



The Application of Image Processing Technique to Separate the Rock Salt with Impurity

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ABSTRACT

With the increasing awareness of consumers and complexity of the application, the application of modern methods of quality control is inevitable. Long traditional methods of identification and separation of impurities have been used in the production of food products. However, after increasing the production, these methods appearing to be cheap are not responsive to the needs of industries. In contrast to traditional methods, the computer inspection of food products is affordable, sustainable and more effective. With respect to the consumer demand, in order to have access to safe and high quality food products and also due to dramatic advances in image processing in recent decades from both theoretical and practical aspects, in this paper, a machine vision system based on image processing is proposed to separate the gross rock salt based on calibration. The results indicate that the accuracy of detection applied algorithm is 67% that given the so likelihood of salt sample is an acceptable result. Based on the detection appropriate accuracy of the presented algorithm, adaptation of the system to perform the calibration of the salts, is possible to be done as online.

Key words: rock salt, image processing, impurities, food safety





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INTRODUCTION

Food has always been the case in all ages and as one of the most basic human needs has been most essential. Production, processing, storage and distribution of community have been the challenges of yesterday and today. Food Ingredients have not been usable without treatment and if they are usable they are needed to be added with appetizers. One of them is table salt (Saied Niyayesh et al., 1385). Salt is an English word that has been derived from the Latin word Sal. Salt from ancient time used by humans as since 3000 BC, the Chinese identified salt. Salt is obtained from various sources with various impurities that are added during formation of the crystals or during collection. The impurities are classified as physical impurities (sand, gravel, soil, etc.), chemical impurities (sulphate, calcium, magnesium, heavy metals, etc.) and microbial impurities (Halophiles that even can live in salt water saturation). The salt can be a carrier of pollution and contamination are constantly entering the human diet can cause serious problems (Omid Mola et al. 1387). Therefore, given the need to maintain the safety of consumer, it is necessary to identify and separate out impurities during the purification. With the increased awareness of the consumers and their complicated demands, it is inevitable to use the modern QC methods. Quality can be considered as a complex of features that the integration of them according to the consumer will result in production reception. The quality assessment base is mostly mental and the features like color, appearance, aroma, tissue and taste are considered by the experienced arbitrators. Human general conceptions are easily involved with mistake.

Image processing techniques are used in order to predict and describe the physical and chemical features (Hung et al, 1997 Taybo et al, 2044) and assess and determine the sense features (Sernadas, Karyon, Rodriguez, Muriel, Antkora, 2005 with Ghazanfari, Dayaraj, 1996) of food materials. During various steps of image processing, some results are obtained that we can measure the efficiency of processing system by assessing the correlation rate with the laboratory results. Image processing has been used in many cases to assess the tissue and appearance properties of food products.

Image processing steps, as shown, include taking image, pre-processing, image scanning, measurement and classification (Figure 1) and the hardware required for the systems usually consists of five components that are: Lighting, camera, image capturing range, a computer and related software. Similar to the human eye, the visual system is affected by the level and quality of lighting. By adjusting the lighting, the appearance and features extracted from object will be changed. So, lighting quality has important impact on the efficiency and function accuracy of the image processing system. In some researches to prevent light-induced changes, the scanner is used for taking image.

Therefore, given the importance of consumer safety and consumer demand for safe and quality products in this paper we present a method for the determination of impurities rock salt that is based on image processing techniques. The system will be designed to determine the amount of mined rock salt impurities and classify the product given the impurity rate and use in particular and application field. In addition, companies can use this method to significantly reduce the cost of washing in the salt treatment.

MATERIALS AND METHODS

The machine vision system hardware consists of the computer (Core i7 950 Memory Ram 6 MB), camera (Canon Digital d600) and the lighting unit. The 2013 Matlab software was used for image processing. It was chosen because of its high power applications in the analysis of color images and there is also a strong function of the image processing. The used rock salt was from the Amarlou mine in Khorasan Razavi, Iran.





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The sample preparation and imaging:

At first, 50 salt stones were selected randomly. Then, in the same light conditions, images were taken with 3456 × 5184 pixels from each of the salt stones. All images were brought to the working environment Matlab software, then the image matrix got binary and according to the algorithm, the program was written in Matlab programming language. Since the images are in black and white, we do not need the gray images with pixel values between [1 and 0]. The images were divided into 4 groups based on the amount of impurities (Fig. 2).

The image processing process:

LBP operand is theoretically simple and powerful method for analyzing tissue. To obtain the LBP operand that is variable to the rotation and monotonic variation of gray levels, by definition of T in the neighborhood we start a monochrome image. T is named the joint distribution of gray levels of p pixel (p > 1) and is defined as follows:

$$T = t(g_c, g_0, \dots, g_{p-1})$$

In the above equation, g_c is the grey surface of the central pixel and $g_p (p = 0, \dots, p - 1)$ is the grey surfaces of pixel p that these pixels are located on a circle at R radius with an equal distance with each other. In fact, these pixels form a rotational symmetric neighbor set. If the coordinate of g_c is equal to (0, 0), therefore the coordinate of g_p is measured by the following equation:

$$(1-1)g_p = \left(-R \sin \frac{2\pi p}{P}, -R \cos \frac{2\pi p}{P} \right) p = 0, 1, \dots, P-1$$

In the following figure, the set of rotating symmetric neighbors are shown according to the different pairs (P, R). Gray surfaces of neighbors that are not exactly in the center of the pixels are obtained by interpolation.

In order to obtain the operand that is invariant to the monotonic changes of the grey surfaces, we should take some steps. At the following, I will explain it. At first step, we subtract the grey surface of the central pixel from its neighbors.

$$(1-1)T = t(g_c, g_0 - g_c, g_1 - g_c, \dots, g_{p-1} - g_c)$$

Then we suppose that the difference of $g_p - g_c$ is independent of g_c . Then we can factorize g_c .

$$(1-1)T \approx t(g_c) \cdot t(g_0 - g_c, g_1 - g_c, \dots, g_{p-1} - g_c)$$

In practice, there is no guarantee that this independence must be established. However, little information is lost about the joint distribution and this information is used for invariance toward the changes of the grey surfaces. $t(g_c)$ in the above equation indicates the general lightness of the image. This general lightness has no impact on tissue and does





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not provide useful information to analyze the tissue of the image. Therefore we can forget $t(g_r)$ and find the following equation.

$$(1-1)T \approx t(g_0 - g_c, g_1 - g_c, \dots, g_{F-1} - g_c)$$

This is called the joint difference distribution equation. For fixed areas, the difference at all directions is zero. For a low-slope edge, the greatest difference is for gradient direction and zero is obtained along the edge. For a point the difference at all directions is high. If we consider the difference sign instead the difference amount, we can find stability at scaling the grey surfaces.

$$(1-1)T \approx t(s(g_0 - g_c), s(g_1 - g_c), \dots, s(g_{F-1} - g_c))$$

With attribution the factor 2^p to each sign of $s(g_p - g_c)$ the above equation is transformed into a unique number of $LBP_{p,R}$. This number describes the location structure of the image local tissue and is defined as follows:

$$(1-1)LBP_{p,R} = \sum_{i=0}^{F-1} s(g_i - g_c) 2^{ip}$$

The operand $LBP_{p,R}$ is not variant against any monotonic transformation of the grey surfaces. It means that until when the order of the grey surfaces of an image is stable, the output of the operand $LBP_{p,R}$ is constant. Therefore, we explained how we achieve unchanging against the monotonic changes of the grey surfaces. At the following, we will debate how we can achieve the stability against rotation.

The operand $LBP_{p,R}$ generates 2^p of different output. When the image is rotated, the amount of the $LBP_{p,R}$ is changed because the neighbors of the central pixels are displaced. But when the patterns includes only 0 or 1, the rotation has no impact on the value of the operand. In order to remove the rotation impact, $LBP_{p,R}$ should be changed as follows:

$$(1-1)LBP_{p,R}^{rot} = \min \{RoR(LBP_{p,R}, i) \mid i = 0, 1, \dots, F\}$$

At this equation $RoR(x,i)$, the number of p shifts the bit of x to right direction i times (rotation shift). Figure 4, shows 36 unique binaries for $p=8$ that are not changed because of rotation. It means that $LBP_{8,R}^{rot}$, it can have 36 different values. For example, the pattern No. 0 identifies the light points; the pattern No. 8 identifies the dark points and the constant areas and the pattern 4 finds the edges.





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The criterion called U is also introduced in this regard. U in fact, is the quantity of passes from 0 to 1 and vice versa. For example, the patterns 0000000_2 and 1111111_2 have monotonic value equal to 0, while the other 7 patterns in the first line of the above figure have a U equal to 2. Similarly, the other 4 patterns have a monotonic value at least equal to 4. So an improved operand is defines as follows that is constant to rotation and grey surface change:

$$(1-1)LBP_{P,R}^{im2} = \left\{ \sum_{v=0}^{P-1} s(g_v - g_c) \text{ if } U(LBP_{P,R}) \leq 2, \text{ Otherwise } P \right.$$

$$(1-1)U(LBP_{P,R}) = |s(g_{P-1} - g_c) - s(g_0 - g_c)| + \sum_{p=1}^{P-1} |s(g_p - g_c) - s(g_{p-1} -$$

Therefore, $LBP_{P,R}^{im2}$, has P+2 possible output. This operand is established by a Lookup Table with 2^P easily. Now we debate how the features of $LBP_{P,R}^{im2}$ are obtained. If we measure the histogram of these operands on an image, we will have a histogram with intervals P+2 that each interval of this histogram can be a feature of the final feature vector. In this project for each area 3 histograms were obtained. These histograms were calculated for (P, R) s equal to (8, 1), (16, 2) and (24,3). The histogram of (8,1) has 10, (16,2) has 18 and (24,3) has 26 intervals. Each of these intervals presents a feature at general feature vector. So, 54 features for each area are obtained based on LBP. Then after obtaining them, classification is performed using K-NN (the K method of the closest neighborhood). Also, at LBP instead of comparison the LBP is used.

CONCLUSION

Designing a system to separate the impure salts based image processing to increase the safety of the consumer and producing a quality product, was studied in this research.

With respect to the results of this study, the algorithm detection accuracy was 67% that is an acceptable result according to much similarity of the salt samples. Based on detection appropriate accuracy of the presented algorithm, the system can be adapted on-line to calibrate the salts. The designed system, in addition to the advantages mentioned by the factories, can reduce the cost of wash to purify the salt significantly using this method. Also, economic calculation before implementing the scheme represents the relative efficacy than the traditional methods.

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Figure 1. Image processing steps



Figure2- Images of salt stone

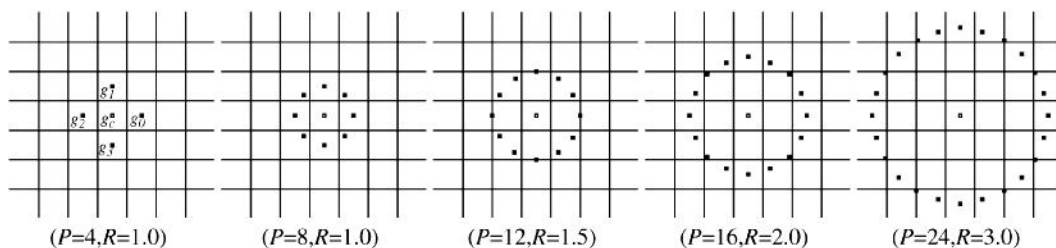


Figure 3. The set of rotating symmetric neighbors for various (P, R)





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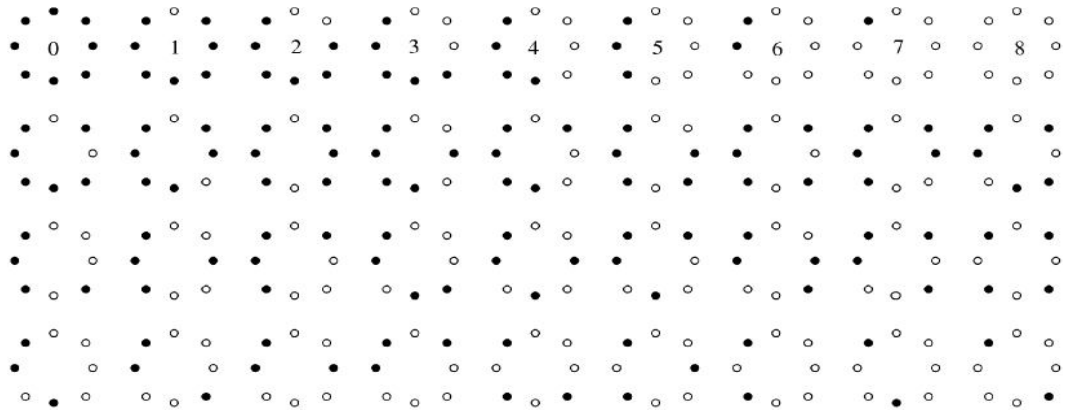


Figure 4- the unique binary pattern (black and white circles are corresponding to the values 0 and 1)





New Processes for Forging Industries Waste Water Treatment

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ABSTRACT

The selection of a proper and optimum process with the lowest cost is one of the basic purposes in the industries, because the separation process is expensive. This research has been done in order to investigate the effect of trans-membrane pressure and surfactant concentration in MEUF process on the permeate flux and rejection percentage of TDS, oil and grease, iron, turbidity and COD of wastewater of forging industries. In this process, membrane pilot with disc module and commercial polyacrylonitrile membrane have been used. Also cationic surfactant of cetylpyridinium chloride (CPC) has been applied in the process. Taguchi method has been used for the experiments design and the results have been analyzed by ANOVA. The results show that the process efficiency is increased and the values of contamination parameters in the permeate are decreased by increasing the surfactant concentration. Also the rejection percentage of all contamination parameters is increased by increasing trans-membrane pressure up to its optimum value, and after that the rejection percentages are decreased due to the micelle structure collapse. The rejection percentage values of 1mM surfactant concentration and 3 bars trans-membrane pressure for TDS, oil and grease, iron, turbidity and COD are 69.34%, 79%, 75.9%, 99.12% and 68.5%, respectively.

Key words: Micellar enhanced ultrafiltration, surfactant, micelle, membrane, Taguchi method.

INTRODUCTION

In recent years, the environmental aspect is one of the most important issues in most industries, for this reason and pollution reduction, they are required to develop new separation methods. Industries wastewater treatment is



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performed in different ways. The combination of surfactants and membrane for wastewater separation helps to develop a new technique in the future. Micellar-Enhanced Ultrafiltration (MEUF) is a process that uses this combination. This process uses ultrafiltration (UF) membranes for the separation of inorganic and organic pollutants in wastewater. This process compared with the traditional separation processes, extraction, distillation or fixed-bed adsorption for low power consumption and no need for purification in the next stage are more appropriate.

Usually, organic compounds with low molecular weight of pollutants in the feed stream will not be separated by ultrafiltration. As an advantage of MEUF, it is usually suitable separation method for low molecular weight organic pollutants. The sizes of the particles which are separated by this process are very small and sometimes it is in nano range. Nanofiltration (NF) or Reverse Osmosis (RO) membrane separation processes are suitable for small particles. However, this process due to the high operating pressure, are expensive and not affordable. But for UF process lower pressure are utilized.

On the other hand, production of membrane for NF or RO processes is harder than UF process. In general, the water flow rate at the UF, while the operating pressure is lower than the NF, is greater than NF or RO. One of the great advantages of this process is that the energy consumption is very low. This process is too cheaper and more convenient compared to the NF membrane.

Mechanism of the MEUF

In the MEUF process, surfactants are added to the water in order to increase its concentration more than the critical micelle concentration. In these conditions the monomers of surfactant are aggregated until the hydrodynamics diameter greater than the diameter of the ultra-filtration membrane. Ions absorbed by the hydrophilic part of Micelle and oils and organic substances solve in hydrophobic part of it, and finally separation is done by a suitable membrane. Fig. 1 shows the MEUF wastewater treatment process and the mechanism of it.

In this study after investigating the properties of surfactant, the rejection percentage of TDS, COD, iron ions, turbidity, oil and grease and also the flux changes through the membrane were examined. And it has been determined that using MEUF method for removing contaminants from wastewater mentioned will be very efficient.

MATERIALS AND METHODS

CPC cationic surfactant manufactured by MERCK Company, Poly Acrylonitrile membrane manufactured by Sepro (Table 1). Wastewater provided from one of the forging factories in Khorasan Razavi, Iran.

Pilot membrane consist of 4 main parts: membrane module, feed tank, pressure gauge and a reciprocating pump, which is schematically presented in Figure 2. Membrane module is a disc module and made of stainless steel (316) with a diameter of 11cm. Other equipment used for the analysis of samples is presented in Table 2.

COD analysis was conducted by AQUALYTIC AL800 spectrophotometer, using high range vial (0–15000 mg). In a vial, 2mL sample was put into contact with the oxidizing acid solution that was then held in AQUALYTIC ET125 thermo reactor at 150°C for 2 h. After cooling, the sample was then analyzed in AQUALYTIC AL800 spectrophotometer. Also, Oil & grease measured by Knechtges, et al. method.





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Experimental design

Taguchi method, also called Taguchi quality engineering, is founded in 1949. The founder is Dr. Genich Taguchi, and he developed this method in Nippon Telephones and Telegraph Company when he was doing the research of a communication system. A set of experiments was designed by MINITAB 16 using Taguchi method (Table 3). The factors to be studied were pressure at 2, 2.5 and 3 bar and CPC feed concentration (C_{CPC}) at 0, 0.3, 0.6, 1, 2, 7mM (CMC value, calculated by conductivity meter in distilled water). The measured responses were the rejection percent (%R) of oil and grease, COD, Turbidity, TDS and Fe ion and the absolute permeate flux (J_v), which were calculated with equation 2 and the rejection percent of oil & grease, Turbidity, COD and iron were calculated using equation 1:

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

$$J_v = \frac{V}{t \times A} \quad (2)$$

Where J_v is the absolute permeate flux, V is the volume of the permeate sample collected, t is the time needed for collecting the permeate sample, and A is the membrane effective area. For permeate flux measurement, initially the permeate volume was measured. At the desired time interval, the permeate stream was sampled and permeate flux was calculated from the permeate volume.

Signal to noise ratio

Signal-to-Noise ratio (S/N) was used to measure the product performance index. The Taguchi method presents a response to an analytical approach to divide average factor levels, then determines which factor level has significant variance and predicts the combination standard factors of optimal factor level. There are several S/N ratios available depending on the interested type of characteristics: Nominal the Best, Smaller the Better, and Larger the Better. In this paper, Larger the Better is used to evaluate the optimal rejection percent's.

$$S/N = -10 \log \left(\frac{1}{n} \sum_{i=1}^n y_i^{-2} \right) \quad (3)$$

Where, y_i and n represents the experimental value of the i^{th} experiment and the number of experiment, respectively.

PROCEDURE

The initial feed volume was 6 liter and the ultrafiltration experiments were carried out until 150 cm³ of the total sample was filtered. The permeate flux was calculated by measuring volume of permeate in desired time interval, measuring operation was continued until the volume in different time intervals, same. The UF cell was made of stainless steel. Effective diameter of the membrane was 90 mm. Experiments were designed to study the influence of applied pressure and CPC concentration on permeate flux and retention of TDS, oil & grease, Turbidity and COD.

In this experiment, pressure and CPC concentration was changed. At first, CPC concentration was held constant and different parameters were measured for three different pressures (2, 2.5 and 3 bars). After that, other surfactant concentration was investigated. After each experiment the membrane was washed successively using deionized water, 0.1M NaOH, finally in deionized water. The deionized water was filtered to determine the permeate flux and to check the permeability of the membrane.





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RESULTS AND DISCUSSION

In this section the results of the experimental data is discussed. Experimental results is represented as the MEUF Membrane Process Flow index, means the permeate flux, and index of wastewater treatment, means the percentage of reject or amount of decrease in total dissolved solids, iron, COD, oil and grease, and turbidity versus changing the pressure and surfactant concentration. Finally, in order to investigate the effects of concentration and pressure, the results of experiments were analyzed by ANOVA analysis.

The effect of time, pressure difference and surfactant concentration on the volume of permeate flux

The effect of pressure difference and concentration of surfactants on the volume of permeate flux at pressure difference of 2, 2.5, 3 bar and concentrations of 0, 0.3, 0.6, 1, 2 and 7 at 20°C is shown in figure 3 to 5. As seen permeate flux decreased with increasing time until it reached to a constant value.

The primary reason for the decline in the permeate flux is micelles and solids in waste water which are blocking the pores of the membrane. In the first 5 minutes, permeate flux decline is fast and then decrease. The reason for this is that the amount of material and micelles that has accumulated on the surface of the membrane increased with time and Leading to the formation of the polarization layer and membrane fouling, which causes a initial sudden drop and gradual decline of permeate flux in the filtration operations.

In fact, by the formation of polarization layer near the surface of the membrane, in addition to membrane strength, R_m , and resistance of membrane fouling, R_f , concentration polarization layer resistance also leads to a reduction of the permeate flow and with the passage of time and the development of gel on the surface of the membrane, the permeate flux will tend towards a constant value.

Also Figures 3 to 5 show that at the higher pressure difference, permeate flux will be increase which is because of the increasing in propulsion of process that is the pressure difference. Increase in the pressure difference causing more passage of the solution on the membrane and subsequently increase in permeate flux. Increasing the surfactant concentration, due to the accumulation of large amounts of surfactants and Micelles on the membrane and increasing polarization concentration and fouling of the membrane, permeate flux will be decrease. According to figures 3 to 5, the effect of pressure difference is almost negligible and the optimum pressure is 2.5 bars.

Effect of pressure difference and concentration of surfactant on rejection

The effect of pressure difference and concentration of surfactant on the rejection rate of pollution index such as total dissolved solids, oil and grease, turbidity, COD and iron has been checked and provided in Figures 6 to 10. Generally, increasing the pressure difference is partly leads to increase in rejection percents.

Increase in rejection percentage with increasing of pressure difference is because of the increase in the permeate flux and solvent and dissolved material which passing through the membrane. In addition, increased flux of dissolved material is proportionally less than the increased in the solvent flux which cause increasing in the percentage of rejection. Increasing the operating pressure greater than the optimum pressure, make the micelles compressed out of the normal, so solubility of contaminants in micelles are reduced, causing a small amount of organic contaminants dissolve in the micelles, which leads to a reduction in the rejection of oil and grease, COD. Figures 7 and 9 show the increase and then decrease in the rejection percentage at the pressure more than optimum pressure.



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Also, by increasing the operating pressure difference of compressed Micelles, the effective bonding sites for metal ions are reduced. Thus the rejection percentage of TDS and iron in concentration higher than critical concentration and pressure higher than 2.5 bars will be decrease, but in the concentration less than the critical concentration it will be occur at higher pressures.

Determintion significant factor in MEUF process by taguchi method

To evaluate the significant factors in Taguchi method, the signal to noise ratio was used. As shown in Figures 11 and 12, the concentration has main effect on the removal of TDS and trans-membrane pressure has main effect on iron ion removal.

Results of Taguchi method shows that the surfactant concentration is the most important parameter in the rejection of several factors. Also according to Figure 11 the optimum levels of surfactant concentration for rejection of COD, TDS, Fe and oil and grease is 7ppm and for the rejection of turbidity is 1ppm. Also optimum operating pressures for maximum rejection of all factors is 3bar (Fig. 2) with respect to the p-values (significancy) obtained by the ANOVA analysis, the above statement is true.

As noted above, we can see that increasing the trans-membrane pressure hasn't a very large and significant effect on the rejection percentage of turbidity. Because rejection percentage of turbidity is very high and it isn't possible to change it a lot. Membrane processes has the most rejection percentage for turbidity, indicating that microorganisms and suspended factors which cause turbidity are well removed by this type of membrane.

As seen in Figures 6 to 10 with increasing surfactant concentration in the wastewater, Rejection rate at lower concentrations increased rapidly, but gradually by approaching to the critical concentration of micelle formation (about 0.9 mM) it has been slowed. The main reason for the increase in the rate of Rejection in lower concentrations is the polarization concentration phenomenon. The polarization concentration phenomenon arises from the accumulation of particles in the vicinity of the membrane caused by the influence of the solvent. This phenomenon increases the concentration between the membrane surface and wastewater solution. During the process, the surfactant molecules rejected by membrane place on the surface of the membrane.

Over time, gel is created near the membrane surface which causes the concentration of surfactant in the solution reach to the micelle critical formation concentration. Then, the minerals place on the surface of the micelle and Reject by the membrane. The effect of increasing the concentration of surfactant at concentrations above the critical concentration could be justified as follow; by increasing the concentration of surfactant the number of molecules in the micelle at the micelle critical formation concentration will be change, but the number of effective places for ions binding does not increase at the same ratio, as a result, at the higher concentrations of the micelle critical formation concentration by increasing surfactant concentration, increase in rejection is lower. Thus increasing of the surfactant in this range is not recommended, because it can bring large economic costs.

According to the provided figures, increase in the rejection percentage of various indices occurs as bellow:

TDS > Fe > COD > Oils and grease > Turbidity

This process is a good alternative for the NF wastewater treatment process because TDS and Fe cannot be greatly reduced by UF and NF processes is needed. Furthermore, NF in the wastewater treatment process will be severe fouling and low flux decreases.





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CONCLUSION

The quantity and quality of treated waste water using MEUF analyzed by the permeate flux turbidity, oil and grease, COD, TDS and iron in the sample. The results of the studying permeate flux show that with increasing operating pressure due to increasing the driving force of the process, the permeate flux increased. But increasing trans-membrane pressure to an optimum pressure increased the rejection percents. Because at high pressures due to the micelles structure collapse and loss of active sites, the possibility of separation and rejection will be decrease.

By increasing CPC surfactant concentration at constant operating trans membrane pressure because of the increase in the micelle mass at the surface of membrane, the resistance across to solvents flux has increased, resulting in reducing flux, in the other hand, by increasing the concentration of CPC, the number of formatted micelle increased and the possibility of charged particles absorption and oils dissolution in the micelle enhanced and hence better separation is done.

According to the result found that both parameters, trans membrane operating pressure and CPC concentration are effective on permeate flux and rejection percentage of CPC, TDS, COD, oil and grease, turbidity and iron, but surfactant concentration would be more effective parameter. On the other hand, according to results presented reveals that the rejection percentage for the various indicators will be as follows:

TDS > Fe > COD > Oils and grease > Turbidity

This process is a good alternative for the NF process in treatment of wastewater because TDS and Fe can't be much reduced by UF and NF processes is needed. Furthermore, NF in the wastewater treatment process get severe fouling and low flux will be decrease. However, this fouling is lower in ultrafiltration membrane.

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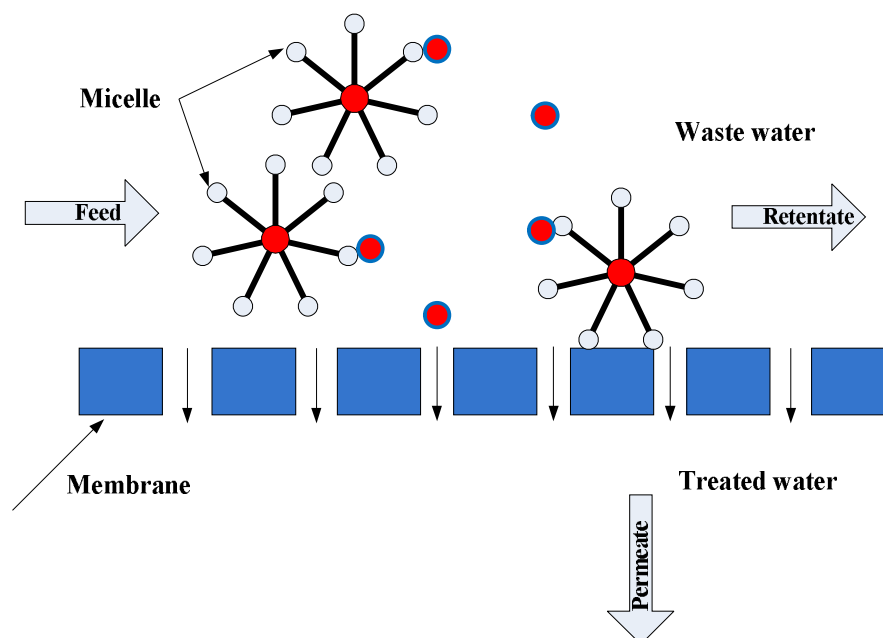


Fig. 1. The separation mechanism of pollution by the MEUF process.





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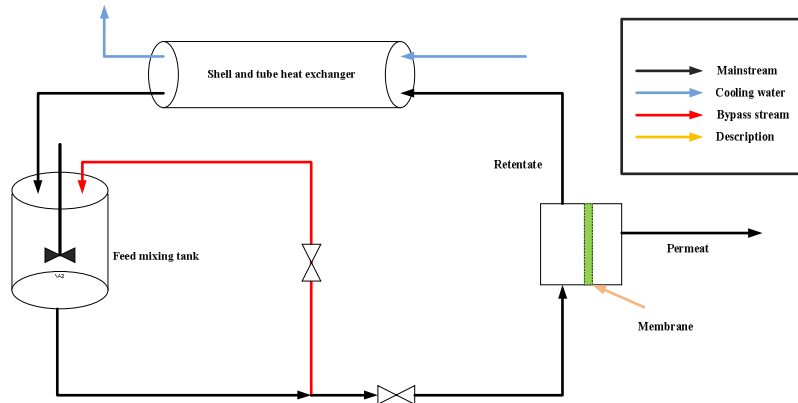


Fig. 2. Schematic of the pilot membrane.

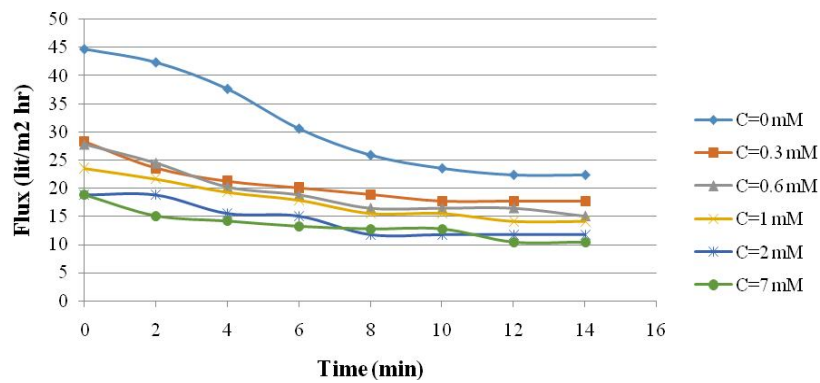


Fig. 3. Diagram of permeate flux versus time at various concentrations of surfactants and trans-membrane pressure of 2bar

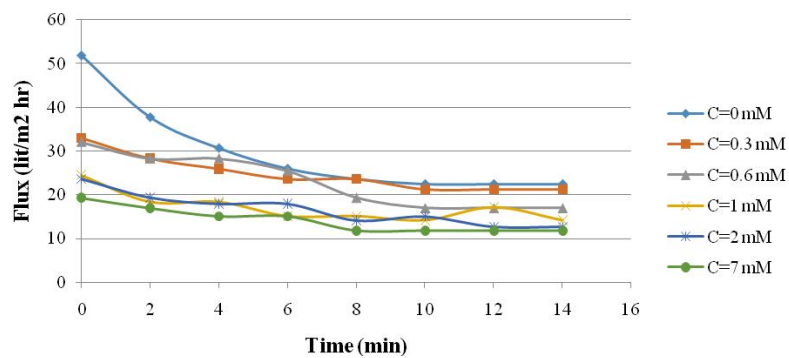


Fig. 4. Diagram of permeate flux versus time at various concentrations of surfactants and trans-membrane pressure of 2.5bar





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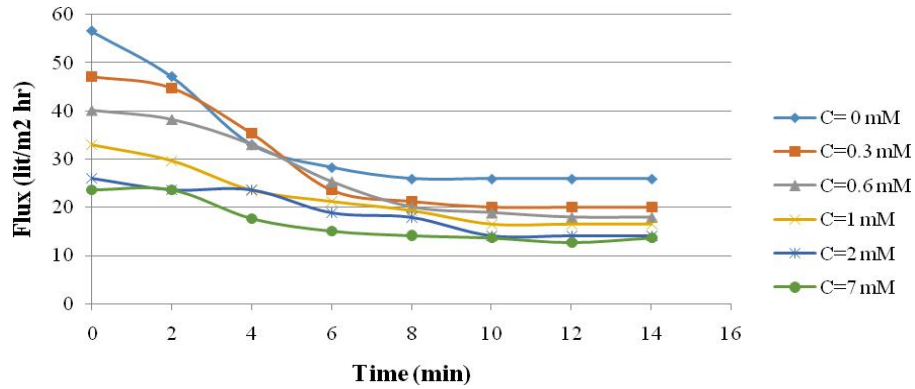


Fig. 5. Diagram of permeate flux versus time at various concentrations of surfactants and trans-membrane pressure of 3bar

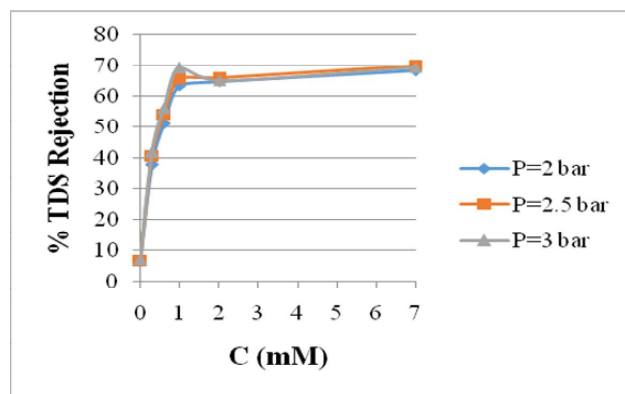


Fig. 6. Diagram of the rejection percent of TDS versus concentration of surfactants at different trans-membrane pressure

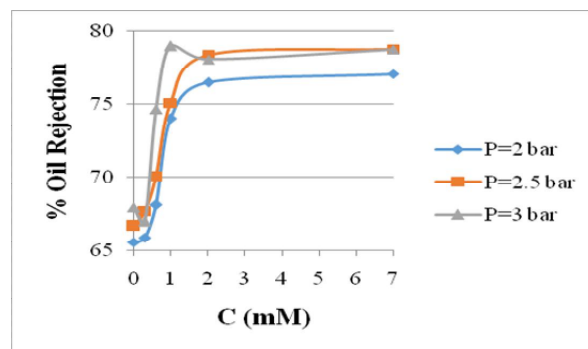


Fig. 7. Diagram of the rejection percent of oil and grease versus concentration of surfactants at different trans-membrane pressure





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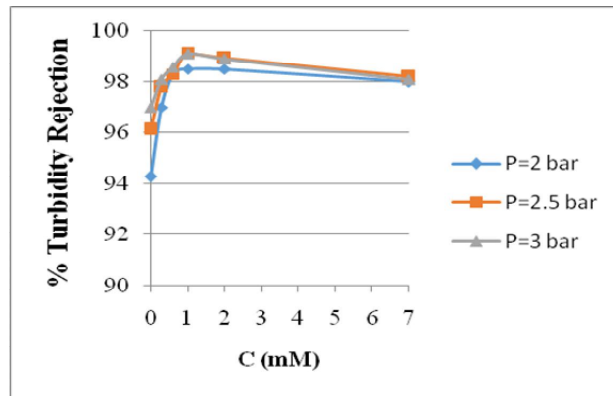


Fig. 8. Diagram of the rejection percentage of turbidity versus concentration of surfactants at different trans-membrane pressure

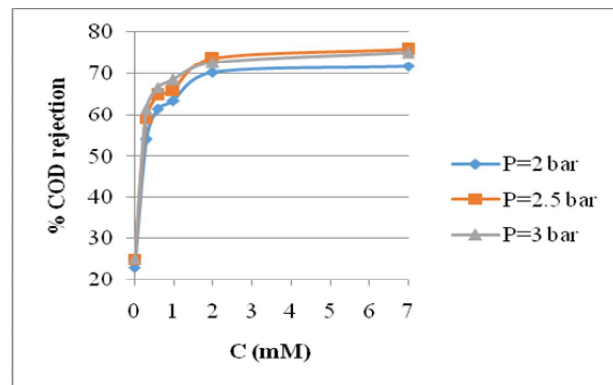


Fig. 9. Diagram of the rejection percentage of COD versus concentration of surfactants at different trans-membrane pressure

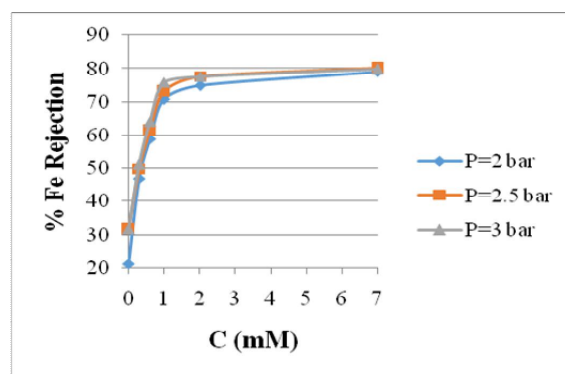


Fig. 10. Diagram of the rejection percentage of iron versus concentration of surfactants at different trans-membrane pressure





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Table 1. Characteristics of ultrafiltration membrane

Country	Firm	Model	Material	Thickness (mm)	P _{max} (MPa)	T _{max} (°C)
USA	Sepro	PAN-350	PAN	0.165	8.3	100

Table 2. The equipment needed for the analysis of samples

Responsibility	Characteristic	Equipment
For mixing and uniform the solution	IKA	Magnetic stirrer
Measurement of electrical conductivity and total dissolved solids	JENWAY	The device measures the electrical conductivity and TDS
The measurement of turbidity in Term of NTU	WTW TURB 355 IR	Turbidity Meter
To perform digestion vials	AQUALYTIC ET 125	Digestive device
Measure COD	HACH DR 2800	COD meter
Measurement of iron ions in the sample	Shimadzu AA-670	Atomic Absorption Spectrometry

Table 3. Design of experiments for MEUF process

Experiment Number	CPC Concentration (ppm)	P (bar)
1	0	2
2	0	2.5
3	0	3
4	0.3	2
5	0.3	2.5
6	0.3	3
7	0.6	2
8	0.6	2.5
9	0.6	3
10	1	2
11	1	2.5
12	1	3
13	2	2
14	2	2.5
15	2	3
16	7	2
17	7	2.5
18	7	3





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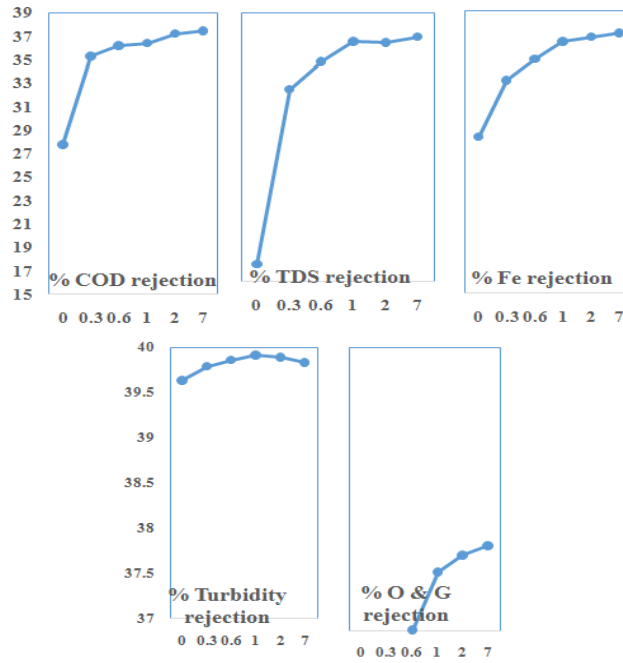


Fig.11. Signal to noise ratio at six different surfactant concentrations

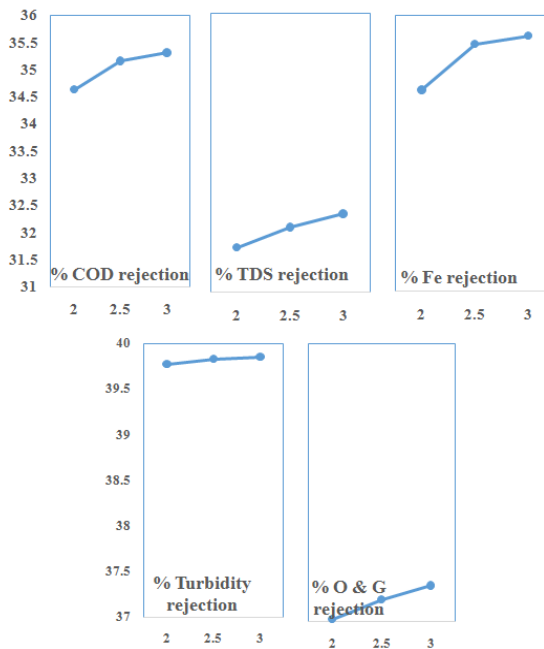


Fig.12. Signal to noise ratio at three different trans-membrane pressures.





Simultaneous Determination of Diclofenac and Naproxen in Environmental Water Samples with Carbon Nanotubes-Assisted Pseudo-Stirbar Hollow Fiber Solid/Liquid-Phase Microextraction and Uv/Vis spectrophotometry by Partial Least-Squares Calibration

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ABSTRACT

In this paper, a method based on Hollow Fiber Solid/Liquid Phase Microextraction (HF-SLPME) for sensitive determination of Diclofenac and Naproxen in environmental water samples was demonstrated. The extracted drugs were then quantified by Uv/Vis spectrophotometry using Partial Least Squares (PLS) calibration. Related parameters that may influence the enrichment efficiency of microextraction such as donor phase volume, agitation speed, extraction time, pH of the aqueous feed, ionic strength and MWCNTs content were investigated. Under the optimum conditions, the detection limits of Diclofenac and Naproxen were 0.01, 0.03 mg L⁻¹ respectively. The Relative Standard Deviations (RSDs) of Diclofenac and Naproxen were 5.3 and 4.7%, respectively. The established method also was applied to the analysis of the real water samples and excellent achievements were obtained with average spiked recoveries from 95 to 103%. All the results indicated that this procedure could allow the simultaneous determination of these two compounds in environmental water samples at trace levels.

Key words: Carbon Nanotubes, Chemometric method, Diclofenac, Hollow Fiber Solid/Liquid Phase Microextraction (HF-SLPME), Naproxen, Non steroidal Anti-inflammatory Drugs (NSAIDs), PLS, Uv/Vis spectrophotometry.



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INTRODUCTION

Carbon Nanotubes (CNTs) are a new type of carbon material first found in 1991 by Iijima. Recently, CNTs are applied for preconcentration of heavy metals, organics, and biological impurities due to its large specific surface areas, outstanding thermal and chemical stabilities and ease of separation [1]. Nevertheless, the CNTs are insoluble and hard dispersible in all solvents due to strong van der Waals interactions that tightly hold them together, forming bundles, so functionalization of CNTs to enhance solubility has excited broad interests and lots of strategies were developed. Meanwhile, for Solid Phase Extraction (SPE) extractants, superior selectivities and capacities are always expected. Multi wall Carbon Nanotubes (MWCNTs) have been characterized as superior sorbent for removing dioxins for environmental protection. The amount of dioxin adsorbed on CNTs is 10^{34} times greater than that on activated carbon. It is believed that reasons for its adsorption may be primarily due to their highly hydrophobic surface and unique structure with internal tube cavity.

More recently, Es'haghi et al. combined Hollow Fiber Liquid-Phase Microextraction with solid phase extraction, introduced a new method namely Hollow Fiber Solid-Liquid Phase Microextraction (HF-SLPME) and have benefited from the advantages of both. In this technique, incorporation of bundles of chemically modified CNTs in organic solvent that was supported by a piece of polypropylene hollow fiber improved extraction performance. MWCNTs incorporated in the membrane system could act as a nano-scale solid-phase extractant with high surface area. It has provided more homogenous phase, large number of active adsorbent sites, stronger, and thereupon chemical bonds between analyte and extractor and very high pre-concentration factors of analytes. HF-SLPME in implementing two-phase and three-phase modes is used. The membrane extraction with a solid/liquid interface that is used in this work is a two-phase supported liquid membrane consisting of an aqueous phase (feed) and organic solvent/nanosorbent (acceptor) operated in direct immersion sampling mode.

Multivariate calibration methods such as Partial Least Squares (PLS) and Artificial Neural Networks (ANNs) are useful means of resolving different overlapping spectra and eliminating matrix interference in the assay of various multi-component mixtures. The principle advantages of applying these methods to spectrophotometric data are; the improvement of sensitivity and selectivity as well as the significant economic advantages over other sophisticated instrumental techniques such as HPLC and GC. The basis of these methods along with their applications, have been reported in the literature.

In this article, we used two-phase HF-SLPME for analysis of Nonsteroidal Anti-inflammatory Drugs (NSAIDs) namely Diclofenac and Naproxen in water samples. Different aspects of the extraction procedure such as donor phase volume, agitation speed, extraction time, pH of the aqueous feed, ionic strength and MWCNTs content were optimized.

Experimental Section

Reagents and stock solutions

Diclofenac and Naproxen were obtained from DarouPakhsh co. (Tehran, Iran). Methanol (HPLC grade) was purchased from Fluka (Buchs SG, Switzerland). All other chemical and solvents were of analytical reagent grade. Deionized water was purified by a Milli-Q system (Millipore, Bedford, USA). Stock solutions of Diclofenac and Naproxen (1000mgL^{-1}) were prepared in MeOH. The MWCNTs employed herein were obtained from the Research Institute of the Petroleum Industry (Tehran, Iran). The mean diameter of the MWCNTs was 10–15nm, and the length was 10–50nm. Working solutions were prepared daily by dilution of the stock solutions with deionized water. All the solutions were protected from light throughout the experiments.





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Instrumentation

All spectrophotometric measurements were carried out with a UUIKON-922 (Italy) double beam spectrophotometric equipped with 1 cm quartz matched microcell (with volume of 400 μ L). PLS program was modeled using ParLeS v3.1 software.

PLS calibration

PLS method involves the decomposition of the experimental data, such as spectrophotometric data in our case, into systematic variations (latent variables) that explain the observed variance in data. The purpose of PLS method is to build a calibration model between the concentration of the analytes under study (Diclofenac and Naproxen in our case) and the latent variables of the data matrix. PLS performs the decomposition using both spectrum data matrix and analyte concentration. Including extra latent variables in the model increases the possibility of the known problem of overfitting. Therefore optimization of number of the latent variables is a critical issue in the PLS method. Optimisation of Number of Latent Variables for PLS Model Cross validation (CV) is applied to predict how many are the optimum number of PLS latent variables. CV involves repeatedly dividing the data into two sets, a training set used to determine a model and a test set to determine how well the model performs so that each sample (or portion of the data) is left out of the training set once only. The Root Mean Square Error of CV (RMSECV) is calculated as:

$$RMSECV = \sqrt{\frac{\sum (C_{pred} - C_{act})^2}{n}}$$

Where n is the number of objects in the calibration set, C_{pred} is the predicted concentrations and C_{act} is actual concentrations of the components. Mean centering is performed on the training set each time successive samples are left out.

A four-level factorial design was used to produce a calibration set of 16 samples (Table 1) and a three-level set was derived to produce a prediction set of 9 samples (Table 2). The UV absorption spectra were recorded over the wavelength range of 210–350 nm. The data points of the spectra were collected every 0.2 nm.

The prediction error of a single component in the mixture was calculated as the Relative Standard Error (R.S.E.) of the prediction concentration:

$$R.S.E.(%) = \sqrt{\frac{\sum_{j=1}^N (\hat{C}_j - C_j)^2}{\sum_{j=1}^N (C_j)^2}} \times 100$$

where N is the number of samples, C_j the concentration of the component in the j th mixture and \hat{C} is the estimated concentration. The total prediction error of N samples is calculated as follows:

$$R.S.E.T.(%) = \sqrt{\frac{\sum_{i=1}^M \sum_{j=1}^N (\hat{C}_{ij} - C_{ij})^2}{\sum_{i=1}^M \sum_{j=1}^N (C_{ij})^2}} \times 100$$





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The R.S.E.(%) of the predicted concentrations and other results are listed in Table 3.

HF-SLPME Procedure

Polypropylene hollow-fiber was cut into 1.5 cm segments and sonicated in acetone for 5 min to remove any possible contaminants. The fiber was then removed from the acetone and allowed to dry completely. Organic solvent was mixed with MWCNTs and dispersed by sonification. Subsequently, 5.0 μL of dispersed MWCNTs in 1-octanol (acceptor phase) was injected into the lumen of the hollow fiber with a syringe, after that the polypropylene tube sealed at both ends by iron pin as magnetic stoppers (iron pins; 1.5 \times 0.6 mm). This fiber was placed into the sample solution containing Diclofenac and Naproxen (1.0 mgL^{-1} in HCl 1.0 molL^{-1}) in an appropriate vial. The samples were stirred at 800 rpm for 30 min. The analytes were trapped in the solid/organic solvent simultaneously. Thereafter the fiber was removed from the solution and the two stoppers were removed using a small forceps. Fiber segment was placed into the other clean vial containing 0.5mL of methanol. The fiber was stirred at 1000rpm for 2min for analytes desorption. The UV absorption spectra were recorded over the wavelength range of 210–350 nm. The data points of the spectra were collected every 0.2nm. Then, calculating both analytes' concentration by help of ParLes software and data gained from previous experiment (formed calibration set). All experiments were performed in triplicate, and the means of the results were used in the calculations.

RESULTS AND DISCUSSION

Optimization for the HF-SLPME

In order to reach the optimization of the HF-SLPME conditions, several parameters that influence the extraction efficiency were investigated. Various experimental parameters, such as donor phase volume, agitation speed, extraction time, pH of the aqueous feed, ionic strength and MWCNTs content were optimized.

Membrane solvent selection

In this work, with respect to our previous research, 1-octanol has been selected as the organic solvent because it is consistent with polypropylene and is well established within the fiber pores. Moreover, MWCNTs' diameter is large enough to easily accommodate octanol molecules.

Effect of donor phase volume

Generally, the amount of analyte extracted is proportional to the sample volume. Hence, the sensitivity of the method can be improved by increasing the volume of the sample. However, a much longer equilibration time is required because the extraction rate is controlled by the diffusion of analytes from the sample matrix to the fiber. In order to select the optimum sample volume, four different volumes of 10, 15, 20 and 25mL were assayed. In general, the data obtained demonstrate that an increase in the sample volume improves the extraction efficiency in the target analytes. In the other hand by increasing amount of sample more than 20mL, mass transfer kinetics become weaker. The amount of analytes that can be extracted depend on the partition coefficient of the analyte between the sample and the MWCNTs. This could be due to the possible saturation of the MWCNTs capacity for a large sample volume, or a longer extraction time is needed for a >20mL sample to reach equilibrium (Fig.2). Thus, 20mL of donor solution was selected for subsequent experiments.





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Effect of agitation speed

Agitation of the donor solution reduces the required extraction time and increases extraction efficiency. Stirring provides fresh donor solution for the organic phase to extract and reduces the effect of the stationary boundary layer zone (Nernstian layer) produced close to the organic phase; these factors promote analyte transport from the donor phase to the organic phase. However, agitation in excess of the optimal stirring rate may also cause lower extraction efficiency because the hollow fiber is vibrated by the surrounding turbulent flow and air bubbles reduced absorption for each analyte and a decrease in the precision of the method .

To evaluate the effect of stirring, donor solution was extracted at varying stirring rates (600 - 1200rpm). As seen from **Fig.3**, the extraction efficiencies of these NSAIDs increased at higher stirring rates and reached a maximum at 1000rpm. Consequently, 1000rpm was chosen for subsequent extractions.

Effect of extraction time

To increase the precision and sensitivity of the HF-SLPME method, it is necessary to select an exposure time that guarantees the equilibrium between the aqueous and organic phases and subsequently, between the organic solvent and MWCNTs. Therefore, the extraction time plays a very essential role in the whole process. The range of extraction time investigated was 10-40min with other extraction conditions being constant. **Fig. 4** shows that there was a corresponding increase in concentrations from 10 to 30 min. Above 30 min there was no significant increase in the concentrations. An extraction time of 30 min was selected as a reasonable compromise between enrichment factor and analysis time.

HCl concentration

Sample pH plays a unique role to transfer the target analytes into organic phase in many LPME methods. Because of acid-base properties of NSAID compounds and the importance of the pH effect on their extraction. Generally for NSAIDs the donor phase should be strongly acidic in order to ensure that the analytes are not ionised and consequently reduce its solubility in the organic solution. We used various concentrations (0.005–0.1molL⁻¹) of HCl. For both compounds, concentrations increased with increasing HCl concentration up to 0.05 molL⁻¹(**Fig. 5**). We used 0.05molL⁻¹HCl for donor phase solution.

Effect of ionic strength

It is well known the beneficial effect of the ionic strength for the liquid microextraction of a wide variety of analytes. When studying the NaCl content, we can take as a general rule that adding a soluble salt to the sample increases the ionic strength of the solution: the organic substances become less soluble, and so the amount of compound released into the fiber increases. Therefore, its influence in the proposed procedure was evaluated by adding different amounts of sodium chloride to the samples in the range 0–15% w/v. The results demonstrated a slight improvement of the extraction for both compounds up to 5%w/v, however a decreasing was observed at concentrations higher than 5%w/v(**Fig. 6**)

Effect of MWCNTs Content

The influences of the amount of MWCNTs on the preconcentration factor have been examined. The idea is to have a membrane protected CNT sorbent that acts as an analyte trap, resulting in higher selectivity and enrichment because the MWCNTs act as solid sorbents in HF-LPME. The investigated range was between 0.01–0.04g/mL and 0.03g/mL was the optimal amount of the CNTs. Although the extraction efficiency was increased with increasing of MWCNTs



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amount but for amounts up to 0.03mg/mL, inserting of mixture into the hollow fiber segment was very difficult and has led to lack of reproducibility of results.

Evaluation of the Method Performance

The characteristic data of the developed HF-SLPME method are summarized in Table 4. Measurements made under the optimum conditions, i.e., donor phase volume: 20mL; stirring rate: 1000rpm; extraction time: 30min.; HCl concentration: 0.05molL⁻¹; and NaCl concentration, 5%, w/v. Pre-concentration Factor (PF), Relative Standard Deviation (RSD %), Limit of Detection (LOD) and Limit of Quantitation (LOQ) have been calculated under optimum experimental conditions.

Real sample analysis

Two samples, drinking water from Zvarm and FajrAbadfountains (bojnourd, Iran) were analyzed to demonstrate the practical applicability of this technique. The analytical results of these samples indicated that the both samples were free from NSAIDs. For recovery, this HF-SLPME method depends on equilibrium rather than exhaustive extraction. Instead of absolute recoveries, relative recoveries determined as the ratio of the real water sample outcome to that of the deionized water sample are summarized in Table 5. These results indicate that the relative recoveries of NSAIDs from the spiked water samples (performed in three replicates on 1.0 mgL⁻¹ of each compound spiked) were 95% - 102% and 99% - 103% for Naproxen and Diclofenac, respectively.

CONCLUSION

A new, simple, rapid and compatible method of Hollow Fiber supported Solid/Liquid Phase Microextraction (HF-SLPME) has been developed for extraction and determination of Non-steroidal Anti-inflammatory Drugs (NSAIDs) in water samples. Compared to most conventional procedures, this extraction technique requires very little sample solution and little expensive and toxic organic solvents. It is a promising pre-treatment method for the fast, trace analysis in many complicated matrixes, such as environmental and biological samples. The method has a high enrichment factor and excellent selective clean up of samples. Good linearity and reasonable relative recovery were also obtained. The disposable nature of the hollow fiber completely eliminates the possibility of sample carry over and guarantees high reproducibility. In addition, the small pore size prevents large molecules in matrixes and unsolved particles in the donor solution from entering the acceptor phase, thus yielding very clean extract. In this technique valuable role of MWCNTs as solid sorbent combined with organic solvent extractor was very significant. Multivariate (PLS) method enable the quantitation of Diclofenac and Ibuprofen binary mixture with good accuracy and precision. All data proved that this method could be effectively applied to the analysis of NSAIDs in water samples.

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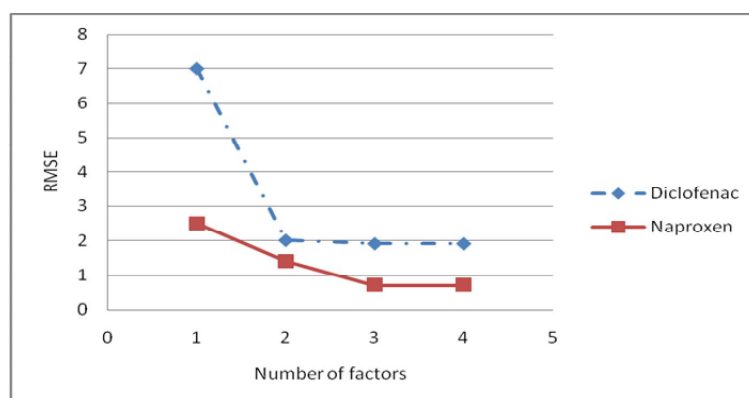


Figure 1. RMSE curve versus number of factors for Diclofenac and Naproxen





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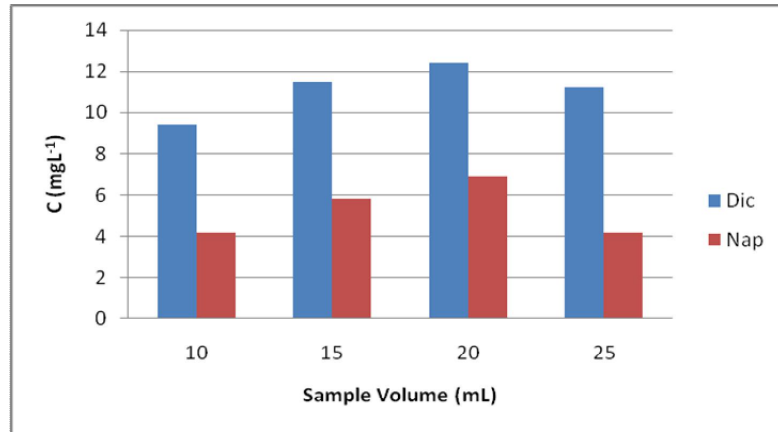


Figure 2. Effect of the donor phase volume on the method performance.

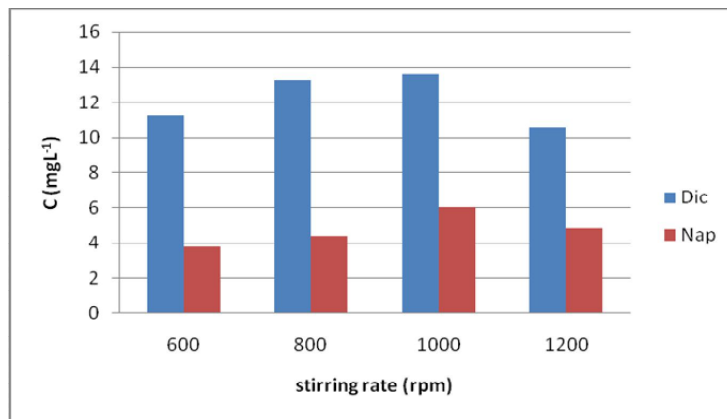


Figure 3. Effect of the stirring rate on the method performance.

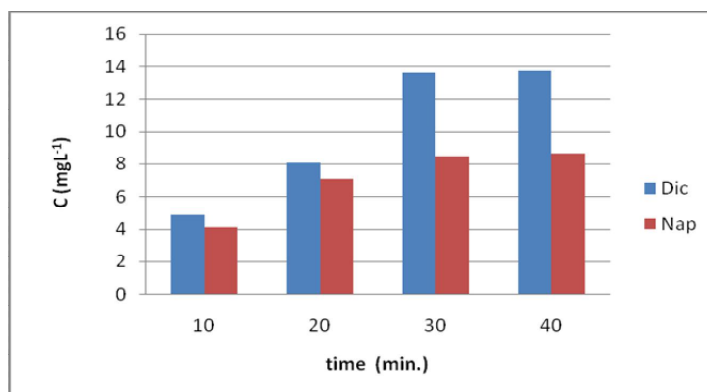


Figure 4. Effect of the extraction time on the method performance.





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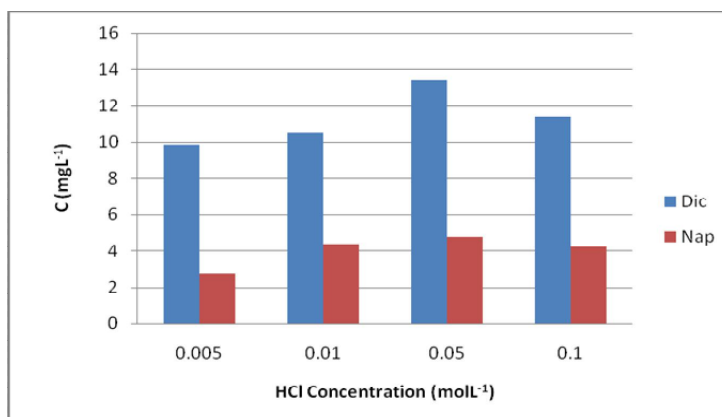


Figure 5. Effect of HCl concentration on the method performance

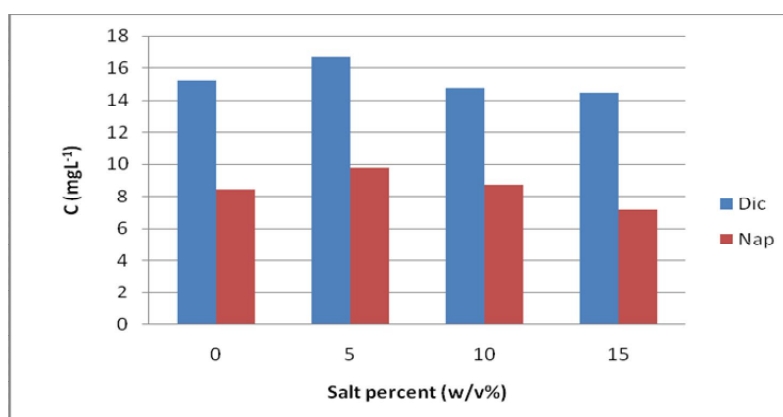


Figure 6. Effect of salt percent on the method performance

Table 1. Calibration set composition

Sample	Concentration(mgL ⁻¹)	
	Naproxen	Diclofenac
C ₁	16.0	4.0
C ₂	0.0	12.0
C ₃	8.0	4.0
C ₄	8.0	8.0
C ₅	8.0	0.0
C ₆	8.0	12.0





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C ₇	24.0	4.0
C ₈	0.0	0.0
C ₉	24.0	12.0
C ₁₀	24.0	8.0
C ₁₁	0.0	4.0
C ₁₂	24.0	0.0
C ₁₃	16.0	8.0
C ₁₄	16.0	12.0
C ₁₅	16.0	0.0
C ₁₆	0.0	8.0

Table 2. Prediction set composition

Sample	Concentration (mgL ⁻¹)	
	Naproxen	Diclofenac
P ₁	10.0	5.0
P ₂	20.0	10.0
P ₃	20.0	2.0
P ₄	4.0	5.0
P ₅	4.0	2.0
P ₆	20.0	5.0
P ₇	10.0	2.0
P ₈	4.0	10.0
P ₉	10.0	10.0

Table 3. Statistical parameters for PLS-1 analysis of Diclofenac and Naproxen

Parameter	Naproxen	Diclofenac
Optimum spectral range (nm)	210–350	210–350
Number of PLS Factors	3	2
R.S.E.(%)	6.7	4.1
R.S.E.T (%)	5.4	
Recovery (%)	98.2	99.8
Recovery _T (%)	99.0	





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Table 4.Characteristic data of the established HF-SLPME-UV-PLS method

Analyte	LODs (mgL ⁻¹ , S/N=3) (n=7)	LOQs (mgL ⁻¹ , S/N=10) (n=5)	RSDs (%) (n=5)	PF (n=3)
Diclofenac	0.01	0.03	5.3	418
Naproxen	0.03	0.1	4.7	408

Table 5.Relative recovery of Naproxen and Diclofenac in real water samples by use of HF-SLPME-UV-PLS method

Sample	Naproxen	Diclofenac
Zvarm fountains Water	102	103
FajrAbad fountains Water	95	99





Synthesis of Hematite (α -Fe₂O₃) Nanoparticles by Wet Ball Milling and Studying its Morphological and Microstructural Properties

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ABSTRACT

This study investigated the morphological and microstructural characteristics of hematite nanoparticles synthesized by ball milling in wet medium. The structure and morphology of samples were determined during milling by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Vibrating Sample Magnetometry (VSM). The crystallite size of synthesized nanoparticles was evaluated according to XRD patterns by Scherrer's Formula. Obtained results showed that the lattice strain of synthesized hematite nanoparticles improves with increasing of milling time, while their average particle size decreases. Based on XRD and TEM results, the grain size of the synthesized nanoparticles was estimated about 12-30 nm. SEM micrographs indicated a steady distribution and spherical morphology of the synthesized powder. Also, it was found that the nanoparticles size decreased with increasing the weight ratio of fluid to powder(R) and magnetic saturation increased as a result of ball milling process.

Key words: Synthesis, Wet ball milling, Nanoparticle, Hematite, Microstructure.

INTRODUCTION

Ball Milling (BM) is a simple method for synthesis of large quantities of metallic nanomaterials that involves the repetition of cold welding and particle fracturing which leads to nanoparticle production by passing the time[1]. During the hard collision of balls together in a high-energy milling process, the size reduction will be continued to



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attain nano dimensions[1]. Wet ball milling through accelerating the kinetic of a series of chemical reactions leads to metallurgical conversions, therefore their occurrence will be possible in ambient temperature[1]. Simple equipment, none necessity to high temperature, ability to production of large quantities and only one step production are specific characteristics of ball milling which make it more economical than conventional methods for synthesis of many nanometals and alloys[1]. Between metallic materials, the iron oxide nanoparticles have been considered strongly because of their unique characteristics such as availability, cheapness, superparamagnetism, high saturation fields and extra anisotropy contributions[2, 3]. Among the different methods that have been used to synthesize iron oxide nanoparticles, ball milling has received considerable attention because of its benefits[8]. α -Fe₂O₃ (hematite) is a strategic industrial material with various applications in different sciences and industries including catalysis in chemical industry [4], electrochemistry, biochemistry, biomedical applications, various facilities for laboratory diagnostics, or in medical medicine delivery[5].

Many studies have been done on the synthesis of hematite(α -Fe₂O₃) nanoparticles. Lemine has determined microstructural properties of hematite nanoparticles synthesized by ball milling. He indicated that ball milling process of micrometric hematite powder can be used to produce hematite nanoparticles without phase change and the lattice strain improves by increasing the milling time[3]. Ding et al., studied the structure and magnetic properties of iron and hematite milled powders. They observed that Semi-stable FeO nanocrystals are decomposed into Fe₃O₄ nanocrystals after annealing in 250–400 °C and then reconvert to FeO in temperatures higher than 500 °C. Also they reported that Fe₃O₄/Fe nanocomposites which are obtained through decomposition after annealing in 300 °C, have higher magnetic property[6]. In other research, Ding et al., indicated that ball milling of FeCl₃+Ca(OH)₂ and FeCl₃ can leads to forming FeOOH mixture that after annealing in 200°C or higher temperatures converts to hematite nanoparticles with dimension of 20–50 nm [7]. Goya, puts the Fe₃O₄ micron powder with average particle size of 0.5micrometer in planetary ball mill model Fristch Pulverisette4 in presence of methanol. He changed the weight ratio of magnetite powder to the total weight of powder and methanol in his experiments. He synthesized nanoparticles with particle size of 7–10nm[8]. Zdujić et al., studied the behavior of α -Fe₂O₃ nanoparticles in air and oxygen atmospheres using planetary ball mill. They observed that α -Fe₂O₃ is completely converted to Fe₃O₄ and then converted to Fe_{1-x}O during the time[9]. Wang et al., synthesized hematite nanoparticles by ball milling of α -FeOOH powder for 90hours with high-energy mill. Their results showed that after 90 hours ball milling with speed of 200 rpm, hematite nanoparticles will be formed with grain size of 20 nm. The reaction mechanism involves the reduction of α -FeOOH particles during the ball milling process and finally their conversion to superparamagnetism α -FeOOH particles. The separticles are dehydrated through a mechanochemical process and convert to hematite nano particles during ball milling. Snachez et al. studied the magnetic and structural properties of pure hematite submitted to mechanical milling in air and ethanol[10]. Randrianantoandro et al., investigated the direct phase transformation from hematite to maghemite during high energy ball milling. They showed that maghemite can be produced directly from (α -Fe₂O₃) hematite after 48h[11]. Woo et al., synthesized rod-shaped hematite and maghemite nanoparticles with diameters of 5nm and lengths of 16 and 17nm by a newly designed sol–gel mediated reaction. The hematite nanorods showed ferromagnetic behavior from 5 to 300K, while the maghemite nanorods exhibited superparamagnetic behavior with a blocking temperature at around 130K[12]. Akbar et al., synthesized Fe₂O₃ nanoparticles of different sizes ranging from 22 to 56nm chemically by a modified sol-gel method. They observed that the average size of the particles decreases with increased annealing temperature of the gel and decreases with the increase in the concentrations of the citric acid. The annealing temperature affects the relative fractions of the two phases and consequently the magnetization of the particles[13].

In this paper, the structural characteristics and magnetic properties of hematite nanoparticles synthesised by wet ball milling have been investigated. The final products have been characterised by chemical analysis, SEM, TEM and XRD. Magnetic properties were measured by vibrating sample magnetometer (VSM). The crystallite size was evaluated by XRD patterns using Scherrer method. The effect of milling time, weight ratio of methanol to powder (R) and precipitation time of solution containing synthesized nanoparticles on particles size has been investigated.



**Esmaeil Koohestanian et al.****Experimental****Material**

α -Fe₂O₃ powder with 99.99% purity and average particle size of 5 μ m was used as the starting material. Methyl alcohol (CH₃OH) having purity higher than 99% was used as carrier liquid. Both chemicals were provided by Germanys' Merck Company.

Experimental setup

Mechanochemical treatments were performed in a Fritsch Pulverisette 5 planetary ball-mill. Different weights of hematite (α -Fe₂O₃) powder (according to the corresponding run of experiments) were dispersed in carrier liquid (CH₃OH). Hardened steel vial were charged with 60 mL of the hematite powder and methyl alcohol mixture. The vial was loaded in a glove box filled with argon. It was sealed with an O-ring to minimize contaminants during milling. Ball mill process was performed at a speed of 300 rpm and grinding durations of 10, 30 and 60 h. In order to avoid an excessive temperature rise within the vial, 60 min ball milling was followed by a 10 min cooling interval. Milling parameters are summarized in table 1 that R is mass of methanol to mass of hematite powder and is function of balls weight ratio to powder (BPR).

Characterization**X-Ray Diffraction (XRD)**

X-ray diffraction (XRD) measurements were performed in a X-ray diffractometer Philips Analytical X-Ray BV using a Cu K α radiation ($\lambda=1.5406\text{\AA}$) in the 2θ range from 20 to 80°. The Fe₂O₃ crystallite size (D) was determined using the Scherrer formula [14]:

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos\theta} \quad (1)$$

where k is a constant and generally assumed to be 0.9, λ is the wavelength of Cu K α radiation, θ is half of the diffraction angle, and β is the full-width at half maximum intensity (in Radian).

Scanning Electron Microscopy (SEM)

Particles morphology was investigated using kyky-EM3200 scanning electron microscope (SEM) at accelerating voltage of 25 kV. All the specimens were sputter-coated with gold in a sputter coater.

Transmission electron microscopy (TEM)

The average particle size and morphology of the samples were observed by TEM using a JEOL model JEM-1600F AT 80 KV



**Esmaeil Koohestanian et al.****Vibrating sample magnetometry (VSM)**

Magnetic properties were estimated at room temperature using a vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Co., Iran).

RESULTS AND DISCUSSION**The structural and morphological characteristic of nanoparticles****XRD analysis of films**

X-ray diffraction patterns of the raw powders and powders in the milling vessel during 10, 30 and 60 h and R=8 and 30 are shown in Fig. 1. All Bragg peaks of the XRD patterns showed only the hematite reflections, indicating that there are no phase changes during the milling. X-ray diffraction line broadening was influenced by the crystallite size[3]. X-ray diffraction results indicate broadening and reduction of peaks intensity with increasing the duration of ball milling. Broadening of peaks by increasing the duration of ball milling indicates that the grains size is reduced. According to the results, in early step of ball milling process, the reduction of grains size was faster and by increasing the time, it slowed down. By increasing the ball milling time from 10 to 30 and 60h, peaks are broadened and grains size will be smaller. As grains size gets smaller, grains boundary increases and the number of atoms at the surface increases. Therefore the number of free bonds in atoms increases and the average force per atom from other atoms decreases and this makes the lattice strain increase in smaller grains.

The results reveal that in ball milling, the crystallite size of hematite is decreased by milling time and R value. The evaluated crystallite size of the obtained samples by the Scherer equation (milled for 60 h and R=30) was about 30 nm. In addition, an increase in the lattice strains was observed with increasing the milling time. With increasing milling time, the diffraction peaks broaden and their relative intensity decreases, thus the grain size decreases and the lattice strain increases. These results are in agreement with previous reported results [3, 15]. Obtained results are summarized in table 2.

SEM analysis of films

SEM micrographs of the samples before and after milling are shown in Fig. 2. As it is seen, not milled powder(Figs. 2a & 2b) has a non-homogeneous structure and particle size distribution. After milling and particle size reduction of samples, complete homogeneity is observable. In these figures (Figs. 2c to 2h), fine sub-rounded α -Fe₂O₃ particles with limited particle size distribution can be observed. With increasing milling time, a significant reduction in particle size due to both an increase in the number of collisions and increase the energy of balls during wet ball milling is evident. Morphology of this particles are spherical or semi spherical. Due to the high surface to volume ratio in spherical shape it is the best morphology for different applications.

Fig. 3 shows that the size of the synthesized nanoparticles decreases with increasing R. Since R is a function of ball to powder weight ratio (BPR), by increasing of this ratio, a more energy is applied to the powder and particles become finer.

In Fig. 4, SEM images of milled samples for 30 hours and weight ratio of methanol to powder R=8 have been shown. Both images are related to identical synthesized samples that only their precipitation time is different. Comparison of the images shows that with increasing precipitation time, particles size will be smaller and their distribution will be more uniform.





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TEM analysis of films

In order to determine the size and morphology of the prepared nanoparticles Transmission Electron Microscopy (TEM) images were recorded. The TEM images of α -Fe₂O₃ nanoparticles are shown in Fig. 5. As it is seen, the synthesized hematite nanoparticles have a spherical morphology with average particle size of 12nm. It is noteworthy that to prepare samples for TEM analysis, the ultrasonic homogenizer was used, that's why the particles appear more homogeneous in TEM images compared to SEM ones.

Magnetic properties

Diminution in magnetocrystalline anisotropy due to smaller average crystallite size, leads to an easier rotation of the magnetic vector. When the grain size is larger than the magnetic exchange length L_{ex} , the coercivity depends on the crystallite size and the magnetization saturation as [16]:

$$H_c \approx 3 \sqrt{\frac{kT_c K_1}{\alpha M_s D}} \tag{2}$$

where H_c is the coercivity, D is the crystallite size, M_s is the saturation magnetization, K_1 is the magnetocrystalline anisotropy constant, T_c is the Curie temperature, k is the Boltzmann constant and a is the lattice constant. L_{ex} can be expressed as [17]:

$$L_{ex} = \sqrt{\frac{A}{K_1}} \tag{3}$$

where A is the exchange stiffness constant. At the grain sizes above L_{ex} the grain boundaries result in the pinning of the domain walls [18]. Increasing the volume fraction of grain boundaries through grain refinement impedes the domain walls movement, thereby increasing the coercivity. On the other hand, when the grain size is smaller than the magnetic exchange length, domain wall effect diminishes and each grain behaves as a single domain. Based on the random anisotropy model, the coercivity can be expressed as [19, 20]:

$$H_c = \frac{P_c K_1^{\frac{1}{2}} D^{\frac{3}{2}}}{\mu_0 M_s A^{\frac{1}{2}}} \tag{4}$$

where P_c is a constant of the order of unity, μ_0 is the permeability of free space and A is the exchange stiffness constant.

Fig. 5 shows the hysteresis curve for samples 1 and 9 from hematite powder in different conditions BM and ± 8500 Oe applied field. Noticing the figure, it can be observed that the saturation magnetizing rate has been an increase in BM time. Generally speaking the hysteresis curve has been narrowed down because of micrograins effect (random anisotropy model) as a result of increase in BM time to 60h. The transformation of this curve with increasing of BM time shows dependence of magnetic properties in microstructure. In fact, compared to a microstructure material, in a nanocrystal structure, the number of magnetic fields in each particle has been decreased and thus, the interactions of magnetic moments among atoms and their magnetic effectiveness have been increased, and also exchangeable interaction among magnetic fields has been decreased and as a result, the material is magnetized with low energy



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[21]. Generally, different factors affect the coercive force in BM, including: internal microstrains, grossness, cavities and faults obtained inevitably during BM process, and can increase coercivity force which is one of the magnetic properties, sensitive to microstructure[22]. On the contrary in this step, the effect of micrograins which is explainable by random anisotropy model is a predominant mechanism. As it was already mentioned, according to Herzer model, when grains size is smaller than magnetic exchange length (L_{ex}), there is a direct relation to grains size (eq. 4) thus the coercive force decreases by decreasing of grains size which is one of the advantages of nanocrystal and amorphous material. In other words, the crystals which have oriented randomly don't resist against Bloch walls motions and coercivity decreases a little[19].

CONCLUSIONS

In wet ball milling procedure that is a low cost method to produce mass of nanoparticle, because of both cold welding and fracturing, the final product will have wide range of distribution (from nanometer to micrometer) which is a basic defect of BM. Interestingly in this study, it is obtained that more uniform particles in a limited range and selective distribution using of wet ball milling and giving optimum precipitation time for separation various phases of synthesized nanoparticles with different sizes. Furthermore, another BM problem is pollution of powder because of mill grind components (ball and vial mill). As BM was performed in wet medium, friction between mill grind components and vial mill were decreased. Moreover, because of desirability of vial and used balls, there was no deviation in XRD results hence one of other faults in material synthesis process through BM and by taking into consideration of special plans. In addition, XRD analysis results confirm that wet ball milling of hematite micrometric powder processing can be used to synthesize hematite nanoparticles without oxidation and phase transformation. However, using XRD and TEM, the average size of the hematite nanoparticles was estimated about 30 and 12 nm, respectively that put them into the category of superpara-magnetism iron oxides ultrafine particles that their diameter is less than 50 nm. Results of VSM also show that magnetic saturation increases as a result of BM time. Morphology of these particles were spherical or semi spherical. Results of SEM and XRD shows that influence of milling time parameter is more than other parameters in shape and size of synthesized particles. Comparing our findings with other studies, confirms the ability of wet ball milling method for Synthesis of metallic nanoparticles more economically than the other methods such as sol-gel.

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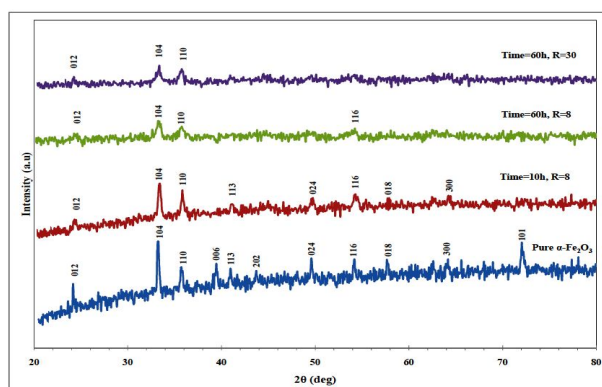


Fig.1. XRD patterns of the powders in the milling vessel milled for various condition of milling at fixed speed of milling of 300 rpm.





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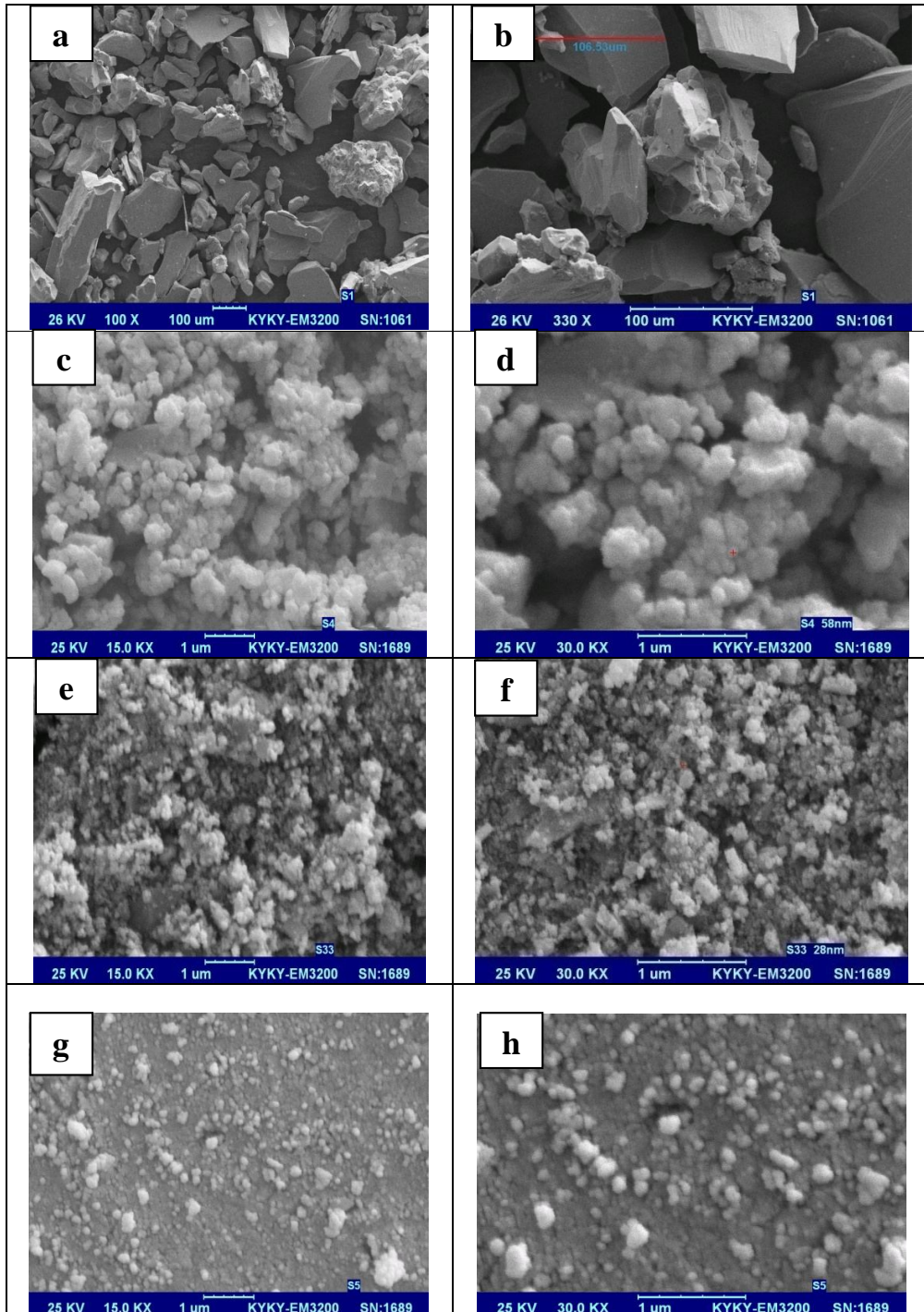


Fig. 2. SEM images of α -Fe₂O₃ powder for R=15 and different milling time: (a) as received; (b) as received at high magnification; (c) milled for 10 h; (d) milled for 10 h at high magnification; (e) milled for 30 h; (f) milled for 30 h at high magnification; (g) milled for 60 h; (h) milled for 60 h at high magnification.





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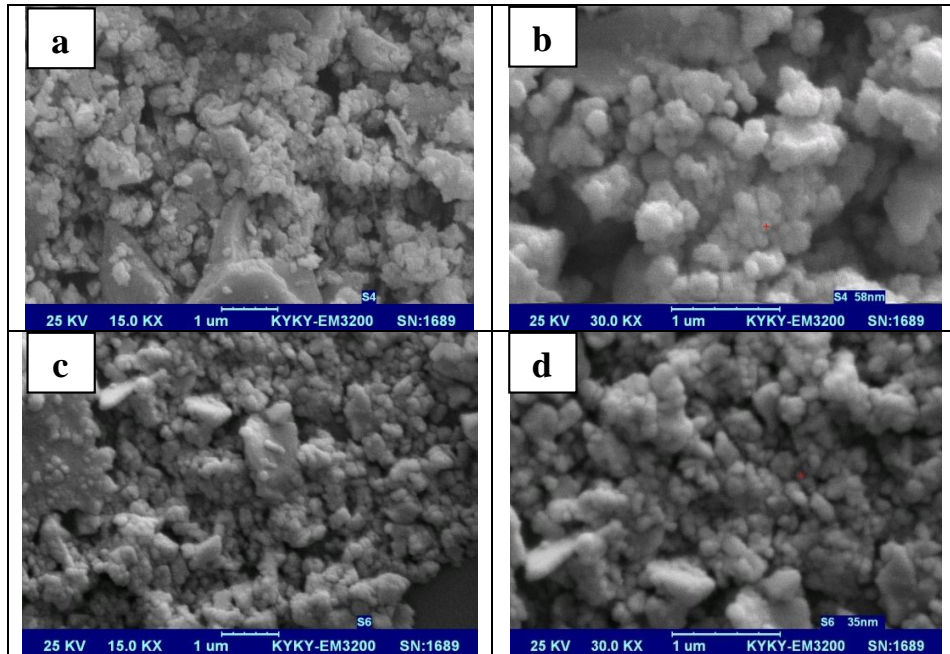


Fig. 3. SEM images of α -Fe₂O₃ powder for 10 h milling time and different amount R: (a) R=15; (b) R=15 at high magnification; (c) R=30; (d) R=30 at high magnification.

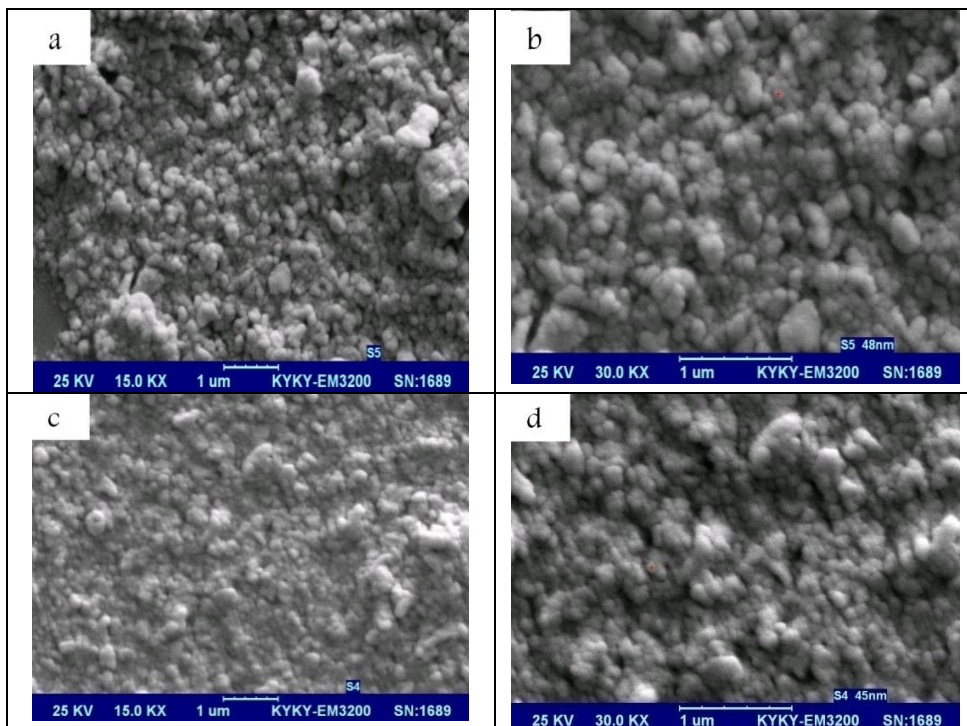


Fig.4. SEM images of α -Fe₂O₃ powder at 30 h and R=8 for different precipitation time: a) 45 min; (b) 45 min at high magnification; (c) 75 min; (d) 75 min at high magnification.





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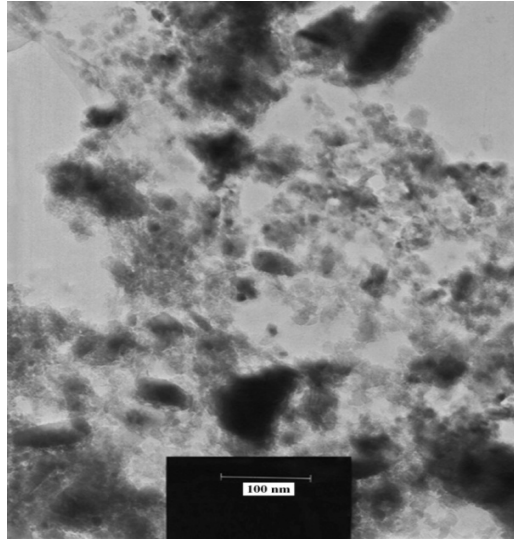


Fig. 5. TEM image of α -Fe₂O₃ powder for 60 h milling time and R=30.

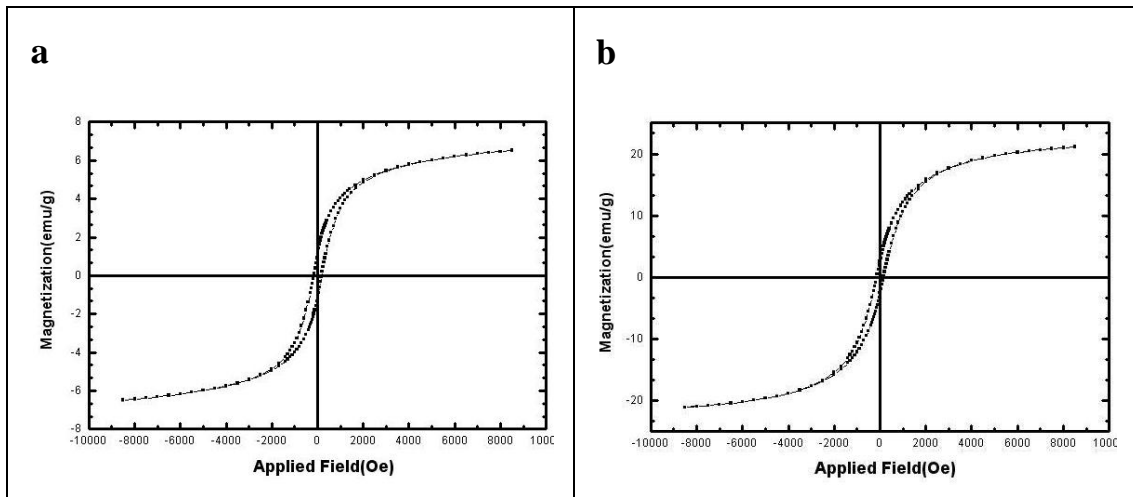


Fig. 6. Hysteresis loops of α -Fe₂O₃ powder at: a) 10 h milling time and R=8; b) 60 h milling time and R=30.





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Table 1: Milling parameters

Sample Number	R (g fluid/g powder)	Duration of Milling (h)
1	8	10
2	15	10
3	30	10
4	8	30
5	15	30
6	30	30
7	8	60
8	15	60
9	30	60

Table 2: Lattice strain and crystallite size of synthesized nanoparticles in different ball milling conditions.

sample	Raw powder	1	8	9
Milling time (h)	0	10	60	60
R (g fluid/g powder)	-	8	8	30
Crystallite size	5 μ m	40 nm	30 nm	30 nm
Lattice strain (%)	0.259	0.302	0.400	0.401





Comparison between Experimental and Theoretical Heat Losses on Thermosyphon Pipe

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ABSTRACT

Thermosyphon is a simple type of heat pipe has many applications in industries. An important application of it is using thermosyphon heat exchanger for recovering waste heat from stacks. Recovering waste heat is very important due to energy crisis and air pollution reason. Many factors effect on heat transfer of thermosyphon, such as Filling Ratio, heat loss and overall heat transfer coefficient. In this paper the thermal performance of a copper thermosyphon with outside diameter of 22mm and 620mm length were investigated. Filling ratio of 60 percent is an appropriate amount of thermosyphon. Thermosyphon efficiency was increased to 300 W heat input, and for higher temperatures it remains almost constant. Rate of theoretical and experimental heat loss from evaporator section are 5.9 and 7.5 W. Waste heat calculated according to the theoretical and experimental had acceptable difference.

Key words: Thermosyphon, Filling Ratio, Heat Loss

INTRODUCTION

Thermosyphons and heat pipes have been applied in many ways since their introduction in 1964.

A heat pipe consists essentially of an evacuated container within which a wick may be inserted and to which a small amount of working fluid is supplied. When energy is applied to the evaporator section, a part of the working fluid is vaporized. Soon the interior of the container is saturated with the pure vapor. As the walls of the chamber are slightly cooler on the condenser side due to heat extraction, some of the vapor condenses, thereby releasing the latent heat of





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condensation. The condensate is trickled back to the evaporator by gravity and/or the wick, thus completing the cycle as shown in Figure 1.

A gravity-assisted heat pipe without a wick is frequently called a two-phase closed thermosyphon. The length of the thermosyphon is divided into three parts: evaporator section, adiabatic section and condenser section, as shown in Figure 2.

Thermosyphons have a lot of advantages. Some of these are:

Simplicity of design and manufacturing.

Small end-to-end temperature drops.

Extremely wide temperature application range (4-3000K).

Ability to control and transport high heat rates at various temperature levels.

Low cost and efficient heat transport equipment [1-7].

Experiments

Thermosyphon tested a copper tube inner diameter of 19.2 mm and outer diameter of 22mm and 620mm length is formed. At the top of the tube, a copper tube diameter of 41.3 mm and 240 mm length in the center of the tube has been having an inlet and outlet duct for water passes. The two ends of the main tube thermosyphon are covered by brass caps. In the middle of the brass caps a thin copper tube length of 40 mm has been to create a vacuum in the system and also the fluid injection is used. Thermosyphon consists of two parts:

Evaporator and adiabatic section at the bottom of thermosyphon and insulation of rock wool is placed around them is their length are 380 mm. Condenser section is located above the center tube of the tube located around the area, and its length is 240 mm.

In evaporator and adiabatic region 5 bush brass is installed to connect the thermocouples are used thermosyphon body. In thermosyphon two parameters are important:

Filling Ratio $(F.R. = \frac{V_f}{V_e} = \frac{L_f}{L_e})$ is the ratio of the volume of working fluid filling the evaporator volume.

Aspect Ratio $(A.R. = \frac{L_e}{D})$ which is the ratio of length to diameter of the thermosyphon in evaporator section.

Experiments on thermosyphon available with different filling ratio of 60, 70, 80 and 90% and the aspect ratio 9.8 for working fluid water have been made. Temperature on different parts of the thermosyphon by a thermocouple is measured. The experiment must be electrically heated with electrical insulation is covered with a closed system is entered on the total heat flux. The thermocouple in the bushes close and rock wool insulation is placed around the evaporator and adiabatic section. To start testing the thermosyphon vacuumed with laboratory vacuum pump then the working fluid is injected. Thermosyphon according to figure 3 is closed.

After equilibration of the system input voltage, condenser inlet water temperature, water temperature output from the condenser, evaporator and adiabatic surface temperature, resistance heating elements, insulation and temperature at three points of the outer wall of the thermosyphon two points located at the condenser is recorded. The results obtained in the analysis of the graph in the relations below, is shown.





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$$Q_{in} = \frac{V^2}{R} \quad (1)$$

$$Q_{out} = \dot{m}c_p\Delta T \quad (2)$$

$$\Delta T = T_i - T_o \quad (3)$$

$$T_{ave} = \frac{T_i + T_o}{2} \quad (4)$$

$$T_f = \frac{T_\infty + T_{ave}}{2} \quad (5)$$

$$Q_{Loss(Experimental)} = Q_{in} - Q_{out} \quad (6)$$

$$Q_{Loss(Theoretical)} = Q_{convection} + Q_{radiation} \quad (7)$$

$$U = \frac{Q_{out}}{T_e - T_c} \quad (8)$$

$$T_e = \frac{T_1 + T_2 + T_3 + T_4}{4} \quad (9)$$

$$\varepsilon(\%) = \frac{Q_{out}}{Q_{in}} \times 100 \quad (10)$$

Theoretical analysis and experimental results in terms of heat loss and heat transfer coefficient of the evaporator or condenser temperature difference of heater or electrical input powers are given. In the analysis of thermal load of thermosyphon heat loss from the condenser and evaporator of the thermosyphon, which is the sum of losses, respectively, are examined.

Heat loss in condenser section

Due to the lack of insulation on the condenser section and the heat transfer between the water and the laboratory environment, there is heat loss in the condenser section. Specifications of condenser section of thermosyphon in these experiments are shown in Table 1.

Mass flow, \dot{m} and heat output, Q_{out} are calculated as follows:

$$\dot{m} = \frac{995 \times 70 \times 10^{-6}}{15} = 4.64 \times 10^{-3} \text{ kg/s}$$

$$Q_{out} = 4.64 \times 10^{-3} \times 4178 \times (34.5 - 26) = 164.9 \text{ W}$$





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Outer wall temperature of the condenser, the condenser inlet and outlet water temperature of the medium is assumed. The value according to Eq. 4 is 30.25 oC. The average temperature of the outer wall temperature of the condenser and temperature of the air on the outer wall of the condenser is considered film temperature according to Eq. 5 the value is 28.7 oC.

Nusselt number in free convection flow on a vertical cylinder is calculated from the following equation [11].

$$Nu_L^{1/2} = \left\{ 0.825 + \frac{0.387 Ra_L^{1/6}}{\left[1 + \left(0.492 / Pr \right)^{9/16} \right]^{8/27}} \right\} \quad (12)$$

Heat transfer coefficient from equation 13 obtained.

$$h = Nu_L \frac{k}{L} \quad (13)$$

Condenser section heat loss is calculated from the following equation.

$$Q_{Loss} = hA\Delta T \quad (14)$$

Thus, the thermal losses in the condenser section approximately 0.1 % of the energy input to the electric heater are calculated. Waste heat to the condenser (that is test condition) were insignificant compared to the input power and can be ignored.

Heat loss in evaporator and adiabatic section

Since almost completely insulated evaporator end cap, there is no other waste from the external wall insulation only heat loss from convection and radiation are two ways. To calculate the heat loss in the evaporator and adiabatic section, insulated external wall temperature T_w is measured by a digital thermometer. Mean temperatures were measured at three points separate the 70, 200 and 300 mm end pipes have been. Specifications of evaporator and adiabatic section of thermosyphon in these experiments are shown in Table 3.

$$T_f = \frac{T_\infty + T_{w_{ave}}}{2} \quad (15)$$

Thermal properties of air and thermal calculation of used thermosyphon for evaporator and adiabatic section are shown in Table 4.

Since the insulator length 38cm, 13cm in diameter and 0.155m² of the surface heat losses through free convection heat transfer is calculated using the following equation:

$$Q_{conv} = hA\Delta T \quad (16)$$





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The radiation loss rate obtained by the following equation:

$$Q_r = \varepsilon \sigma A (T_w^4 - T_\infty^4) \quad (17)$$

The rate of theoretical heat loss from evaporator section to input energy to an electrically heater is 3.5%. The results are compared with experimental methods.

$$Q_{Loss(Theo)} = Q_c + Q_r = 5.9 \text{ W}$$

$$Q_{Loss(Exp)} = Q_{in} - Q_{out} = 172.4 - 164.9 = 7.5 \text{ W}$$

The good agreement between theoretical and experimental results is made [12-15].

DISCUSSION AND CONCLUSIONS

In this study, the thermal performance of thermosyphon copper tube outer diameter 22mm and length 620mm with water as the working fluid has been studied experimentally. Thermosyphon heat transfer coefficient distribution plots of the evaporator and condenser temperature difference between the two parts plotted in Figure 4, the distribution of heat transfer coefficient based on the average temperature in the evaporator section in Figure 5, the distribution of efficiency in Figure 6 and distribution of heat loss in Figure 7 is shown [16-18].

According to the diagrams obtained under following results:

Overall heat transfer coefficient between the evaporator and condenser section is directly related to increasing temperature difference. Filling ratio of 60 percent is an appropriate amount of thermosyphon. Because of the temperature difference less overall heat transfer coefficient is higher.

Heat transfer coefficient in the length of thermosyphon increases with increasing mean temperature evaporator section. Also in this case the filling ratio of 60% is a good result.

Thermosyphon efficiency was increased to 300 W heat input, and for higher temperatures it remains almost constant.

Convective heat loss in the condenser section and the minimal amount of power that can be ignored.

The rate of heat loss from insulated outer walls of the evaporator section is to both convection and radiation. Which is 3.5% of the input energy into electrical heater and a considerable amount

Waste heat calculated according to the theoretical and experimental, acceptable difference. In this case, making use of the thermosyphon, heat pipe and heat exchanger, is effective for industrial applications.

NOMENCLATURE

Q_{in} : Heat input

Q_{out} : Heat output





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Q_{Loss} : Heat loss

T: Temperature

C_p : Specific heat of water

ΔT : Differences temperature of water passing condenser

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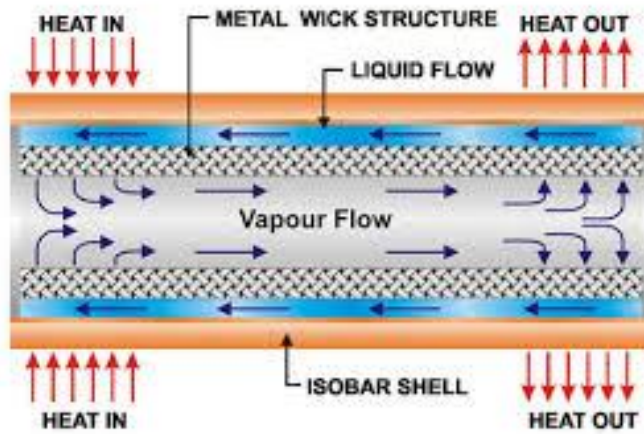


Figure 1: The schematic description of a heat pipe

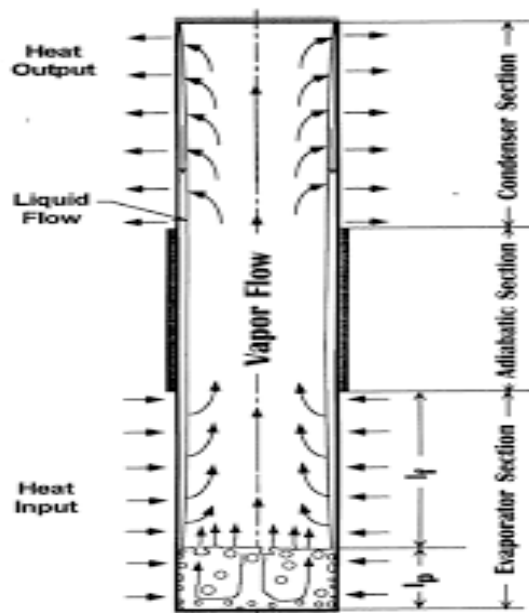


Figure 2: Schematic of a two-phase closed thermosyphon





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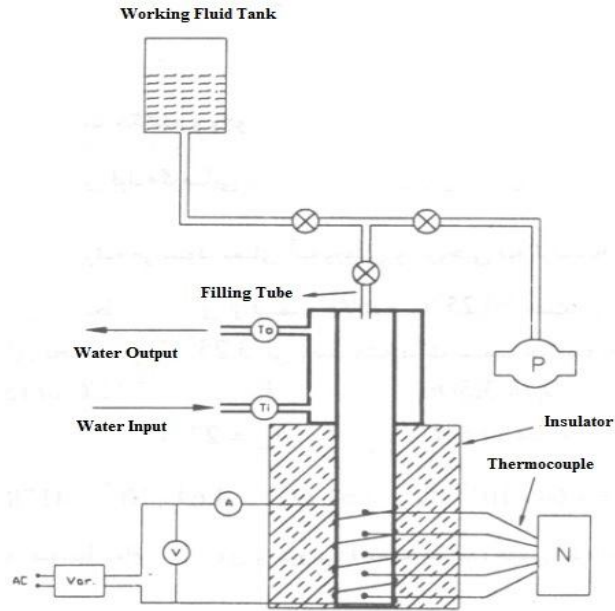


Figure 3: The test circuit (P: Vacuum pump, N: Temperature indicator, A: Ammeter, V: Voltmeter, Var: Variable Resistance)

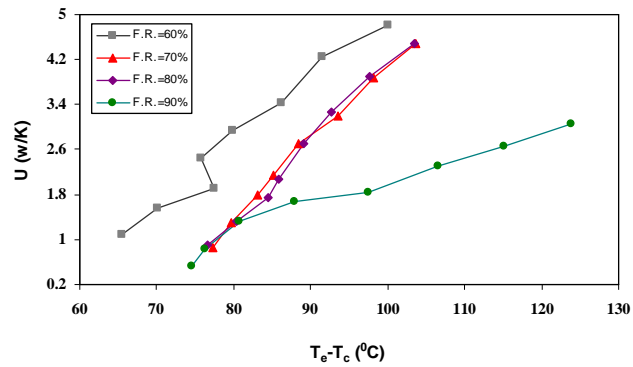


Figure4 :Distribution of overall heat transfer coefficient between the evaporator and condenser temperature difference of thermosyphon





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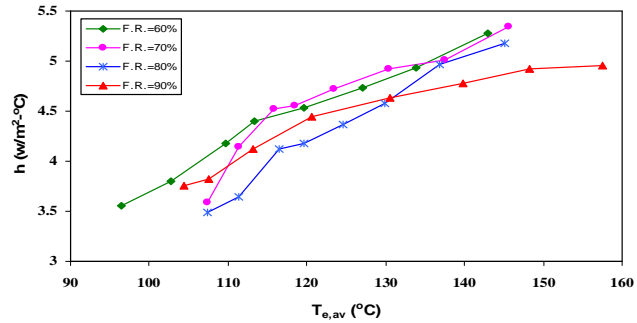


Figure 5: Distribution of thermosyphon heat transfer coefficient to mean temperature of the evaporator section

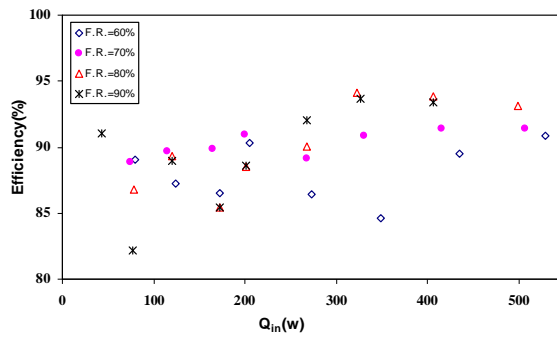


Figure6: Distribution efficiency in terms of heat input to the evaporator section of thermosyphone

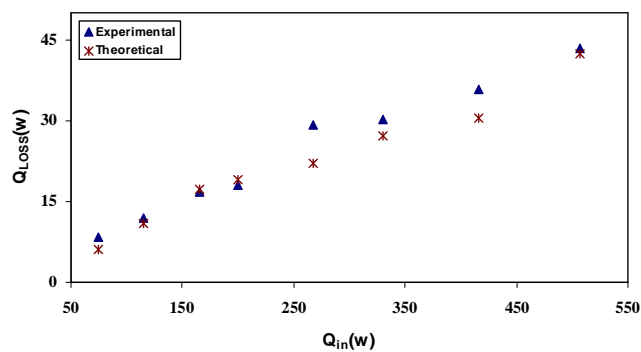


Figure7: Distribution of heat loss in by heat input to the evaporator section in both theoretical and experimental





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Table:1 specification of condenser section of Thermosyphon

Parameters	Units
Working fluid	water
Filling Ratio, F.R.	90 %
Aspect Ratio, A.R.	9.8
Voltage	100 V
Resistance	58 Ω
Heat input, Qin	172.4 W
Specific heat water, CP	4178 J/kg. oC
Density, ρ	995 kg/m ³
Inlet water temperature, Ti	26 oC
Outlet water temperature, To	34.5 oC
Environment temperature, T∞	27 oC
Average temperature of water passing condenser, Tave	30.25 oC
Differences temperature of water passing condenser, ΔT	8.5 oC
Diameter of condenser section, Dc	35 mm
Length of condenser section, Lc	167 mm
Water volume outlet from condenser section	70 cc at 15 sec
Mass flow, <i>ṁ</i>	4.64 ×10 ⁻³ kg/s
Heat output, Qout	164.9 W
$Q_{Loss(Experimental)} = Q_{in} - Q_{out}$	7.5 W

Table: 2 thermal properties of air and thermal calculation of used thermosyphon for condenser section

Parameters	Units
Film temperature, <i>T_f</i>	28.7°C
Thermal diffusivity, α	$23.0032 \times 10^{-6} \frac{m^2}{s}$
Cinematic Viscosity, ν	$16.232 \times 10^{-6} \frac{m^2}{s}$
Thermal conductivity, K	$26.552 \times 10^{-3} \frac{W}{m.K}$
Prandtl number, Pr	0.7065
Volumetric expansion coefficient, $\beta = \frac{1}{T_\infty}$	$\frac{1}{27 + 273} = 3.33 \times 10^{-3}$
Rayleigh number, <i>Ra_L</i>	1.37×10^6
Nusselt number, <i>Nu</i>	18





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Heat transfer coefficient, h	$2.862 \frac{W}{m^2 \cdot ^\circ C}$
Heat loss, Q_{Loss}	0.17W

Table :3specification of evaporator and adiabatic section of Thermosyphon

Parameters	Units
Length of evaporator section, L_e	188mm
Length of evaporator and adiabatic section, L_e+L_a	380 mm
Temperature of external wall insulation in point 70 mm, T_{w_1}	38.1°C
Temperature of external wall insulation in point 200 mm, T_{w_2}	40.6°C
Temperature of external wall insulation in point 300 mm, T_{w_3}	35.4°C
Environment temperature, T_∞	28.5°C
Average temperature of external wall insulation, $T_{w_{ave}}$	38.03°C

Table: 4 thermal properties of air and thermal calculation of used thermosyphon for evaporator and adiabatic section

Parameters	Units
Film temperature according to Eq. 15, T_f	33.3°C
Thermal diffusivity, α	$23.64 \times 10^{-6} \frac{m^2}{s}$
Cinematic viscosity, ν	$16.66 \times 10^{-6} \frac{m^2}{s}$
Thermal conductivity, K	$26.87 \times 10^{-3} \frac{W}{m \cdot ^\circ C}$
Prandtl number, Pr	0.706
Rayleigh number, Ra_L	43.16×10^6
Nusselt number, Nu	47.59
Convective heat transfer coefficient, h	$3.37 \frac{W}{m^2 \cdot ^\circ C}$
Convection heat loss, Q_{Conv}	4.98W
Stefan Boltzmann constant, σ	$5.67 \times 10^{-8} W / m^2 \cdot K^4$
Emission factor, ϵ	0.087
Radiation heat loss, Q_r	0.85 W
$Q_{Loss(Theoretical)} = Q_{convection} + Q_{radiation}$	5.9 W





An Approach to Employees' Empowerment and its Role in Business Excellence

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ABSTRACT

In recent years, a large part of time and capital of leading organizations have dedicated to attention to human resources. Nowadays, smart managers are aware that the more they invest in the development of human resources, the higher the efficiency and competitive advantage of their organizations will be. In Iranian administrative system, employee empowerment is taken into consideration so that it could be found in the administrative development and transformation policies and programs and state services management law. This paper aims to study the role and status of empowerment of human resources in Iranian administrative system. The result obtained is that in Iranian administrative system, increased productivity and efficiency of operations is possible through increasing and updating knowledge, insight and skills of human resources and in other words by empowering employees.

Empowerment is a constant movement with increasing importance because now the basis of business development is to come up with social changes, technological achievements and competitive environment demands. The main wealth of any organization is made up its employees in the form of knowledge, skills, and their motivations. Such a wealth is important because in the last decade and perhaps in the next century the main source of competitive advantage won't be new technology, but initiative, creativity, commitment and capability of workforce. Organizations need people who can make the best use of high technology, find innovation and improve their products and services.





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Keywords: empowerment, organization excellence, employees, productivity, administrative transformation

INTRODUCTION

In today's stressful business environment, managers face with multiple challenges. They should guide and lead their organizations such that they can survive in the face of tough competitors. Technological changes and innovation in product on one hand and management complexity on the other hand have left the only choice which is reliance on the main capital, human resources. Accordingly, employees become more and more important and the period of looking labor as a tool has spent. Believing in the ability of employees has led them to be as companions so managers have sought mechanisms to foster empowered people. More importantly, the measures considered by managers to empower themselves has been an effective movement to fulfill this mission. There is no doubt that in successful organizations, managers first empower themselves. Synergy of managers and employee empowerment may facilitate understanding and awareness of changes and taking step for quality of thinking has converted change management into transformational leadership. Meanwhile, individual, group and organizational learning is inevitable as a sustainable approach to empowerment of managers and employees. Enjoyment of learning for organization is associated with a sustainable competitive advantage. Organizations where analyst, activist and knowledgeable employees are fostered make the knowledge-oriented objective; the process putting people and society in dynamic and excellence direction.

The most important step in the process of employee empowerment is to provide an environment in which there is an opportunity for people to practice with a degree of authority, power and intrinsic motivation within employees. Many studies on empowerment show that the environment provides some opportunities for employees. Therefore, enabling environments provide opportunities and restrictive environments bring limitations for employees. It depends on the amount of influence exercised for business outcomes to be effective. If employees are empowered but don't have required influence, they still lack of possible effect of opportunity or environmental support. In other words, employees should have a sense that they are supported to be able to provide opportunities to influence in an effective manner; this environment and support can be created by suggesting an appropriate model (Aghayar, 2007).

The need for empowerment

The necessity of fostering employees who have self-management ability has caused human resources empowerment to attract the attentions of many management experts as a new paradigm.

Theses experts believe that both managers and employees benefit from the advantages of employee empowerment. On the other hand, by fostering motivated and enabled employees, empowerment allows managers to respond quickly and appropriately to the dynamics of competitive environment. Furthermore, in the current era empowerment is considered as a tool by which managers can manage today's organizations effectively (Jazini, 2006,7).

The reasons implying the need for empowerment can be summarized as:

Developments in data processing or information technology

Changes in performing management information systems-information technology and computer use may affect on organizations to eliminate the middle level.

The growing competition and as a result an increase in the need to meet customer demand

Personnel who have now a higher level of education and expectations

Generally at the community level and in particular an increase in democratization desire





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Emerging knowledge and human element as the most important source of competitive advantage and strategic look to human resources (human capital) (Amirkabiri, 2006, 351).

Therefore, to achieve the goals of organization requires effective management of these valuable resources. In this regard, growth, progress, prosperity and promotion of employee empowerment have attracted the attention of scholars and experts in recent years as employee empowerers. So to empower employees, the efforts should be done to foster employees who have self-management ability to both employees and managers will benefit. On the other hand, empowering motivated and enabled employees allow managers to respond more quickly and appropriately to dynamics of competitive environment (Jazini, 2006: 7).

Eventually, in addition to abovementioned, the reasons for choosing this subject can be stated as it is an up to date issue and organization willingness to use it to respect for the dignity of human resources and improvement of individual and organizational productivity.

Keywords of empowerment

The concept of empowerment

The first step in defining the concept of empowerment is designating its boundaries. Some believe that empowerment is giving power to employee. Others reject this and believe that since employees are a capital of knowledge and motivation so they by themselves have the power to work best; hence empowerment is defined as providing a context to release this potential power.

Terlacson defines empowerment as the process of interpreting employee performance from the situation and what they were told to do. According to Baruch, empowerment is not only making a new verbal, but an imaginative introduction of current trends of recent management science; it is a story of working with people and changing top-down management style the importance of which has increased by the introduction of new issues, such as reengineering and restructuring (Baruch, 1998).

Empowerment aspects

For the managers can empower others successful, they should create these five features in them. Successful empowerment means creation of the following features:

- A sense of competency (self-efficacy)
- A sense of having a franchise (self-organizing)
- A sense of efficacy (Personal accept of result)
- A sense of being meaningful or importance (be valuable)
- A sense of having trust

When managers can develop these five characteristics in others, they are empowered successfully. Empowered individuals can not only carry out their duties, they think about themselves differently. These five dimensions describe the difference.





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A sense of competency (self-efficacy)

In fact, the self-efficacy is the sense of individual's ability to perform their tasks with high skills. When people are empowered, they feel a sense of self-efficacy and feel that they have the necessary ability and skill to perform the job successfully. They feel personal superiority and believe that they can learn and grow to face with new challenges (Bines and Nanus, 1985). Some authors believe that this feature is the most important element of empowerment, because a sense of competency determines whether people will try to do a hard work and will have perseverance or not?

A sense of having a franchise

Empowered people are also feeling self-organizing. Whereas self-efficacy refers to the sense of ability, self-organizing attributes to the sense of having a franchise. Self-organizing means experience of feelings of chosen to run up and organize the person's activities. When people instead of being forced to do something, engaged in their duties voluntarily and knowingly, they feel they have a franchise (Deci et al., 1989).

A sense of efficacy (Personal accept of result)

Empowered people have a strong sense of personal control over outcomes, they believe that they can create change by influencing the environment in which they work or the results that are achieved. A sense of efficacy is the beliefs of an individual within a specified period of time about ability to produce better results.

A sense of being meaningful

Empowered people have strong feelings of being meaningful. They valorize their purpose, objectives or activities which they are employed, its ideals and standards are homogeneous with what they are doing, activity in their value system is important, take care about what they produce, and believe it. They have a sense of personal importance in their conflict and employment and as a result of employment in that activity, experience the link and personal relationship. Therefore, being meaningful refers to value-focused attitude. Activities infusing meaningfulness create a kind of purposeful feeling, emotion, or mission for individuals and provide a source of energy and enthusiasm for them rather than wasting energy and enthusiasm of the people.

A sense of having trust in others

Finally, empowered people have a sense of trust, they are sure that they will be treated fairly and equally. These people are sure that even as the subaltern, the end result of their work is not damaging but it would be justice and peace. Usually this feel means they are sure that the officers of authority or authorities will not damage or loss them, and will be treated impartially with them. In other words, trust means having a sense of personal security.

Indicators of Empowerment

Since empowerment is a long term process and senior managers can't observe its positive effects immediately, they need ways on which to assess whether empowerment plans move in the right direction or no? One way is to study the behaviors of empowered individuals compared with un-empowered ones. Table 1 refers to the behavioral characteristics.





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Empowerment history

The Empowerment term has been day motto in two decades of 1980 and 1990. In the past few years, many books and articles have referred to the concept of empowerment. Empowerment has roots in psychology, sociology and the sociology and religion that go back to decades, even centuries past. (Monavvarian, 2005).

Before this term would be current in management, it was used in above fields and also in the form of dative help to third world country. The writers of these fields have exploited the term of empowerment as meaning of making available of necessary resources and tools for individuals so that be invisible for them and make use of them in their interests direction (Monavvarian, 2005).

Since then, the term has been widely used in humanities. In the early stages there was no agreement on the definition of empowerment and in 1988 Conger & Kanungo took an important step to clarify this concept that it would be defined as motivational processes of employees. This approach later allowed such scholars as Thomas & Velthouse to suggest another operational definition of empowerment. Following the definition of Thomas & Velthouse, the term was used to measure validity and reliability. In psychology, the concept of "mastery motivation" was suggested which focuses on attempts done by people to master in dealing with world. (Khodadadi Nejad, 2002).

Similar concepts were introduced decades ago including "effectiveness motivation" which is an intrinsic motivation that makes things happen; "psychological reactance" which refers to the struggle for freedom from restrictions; "Motivation to master ", an effort to meet the challenges and overcome them; and "personal causation", the motivation to practice freely (Sheykhi, 1994).

In each of these studies, the concepts resemble to empowerment; the tendency to experience a sense of self-control, self-importance and self-liberation. In sociology, the concept of empowerment is the basis of most of movements and rights, for example, human rights in which people struggle for freedom and control of their personal situation and circumstances. Furthermore, most of literatures attacked social problems through social change primarily focused on group empowerment (Soleiman Poor, 2002).

It means that people make efforts for social changes in order to increase their access to an empowered state. Before this term would be current in management, it was used in field of political and social science, feminist view and also in the form of dative help to third world country was used. The writers of these fields have exploited the term of empowerment as meaning of making available of necessary resources and tools for individuals so that be invisible for them and make use of them in their interests direction (Sheikhi, 2004).

In management, the antecedent of using term of empowerment refer to industrial democracy and employees interfering in organizations decision making under various titles of team making, participation and total quality management. The latest changes that have been accomplished on this subject were named by employees' empowerment.

Empowerment is not a new concept. This concept has come in different forms in most of new scientific resources literatures of management. For example in 1950s, the scientific resource of management was full of such prescriptions as managers should have friendly behavior with their employees (human relationships). In 1960s, managers had to be sensitive as regard to employees needs (sensitivity training). In 1970s, managers had to ask employees helps (Employees involvement) and in 1980s, mangers had to organize a group and hold meetings (Soleiman Poor, 2002).





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Pursuing these subjects in 1990s and thereafter is indicative of that managers should learn that how expand empowerment. But in spite of emphasis on different forms of employees' involvement and empowerment, it is still not common in skills repertoire of most of managers so empowerment is very rarely found as advised.

Finally, humanities experts discussed empowerment from the following three viewpoints.

DISCUSSION AND CONCLUSION

In recent decades, employee empowerment has become one of the concerns of managers because managers' workload has increased rapidly. Therefore, managers should rely on their subordinates. In fact working conditions and competition more than anything else force managers to empower employees. So today employee empowerment is one of the most miraculous approaches to human resource development leading to the development of human resources and organization. Empowerment is a constant movement with increasing importance because nowadays the basis of business development is to come up with social changes, technological achievements and competitive environment demands and organizations need people who can make the best use of high technology, find innovations and improve their products and services.

Empowering human resources is a very efficient tool based on transformational attitude of management so that by employing it, organizations can take steps toward rapid development and growth. Since organizational change is human-centered, to achieve an acceptable level of organizational excellence, human resources should be promoted and developed intrinsically which is possible through the followings: Meritocracy system, career development system, job enrichment system, participation system, human resources rehabilitation system, behavioral rational system and creation of philosophical mentality. Employee involvement and empowerment is also a new technique to make human talents and abilities to be released in organizations that include four key components, power, information, knowledge and skill, reward.

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Table1: Indicators of empowerment

Characteristics of empowered employees	Characteristics of un-empowered employees
1. Have initiative in important situations and define problems in the ways that can better analyze and achieve better facilities	1. Waite for making decisions by superior that who has is responsible to address the problems so they are always waiting for the referendum
2. Are able to recognize opportunities in important situations such as when customer complaints and competitive threats increase	2. Are able to deal with problems effectively but can't recognize social opportunities
3. Are able to apply critical thinking skills, such as uncovering, testing assumptions and assessing reasons offered. They also able to offer strong reasons that their decisions and actions are within the framework of common goals	3. Accept information, evidence and conclusions offered by others particularly influential individuals quickly and without required investigations. Argue on the information they have, but they are not able to use this information in order to achieve common goals.
4. Work on the opportunities and identify them to be able to systematize activities, documentations, communication and information systems and identify and solve problems systematically, and finally modify or remove systems unable to add value to customer	4. Focus on individual improvement or team effectiveness, but are not able to understand problems. Able to give disposable solutions, but have difficulty to systematize them, rely heavily on existing systems even if these systems have lost their effectiveness
5. Try to optimize resources through cost reduction or even opportunities for investment in new fields (such as improvement process and high technology)	5. Turn their attention to the issue of resources only when they are obliged to do them by authorities
6. Are self-confident and think they are talented, creative and trusted.	6. Lack of self-confidence and think they do not have the necessary talent and creativity and may not be trusted.
7. Feel that they are well able to decide when and how to perform their duties	7. Feel incapable to choose how they do their works
8. Able to socialize both in functional groups and multitasking groups for making decisions and actions	8. Expect the efforts be made to reach consensus, but if it fails in this regard, resort to hierarchical authority





Solidified Floating Organic Drop Micro Extraction and Spectrophotometric Determination of Dextromethorphan in Water Samples

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ABSTRACT

In this study, Solidified Floating Organic Drop Microextraction (SFODME) followed by spectrophotometric determination was applied for determination of Dextromethorphan in water samples. For this purpose, the influence of different parameters affecting the procedure (type of extraction solvent, volume of extraction solvent, sample volume, NaOH concentration, extraction time, stirring rate and ionic strength) was evaluated in order to optimise the efficiency of the process. Subsequently, the linearity, detection and quantification limits, precision and applicability to real water samples were studied. Under the optimized conditions, an Enhancement Factor of 61.4, detection limit of 0.13 mgL^{-1} , and good relative standard deviation of $\pm 5.9\%$ at 1.0 mgL^{-1} were obtained. The method was successfully applied to the determination of Dextromethorphan in two tap water samples. Relative recovery of Dextromethorphan in Quchan tap water was 94.0% and for Esfarayen tap water was 92.0%.

Key words: Solidified Floating Organic Drop Microextraction, Spectrophotometry, Dextromethorphan.

INTRODUCTION

Dextromethorphan, ((+)-3-methoxy-17-methyl-(9 α , 13 α , 14 α)-morphinan), is used as an effective non-narcotic antitussive drug. It is a cough suppressant, which has a central action on cough center in medulla. It is an over-the-



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counter, highly effective antitussivedrug that is widely prescribed for temporary relief of cough caused by minor throat and bronchial irritation (such as flue and common cold) which it mainly acts on cough center in the medulla to treat mentioned respiratory disorders . Various analytical methods for the determination of Dextromethorphan and/or its metabolites in biological matrices have been reported, such as High Performance Liquid Chromatography (HPLC) combined with fluorescence detection or ultraviolet detection ,Capillary Electrophoresis(CE), Gas Chromatography(GC) coupled with different detectors and Liquid Chromatography–Mass Spectrometry (LC/MS).

Generally, analysis of pharmaceutical compoundsrequires preconcentration and cleanup of samplesprior to the instrumental analysis.The most common extraction techniques used in environmentalanalysis are Liquid-Liquid Extraction (LLE) andSolid-Phase Extraction (SPE) . LLE is labor-intensive,tedious, time-consuming and requires large volume oforganic solvents that are toxic to our health. SPEconsumes much less solvent than LLE, but can be relativelyexpensive . These drawbacks have led to thedevelopment of the miniaturization of sample preparationprocess, such as Solid-Phase Microextraction (SPME) Single Drop Microextraction (SDME) Liquid PhaseMicroextraction (LPME). SPME is a rapidand solvent-free extraction technique. However, the fiber isexpensive and fragile in the SPME. The droplet is instablein the SDME. LPME is a solvent-minimized samplepretreatment procedure. Nevertheless, some disadvantagesstill exist in the LPME. This technique is a simple, low-cost, and rapidprocedure requiring lower sample and extractant volumes. Different operational modes have developed fromLPME; the most commonly used of which are as follows:Single Drop Microextraction (SDME) [**Error! Bookmark not defined.**], HeadspaceSolvent Microextraction, Hollow Fiber-based LPME (HF-LPME), Directly Suspended Droplet Microextraction, Ionic Liquid-based Single-Drop Microextraction and Dispersive Liquid-Liquid Microextraction. In 2007, Khalili Zanjani andco-workers introduced a novel liquid phase microextraction called Solidification of Floating Organic Drop Microextraction(SFODME). This method has been successfully used for the extraction of organic compounds and metal ions from water and other matrices.In this method, small volume of an organic solvent with a melting point near room temperature (in the range of 10–30°C) was floated on the surface of aqueous solution. The aqueous phase was stirred for a prescribed periodof time, and then the sample was transferred into the ice bath. When the organic solvent was solidified (about 5 min), it was transferred into a small conical vial, and the melted organic solvent was used for analytes determination. The SFODME is a modified solvent extraction method which has the advantages of simplicity, short extraction time, minimum organic solvent consumption, achievement of high enrichment factor, and being very inexpensive.

Experimental**Reagents and samples**

The organic solvents(HPLC-grade) and sodiumchloride (analytical reagent grade) were purchasedfrom Merck (Darmstadt, Germany). Ultrapure water was prepared by a Milli-Qsystem (Bedford, MA, USA). Stock solutions(1000 mgL⁻¹) of Dextromethorphan wasprepared by dissolving an accurate mass of 0.1 g of this compound into a 100 mL flask and diluting to themark with methanoland stored at 4°C in the darkness. Standard solutions were prepared daily from the stock solutions by serial dilution withwater. Dextromethorphan, 1-undecanol, 1-dodecanol, and n-hexadecane were obtained from Merck (Darmstadt, Germany).

Instrumentation

All spectrophotometric measurements were carried out with a UUIKON-922 (Italy) double beam spectrophotometreequipped with 1 cm quartz matched microcell (with volume of 400μL).





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Extraction procedure

An aqueous solution (15mL) containing analyte (1.0mgL^{-1} in $\text{NaOH } 1.0\text{molL}^{-1}$) was introduced into a 25.0mL vial containing a magnetic stirrer. Then $30\mu\text{L}$ of an immiscible extracting solvent was added, the magnetic stirrer was turned on, and the solution was mixed for 15min. at 800rpm. In this step the analyte was extracted into organic solvent. After the extraction time was up, the sample vial was kept in an ice bath until the organic solvent was solidified (~5 min). The solidified solvent was then transferred into a conical vial with a glass spatula where it melted immediately. The extract was then diluted to $400\mu\text{L}$ with methanol and its absorption was measured at 216 nm against a reagent blank treated in the same way.

RESULTS AND DISCUSSION

In order to optimize the SFODME procedure for analysis of Dextromethorphan in aqueous samples different parameters such as type of extraction solvent, volume of extraction solvent, sample volume, NaOH concentration, extraction time, stirring rate and ionic strength were investigated.

In the SFODME method, the Enrichment Factor (EF) and the percent of extraction were calculated as described before

$$\text{Percent of extraction} = \left(\frac{C_o V_o}{C_{aq} V_{aq}} \right) \times 100 \quad (1)$$

$$\text{Enhancement Factor} = \frac{C_o}{C_{aq}} \quad (2)$$

where V and C are the volume and concentration, and the suffixes o and aq stand for the organic and initial aqueous phases, respectively. C_o was calculated from the calibration curve.

Type of extraction solvent

The selection of organic solvent is a critical factor in the development of an efficient SFODME procedure, as the physico-chemical properties of the solvent govern the distribution ratio and consequently the extraction efficiency of analytes. The extraction solvent should meet the following requirements: (a) lower density than water, (b) melting point near the room temperature (in the range of $10\text{--}30^\circ\text{C}$) [Error! Bookmark not defined.], (c) high boiling point and a low vapor pressure in order to reduce the risk of evaporation (d) low water solubility, (e) high extraction capability of target compounds and (f) it must not interfere in the analytical techniques used for the determination of analytes. According to these criteria, several extracting solvents, including 1-undecanol (mp $13\text{--}15^\circ\text{C}$), 1-dodecanol (mp $22\text{--}24^\circ\text{C}$), and n-hexadecane (mp 18°C) were investigated. Among the tested extracting solvents, 1-undecanol presented the best extraction efficiency. According to the LLE equation, the rate of transport of analyte into the organic phase is directly related to the interfacial area between the two liquid phases. As the melting point of 2-dodecanol is close to room temperature, it did not disperse properly in the aqueous solution; thus, its interfacial area was lower, and under a fixed extraction time, the amount of analyte extracted was lower. The lower extraction efficiency of n-hexadecane in comparison to 1-undecanol is due to its lower polarity. Thus, in the present study, 1-undecanol was selected as an extracting solvent because of its sensitivity, stability, low water solubility, low vapor pressure, and lower price.



**Mohammad Rouinfard and Mohammad Reza Abedi****Volume of extraction solvent**

In order to obtain the highest extraction efficiency, different extraction solvent volumes were examined within the range of 20–50 μL . The volumes of 1-undecanol smaller than 20 μL could not form droplets. When the volume of extraction solvent was increased from 20 to 50 μL , the analytical signal decreased. Hence, the volume of 1-undecanol was optimized at 20 μL for further studies.

Effect of sample volume

In the present article, the phase ratio of donor and acceptor solutions was optimized by changing the volume of the donor phase between 10 and 25 mL while the volume of acceptor phase was kept constant at 20 μL (Fig. 2). The results however indicate that the best extraction efficiency was obtained when 20 mL of donor phase was used. Commonly, the extraction efficiency can be improved by increasing the volume ratio of donor to acceptor phase, but a larger sample volume can be disadvantageous due to poorer mass transfers kinetics that result in a poor extraction efficiency. This would lead to a decrease in the microextraction output. Also, with an increase in the aqueous donor phase volume, organic phase dissolution may also be a concern.

NaOH concentration

The pH value plays an important role in this extraction method. A suitable pH can improve the extraction efficiency and reduce matrices interferences. Since Dextromethorphan is a basic nitrogenous compound, the basicity of the donor phase should be high enough to deionize this analyte, and consequently reduces its solubility in the solution. The effect of basicity of the sample on the extraction efficiency was studied by changing the sample NaOH concentration from 0.001 to 0.1 molL^{-1} . The maximum extraction efficiency of the analyte is achieved at the concentration of 0.05 molL^{-1} NaOH in the donor phase. The results are shown in Fig. 3.

Effect of extraction time

LLE is a type of equilibrium extraction, and the optimal extraction efficiency is obtained when equilibrium is established. In order to have good precision, sensitivity, and speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between aqueous and organic phases. The effect of extraction time on extraction efficiency was examined by varying the extraction time from 5 to 30 min. in the constant experimental conditions. Fig. 4 shows that there was a corresponding increase in analytical signal from 5 to 20 min., followed by a period of stability. An extraction time of 20 min. was selected as a reasonable compromise between enrichment factor and analysis time.

Effect of sample stirring rate

Sample stirring rate is one of the important parameters that improves the extraction efficiency and lowers extraction time. The agitation can regenerate a new sample solution surface, accelerating the mass transfer from the donor phase to the acceptor phase. In this study, the stirring rate was varied between 600 and 1000 rpm at a constant extraction time of 20 min. The extraction efficiency was found to increase as the stirring rate was increased up to 1000 rpm. Higher stirring rates were not used because the microdrop was spattered on the vial wall and damaged. Therefore, an optimum stirring rate of 1000 rpm was selected (Figure 5).



**Mohammad Rouinfard and Mohammad Reza Abedi****Effect of ionic strength**

Depending on the target compounds, the presence of salt in aqueous sample can potentially result in contrary effects: it may improve, not influence, or diminish extraction. In order to investigate the effect of ionic strength on the SFODME performance, several experiments were performed with different NaCl concentrations (0.0-10.0 %w/v) while keeping other experimental parameters constant. The results confirmed that salt addition up to a concentration of 5%w/v causes an increase in extraction efficiency. However, a further increase in NaCl causes a decrease in the extraction efficiency, possibly due to the decrease in analyte mass transfer from the aqueous solution into the organic drop. Therefore, in all the further experiments the NaCl concentration was adjusted to 5%w/v.

Method validation**Analytical features of the presented SFODME method**

The calibration curve was constructed by extracting the analyte from 20.0mL sample standard solutions. Under the optimum conditions the calibration curve was linear in the concentration range of 0.5-5.0mgL⁻¹ with a coefficient of determination (r^2) of >0.9982 (n = 3). The Relative Standard Deviation (R.S.D.) for 5 replicate measurements at 1.0mgL⁻¹ was $\pm 5.9\%$. LOD was determined using equation $3S_b/m$; where S_b is the standard deviation of the blank signal and m is the slope of calibration curve after extraction which was 0.13mgL⁻¹. Furthermore, The Enhancement Factor (EF) determined as the ratio of the slope of calibration curve with and without preconcentration was 61.4; however, a higher enrichment factor can be obtained by the use of a smaller microcell for the measurement of the absorbance of the analyte. The results have been presented in Table 1.

Application to real samples

The efficiency of the proposed method (SFODME-UV) was evaluated by the analysis of the real samples including two tap waters from Quchan and Esfarayen. The results indicated that no Dextromethorphan has been detected in analyzed samples using the proposed method. All the real water samples were spiked at concentration level (1.0 mgL⁻¹) to assess the matrix effect. The relative recoveries determined as the ratio of the real water sample outcome to that of the deionized water sample, are given in Table 2, which varies from 92.0% to 94.0%. This demonstrates that the matrices of the tap water samples had no effect on the SFODME method for the determination of Dextromethorphan.

CONCLUSION

The results of this investigation demonstrate that Solidified Floating Organic Drop Microextraction (SFODME) combined with spectrophotometry can be used as a simple and powerful tool for the preconcentration and determination of Dextromethorphan from aqueous samples. This technique provides good precision, high enrichment factors, simplicity, ease of operation, low detection limits and good recovery within a short time compared to other techniques. In this method we used 1-undecanol as extraction solvent which is less toxic and dense than the solvents used in other methods. Due to the melting point and density of the extracting solvent, extractant droplet can be easily collected after solidified on the surface of the sample at low temperatures. Furthermore, the solidified phase can be easily separated from the aqueous phase. The developed method has been successfully applied to the preconcentration and determination of trace Dextromethorphan in tap water samples, and the precision and accuracy of the method are satisfactory.



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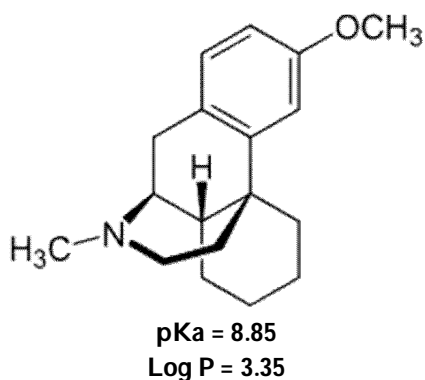


Figure 1. The chemical structure and properties of Dextromethorphan.

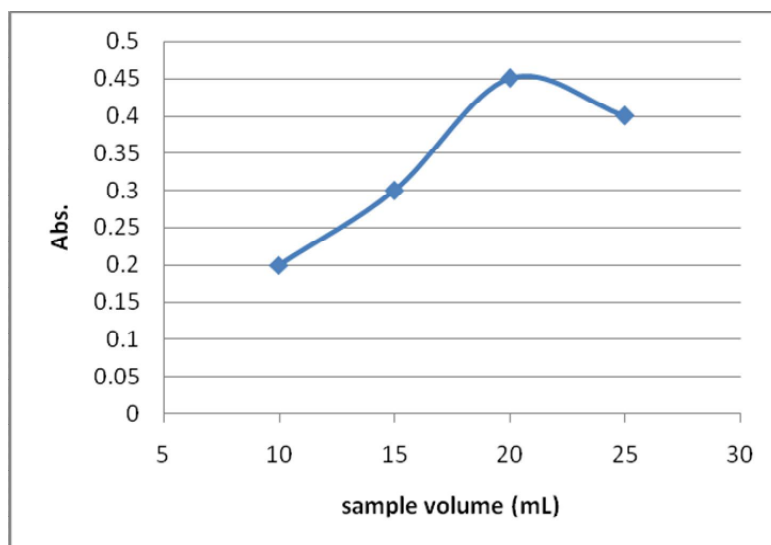


Figure 2. Effect of sample volume on the extraction efficiency.





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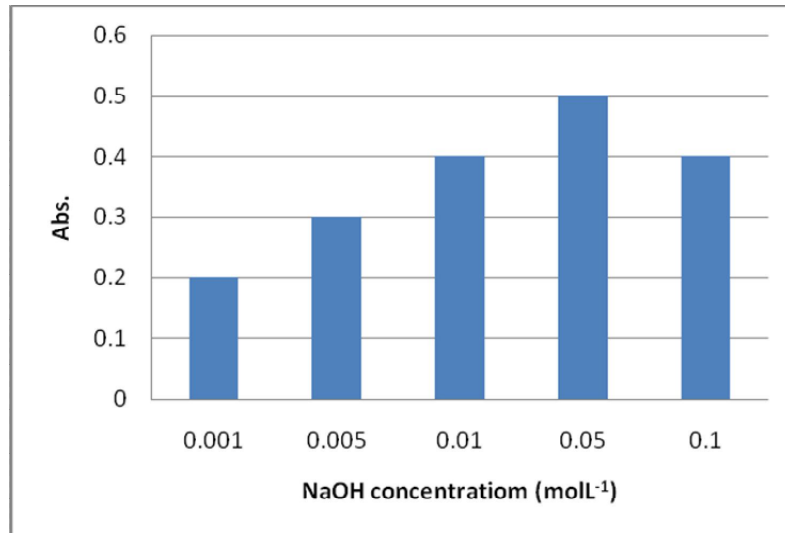


Figure 3. Effect of NaOH concentration in sample solution on the extraction efficiency.

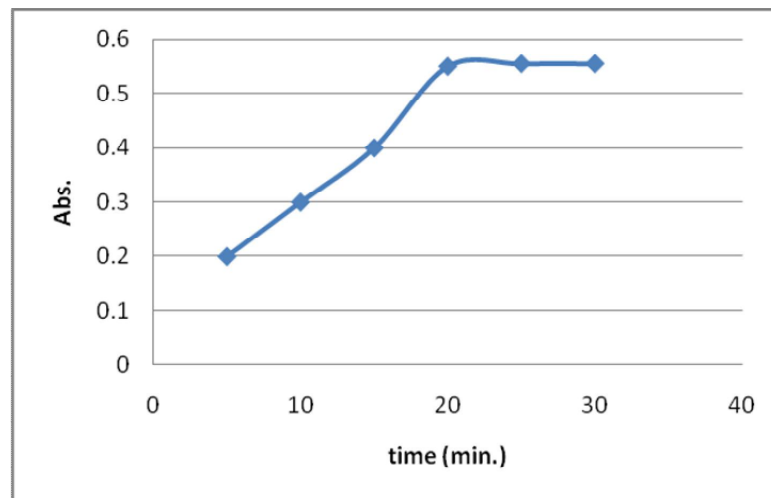


Figure 4. Effect of extraction time on the extraction efficiency.





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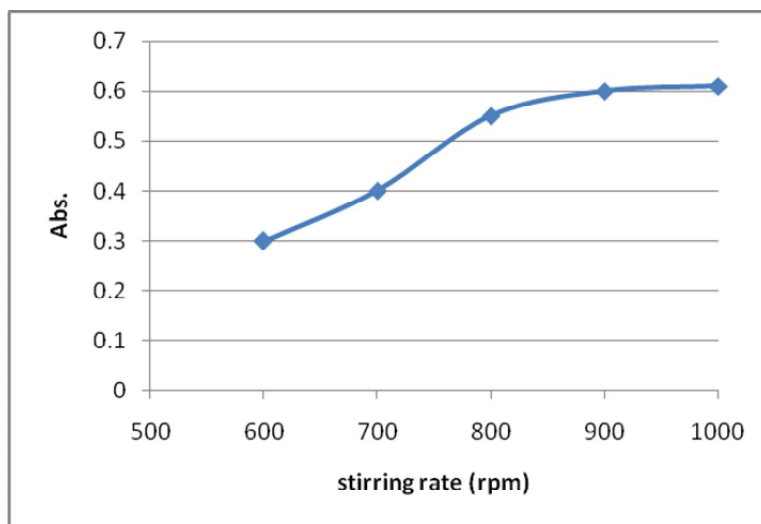


Figure 5. Effect of stirring rate on the extraction efficiency.

Table 1. Characteristic data of the established SFODME-UVmethod

Analyte	LOD (mgL ⁻¹)	LOQ (mgL ⁻¹)	LR (mgL ⁻¹)	r ²	RSD (%)	EF (n=3)
Dextromethorphan	0.13	0.5	0.5-5	0.9982	5.9	61.4

Table 2. Relative Recovery of Dextromethorphan in real water samples by use of proposed method

Sample	Relative Recovery%
Quchan tap water	94.0
Esfarayen tap water	92.0





TSS and COD removal from Waste Water by Hybrid Electrocoagulation-Membrane Process

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ABSTRACT

There are several methods for wastewater treatment. One of the most important processes for water and wastewater treatment is membrane processes. Despite the many advantages of membrane processes, one of the problems which limits the use of this technology is membrane fouling. Using membranes in appropriate operating condition, hybrid processes and pretreatments like electro coagulation are solutions to reduce membranes fouling.

In this paper, first contaminated waste water by electro coagulation process with iron, aluminum and stainless steel electrodes in residence time of 20, 30 and 40 minutes, and the voltages of 5, 10 and 20V pretreated, and its COD and TSS were removed. At the next step the pretreated waste water was treated by membrane at pressures of 9, 12 and 15 bar. The results show that increasing the residence time and voltage in electro coagulation process and raising pressure in the membrane process increase the removal efficiency.

Key words: membrane process, electro coagulation, operating pressure, residence time, voltage, wastewater treatment.





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INTRODUCTION

Electro coagulation (EC) involves the generation of coagulants in situ by electrical dissolving of aluminum or iron electrodes. Metal ions at the anode and hydrogen gas at the cathode are produced. In this method, a convenient current is imposed on soluble anodes like aluminum, iron or their alloys in an electrochemical cell acting as the reactor for the experiment separated by filtration, depending upon their density. The electro coagulation results in the dissolution of the electrode to yield metal ions (Fe^{2+} , Fe^{3+} or Al^{3+}) which are active coagulants precursors involved in the neutralization of the negative charges on the colloids of the effluent. These metal ions then react with the hydroxyl colloidal particles is specific in each of these processes. The process for the water and wastewater treatment in various industries such as pulp and paper, metal industry, automotive, chemical and pharmaceutical industry has been designed and implemented in real scale [1-3].

In the membrane filtration process the two-phases, which are not in equilibrium thermodynamically with each other, are separated by a semi-permeable membrane. Mentioned membrane acts like a physical barrier which can control passing or not passing substances from one phase to the other. A membrane is defined as a perm selective phase. In other words, a membrane acts as a phase that detachable components of feed with different rates pass through it. In this method, the phase change is not taking place and products are soluble in each other [4, 5].

Membrane processes have advantages such as low energy consumption due to the lack of phase change, low volume and not requiring much of space, the variation in size and shape, low pressure drop and high mass transfer, high separation efficiency for dilute solutions, low demand for additives and solvents, simple design of membranes and ease of their application in industrial scale, and because they are environment friendly; membranes have been distinguished from other methods. However, this method has some disadvantages, such as concentration polarization and membrane fouling, low membrane lifetime, selectivity and low flow rate through the membrane and the high cost of its construction [5, 6].

By the help of membrane technology many water-soluble impurities can be removed. Accumulation of colloids at surface or near the pores of the membranes (ie, colloidal fouling) lead to high energy dissipation during filtration and subsequently operating costs rise which limits application of membrane technology. Adding a coagulant before membrane filtration results in increasing the quality of effluent water from membrane and reducing fouling on the membranes. Nevertheless, electrocoagulation is another proposal.

The colloidal particles are effectively eliminated by EC compared with other conventional methods. Small particles are more likely to be concluded in the electric field. Gas bubbles are produced due to electrolysis, which can enhance flotation. Floc formed by EC is similar to the floc formed by chemical coagulant, but the EC floc contains less bound water and tends to be much larger, more stable, and acid-resistant. For these reasons, the floc caused by EC process separate faster by filtration operations. Few studies have been done to investigate the hybrid process of electrocoagulation and membrane [1, 7].

Results of previous studies show that the use of electrocoagulation pretreatment prior to membrane processes for water and wastewater treatment method is very effective which cause a reduction in fouling rate, increase removal of impurities, reducing the pressure difference on both sides of the membrane, reducing energy consumption and consequently they will reduce costs [8-13].

In this paper, the effect of three parameters, residence time, type of electrode and voltage on the results of wastewater treatment by electrocoagulation process is checked, then the pretreated wastewater by EC at best condition of efficiency, by nanofiltration process can be refined with three different pressures.





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MATERIALS AND METHODS

In this study, research has been done based on a sample of the effluent with 1280 (mg / L) TSS and 3328 (mg / L) COD.

Electrocoagulation

The experiment was setup in the static method where the EC and wastewater batch test are performed in a glass cell (volume 5,000 mL). Iron (Fe), aluminium (Al), and stainless steel (SS) plates with side area of 400 cm² as the anode and cathode electrodes were connected in parallel and the monopolar to a digital DC power supply (0-50 V, 30 A). In each test, three electrodes were used as the anode and three electrodes were used as the cathode. In EC process three parameters of residence time, electrode type and voltage were studied. Then TSS and COD removal rates were measured in each case. Different scenarios of experiments can be seen in Table 1.

Then the effluent from the EC process with the highest percentage of removal was purified by nanofiltration process.

Membrane Process

The nanofiltration membrane (NF1) was used in this investigation. The membrane was supplied by Sepro. In order to determine the amount of TSS and COD removal by nanofiltration process, a nanofiltration pilot plant with a cross-flow cell was used. The cross-flow cell housed flat sheet membrane pieces with an effective area of 28 cm². The experiments were carried out at three pressures of 9, 12 and 15 bar. The volume of droplets that permeate through the membrane were recorded as a function of time. The process continued to reach a steady state.

Measurement of TSS and COD

Solids can be present in the water in the form of suspended. They can be formed from organic or inorganic particles. There are different tests to measure the amount of solids. Most of these tests are included gravimetric measurement of the mass of sediment. To determine the TSS, a filter paper was located in a certain temperature inside the oven to dry completely then accurately was weighed. In the next step, 100 CC from wastewater samples which is quite uniform was poured on a filter paper and was filled with a funnel and vacuum pump, then the filter paper was located in the oven for about an hour until completely dried. At the end the final weight was measured and TSS values were calculated from the difference weights according to the following formula:

$$\text{TSS (mg/lit)} = \frac{(B-A) \times 1000}{V}$$

Where B is final weight of filter paper (mgr), A is basic weight of filter paper (mgr) and V is the volume of wastewater samples (lit).

Moreover, in this study in order to measure the COD, the open distillation method was used according to test methods for water and wastewater which were presented in the standard book [14].

RESULTS AND DISCUSSION

In this study, wastewater by the use of EC was pretreated, and then was treated by nanofiltration. The effects of residence time, types of electrode and voltage on the TSS and COD removal in electrocoagulation process are investigated. The pretreatment wastewater by EC in the maximum amount of removal from nanofiltration pilot at three pressures of 9, 12 and 15 bar was passed. Also in this section, the effect of operating pressure in the nanofiltration process on TSS and COD removal was also examined.



**Nadia Shebjamee and Ehsan Shekarian****Effect of electrode types and voltage on the EC**

In Figures (1 and 2) changes in COD and TSS removal rate as a function of types of electrode and voltage can be observed. The results show that the type of electrode and the voltage on COD and TSS removal are efficient. The appropriate electrode to achieve maximum removal rates of COD and TSS, in this study, is Al-SS. This could be due to differences in the structure and nature of clots formed in the presence of different electrodes and the nature of the available contaminants.

Also in Figures (1 and 2) observed that TSS and COD removal rate increased with increasing voltage. Based on the results, in the case of Al-SS electrodes and residence time of 40 minutes, at a voltage of 5 volts, 84.50% and 77.83%, at the voltage of 10 volts, 92.30% and 83.15%, and 97.23% and 90.00% at the 20 volt, removed from TSS and COD, respectively.

By increasing voltage the generation of coagulants, the rate of bubble production, size and growth of the clot will change. Rise in voltage increases the production of metal hydroxide which increases precipitates and clots. In addition, the density of bubbles increases and their size decreases and this leads to a faster removal of the contaminants.

Like rising in residence time, increasing voltage generates more coagulants in the wastewater. From hydrolysing water, more oxygen molecules will be generated that increase the percentage of COD removal. Moreover, by increasing the voltage generated bubbles in the wastewater become smaller, consequently, the level of exposure to pollutants can be increased which increases the percentage of COD removal.

Effect of residence time on EC

In Figures (3 and 4) the effect of changes in residence time on the removal of COD and TSS in the voltage of 10 V with the electrode of Al-SS can be seen. With increasing residence time, more coagulants is generated in the wastewater, which enhances further coagulation and removal of COD of the wastewater. Also, at higher residence time, because of the hydrolysis of water, more oxygen molecules produced which will increase the percentage of COD removal. With increasing voltage and residence time, due to rising of oxidation potential, the separation of metal ions from the anode electrode increases and causes the concentration of hydroxide of the metal species in the environment increases. This species through neutralization of surface charge of particles and substances in the wastewater and by absorbing them result in reducing the pollution. As shown in Figure 4, rise in voltage and residence time cause the TSS in the effluent significantly reduced. The reason can be attributed to the fact that the major part of the wastewater pollutants are absorbed by metal hydroxide clots.

According to the results, the highest percentage of TSS and COD removal were taken place by using Al-SS electrode, residence time of 40 minutes and voltage of 20 volt; the amount of removal were equal to 90.00% and 97.23%, respectively.

Effect of operating pressure on the nanofiltration process

After pretreatment by EC, effluent with the highest removal percentage (residence time of 40 minutes, voltage of 20 volt and electrode type of Al-SS) by nanofiltration process at three pressures of 9, 12 and 15 bar was filtered.

TSS and COD removal rate as a function of pressure in Figure (5) is shown. As can be seen in this figure, by increasing the pressure, the removal rate increases. By increasing the pressure, the water flux through the NF increases, while the impurity flux remains unchanged. Therefore by increasing the feed pressure, the concentration of impurities in the water passing through the NF decreases.





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CONCLUSION

In this study, COD and TSS removal of a sample wastewater with changes in voltage, residence time and type of electrode in EC pretreatment process was studied. Based on the observations, the following conclusions can be mentioned:

1. With increasing residence time and voltage, COD removal rate increases. By increasing residence time, more coagulants are generated in wastewater, which enhances further coagulation and COD removal of the wastewater. Moreover, in higher residence time, because of the hydrolysed water more oxygen molecules produce, which increase the percentage of COD removal.

Rising in voltage like increasing residence time, produce more coagulants in wastewater, and by hydrolysis of water, more oxygen molecules will be produced which will increase the percentage of COD removal. Moreover, by increasing the voltage bubbles generated in the wastewater become smaller and thus their contact surface with pollutants increases, so the COD removal rate increases.

2. With increasing residence time and voltage, TSS removal rate increases. With increasing voltage, coagulants production rate, bubbles production rate, the size and the growth of the clot will change. Increasing the voltage increases the production of metal hydroxide can be used to increase precipitates and clot. In addition, the density of bubbles increases and its size is reduced and this leads to a faster removal of the contaminants.

By increasing voltage and residence time, due to increased oxidation potential, the separation of metal ions from the anode electrode is increased and causes the concentration of the metal hydroxide species in the environment increases. These species through neutralization of particles and substances surface charge in the wastewater and also by attracting them reduce pollution.

3. Effect of the electrode type in three states (Al-SS, Fe-SS and Fe-Fe) were studied. To determine the effect of the electrode type, the tests were performed under identical conditions of voltage, residence time, plates size and the distance between the plates and only by changing made to the material of plates, the impact of this factor was evaluated. Observations showed that at the EC process, the Al electrode compared with Fe anode electrode have higher yields. By using of aluminum electrode and a residence time of 40 minutes with voltage of 20 volt, the highest removal rates of COD and TSS values 90.00% and 97.23% were obtained, respectively.

- Next, the effect of operating pressure in nanofiltration process on COD and TSS removal was investigated. After pretreatment by electrocoagulation process, effluent with the highest percentage of removal was refined by nanofiltration process at three different pressures of 9, 12, and 15 bar. Based on the observations, the following result is noteworthy:

4. By increasing the operating pressure, the water flux and removal rate increases which both of them are desirable, but the operating costs because of using more energy increases. By increasing the pressure, the water flux through the NF increased, while the impurity flux remains unchanged. Therefore increasing the feed pressure the concentration of impurities in the water passing through the NF decreases.

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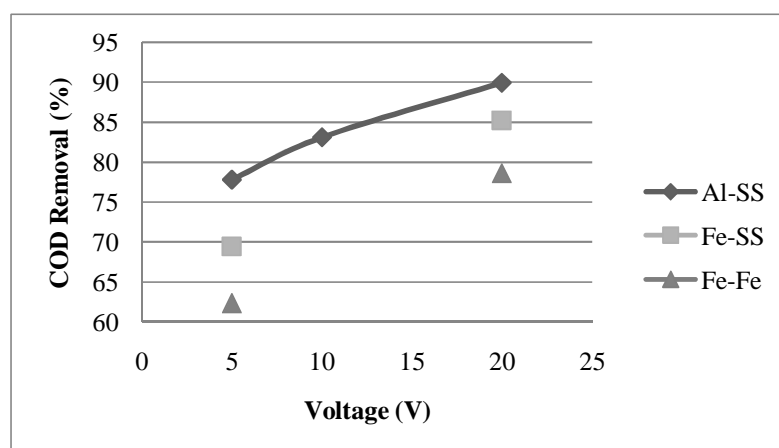


Figure 1 - The effect of voltage and electrode changes on COD removal at residence time of 40 min





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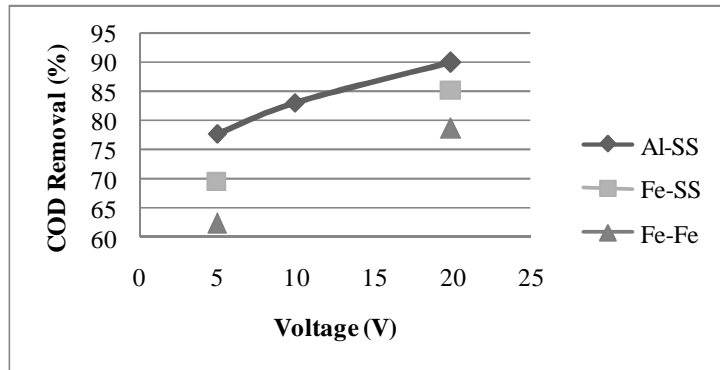


Figure 1 - The effect of voltage and electrode changes on COD removal at residence time of 40 min

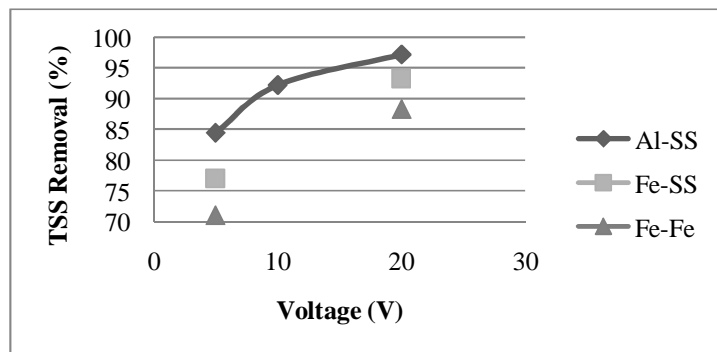


Figure 2 - The effect of voltage and electrode changes on TSS removal at residence time of 40 min

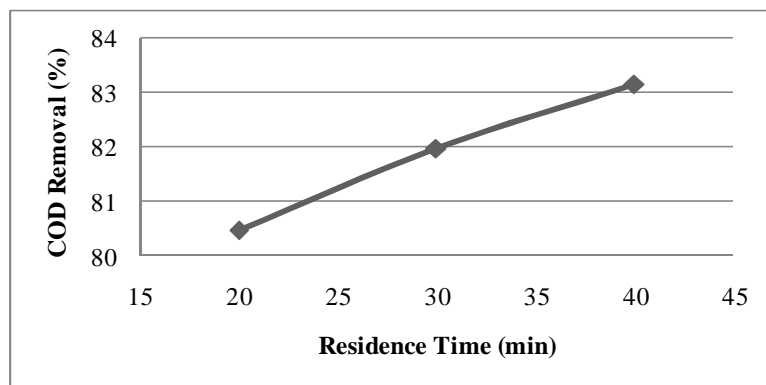


Figure 3 - The effect of changes in residence time on COD removal at voltage of 10 V and Al-SS electrode





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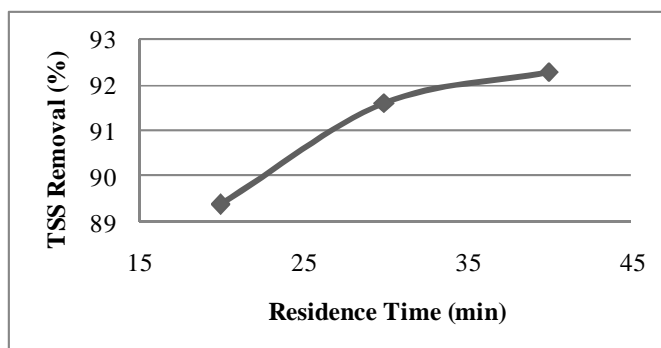


Figure 4 - The effect of changes in residence time on TSS removal at voltage of 10 V and Al-SS electrode

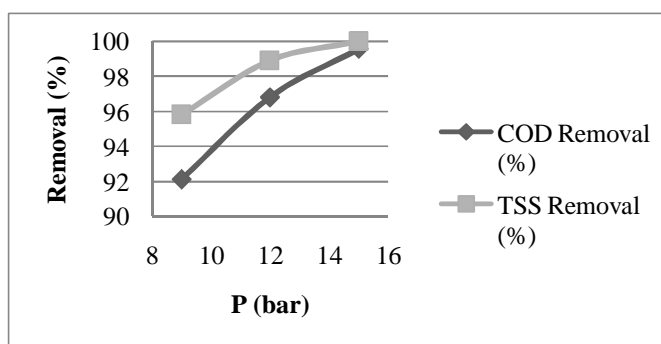


Figure 5 - Effect of operating pressure on the removal of COD and TSS

Table 1. Different scenarios of experiments

Number	Types of Electrode (Anode-Cathode)	Residence Time (min)	Voltage (V)
1	Fe-SS	40	5
2	Al-SS	40	5
3	Fe-Fe	40	5
4	Fe-SS	40	20
5	Al-SS	40	20
6	Fe-Fe	40	20
7	Al-SS	40	10
8	Al-SS	30	10
9	Al-SS	20	10





Sadegh Chubak as a Real Reflection of Naturalism in Iran

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ABSTRACT

Sadegh Chubak was among the pioneers who dare to break the tradition in Persian Literature. Sadegh Hedayat and Jamalzadeh accompanied him as well. It is thought that Sadegh Chubak and his works are considerably influential in Persian Literature. Miserable and poor people and those who have never tied to change their life style are considerably highlighted in Chubak's works; they are not palpable in the real world though. He has looked through immortality and sinfulness from naturalism point of view. In this paper, at the first place we will go through the appearance of Naturalism in France and its infancy and adulthood in other European countries and briefly we will look at Naturalism and Realism Works individually. Then Sadegh Chubak and his works have been taken into account. Finally, Sadegh Chubak's works have been analyzed regarding Naturalism features. His genre and style in writing is a palpable witness of Naturalism, his unique and extraordinary features in writing has turned him into a prominent figure in Naturalism.

Key words: Chubak, Naturalism, Realism, Story characters

INTRODUCTION

Sadegh Chubak was the one who brings novelty in Iran, it is worth mentioning that his works and his effects in story writing are not revolutionary, there is no huge difference between his works and Sadegh Hedayat and Jamalzadeh's and those who have tried to improve this genre. His early works have been published in "Sokhan" magazine. Apparently it has been proved that Sadegh Chubak was greatly influenced by Sadegh Hedayat's works. Chubak's outlook about Hedayat gave validity to this effect, "I personally believe that Sadegh Hedayat is a perfect man in all





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fields, his story characters are captives and miserable people who have never tried to free themselves" (Dastgheib, 1974, p. 65).

In his short stories, all characters are doomed to be miserable; they never try to change their destiny even if they are allowed to. They are slaves of pessimism and fear, they are too petrified to take small challenges and this is Naturalism.

He highlighted bad and hatred features in his works, it is a considerable feature of Naturalism. Sadegh Chubak was greatly accustomed to all these features. Surprisingly he tried to prevent readers from getting used to routine although he himself was imprisoned in his routine and habits. In other words, he has buried himself in ugly and disgusting realities; he has gone far away in such a way which beauty has been quite neglected in his life. "Sang e Saboor" "The Patient Stone" is a tangible example of this feature. He has over emphasized on describing ill mannered characters and their ugly and dirty social lives. This imbalance is a prominent character of all Naturalism writers. Sadegh Chubak is not excluded, though. He was really faithful to Naturalism to a degree that all naturalism elements mirror in Sadegh Chubak's works.

From others' point of view, Chubak was not a western naturalism, since Chubak has not given a fig to Genetic and inherency; however, western naturalism has. His works carry some other features as his focus was on ugliness and immoralities; therefore he can be counted as an Iranian Naturalism.

A group has been scrutinizes Chubak's works though roughly although they have not gone through close comparison of his works and Naturalism features. Surprisingly, some people strongly believe that Chubak is in no way a western Naturalist, they totally agree that his works do not mirror a single characteristic of Naturalism. They claim that Chubak was lion hearted enough to shout society's problem as they are in reality whereas former writers failed to do so.

This paper sets out to discover the effects of Naturalism in his works since he has been mentioned as a well known writer in Persian Literature. Many of his works such as "A keyma- sab bazi" "The puppet show" and "Antari e Ke Lutyash Murde bud" "The Baboon whose Buffon was dead". And some of his novels as "Sang e Saboor" "The Patient Stone" and "Tangsir" can vividly witness that he was a great Naturalism.

Naturalism can be defined as a magnified form of realism of philosophical naturalism. Naturalism believes in absolute power of nature, they claim that human beings are controlled by their emotions and instincts. All his thoughts and actions are affected by his instincts as well. Naturalism Literature overstated on nurture effects and it pictured life in such a way which ambition and enthusiasm have no identity. Naturalism described every single element in spite they are ugly and not likeable. Its main and first focus is on science.

Naturalism features:

The first focus is on Physiological science.

They strongly believe that if one wants to know about characters' attributes and features, it is not necessarily recommended to mention his mental characteristics. In other words, his taste is a good judge. As to this matter, Zola in his book "Teresa ken" has mentioned that "In this book I never describe people by their mental features; I simply know them by their tastes. (Seyed Hosseini, 1992, p. 422)





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Inheritance:

Naturalism highlighted inheritance matter; they believe that people inherit most of his characteristics and features from their parents. They strongly believe in nature and nurture and human being is surrounded by these two feature. Zola has been considerably inspired by "Loco", it is worth mentioning that regarding this theory Rogan Maker's novels "social and historical aspect of life in a family in 2nd Emperor" have been published.

Contradiction with morality and religious point of view:

It is believed that human being is controlled by nurture and nature, spirituality is not considered a big deal.

Pessimism and ugliness have been highlighted:

The naturalist author has an authority to describe reality as it is whether it is immoral or moral, black or white.

No limitation in diction:

The naturalist author uses the words and structures were considered taboo and inappropriate before then.

Poverty, unfairness, evil, and ugliness are prominent features of naturalism:

Naturalism authors attempt to describe world realities exaggeratedly.

Love is considered hocus-pocus and it is shallow weighted in naturalism:

In other words, naturalism can be counted as a destructive criticism to world's society.

Contradiction with superstition:

Vividly naturalism authors have gone far away, any belief even a religious one can be considered a superstition.

Freedom has been neglected in naturalism literature:

It is believed that human being is doomed to its destiny and there is no getting away from nature and nurture.

Physical features and neurons are the controllers:

Naturalism believes that human beings are controlled by their physical features, neurons to be more precise. "Human beings are under a close control of their inheritance and physical features." Zola said. As Nietzsche has remarked that human being looks as a system of neurons.

Slang and colloquialism:

Naturalism was a reformist movement against formal speech. Slang has been introduced by the appearance of naturalism. Slang and colloquialism have been supported by other authors and thinkers. They have been survived even after naturalism disappearance.





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Detailed descriptions and clarification:

Naturalism authors details out reality. They are enthusiastic about details not general features.

Animal features:

Naturalism authors are mostly interested in immoral features such as greed and lust.

Sad ending:

All the characters in naturalism stories are destined for a doomed destiny.

Naturalism, behavior, and society:

Zola claimed that a scientific work can be counted as an artistic masterpiece. It has not been supported by many thinkers, though. "An author can be an inspector, an author deals with people's emotion and feelings. He must sit on the fence as he is counted as a judge and a judge is supposed to be indifferent." (Seyed Hosseini, 1992, p. 41)

Naturalism literature advocated morality. It has tried to provide human beings with constructive resolutions to deal with immorality. Generally speaking, it has been thought that naturalism is an exaggerated form of realism. Some thinkers have attempted to develop realism; as a result some of naturalism works have been turned out to be simply photography and dairy. From 1850 to 1890, there were some movements against Romanism which all led to Realism movement. To sum up, all these movement were the foundation of Naturalism appearance. (Seyed Hosseini, 1992, p. 290)

In the mid 20th, Naturalism has been remarked as a significant issue, it has touched some thinkers' minds to look through it. By the passage of time, thinkers have drawn a line between naturalism and realism. These two schools were considered a single concept, though. It is worth bearing in mind that regardless all those differences, they share some commonalities. "These two concepts look as if a twin who are independent in some parts. (Forest, 1997, p. 27)

Naturalism has been surfaced since mid 19th century. It was considered a movement against Romanism in France. Gradually it has been brought up and has passed his infancy. "Naturalism set out to expose people to reality rather than a man made story. (Radfar and Hassanzadeh, 2004, p. 30). "Literature is a window through life; reader will realize the identity of life by literature." (Payandeh, 2010, p. 27)

Naturalism and Realism:

Realism and Naturalism have some features in common, they are as following:

Similarities:

When it comes to talk about the features of Naturalism and Realism, reality comes to limelight. All the stories and novels in these two genres deal with actual happenings which take place in the real world. All the characters are quite palpable. Even the language has been used is not the former formal one, it informal speech which is mostly used in every day dialogue. (Forest, Screen, 1978, p. 16)





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The mentioned issue is the common feature of Realism and Naturalism. Naturalist authors work as a camera and record all the scenes they are exposed to, they never try to interfere or judge on their records. They are quite faithful to reality. Time is the important element in this genre, the authors are too fussy to schedule the events and timing is a big deal in naturalism.

Differences:

There is a galaxy of difference between Naturalism outlook and Realism point of view. They look through life from different windows. Realism can be defined as looking for reality in the real world, through this inspection, some problem may be surfaced, ultimately all these may lead to a remedy to society' problems. However, naturalism looks at a single aspect of life, to be more precise it is tried to exaggerate what has been witnessed. Exaggeration is the main feature of naturalism characteristics. Society problem are mentioned in such a disastrous way that seem to be impossible to find any solution for.

The major difference which draws a line between Realism and Naturalism is their attitude toward reality. It is generally thought that the reality is not definite, it is proportional and relative. The real world reality is different from story like. (Madanipour, 2003, p. 131)

Naturalism looks at immoralities and ugliness as realism does. The difference is that Naturalism exaggerates all those darkness. The second feature which sounds to be important is the characters. All the naturalism characters are indecisive and miserable; they strongly believe in destiny and claim that they all are doomed in destiny, a malevolent destiny. On the other hand, Realism characters are free to live their own lives; they are determined to make their own destiny.

In a quick overview, natural science and philosophy are the foundation of Naturalism, naturalism is a mean to get to reality; however, only philosophy is the modality of Realism, Realism describes the goal of reality. Naturalism believes what makes human beings superior than other creatures is their animal features and immoral behavior. To their mind, weak people are destined to be died out by power. (Radfar, Hassanzadeh, 1995, p. 29)

Sadegh Chubak was born in August 1916, in Bushehr. His father was a well-known merchant of bazaar. He received his early education in Bushehr and Shiraz. Later on he moved to Tehran and attended the Alborz High School. After completing high-school, he was employed as a teacher by the Ministry of Education and sent to Khorramshahr in oil-rich province of Khuzestan, he got married in the same year. He later joined the National Oil Company. Chubak was widely considered as the greatest naturalist writer in Persian literature, he has written a large amount of works including novels, short stories, and plays. His collected stories of "Kheymeh Sab Bazi" "The Puppet Show" in 1945 and "Antari Ke Lutiash Murdeh Bud" "The Baboon whose Buffon was dead". In 1949 did profoundly influence the modern Persian literature. Then he travelled to England and America, he has spent the rest of his life in California, he died in July 1998, in Berkeley, United States. His works include novels, short stories, drama, and some translated prose. Chubak has translated some works internationally known writers such as Balzac and Shakespeare into Persian.

"Once one of my father's fiends was invited to our place, he was a merchant too. They went to a cozy place and read a book. I followed them because it sounded to be intriguing to me, I was just nine. Sometimes they burst into laugh, sometimes they elapse into silence and sometimes they whisper. As I was following the story, I gathered they were back biting and making fun of other people, especially Ayatollah Majlesi' writings. I mostly found all those books interesting enough." Chubak maintains.

Chubak believed that Amir Abbas Hoveida was the most influential figure through his life.





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He was also impressed by Mirza Ali Mazandarani who was his father's friend. Mirza Ali Mazandarani was a knowledgeable and noble man; Sadegh was really inspired by him in the idea of anti superstition. He has been accused of taking originality too far. Chubak was really keen on describing every single detail. He looked through life from naturalism angle; this naturalistic feature obliged him to zoom in the ugliness and immoralities. Sadegh is known as a Naturalist author, some of his works which verify this fact are as follows: "Kheymeh Sab Bazi" (Puppet Show) in 1945 and "Antari Ke Lutyash Murdeh Bud" "The Baboon whose Buffon was dead" , and "Sang e Saboor" "The Patient Stone". His genre in writing gave a dimension unusual in Persian writings.

Naturalism features and its impact on Chubak's works:

Physiological science has been remarked:

When Chubak wants to describe death, he never mentioned it directly. He always chooses an indirect method to go through the description in order to let his readers think freely. "Sikh tried to speak a word but he failed to open his mouth, it looks as if he got stammered, even a word was not uttered. He got shocked and unable to move a muscle. All his words were imprisoned in his mouth, Mohammad was waiting for his reply but he did not say a single word." (Chubak, 1973, 146,147)

Or:

" Kahzad was quite hopeless, has no more hopes and wishes. His eyes and nose were itchy. No sense, no feeling, no smile, and no tear. Finally he ended up in a cold smile.

Inheritance:

"Jalal Parents and his sibling who are smirking are waiting for them in the yard. When the woman saw them, she got gobsmacked since they all have been changed totally since the time she met them in Paris. Now they all are pale and have a big belly hanged out. It seems as if a sickness runes in the whole family."

Contradictory with morality and religious point of view:

In "Cheragh e Akhar" "The last light" Chubak has mentioned a verso of Molavi, and has pointed out that " He was naïve and he just tried to do snow job on himself." (Chubak, 1966, p. 216)

These ideas are too disappointing; they all obviously ridicule human values. All these ideas result in pessimism. (Dastgheib, 1975, p. 41,40)

Or:

At the end of "Sang e Saboor" "The patient stone" The evil murders God, "God is dead."

Or:

In " Asb e Choobi" "The Rocking Horse" the married people affairs are ridiculous and they are counted as revolutionary movement against the former existed ideas.

Pessimism and ugliness have been highlighted:





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In “Sang e Saboor” “The Patient Stone”, the reality has been surfaced as it is and even uglier and more cynical. All the characters are terribly dealing with all the immoral matters and vividly there is no getting away from it. This story is about a woman who has to pay for her own and 5-year-old son in a dishonest way.

As to this matter, Chubak greatly focused on the instinct and nature. He considerably exaggerated the dark parts of human beings. In “Chera Darya Toofani Shod?” “Why the sea is stormy?” All the characters and their ideas are directly affected by their instinct and their nature.

No limitation in diction.

“Formal structure is a big obstacle in Literature. It was Chubak who made a movement against formal structure. Slang and informal language and unseen and unheard structures have come in to Literature; Chubak can be considered a pioneer in this field. His works are the ones worth naming Literature masterpiece.” Dr. Khanlari said. (Dehbashi, 1380, 93) Chubak has stepped in to an area which was counted taboo. He deconstructed the existed formal structures and used words and structures were not been used former. His bravery in describing taboo structures is quite respectable.

“You were so mean; you never tried to save her from Sikh Mahmood, you just slept with her. You were lying, you have never liked her” (Chubak, 1974, p. 44)

Love is totally unconcerned in Naturalism:

In Naturalism love can be considered as a mean to quench people thirst in physical and sexual affairs. In all of his stories, love is not holly and sacred. His story characters are looking for love but not the one has been mentioned holly. They are looking for Lust and Passion.

Superstition is let aside:

Chubak was against superstition, he neglected all the religious beliefs and ideas.

“It is all dead loss; we have to destroy it completely. Superstition has to be eradicated; otherwise it will destroy human beings.

Freedom is shirked in Naturalism:

Naturalism believes that human beings have no authenticity to change their life style since they all are surrounded by their nature and nurture. This absolute power which has been mentioned in Naturalism has been broken into two different parts, naturalism believe that the absolute power is inheritance and nature of each human being. However, the one has been advocated by Chubak is nurture and environment.

To some people point of view, Chubak is a western naturalism.

Those two outlooks regarding the naturalism overlap each other. To be more precise, if we take the first one, nature we undoubtedly end up in the nature. The Vice versa can be applicable as well.





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Poverty, dishonesty, and injustice are highlighted.

Lower society classes have been emphasized by Chubak. In all his stories, he pictured poor and miserable people. Among all those stories, I can refer to “Bad az Zohr e Akhir e Paez” “The late autumn evening”, “ Sang e Saboor” “ Patient Stone”, and “ Pirahan e Zereski” “ The Maroon Dress”

He pictured people in brothel, cemetery, and some other similar places.

For example:

“Pirahan e Zereski” “The Maroon Dress” is a tangible example of these ugly and unpleasant features. It is about undertakers who work in a Murde Shur Khane (A place where dead bodies are dipped). The undertakers have been characterized in a way that have been totally ignored by Chubak. They are less respectable than those dead bodies. The climax of this story is when one of the undertaker looked into one of dead body’s mouth to find a golden tooth but he failed to find any; therefore, he sighed, “ everything is doomed.”

Naturalism believes that human beings are surrounded by physical elements. No spirituality:

Since Chubak was considerably impressed by Naturalism, he makes comparison between human and animal and he drew no line between these categories. He strongly believed not only animals but human beings are influenced by their nature and nurture.

“Pity on him.... This mankind is too poor and miserable; he has no authority on his needs. He has to wait hours and hours in disgusting and disgusting loo for whatever he has gulped down before.” (Chubak 1976, p. 112)

Slang and colloquialism:

Naturalism believes that formal language does not work out when it comes to short stories. It has been claimed that a text is supposed to be as plain and simple as possible. Sadegh Chubak was the one who can be considered as a pioneer in entering slang and colloquialism languages in to stories. His stories are quite casual and less formal. For example:

“Jesus’ mercy....what the heck he’s gonna do? It’s been uneventful for a long time.” (Chubak 1973, p. 101)

Detailed descriptions and clarification:

Description and clarification are some of Chubak’s characteristics. He prefers to revolve around describing events rather than dealing with spirituality. In other words, he was keen on concrete concepts, not the abstract and non tangible ones. He described immorality and ugliness and the realities surround the world. This feature is known as dark realism or it would be better to say it is naturalism.

He paid close and conscious attention to every details, he looked at every corner and tried not to lose any interesting fact.





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Animal features, such as Greed, Lust, and immorality:

In his book "Sang e Saboor" "Patient Stone", Chubak has remarked that human being assembles to animals. It is generally believed that any human being has been parted into two sections, Evil and God. The evil is the main focus of Chubak's stories. He insists on the evil and immoral part of human being. The characters all are insane, miserable, poor, and idiot.

For example,

"Once I came across a good looking and handsome man, I murder and behead him, then gave him to Atma to be eaten." (Chubak, 1966, p. 180)

Sad ending:

In naturalism, all the characters are doomed and their historical backgrounds and society decide on any single part of their lives. Most of Sadegh Chubak's works do not have a happy ending. Among all I can refer to "Antari ke Lutyash Murde bud" "The Baboon whose Buffon was dead". At the end of this story, the Baboon could not be survived from the doomed destiny.

There are some other stories which end up in a sad ending, "Late Night" and "Why the sea was stormy" are a few among many.

Naturalism, behavior, and society:

Chubak has looked through society from Realism window; he described reality as it is without any censorship. His words are in no way likeable, they are chosen among the most disgusting ones. Chubak looked at people from a single window, society has many aspects and all those have neglected by Chubak. He did not give a damn to the cruelty. In all his life, he was seeking for reality but to his mind reality cannot be found easily buy in brothel, cemetery, and loos. His characters are indecisive, doomed, poor, and cynic. (Dehbani, 2001, p. 161)

"Sang e Saboor" "The Patient Stone" is about a couple who speak freely and impudently about sexual matters. These subjects were considered taboo before then. This characteristic puts Sadegh Chubak into lime light.

In Persian Literature, Sadegh Chubak is well known as a Naturalistic author. Some of his works such as " A keymasab bazi" " The puppet show" and " Antari e ke Lutyash Murde bud " " The Baboon whose Buffon was dead", and some of his novels as "Sang e Saboor" " Patient Stone" and " Tangsir" can vividly verdiccate that he was a great Naturalism.

Other authors commented on Chubak, the followings are a few among many:

Khanlari

Chubak and his works must be respected world widely. He can inspire million authors. I can give my words he is the one and only in Literature. There might be some people to follow him in footstep to make a masterpiece but no one's is comparable to him. He was unique in his diction, his words and structures are chosen delicately. His characteristics differentiated him from the others, he as stubborn and pig-headed.(Dehbashi, 2001, p. 99,100)





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Najaf Daryabandi

“To my mind, “Sang e Saboor” “The Patient Stone” has attempted to be mentioned among the best works. The author is bewildered and has no authority; he is just inspired by western authors, such as James Josie, William Faulkner. Sadegh Chubak did not have a clear idea about the genre but he went through it, that’s why his works are light weighted.

Abdul Ali Dastgheyb

Chubak is considered both a naturalism and realism. When his works are counted as realism, they carry a moral lesson for readers. But when the naturalism stepped in to his works, he is not considered a faithful author. Chubak’s works yield both betterments and drawbacks. One of the biggest disadvantages is that he describes the reality as it is without making any judgment. And the greatest advantage is that he made a detailed record of the current events. It is worth bearing in mind that he always did not succeed as he tried to do so; it is naturalism limitation, tough.

Michel Hillman

Chubak is the most significant Iranian author. He is really professional in his own genre. All his short stories and novels are the prominent ones in Literature. He sometimes is inspired by Sadegh Hedayat. (Hillman, 1971)

Peter Chelkouski

Chubak used slang and informal language in his poetic works although they may sound immoral and unfavorable. His main focus in all of his works is on social aspect of human beings. (Dehbashi, 2001, p. 44)

Jalal ale Ahmad

Bozorg e Alavi and Chubak are both inspired by Sadegh Hedayat. They both are counted as western authors. Their works mostly revolve around immoral issues. In some their works, some parts have been allocated to women. If anything about religion and tradition is mentioned in their works, undoubtedly their ideas are all against religion. (Jalal ale Ahmad, 1985, p. 186)

Mahmood Dolat Abadi

Firstly he was inspired by Hedayat a; however, he was not as skilled as Hedayat was, and he turned to be Naturalism. (Dastgheib, 1975, p. 10)

Foot note:

These two books set out to over emphasize superstition. And the belief has been spread all around the world. (Sadegh Chubak, the pioneer of Naturalism in Persian Literature. Heidar Jamali)

The critique of Sadegh Chubak ‘s Works (Dastgheyb, A. 1975, p. 5&6)

Taken from “Cheragh e Akhar” “The Last Light” (Etma, my puppy)

Dehbashi, A (1968, p. 115& 129), About Sadegh Chubak’s life and works.





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The Description of Lover and Beloved in “Layla and Majnun” Stories by Nezami and Jami

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ABSTRACT

Description of beloved in Nezami’s “Layla and Majnun” and Jami’s “Layla and Majnun” are examples of fine descriptions. The virtues of these two poets describe the lover uniquely as examples of eastern literature. The description of beloved (Layla and Majnun) in Nezami and Jami poetic collection and also the features of description in each of Layla’s and Majnun’s organs such as scalp, face, mouth, hair, lips, height and body have been studied and the comparison between both poetic collections has been done. In this paper, a general description has been consecutively done through some lines with the same contexts and a description of the lover and beloved has been shown and also descriptions of terms have been presented through metaphor and simile. On the background of this study it should be noted that some papers have been written about storied context and the Masnavies which have been composed by imitating Nezami and also their similarities and differences. Moreover, the description of beloved and the evaluation of love in “Layla and Majnun and Juliet” have been done in comparative but there is no comparative study between Nezami’s “Layla and Majnun” and Jami’s “Layla and Majnun” or at least the researcher has not achieved to it.

Key words: Description, Layla and Majnun, Lover, Beloved





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INTRODUCTION

In this article, the researcher has discussed the similarities and differences between lover and beloved in Nezami's "Layla and Majnun" and Jami's "Layla and Majnun". Both stories are similar in Qais' love to Layla, Majnun's father proposal and rejecting his request by Layla's father, Majnun's going on a pilgrimage to Mecca, written relationship between lover and beloved, Layla's death in autumn and other main sections like these. However, there are differences between some parts such as Layla and Majnun's visiting which have occurred once in Nezami's story and four times in Jami's story or the fidelity of beloved which has been represented by describing the middle organs of body when Layla declared her loyalty to Majnun in a letter and says:

My unique pearl is a hidden treasure

Like a bud with a concealed secret

These similar parts have been described with highlighted differences. Jami has described Qais _Majnun_ with many good characters of a true man. It should also be noted that Jami's Majnun is clearly different from Nezami's Majnun. Jami's Majnun is the authority from the beginning but Nezami's Majnun is dependent on his father for a certain period of time. Jami describes the liberality, honesty, loyalty and philanthropy of eastern women through describing Layla (Khadivar & Sharifi, 2011, p. 49).

The poet clearly shows that Layla has natural elegance because she is a tall, extremely beautiful and enchanting girl. Layla's belief about lover and beloved is totally different, she believes that lover and beloved are one. In Nezami's story, Layla is not satisfied with getting married with Ibn Salam. In Jami's story, Layla's parents ask her about getting married with a man from Bani Thaqif tribe but because of her silence she has to do that. All these cases have their own specific description.

"Layla and Majnun": It is Nezami's third Masnavi which has been made for the Shervan King Abol Mozaffar Akhestan Ben Manuchehr in 1206. Nezami has composed this story in 4700 lines and in a short term (less than four months) and later it has been appealed by him and has been completed around 1210 (Ibn Nadim, 2003, p. 425).

But Jami's "Layla and Mjnnun" is the sixth Masnavi of "Haft Orang" in which he has imitated Nezami. The remarkable point is that Jami particularly has used an eloquent, expressive and easy to take language in descriptions:

Two companions, two faithful to a secret who sits with another
Two lover and beloved who joined with each other

Layla in throne of monarchy
Majnun in the presence of strangers pleading for justice

Layla is in the heavens honorable
Majnun is in the heavens seeking to find his faithful friend and his gift

A joyous laughther on the lips of Layla
Tears like unique pearl on the eyes of majnun

Layla is not similar the light of candle to brights the morn
Majnun is not similar the cloud of sky to increased through blessing





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Both poets have used common senses to describe and to use metaphor and simile such as moon, sun, star and dove, snake, capacitor, morning, flower, lotus, flush, tulip, violet, bud, cypress and pomegranate, jewel, sweetheart and etc.

Comparison between Nezami's and Jami's "Layla and Majnun"

In Nezami's story, Majnun had fallen in love in school when he was ten but in Jami's story, he has fallen in love in the desert when he was fourteen. Due to the Majnun's age, Jami's story is true and also it is almost similar to Arabic news (Isfahani, as cited in Afsahzadeh, 2000, pp. 656-657).

In both stories, Layla and Majnun's visiting has described in different ways. It has come out four times in Jami's Masnavi and once in Nezami's Masnavi.

According to the description of Nezami of this moment:

This appear on his eyes to regret
That reveal for him to moan
Layla like a star hidden in the palace
Majnun like a keeper of treasure
Layla is not similar the light to be turned dark night to bright day
Majnun is not similar the candle to burn himself
Layla was a master of locution as beautiful as a fairy
Majnun began to speak as burning as fire
When Layla come to her lover like a rosebud
Majnun shed tears because of deep gladness
Sweet-smelling reed was on layla's hand

Majnun is not following the wine, on the contrary, he searches the aroma of wine (i.e Layla to get drunk) (Nezami, 1999, p. 449)

In Jami's "Layla and Majnun", this situation is described for four times but with modernization and novelty and takes place in certain conditions. When Layla and Mjnjun come together for the first time:

The beloved on beauteous silk cloth seem so magnificent
As beautiful as the partridge and pheasant
They exhilarate after visitation each other
Such as that gladness full their spirit of love
When Layla take off her face mask
Majnun become impatient however he tolerance
The eyelash like a little arrows shooting to lover's heart
The lover become restless and fidgety
Enjoyment of visitation each other cause they remained cheerful
Companion of good words was a continuation of their love
(Jami, 1988, p. 769)

In Nezami's Masnavi, when Layla comes to watch the groves, a person sings a lyric of Majnun whose context is almost similar to Layla and Majnun's fourth visiting in Jami's Masnavi:

Restlessness of the Majnun's heart raise a tumult
Layla waiting to the end venture
Majnun was tormented for being away from his beloved





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Layla made an abortive attempt to follow her friend
Majnun with white poplar annihilate every thistle(the metaphor of tolerance of offended)
Layla dormant by the fiery eloquent
Thousands ways help Majnun to groan of separation
Jollity and gladness without friend is impossible for Layla
Groan of separation and grief is the companion of Majnun
In the duration of separation there is not spring and happiness for Layla
(Nezami, 1999, p. 472)

In Jami's story, Majnun sings one of his lyrics which is consonant and almost similar to this lyric:

When Layla song a love lyric and conquest
Restless and infatuation companion with Majnun
Lapse of time determine the destiny of lover and beloved
The groan of separation cause Majnun wandering about in mountains and deserts
Layla as beautiful as rose expecting for her lover at castle
Majnun become sad because of separation ,imprison himself in cave
(Jami, Layla and Majnun, p. 25)

That part of the story where Majnun's father and the rich of Bani Amer tribe go to propose to Layla to get married with Mjnnun, is a common event with describing lines and with common context in both stories and it is seen in all stories about Layla and Majnun but it occurs in different situations in each story. For example, in Nezami's story, after Layla and Majnun fall in love and then they are separated, Majnun walks madly around Layla's house day and night. Majnun's father finds out his son's intense love to Layla and goes to propose to her with the elders of the tribe but the tribe where Layla lives in rejects their request and ask them to treat Majnun and then come to propose. In this story, Nezami describes the state of Majnun's father as follows:

The buyer of pearl am I and you sell the jewel

If you're cautious sell the merchandise
Whenever valuable and precious goods to sell
To buy it I eager
Whatever is worth a lot
On the suitable time sell it
(Nezami, 1999, p. 451)

In Jami's story, Majnun's father finds out that his son has fallen in love so totally resist it. Majnun becomes insane and asks the elder of the tribe to go to propose to Layla but they do not succeed. The conversation between Majnun's father and Layla's father are similar in both stories. In Jami's story, Layla's father rejects Ameryan's request as Qais's love poems have taken his family's reputation. Majnun is described as follows:

Is it a real indelible disgrace?
The infamous is rather homely than whatever you think
Cause to rise,become not needy
Don't any word ,deaf and blind against this event
Said swear by God
Necessity and penury is not belong to him any time anytime and anywhere





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In search of love,if anybody seeking something from Layla ,in contrast with thousands like Majnun ,neither Layla,nor Majnun substitute lover and beloved with anything else
(Jami, 1988, pp. 812-813)

The section of the story when Layla and Majnun go on a pilgrimage to Mecca, has been described in different ways by Jami and Nezami.

In Nezami's story, Majnun goes on a pilgrimage to get ride of the pain of love but in Jami's story, he goes on a pilgrimage to keep his promise. The description of these stories are interesting. In Jami's story:

Layla ride the camel-litter herself
Majnun glance far from his beloved cheerlss
In an instant look at his friend
Pain separation cause shed tears
Come to tears and said she who tolerate the sorrow of separation
Did you cherish a desire for meeting?
The sorrow of absence bothering you,however,struggle against it
Waiting for visitation of beloved and desire of meeting give the lover patience
Without beloved,passing of time is impossible
Lacking beloved cause shed tears days and days

Oppressed Majnun said gently ,there is occasion for fear of everybody and anything,sometimes see the forward and sometimes look at the back

(Jami, 1988, pp. 843-844)

Circumambulation of the Kaaba by lover and beloved has been described as follows:

That black stone, give a kiss
The other one,cheerful of imagine the beloved beauty-spot
The beloved drink the water of Zamzam spring
The other one weeping sorrowful
The beloved departure to Safa and Marveh
The other one have a trust on beloved loyalty
(Jami, 1988, p. 844)

As noted in Nezami's story, going on a pilgrimage to Mecca was not optional but to forget the pain of love or to put an end by Majnun's father to this crisis. This circumambulation of the Kaaba has been described as follows:

When his worth of love become widespread
Like the beautiful of Layla embrace the whole of sky
Self-effacing become the part of his essence every day more and more
Entire infatuation embrace his character
(Nezami, 1999, p. 456)

Layla's marriage in both stories are almost similar but in Nezami's story, a man called Ibn Salam proposes to Layla and in this matter , she gets married for her parents' request and there is no force in it but for modesty. On the other hand, she protects her virginity. Layla knows well that there is no love in this circumstance and especially it is a shame for women to express their love. Of course, this belief is still common today and expressing love is one-sided and beloved (woman) cannot express her internal love to the man she loves

Love-making not related to women
Woman not possess of their affairs





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Love affair that become apparent
Relevant to man is art, if the woman express it, indicate a shame

Layla describes her belief about lover and beloved totally different. She believes that lover and beloved are one. But the circumstance inculcates lover expresses his love and beloved should only try to hide this secret, but Layla returns to Majnun and describes her belief as follows:

Said who express liking for love me
Sweetheart desire your love
The pain that captivation of hearts by love
Take possession of heart
Because of the presence of beloved, the garden of love full of joyous laughter
Affliction of me become thousand times as much
However not express liking for
Any movement towards you done
The mystery you can declare
It is a concealed secret for me
Creator who bring into being love
The heart of lover and beloved join
two melody lover and beloved are from the same source
the same origin not to separate
(Jami, Layla and Majnun, p. 7)

In Jami's story, Ibn Salam is not the man who is going to get married with Layla but there is a young man from Thaqif tribe. Unlike Nezami's story, her marriage is not for modesty but because her parents force her to get married with him. However, Majnun is informed of her marriage and it can be seen in both stories but each of them has described nicely and Layla's and Majnun's replies are thinkable. In Nezami's story, when Majnun is informed of Layla's marriage:

In her juniority, turn into a bride
To marry on the time of adolescence
The bride passing the time under the care of loving her mate
Companion and comrade of her mate
Beloved passing time on her married life
Lover become sorrowful is it so wisely
Grief take possession of the entire heart of Majnun
In a fury heart burn his power
When deep sorrow take possessions him entirely
His power become lost
Lover knocked head of himself on the stone
Lover's blood flow on the soil
His body fall on the pumic stone
His wounded bloody with torn dress fall among rock
(Nezami, 1999, pp. 503-504)

And he describes it ironically and complainingly as follows:

Ringdove take offence in the garden
when the fruit garden growth, raven eat it





Ali Heidari

O'fragrant bosom,when grow like a juniper
Not will any result,nobody eat the fruit of juniper at all
On the first step, companion with me
At the end release me on absement
That days fall in love with you
Never have an apprehension for you
(Nezami, 1999, p. 505)

In Jami's story, when Majnun is informed of Layla's marriage, Jami presents these lines to describe Layla's state:

The friend who not remain faithful
Even give a hundred yilds of brook is not valuable
Because of God's grace you are existence
Impression fine alive you
For the sake of you, decide not marriage
Instead of uique pearl purchase a marble
(Jami, 1988, p. 852)

After he is informed of her marriage, Jami describes him as follows:

Majnun after hearing this story
Cause to dance mystically, like a sufi
From the lover's blood flow on the soil,grow flowers
Became like a freed bird
So much that hard-heartedness's friend influence him
Because of annoyance knocking the stone on his chest
Thousands of sorrow and grif captivation of his heart
Become restlessness and passed out unconseiously
Lovwr not take breath, not movement his lips
Besides can not state at anything
After passingthe time,the lover alive again
Wheras worry and grief captivation of his spirit
At that time respire again
Without any movement just breath" Ah"
(Jami, 1988, p. 853)

Description of beloved in Layla's letter are interesting in both stories.

The beginning of the letter in both stories are almost similar. Both of them are begun in the name of God and it is finished with a description of the state of beloved. In Jami's story, the letter begins with this line.

At the beginning in the name of God
God quiets pain and sorrow of grieved
Is it so solitude and keep aloof from us?
Is become a captive adjectness?
At the age growing like flower minicingly
Struggle with thorn force me to turn a blossom again
I had no right to decision about marriage
Coupling was beyond control of me
Parents's decision was that
Take amiss of them,that offended like a thorn hurt my heart





Ali Heidari

Everybody see your face as beautiful as a rose
Or hear the description of your beauty from zephyrus
Is the beloved show her beautiful face to others?
Is anybody permission to companion with her?
Never sleeping together with me
Never my companion and comrade
(Jami, 1988, pp. 862-863)

But in Nezami's story, the letter begins in a different way because it represents a description of both Layla and Majnun.

This letter is like a painted silk
Through it, the sorrow of grieved transfer to afflicted lover
O'old friend, do you keep your oath of friendship
Do you keep your promise about a compact of loyalty?
O'the origin treasure of friendship
The love bright of your luminosity
O'my beloved, the soil coloured of your blood
Beloved's blood like a red agate settle among the rocks
O'the bright spiring among the deep darkness
Like a butterfly around the morn candle
O'who right to reproach me because of glooms
Companion with me right now until doomsday
O'who relentness about her existence
Yield of herself conflagrat
O'heart who sure on my loyalty
Lover and beloved's conversation accept
Among the lover and beloved "how' and "why" are meaningless
I am just with you,are you stay with me in love?
Our furtun was separation and being away from beloved
Company with you is my aim,restlessly
If I like a moon,actually you're the vanguard of sunshine
Far from distance sstare on you
(Nezami, 1999, p. 534)

In Nezami's story, loyalty represents by describing the middle organs of body and there is a common theme in a line which is similar to another line in Jami's story.

Although he is my spouse
Never sleeping toghether by my side
Precious diamond am I, distinguish the imitation diamond
Diamond to test just by mastery person ,not everyone
My unique pearl is a hidden treausure
Like a bud with a concealed secret
Although company with spouse is magnificence
Without you everything are meaningless
That heart careless against your satisfaction
It is better die in a bad destiny

A few strands of beloved hair is like a world





Ali Heidari

A little thorn on the way of beloved is like a flower garden
(Nezami, 1999, p. 532)

In the story of Jami, Majnun replies Layla by using the context of her letter. Love, loyalty, betrayal, joy, honesty and etc. are interlaced and described as follows:

That is similar requisite book
From the grieved to the compassion
Onetime a letter from you recived
That letter was full of loyalty and your compassion
Sympathetic of beloved calm dawn me
After tranquility, because of sorrow of lonliess increased by grief
The bird that fly to friend's house-top
From the griend's roof eat seeds
Annoyance and grief from morn to night
Accompany with you,if you want or not
Become cheerful of passing time, hope to the future
The times change and cosmos turn into satisfactory axis
Companionship of friends blessed
After absence of me,continuance is light of you
(Jami, 1988, pp. 869-871)

In the story of Nezami, Layla dies first and then Majnun is gone but in Jami's story, Majnun dies first and then Layla is gone. However, death exists in both stories as a truth and Jami describes Layla's death as follows:

Layla after the departure of Majnun
Astonished and confused began to moan, like a tulip wallowing in the blood
Because of the anger of eternity take her offence
Live in pleasure and wining and dining forbidden fr herself
On that time with many regrets
Wining and dining became forbidden
Fever take in her thin body entirely
Her mournful face give evidence of facht that she is in a deplorable condition
(Jami, 1988, p. 899)

Jami's general description of autumn as Layla's death is fine and interesting:

Each flower and plant on the muddy
Became like a working place full of color and florid
The face of lover became pale because of shame
On his face appear the sign of lover's pain
The garden become empty of flowers and blossoms
Baqqad turn into Kofeh
The garden with variegated flowers become death
Layla was the best blossol of the garden now was dyning
Time of death take place
The beloved give up against life

Jami, 1988, pp. 901-902)





Ali Heidari

In Nezami's story, falling leaves in autumn as Layla's death has been described as follows:

Condition is that at the time of autumn
The blood flow after shedding the leaves
On the part of grass, stigma of the soil
Similar the ZAHak's snake rolled
Layla from the summit of the throne
Fall into affliction well
The spring of garden was under a spell
The light was blown out by wind
She began to shudder because of fever
Herpes of the lips disappear her sweet laugh
This happening have broken the stature like juniper
The figure like juniper broke, her body that was like pheasant fell
(Nezami, 1999, p. 560)

Both stories end with the death of lover and beloved who could not be together but the poets represent this image in different ways. Nezami shows Majnun over Layla's tomb hugging the grave crying and soothing himself while he is surrounded by savages in the desert. But in Jami's story, when Layla is informed of Majnun's death, she asks her mother with melting heart and crying to bury her beneath his feet:

The ground under her foot is ripped
The woman fall on huge grave
And she dies at this moment:
She asleep, like the dead, domed woman-litter for bride turn into an absurd desire
Mother for the sake of her, in her way buss the soil

Layla's sad words over the grave of Majnun and Majnun's sad words over the grave of Layla show that lover and beloved have been buried near each other. In both stories, they will be together after death. Most of Jami's and Nezami's descriptions are represented by metaphor and simile.

In most of Nezami's descriptions, he has used metaphor and simile and has not called Layla by her own name. These metaphor and simile are often used to describe the beauty of Layla such as this line:

Exordium of the sign of goodness and kindness
King of kings of fairness and beauty property
The names and descriptions which Nezami has used to describe Layla are as follows:

Moon (moon, phoebe, luna, love, sun, photosphere, stars): These terms are the most applied terms to describe Layla and refer to her unique beauty. In fact, Nezami has described Layla's unique beauty by using these fine literal terms.

Moon:

Arabic beloved cast her beauty in others teeth
Persian beloved is so heart-stealing that ravished all hearts
Accompany with all three friends, every morn
The moon aaley was gone round
The moon am I, and you are the ray the light of sunshine
Having to do with eyes disclosed to you from far

Sun:





Ali Heidari

He mediated between them hopefully
Similar the venus star between moon and sun (the metaphor of lover and beloved)
Photosphere:
Aqua rosae pour on the flowers and blossoms
Moonlight sprinkle light on the sunshine
Phoebe:
When his worth of love become widespread
Like the beautiful of Layla embrace the whole of sky
Love:
At the home of love-making make a stand and persist
They persist until termination the love with elated thoughts
Luna:
Layla is so beauteous, charming and heart-stealing
That Majnun against her surrender
Stars:
Layla like a star hidden in the palace
Majnun like a keeper of treasure

Treasure (treasure, gem, essence, jewel, ruby, crown and agate): Other expressions which have been used to describe the beloved are treasure, gem and other synonyms. Indeed, they present how great Layla means to Majnun.

Treasure:
He suffers pains in searching treasure,
Without resulting in getting it,
Gem:
The one who has the gems like you wealthy and prosperous,
Essence:
Although the essence was wealthy,
But it was in the mouth of dragon like a piece of moon,
Jewel:
It was hidden in the pearl of that ruby when the set out to home
Ruby:
For separating the ruby from granite,
He should suffer hardship,
Ruby:
The decorated ruby looks like a fish,
Watches likes a tall cypress
Crown:
The crown is not on my heart,
The plunder but not my property,
Agate:
That the mournful song causes the agate cries blood

Stag eyes and the eyes of Narcissus: These terms are the only terms which have been used in this poetic collection and only represent Layla's incredible beautiful eyes. It should be noted that these terms have been used to describe her unique beauty.

Stag eyes:
The stay eyes of Layla were so beautiful and unique,
It seems a lion just like an innocent rabbit,
Eyes of Narcissus:





Ali Heidari

These eyes were just like narcissus,
Besides the river,

Hedge: This term has been used to describe the fine stature of beloved and only one case has been found for it.
You and I are both human,
But I am a dry branch and you are the leaf of Shamshad,

Garden (garden and green): As the Term spring refers to the beauty and freshness but with less meaning, the term green has been used to emphasize on freshness and vitality.

Garden:
Her hair likes a dark night,
And the light in the clutch of raven,
But the garden is destroyed not even fresh and vital,
Green:
As much as I take out the tongue like dogs,
They take green from fawn,

Sweetheart (sweetheart, gill, leman and mistress): The meaning of these terms which have been used in this poetic collection are more similar to beloved than other terms. In fact, they have been used as a direct substitute for the term beloved. These terms do not refer to an especial meaning but probably to intimate.

Sweetheart:
The sweetheart was dead,
The enamored of love fall on soil,
Gill:
He gains the cup with so much effort,
In the memory of Gill,
Leman:
The leman sets out with the huge expedition,
Mistress:
When Majnoon sees the beautiful face of mistress,
He falls in love,

Spring: Moreover, the term spring refers to beauty it refers to freshness and vitality. It can be said that the purpose of the poet to use this term is to describe Layla's beauty and vitality especially in her youth and teens.

Layla's beauty reaches to her youth from trees,
Majnoon's desire increases by Layla's beauty,
He comes and refreshes the beauty,
By rose and ambergris,

Idol (idol, fetish, ephod and eidolon): These terms with little apparent difference refer to beloved who is unique in all descriptions. By using these terms Nezami has represented a unique character of Layla.

Idol:
He was impatient with speaking that beautiful idol,
Fetish:
Every one admires the fetish,





Ali Heidari

Ephod:

In passing the way I saw an ephod,

Eidolon:

The eidolon in fence free from any grief (sorrow)

Light (light, morning and day): The formal sense of these terms refer to light and their true meaning refer to hope. Layla who is indeed Majnun's desire and also his only aim in his life is joining to her, has been described as follows:

Light:

When he saw Layla (shining light),

He tried to remedy as quick as a wind,

Morning:

Layla is like a world light morning,

And Majnoon is like a self-burning candle

.Nymph: The term nymph is also one of the terms which refers to Layla's unique beauty.

He continues his way,

Far from jealous people

The Nymph is faithful

And the way to catch her is the way to the gate of paradise

Flower (flower, blossom, violet, basil and petal): The second most applied term in this poetic collection is the term flower which refers to Layla's beauty. This term can also describe the elegance, hence; it is different from the term moon which describes beauty. Indeed, the term moon is stronger in sense to describe the beauty and the term flower is stronger in sense to describe the elegance.

Flower:

Layla grows like a flower and blossom

Majnoon washes his eyes by rose-water

The beauty of Layla calls in requisition the flower

And summons rival

..Blossom:

Teach the cypress tallness

Teach the jasmine blossom

.Violet:

I had some nimble violets

So pure as if they grow up from my heart

.Basil:

I choose a basil face

Nobody has in the world

Petal:

The petal

Wears out in distress

Fawn: This term refers to Layla's beauty and coquetry

When the king's dog went to Nakhjir

The fawn was twinge

Oh, kind god what is the prudence?

The fawn should be in danger!





Ali Heidari

Adornment: This term has been used for the sense of beautiful and it refers to Layla who is the adornment of the clique.

The adornment of the clique
Is lower than the adornment of Layla

Water of life (water of life, treatment, remedy, cure, peace, composure and key): Each of these terms are indicating that Layla is the only solace for Majnun and his only hope, expectation, desire and soothing in his life.

Water of life:
Without sweetheart, I'm afflicted
Portion less from water of life
Treatment:
The sweetheart that is the treatment of soul
Even a smell is booty
Remedy:
The sweetheart is the remedy of every pain
Like Gem and wine
Cure:
The bad and good people are obtrusive
Both pain and cure are from you
Peace:
You are the peace of lovers
And solace of poor-spirited
Composure:
I write this letter from restless lover
To send you, the composure of me
Key:
The rendezvous of spring is beside you
The key of affairs is in your hand
Peacock: This refers to Layla's coquetry and only one case has been found for it.
The coquetry and peacock of Layla
Get the soul of Majnoon
Expectation: This term refers to the true sense of hope and desire.
In presence of you, death is my desire
The death that is completely my choice
Partridge: This term refers to coquetry.
When I fly like a hawk
There is no sign of partridge

Fine: This term is one of the terms which has been used in true sense and only one case has been found for it.

Layla is the beauty of the world
In friendship, she is true and honest

Cypress: This term which is an example of fine stature in Persian literature has been used repeatedly in Nezami's poetic collection to describe Layla.

The forest of cypress
Is hidden in Layla

The cypress with a fine stature





Ali Heidari

Not short or without dignity
The fate got the cypress
That I chose

Description of Majnun by Nezami

Violet and Daffodil:
After passing seven years
The daffodil grew up next to tulip
. Smiling pomegranate:
The new growing flower like smiling pomegranate
The large number of pomegranates and flowers
Gem:
The shining gem
Lit the night by its brightness.
Ruby:
His virtue was learning
The ruby of his lips like a gem
Cypress and bud:
They start speaking
Like cypress and bud
Orange and bergamot:
The Geis city manifested by buds
Like orange and bergamot
Thirsty liver:
Layla likes the water of life
And I like a thirsty liver, as you know
Heaven:
Layla likes a star in heaven
Majnoon likes screens of sky
Candle:
His liver was bloody like a candle
He opened his mouth to speak fiery
Layla likes a world light morning
Majnoon likes a self-burning candle
The green spring in darkness
The morning candle butterfly
.Rose water:
Layla grows like a flower and blossoms
Majnoon washes his eyes by rose-water
Snake:
He jumped like a snake
Made a circle around the hair of beloved
With continuous suffer, he waind on the soil
Like a snake on treasure
Dove:
The dove tolerates suffers in garden
But raven eats fruit when they ripen
.





Ali Heidari

Capacitor:

The familiarity treasure of capacitor
Love got its light from you

Green fountain:

The green fountain in darkness
The morning candle butterfly

Broken-hearted:

He was like a wave of blood
Don't ask how that was broken-hearted

Layla's features in Jami's Masnavi

Jami has used metaphors and similes for descriptions in "Layla and Majnun". These metaphors and similes which have been often used to describe Layla's beauty have also some sub branches. Names and descriptions that he has used to describe Layla are as follows:

Moon (moon, phoebe, luna, sun, sunny, stars): These terms have been used to describe Layla.

Moon:

It is said that in a tribe
The moon looks like an angle exists
The auspicious moon is in the veil
That you can look her through the eyes of heart.

.Phoebe:

The phoebe revealed the secret of night
Talked about the discordant of mother and father
The phoebe like Layla, you have in tower
Majnoon had the wall of grief around himself
Each placed in his position
They concluded an agreement between phoebe and star

.Luna:

Forgive the oppressors
Make free the Luna
The Luna sits alone in her pitch
She is unique like the halo of moon
When he saw the shadow of Luna on the screen
Followed her consciously

Sunny/sun:

He saw a sun in screen
It made the sunny horse moving

Stars:

Layla and Majnoon are meritorious
These two stars are eager to each other
Flower (flower, flush, bud, lotus, tulip, blossom, well-favored).

Flush:

The flush face of Layla
Came out of tent like a flower

Bud:

They start speaking
Like cypress and bud





Ali Heidari

Lotus:

The face of lotus changed to blue
Because of the wound of slap

Tulip:

Because of Majnoon s death
She was drowning in blood like a tulip

Blossom/tulip:

The lung burnt from the flame of grief
The blossom provoked like a tulip

Well-favored:

The enthusiasm well-favored of Baghdad
That is Layla

Stag eyes (stag eyes, eyes of Narcissus): These terms have only been used in this poetic collection and refer to Layla's beautiful eyes.

Stag eyes:

The stag eyes that even fawns
Gazed at them

Eyes of Narcissus:

Because of the seditionaries' eyes of Narcissus
Sat beside while bleeding

Cypress (cypress, palm, fine stature): In Persian literature, there are examples of fine stature and tallness that Jami has used them well.

Cypress:

The fine stature and tall cypress
The partridge that walk with fondle

Palm:

Just the shadow of cypress is satisfactory
A feather of TAZROOM is pleasant

Place beside the straight palm

Take a fancy

Fine stature:

When he saw the fine stature cypress
Jumped and became unconscious

Gem (gem, essence, and ruby, smiling lips): These terms are other expressions which have been used well to describe beloved. In fact, they refer to how great Layla means to Majnun.

Ruby/gem:

All were happy except Layla,
All were smiling to reaching the wishes except Layla
She opened the gem,
And closed the ruby,
They dig the grave beside the friend,
And put her in soil like a gem,
Without Layla, he chose homelessness,
Selected the still as a gem,

Essence:





Ali Heidari

I have a unique essence like an angle,
It was concealed from the injury, caused by evil eyes of time,
They are meritorious,
The shining stars are eager to love and stay together,
Smiling lips:
He became helpless, when he heard,
The promise and oath from smiling lips,

Sweetheart (sweetheart, gill): These terms have more similar senses to beloved than others and they are indeed direct substitutes for the term beloved.

Sweetheart:
The separation that caused by sweet heart,
Is more pleasant than the attainment,
The unfaithful sweet heart, what did you do?
With the lover fell in love, what did you do?
Gill:
For the sake of telling the love story of the Gill,
He got tired,

Spirit (spirit, spirit's desire, water of life): These terms with a little apparent difference refer to intense passion of the lover to the beloved and it is probably the only consolation in his life.

Spirit:
Layla is soul and I am her body,
O God, send greetings to her pure spirit,
Who caused this separation should annihilate,
Because of not caring my spirit's desire,
Spirit's desire:
Layla is the spirit's desire
She is the immortal turquoise
The desire of my spirit
Strength my weak body
She said, I am the desire of your spirit
The fruition of your heart and flourish of your spirit
I am his spirit's desire
And he just said my name
Water of life:
Layla is the answer to my life
I'm thirsty and she is the water of life

Bright Qibla and nymph chamber: These compounds refer to Layla's beauty which the lover praises the beloved fine.

Bright Qibla and nymph chamber:
Layla, who is Bright Qibla and nymph chamber
That the sun concealed in her shadow

Partridge (partridge, camel): These terms refer to the elegance and coquetry of beloved.

Partridge:
The fine stature and tall cypress
The partridge that walk with fondle
Camel:
He knew that efforts are useless





Ali Heidari

The unrestrained camel is powerful

Fire in heart (fire in heart, morning, day): This formal sense refer to the light and their real senses refer to the hope.

Burning heart:

When he set out to the land of burning heart

His soul was convenient

He said you are my burning heart

This day, I reach to you with much sorrow and pain

Day:

By the order of burning heart

Majnoon was deprived of day

Morning:

When he saw the beloved

He greeted with smile like morning

Martyr: It is the only term that Layla has used to describe herself with and refers to the eternal love which exists even after death.

Martyr:

Forgive the white appearance of me

This is the sign of martyr

Description of Majnun in Jami's Masnavi

Moon (moon, phoebe, sun).

Moon:

The auspiciousness of Layla (moon)

Is uncountable and incomparable

Phoebe:

She is from the hopeful world,

The auspicious phoebe like sun,

Sun:

If I see you without veil,

The sun will appear without stars,

Bird, loyal.

Bird:

The heart of flower became bloody in the soil,

While seeing the bird,

Loyal:

He exclaimed loudly, you who are loyal,

Your soul is created on loyalty,

Tulip and flower.

Tulip:

Suddenly, like a tulip with a cauterization on heart,

Accommodate on top of the TALL,

Flower:

Who has seen your beautiful face?

Who has inhaled your smell?

Garnet lips, bud mouth.

Garnet lips:





Ali Heidari

When the garnet lips were extinct,
The secrets were concealed,
Bud mouth:
When the bud mouth opened
Thousands of judicious points got out

CONCLUSION

Both poets have used common themes to describe and to use metaphors and similes such as moon, sun, flower, tulip, violet, cypress, garnet, sweetheart and etc.

Both poets have used the written relationship between lover and beloved with some descriptions of them.

The beginning of love in each stories are different. In Nezami's story, it has taken place in school but in Jami's story it has happened in desert. But there are some similar descriptions such as:

The beautiful who with the fawn eyes
Kills everybody in the world
(Nezami)
The stag eyes that even fawns
Gazed at them
(Jami)

In both stories, the description of lover and beloved is two-sided.

Both poets have also described physical appearances such as hair, stature, eyes, face and etc.

Nezami has described the middle organs of body in the letters of beloved.

The beginning of both letters is almost similar. Nezami says:

The old friend, what is your vow?

And Jami says:

Are you aware of what you have done?

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Determination of Propranolol and Metoprolol by Titanate Nanotubes Reinforced Hollow Fiber Solid/Liquid Phase Microextraction and Uv/Vis Spectrophotometry by Partial Least-Squares Calibration

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ABSTRACT

A new design of Hollow Fiber Solid/Liquid Phase Microextraction (HF-SLPME) was developed for the determination of two β -blockers- Propranolol and Metoprolol. The extracted drugs were then quantified by Uv/Vis spectrophotometry using Partial Least Squares (PLS) calibration. The membrane extraction with sorbent interface used in this research is a two-phase supported liquid membrane consisting of an aqueous (donor phase) and one organic solvent/nano sorbent (membrane) system operated in direct immersion sampling mode. The TiO₂ nanotubes dispersed in the organic solvent is held in the pores of a porous membrane supported by capillary forces and sonification. Both ends of the hollow fiber segment are sealed with magnetic stoppers. This device is placed inside the aqueous feed solution and plays the rule of a pseudo-stir bar. All microextraction experiments were supported using an Accurel Q3/2 polypropylene hollow fiber membrane (600 μ m I.D., 200 μ m wall thicknesses, and 0.2 μ m pore size). The experimental setup is very simple and highly affordable. The hollow fiber is disposable, so single use of the fiber reduces the risk of cross-contamination and carry-over problems. In order to obtain high enrichment and extraction efficiency of the analytes using this novel technique, the main parameters were optimized. The results showed that practical pre-concentration factors varied from 103–577. Under the optimized extraction conditions, the method showed good linearity and low limits of detections, 0.01 and 0.03mgL⁻¹ for Propranolol and Metoprolol respectively. Relative recovery of β -blockers in real water samples were between 96–98 for Quchan tap water, and 94–95 for Bojnourd tap water.



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Key words: β -blockers, Chemometric method, Hollow Fiber Solid/Liquid Phase Microextraction (HF-SLPME), Metoprolol, PLS, Propranolol, TiO₂ Nanotubes, Uv/Vis spectrophotometry.

INTRODUCTION

β -blockers have been used for over 40 years to treat high blood pressure (hypertension), various cardiac arrhythmias, and to treat patients after heart attacks to prevent recurrences. In most of the countries including Iran, β -blockers are prescribed in large amounts. Substantial amounts of these pharmaceuticals and their metabolites get into the wastewater after excretion and finally end up in surface water.

The toxicity of propranolol has been particularly well described, with acute toxicity occurring in aquatic organisms exposed to concentrations in the low milligram per liter range. Previous publications have reported the levels of various β -blocker drugs in municipal wastewater, surface waters, and even in groundwater .

β -blockers have been reported to have a relatively slow rate of degradation so they may persist in surface waters. β -blockers have been forbidden by the Medical Commission of the International Olympic Committee (IOC) for typical concentration of 500 mgL⁻¹ in urine and prohibits the use of these drugs because they reduce heart rate and muscular tremor in archery, billiards, and rifle competitions. Therefore, screening and determination of β -blockers in real samples are required in many circumstances such as clinical control for diagnosis, doping control, forensic analysis, and toxicology.

Consequently, there is a growing need to develop reliable analytical methods, which enable their rapid, sensitive, and selective determination in environmental samples, at trace levels. Several analytical methodologies are already available in the literature for the determination of pharmaceutical compounds in surface and wastewaters, and numerous papers reported occurrence of specific pharmaceuticals at levels ranging from ngL⁻¹ to mgL⁻¹. Nevertheless, the vast majority of them are focused on specific therapeutic classes.

Most of the common β -blockers are weakly basic compounds (pKa 8.7–9.7) and structurally have one secondary amino group and one hydroxyl group situated on adjacent carbon atoms (Figure 1). These similarities suggest the possibility of simultaneous analysis of these compounds. The most widely used technique for the determination of these highly polar and basic compounds is HPLC with UV detection fluorimetric, electrochemical and mass spectrometry (MS) detection Furthermore, most of the methods require laborious cleanup of the biological and environmental samples because β -blockers are generally present at low concentration in these complex matrices. To achieve a more efficient, practical, and reliable method for the analysis of β -blockers, ample preparation is a very important step.

More recently, Es'haghi et al. combined hollow fiber liquid-phase microextraction with solid phase extraction, introduced a new method namely Hollow Fiber Solid-Liquid Phase Microextraction (HF-SLPME) and have benefited from the advantages of both. In this technique, incorporation of bundles of chemically modified carbon nanotubes in organic solvent that was supported by a piece of polypropylene hollow fiber improved extraction performance. MWCNTs incorporated in the membrane system could act as a nano-scale solid-phase extractant with high surface area. It has provided more homogenous phase, large number of active adsorbent sites, stronger, and thereupon chemical bonds between analyte and extractor and very high pre-concentration factors of analytes.



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HF-SLPME in implementing two-phase and three-phase modes is used. The membrane extraction with a solid/liquid interface that is used in this work is a two-phase supported liquid membrane consisting of an aqueous phase (feed) and organic solvent/nanosorbent (acceptor) operated in direct immersion sampling model.

Recently, the research on nanomaterials has achieved great success, and which made many new concepts turned into reality. Based on these facts, nanomaterials have attracted great attention in many fields. On the other hand, these nanomaterials earn good characteristics for enrichment and also have absorbed the highlighted attention of researchers in analytical and environmental fields. Titanium dioxide, a novel nanomaterial, has been in the center of focus and the properties of TiO₂ nanopowder determine that it could enrich some environmental pollutants. TiO₂ nanotubes, another form of TiO₂ nanomaterial, has been synthesized and often used for the photodegradation as the photocatalyst. However it has much higher adsorption capacity than that of TiO₂ nanoparticle and much great potential for the trapping of compounds because it is proved to have larger surface area than that of the TiO₂ nanoparticles. TiO₂ nanoparticles has exhibited good enrichment capacity for heavy metals and etc., and TiO₂ nanotubes have been preliminarily explored in preconcentration and sensitive analysis of DDT and its main metabolites, heavy metals and phthalate esters in environmental water samples.

Partial Least-Squares (PLS) is a powerful multivariate statistical tool that has been successfully applied to the quantitative pharmaceutical analysis by using ultraviolet, near infrared, fluorometric, Fourier-transform-infrared-attenuated total reflectance and polarographic data . The basis of these methods along with their applications, have been reported in the literature.

In this article, we used two-phase HF-SLPME for analysis of two β -blockers- Propranolol and Metoprolol in water samples. Different aspects of the extraction procedure such as donor phase volume, pH of the aqueous feed, extraction time, ionic strength (NaCl %) and stirring speed were optimized.

EXPERIMENTAL SECTION

Reagents and stock solutions

Propranolol and Metoprolol were obtained from DarouPakhsh co. (Tehran, Iran). Methanol (HPLC grade) was purchased from Fluka (Buchs SG, Switzerland). Analyte, solvents, salts, acids, and bases were of analytical grade. Deionized water was purified by a Milli-Q system (Millipore, Bedford, USA). Stock solutions of Propranolol and Metoprolol (1000mgL⁻¹) were prepared in MeOH. Working solutions were prepared daily by dilution of the stock solutions with deionized water. All the solutions were protected from light throughout the experiments.

The hollow fiber polypropylene membrane support Q3/2 Accurel PP (200 μ m thick wall, 0.6mm inner diameter and 0.2 μ m average pore size) was purchased from Membrana (Wuppertal, Germany).

Instrumentation

All spectrophotometric measurements were carried out with a UUIKON-922 (Italy) double beam spectrophotometric equipped with 1 cm quartz matched microcell (with volume of 400 μ L). Measurements of pH were made with a Metrohm 632 pH-meter. PLS program was modeled using ParLeS v3.1 software.





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UV/Vis spectrophotometric determination of Propranolol and Metroprolol by PLS calibration

To verify the governing Beer's law, several standard solutions in the concentration range of 0-100 mgL⁻¹ and 0-50 mgL⁻¹ for Propranolol and Metroprolol respectively were prepared. All dilutions were scanned in the wavelength range of 200-350 nm. Spectrum of Propranolol (5mgL⁻¹) and Metroprolol (10mgL⁻¹) has shown in Fig. 2. Propranolol has λ_{max} of 223.4 nm while Metroprolol has λ_{max} at 214.0 nm. Gained calibration coefficients, 0.995 and 0.994 is representative of good linear changes on concentration range of 0.1 – 40.0 mgL⁻¹ and 0.1 – 50.0 mgL⁻¹ for Propranolol and Metroprolol, respectively.

PLS method comprises two separate stages. In the first step, termed calibration, an empirical model is built, representing the relationship between the data generated from a set of reference samples and the respective concentrations of their component(s) of interest. This is followed by a second step called prediction, in which the calibration model is used to determine the concentration of the components in the unknowns from their spectral data.

A four-level factorial design was used to produce a calibration set of 16 samples (Table 1) and a three-level set was derived to produce a prediction set of 9 samples (Table 2). The UV absorption spectra were recorded over the wavelength range of 200–350 nm. The data points of the spectra were collected every 0.2 nm.

The predicted concentrations of the components (C_{pred}) in each sample were compared with the actual concentrations (C_{act}) in the prediction samples and the Root Mean Square Error (RMSE) was calculated for each method as follows:

$$RMSE = \sqrt{\frac{\sum (C_{pred} - C_{act})^2}{n}}$$

The prediction error of a single component in the mixture was calculated as the Relative Standard Error (R.S.E.) of the prediction concentration :

$$R.S.E.(%) = \sqrt{\frac{\sum_{j=1}^N (\hat{C}_j - C_j)^2}{\sum_{j=1}^N (C_j)^2}} \times 100$$

where N is the number of samples, C_j the concentration of the component in the jth mixture and \hat{C} is the estimated concentration. The total prediction error of N samples is calculated as follows:

$$R.S.E._T(%) = \sqrt{\frac{\sum_{i=1}^M \sum_{j=1}^N (\hat{C}_{ij} - C_{ij})^2}{\sum_{i=1}^M \sum_{j=1}^N (C_{ij})^2}} \times 100$$

The R.S.E.(%) of the predicted concentrations and other results are listed in Table 3.



**Narges Eidi and Mohammad Reza Abedi****HF-SLPME Procedure**

The membrane extraction with sorbent interface used in this research is a two-phase supported liquid membrane consisting of an aqueous (donor phase) and one organic solvent/nano sorbent (membrane) system operated in direct immersion sampling mode. The TiO₂ nanotubes dispersed in the organic solvent is held in the pores of a porous membrane supported by capillary forces and sonification. Both ends of the hollow fiber segment are sealed with magnetic stoppers. This device is placed inside the aqueous feed solution and plays the rule of a pseudo-stir bar. All microextraction experiments were supported using an Accurel Q3/2 polypropylene hollow fiber membrane (600µm I.D., 200µm wall thicknesses, and 0.2µm pore size). The experimental setup is very simple and highly affordable. The hollow fiber is disposable, so single use of the fiber reduces the risk of cross-contamination and carry-over problems. In order to obtain high enrichment and extraction efficiency of the analytes using this novel technique, the main parameters were optimized.

The polypropylene hollow fiber was cut into small segments with a length of 1.5 cm. A disperse mixture (5 µL) of the TiO₂ nanotubes in 1-octanol was gradually injected into the fiber manually by using an HPLC syringe so that the injection speed of the mixture and the evaporation of the sample solvent from the fiber were the same. After that the polypropylene tube sealed at both ends by iron pin as magnetic stoppers (iron pins; 1.5×0.6 mm). This fiber was placed into the sample solution containing Propranolol and Metoprolol (1.0mgL⁻¹ in NaOH 1.0molL⁻¹) in an appropriate vial and it was operated as a pseudo- stir bar sorption. The samples were stirred at 800 rpm for 30 min. The analytes were trapped in the solid/organic solvent simultaneously. Thereafter the fiber was removed from the solution and the two stoppers were removed using a small forceps. Fiber segment was placed into the other clean vial containing 0.5mL of methanol. The fiber was stirred at 1000 rpm for 2min for analytes desorption. The UV absorption spectra were recorded over the wavelength range of 200–350 nm. The data points of the spectra were collected every 0.2 nm. Then, calculating both analytes' concentration by help of ParLes software and data gained from previous experiment (formed calibration set). All experiments were performed in triplicate, and the means of the results were used in the calculations.

RESULTS AND DISCUSSION**Optimization for the HF-SLPME**

In order to reach the optimization of the HF-SLPME conditions, several parameters that influence the extraction efficiency were investigated. Various experimental parameters, such as donor phase volume, pH of the aqueous feed, extraction time, ionic strength (NaCl %) and stirring speed were optimized.

Membrane solvent selection

In this work, with respect to our previous research, 1-octanol has been selected as the organic solvent [17] because it is consistent with polypropylene and is well established within the fiber pores. Moreover, TNTs' diameter is large enough to easily accommodate octanol molecules.

Effect of donor phase volume

The influence of the sample volume used for extraction is markedly different in LPME as compared to SPE. In LPME extraction is an equilibration and not an exhaustive process and therefore, the amount of analyte partitioning into the acceptor solution becomes independent of the sample volume when this volume is much higher than the product of the partition constant and the volume of the acceptor solution. Furthermore, a larger sample volume can even be



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disadvantageous due to poorer mass transfers kinetics, resulting in a worse extraction efficiency. For this aim, extraction performed on 5, 10, 15, 20 and 25mL of sample. As one can see in Fig. 4, by increasing sample volume, the concentration of extracted analytes increase too. This could be due to the possible saturation of the TNT capacity for a large sample volume, or a longer extraction time is needed for a >20mL sample to reach equilibrium. Thus, 20.0 mL of donor solution was selected for subsequent experiments.

Effect of stirring of the sample solution

Generally, faster stirring speed increases extraction efficiency. This is because agitation permits a continuous exposure of the extracting surface to a fresh aqueous sample. As seen from Fig. 5, stirring improved microextraction efficiency. However, with extraction at 800rpm stirring rate, excessive air bubbles at the HF were generated. These adhered to the HF surface leading to poorer extraction precision. Therefore, on the basis of these observations the lower stirring rate 800rpm was selected.

Extraction time profile

The extraction time is a very important parameter in an HF-LPME procedure because it influences the partition of the target analytes between the sample solution and the membrane (in the pores of the fiber) and, subsequently, between the organic solvent and acceptor phase. Extractions were performed in periods of 5, 10, 20, 30 and 40 min, while the other parameters remained the same. The experimental results indicate that the concentration of analytes were increased with increasing the extraction time to 20 min. Above 20 min there was no significant increase in the concentrations.

NaOH concentration

The pH value plays an important role in this extraction method. A suitable pH can improve the extraction efficiency and reduce matrices interferences. Therefore, the pH of the sample solution (donor phase) was optimized. In the present study, we used various concentrations (0.005–0.1 molL⁻¹) of NaOH. For both compounds, concentrations increased with increasing NaOH concentration up to 0.05 mol L⁻¹. β -Blockers consist of both a weakly acidic hydroxyl group and a strongly basic amino group. Generally, for basic analytes, the sample solution should be strongly alkaline to promote dissolution of the analytes and to de-ionize the molecules as neutral molecules.

Effect of ionic strength

Adding salt to the analytes may have contradictory effects. First, one expects a positive effect from salting out when the ionic strength of the donor phase is increased. This is due to the decrease in the solubility of the analytes in the aqueous phase and enhances their partitioning into the organic phase. Secondly, a negative effect is attributed to changes in the physical properties of the Nernst diffusion film, which results in reducing the rate of diffusion of the analytes from the donor phase into the organic phase. In addition, the salting out phenomenon would also reduce the solubility of organic solvent in water, causing the organic phase to exhaustively wall off the acceptor phase from the donor phase, a quite desirable result.

Therefore, its influence in the proposed procedure was evaluated by adding different amounts of sodium chloride to the samples in the range 0–15% w/v. As the experimental results indicated, the addition of 10.0%, w/v of sodium chloride optimally enhanced the extraction of the analytes in water. This quantity of NaCl was therefore used in subsequent experiments.



**Narges Eidi and Mohammad Reza Abedi****Evaluation of the Method Performance**

The optimized HF-SLPME and UV-PLS procedure was validated with respect to Relative Standard Deviation (RSD %), Pre-concentration Factor (PF), Limit of Detection (LOD) and Limit of Quantitation (LOQ) (Table 4). Measurements made under the optimum conditions, i.e., donor phase volume: 20.0 mL; stirring rate: 800 rpm; extraction time: 20 min.; NaOH concentration: 0.05 molL⁻¹; and NaCl concentration, 10%, w/v.

Real sample analysis

To demonstrate the practical applicability of this method, real water samples were analyzed using this technique. Drinking water from Quchan and Bojnourd water-supply network were spiked with 1.0 mgL⁻¹ of Propranolol and Metoprolol and extracted under optimal conditions. Method accuracy was determined by calculating the percent Relative Recovery (% RR) as the ratio of the concentrations found in natural and distilled water samples spiked with the same amount of analytes, under the optimized conditions. The relative recovery of the analytes from these real water samples were higher than 90% compared with that of spiked pure water. This indicates that the matrices effect does not have any significant effect on the extraction efficiency of this method. The relative recoveries for two types of water samples are presented in Table 5.

CONCLUSION

A novel, fast and simple procedure based on equilibrium Hollow Fiber Solid-Liquid Phase Microextraction (HF-SLPME) combined with UV-PLS has been developed to extract β -blockers from water samples. The experimental setup is very simple and highly affordable. The hollow fiber is disposable, so the single use of the hollow fiber reduces the risk of cross-contamination and carry-over problems. In comparison with the other conventional sample preparation methods, the developed method has the merits of considerable analysis speed, good separation efficiency and elevated pre-concentration, notable precision and high sensitivity. TNTs are also compatible with the polypropylene fiber structure. In desorption stage, the pore structure of the polypropylene fiber allows rapid exit of the analytes from the sorbent in the enriched solvent. In this technique valuable role of TNTs as solid sorbent combined with organic solvent extractor was very significant. Multivariate (PLS) method enable the quantitation of Propranolol and Metoprolol binary mixture with good accuracy and precision. All data proved that this method could be effectively applied to the analysis of β -blockers in water samples.

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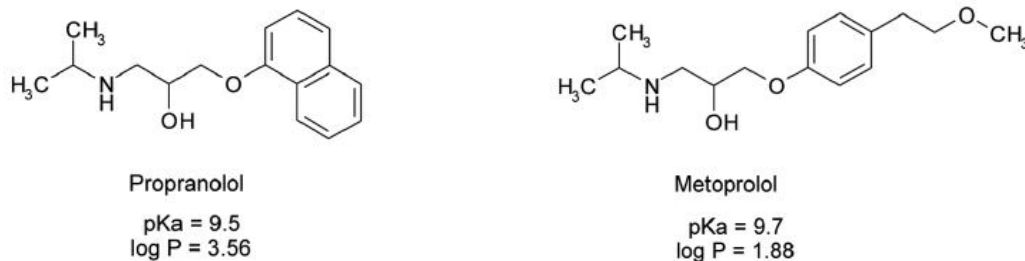


Figure 1. Structures of β -blockers used in this article.

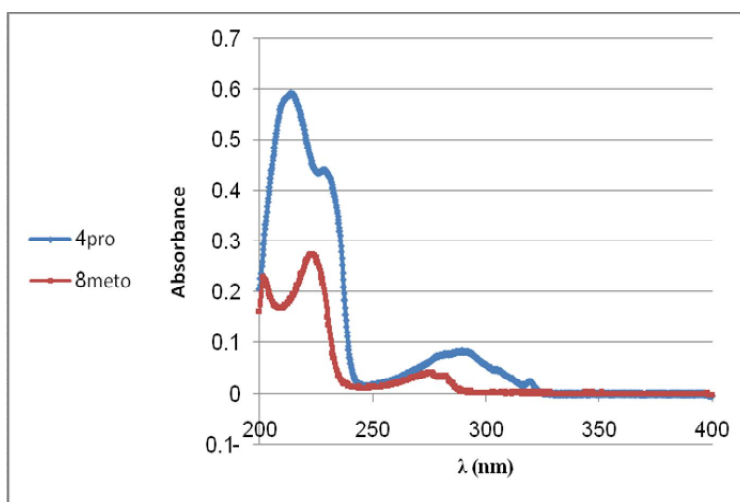


Figure 2. Spectrum of Propranolol (5mgL⁻¹) and Metroprolol (10mgL⁻¹)

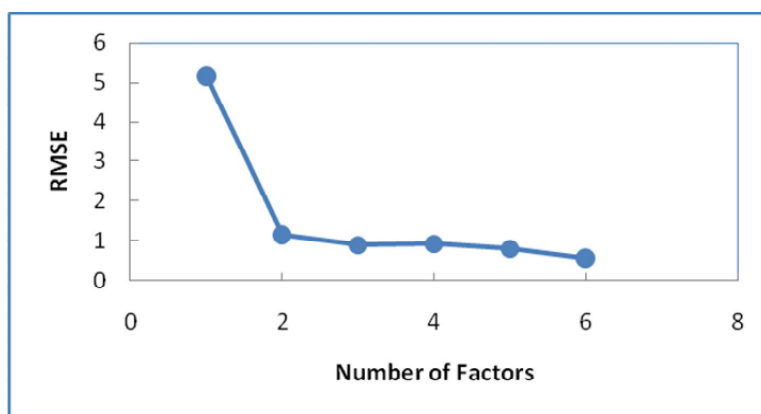


Figure 3. RMSE curve verses number of factors for Propranolol and Metroprolol





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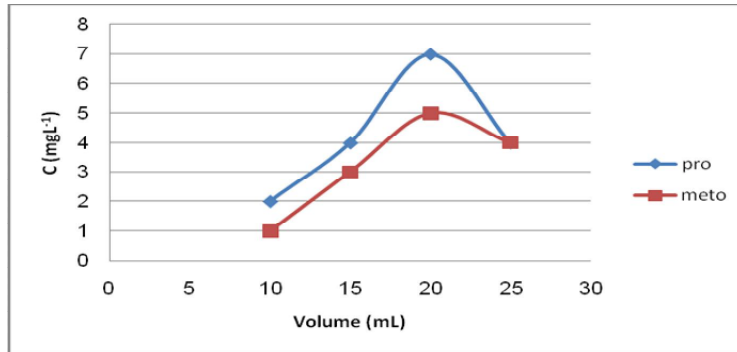


Figure 4. Effect of the donor phase volume on the method performance.

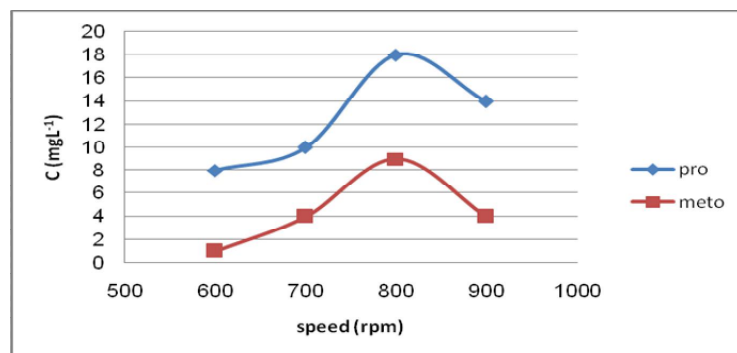


Figure 5. Effect of the stirring rate on the method performance.

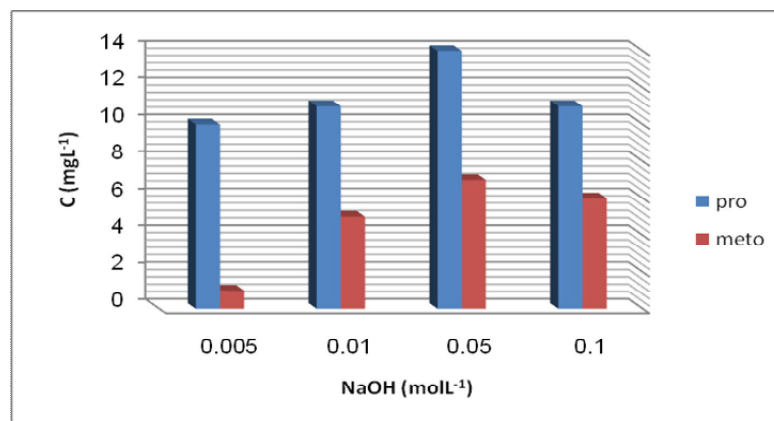


Figure 6. Effect of NOH concentration on the method performance





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Table 1. Calibration set composition

Sample	Concentration(mgL ⁻¹)	
	Metroprolol	Propranolol
C ₁	16.0	4.0
C ₂	0.0	12.0
C ₃	8.0	4.0
C ₄	8.0	8.0
C ₅	8.0	0.0
C ₆	8.0	12.0
C ₇	24.0	4.0
C ₈	0.0	0.0
C ₉	24.0	12.0
C ₁₀	24.0	8.0
C ₁₁	0.0	4.0
C ₁₂	24.0	0.0
C ₁₃	16.0	8.0
C ₁₄	16.0	12.0
C ₁₅	16.0	0.0
C ₁₆	0.0	8.0

Table 2. Prediction set composition

Sample	Concentration (mgL ⁻¹)	
	Metroprolol	Propranolol
P ₁	10.0	5.0
P ₂	20.0	10.0
P ₃	20.0	2.0
P ₄	4.0	5.0
P ₅	4.0	2.0
P ₆	20.0	5.0
P ₇	10.0	2.0
P ₈	4.0	10.0
P ₉	10.0	10.0

Table 3. Statistical parameters for PLS-1 analysis of Propranolol and Metroprolol

Parameter	Propranolol	Metroprolol
Optimum spectral range (nm)	200–350	200–350
Number of PLS Factors	3	3
R.S.E. (%)	3.1	4.4
R.S.E. _T (%)	3.4	
Recovery (%)	101.55	106.50
Recovery _T (%)	104.2	





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Table 4. Characteristic data of the established HF-SLPME-UV-PLS method for determination of Propranolol and Metroprolol

Analyte	LODs (mgL ⁻¹ , S/N=3) (n=7)	LOQs (mgL ⁻¹ , S/N=10) (n=5)	RSDs (%) (n=5)	PF (n=3)
Propranolol	0.01	0.05	6.8	577
Metroprolol	0.03	0.1	7.4	103

Table 5. Relative recovery of Propranolol and Metroprolol in real water samples by use of HF-SLPME-UV-PLS method

Sample	Propranolol	Metroprolol
Quchan drinking water	96	98
Bojnourd drinking water	94	95





Pre-concentration and Determination of Diclofenac and Ibuprofen Using Titanate Nanotubes-Assisted Pseudo-Stirbar Hollow Fiber Solid/Liquid-Phase Microextraction and Uv/Vis spectrophotometry by Partial Least-Squares Calibration

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ABSTRACT

A method termed pseudo-stir bar Hollow Fiber Solid/Liquid Phase Microextraction (HF-SLPME) was utilized to extract two Nonsteroidal Anti-inflammatory Drugs (NSAIDs)- Diclofenac and Ibuprofen- in environmental waters. The extracted drugs were then quantified by Uv/Vis spectrophotometry using Partial Least Squares (PLS) calibration. In HF-SLPME a porous polypropylene hollow fiber filled with TiO₂ nanotubes reinforced organic solvent that acts as an analyte trap to pre-concentrate NSAIDs from water samples. Both ends of the hollow fiber segment are sealed with magnetic stoppers. This device is placed inside the aqueous feed solution and plays the rule of a pseudo-stir bar. The effective parameters are optimized. The results showed that practical pre-concentration factors varied from 355–369. Under the optimized extraction conditions, the method showed good linearity and low limits of detections, 0.02 and 0.03mgL⁻¹ for Diclofenac and Ibuprofen respectively. Relative recovery of NSAIDs in real water samples were between 96–98 for Quchan tap water, and 94–95 for Esfarayen tap water.

Key words: Chemometric method, Diclofenac, Hollow Fiber Solid/Liquid Phase Microextraction (HF-SLPME), Ibuprofen, Nonsteroidal Anti-inflammatory Drugs (NSAIDs), PLS, TiO₂ Nanotubes, Uv-Vis spectrophotometry.





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INTRODUCTION

In the μ -SPE technique described by Basheer et al. a square (15mm \times 15 mm), heat-sealed polypropylene sheet membrane envelope was packed with 6mg of MWCNT. This μ -SPE device may be dropped on stirred aqueous samples; analytes from the sample diffuse through the envelope wall and are adsorbed over the MWCNT filling. After extraction, the device is removed, rinsed, dried, and dipped on organic solvents under ultrasound to desorb the extracted species. They found this μ -SPE method robust, durable and that it is not easily automated. CNTs acts as an analyte trap, resulting in higher selectivity and enrichment because the MWCNTs act as solid sorbents do in SPME fibers.

More recently, Es'haghi et al. combined hollow fiber liquid-phase microextraction with solid phase extraction, introduced a new method namely Hollow Fiber Solid-Liquid Phase Microextraction (HF-SLPME) and have benefited from the advantages of both. In this technique, incorporation of bundles of chemically modified carbon nanotubes in organic solvent that was supported by a piece of polypropylene hollow fiber improved extraction performance. MWCNTs incorporated in the membrane system could act as a nano-scale solid-phase extractant with high surface area. It has provided more homogenous phase, large number of active adsorbent sites, stronger, and thereupon chemical bonds between analyte and extractor and very high pre-concentration factors of analytes.

HF-SLPME in implementing two-phase and three-phase modes is used. The membrane extraction with a solid/liquid interface that is used in this work is a two-phase supported liquid membrane consisting of an aqueous phase (feed) and organic solvent/nanosorbent (acceptor) operated in direct immersion sampling mode[Error! Bookmark not defined.]

Recently, TiO₂ nanotubes (TNTs) have received considerable attention because of its higher surface area, better adsorption ability and higher photocatalytic activity . Zwilling et al. firstly reported that the ordered TiO₂ nanotubes arrays could be obtained through a simple anodization process . Ordered TiO₂ nanotube array has been an attractive approach for many important engineering applications. These potential applications include photoelectrochemical hydrogen generation , solar cells , hydrogen storage , gas sensing , catalyst supports and photoelectrocatalytic activity electrode for organic contaminant degradation . However, to the best of our knowledge, there has very few reports using TiO₂ nanotube array on the enrichment and measurement of environmental contaminants.

PLS regression was originally developed by Wold . Calibration in PLS methods is done by using a set of m mixtures containing known concentrations of n analytes, the absorbances of which are measured at k wavelengths. PLS methodology resolves both the absorbance data matrix, $\mathbf{X}(m, k)$, and the concentration matrix, $\mathbf{Y}(m, n)$, into the product of two smaller matrices. In the process, PLS actively uses the variables included in the concentration matrix as the data matrix being resolved. This entails compressing data to a smaller number of intensities called "scores" in a new coordinate system. The new axes are called "Principal Components" (PCs) and are linear combinations of the original variables. A PC represents a systematic variation detected in the data set. The regression coefficients from each original variable to each PC are called "loadings". PLS methodology assumes concentrations to be linear functions of the scores:

$$\mathbf{X}=\mathbf{TP}^T+\mathbf{E} \quad (1)$$

$$\mathbf{Y}=\mathbf{UQ}^T+\mathbf{F} \quad (2)$$

where \mathbf{T} and \mathbf{U} , of $m \times a$ dimensions, are the absorbance and concentration scores matrix, respectively, and $\mathbf{P}^T(a, n)$ and $\mathbf{Q}^T(a, p)$ the corresponding loadings matrices, superscript \mathbf{T} denoting the transpose of each matrix and a the





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number of PCs [$a \geq \min(m, k)$]. Finally, $\mathbf{E}(m, k)$ and $\mathbf{F}(m, n)$ are the residuals matrices of absorbance data and concentrations, respectively. Absorbance and concentration scores are related by

$$\hat{\mathbf{u}}_h = \mathbf{B}_h \mathbf{t}_h \quad (3)$$

where \mathbf{b}_h denotes the regression coefficient for each PC. Equation (2) can thus be rewritten as:

$$\mathbf{Y} = \mathbf{T} \mathbf{B} \mathbf{Q}^T + \mathbf{F} \quad (4)$$

where $\mathbf{B}(a, a)$ contains the regression coefficients for matrix \mathbf{b}_h .

In order to estimate the concentration of an unknown mixture, its scores (\mathbf{t}^*) are first calculated and then used to obtain the concentration from

$$\hat{\mathbf{Y}} = \mathbf{T}^* \mathbf{B} \mathbf{Q}^T \quad (5)$$

In this work, the PLS1 algorithm was used, so matrix \mathbf{Y} was reduced to the corresponding vector. Provided calibration mixtures are properly chosen, the main step in PLS calibration is the selection of the number of PCs needed to model the system. Several procedures for this purpose have been devised. We chose the significant number of PCs to be that which prediction error sum of squares (PRESS) was not significantly different from the minimum PRESS **Error! Bookmark not defined.**,

$$\text{PRESS} = \sum_{i=1}^m (\hat{c}_i - c_i)^2 \quad (6)$$

where \hat{c}_i and c_i denote calculated and added concentrations, respectively.

One advantage of using multivariate calibration in general and PLS in particular is that they allow one to distinguish those samples that are "different" from those used in the calibration step; this can be accomplished by comparing the variances of the residuals of the spectra for the sample with those for the calibration samples. If a sample is classified as "different", its determined concentration will be unreliable and the origin of the uncertainty (instrumental error, presence of an unexpectedly high level of a given interference, etc.) should be investigated. In this article, we used two-phase HF-SLPME for analysis of Nonsteroidal Anti-inflammatory Drugs (NSAIDs) in water samples. Different aspects of the extraction procedure such as donor phase volume, pH of the aqueous feed, extraction time, ionic strength (NaCl %) and stirring speed were optimized.





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Experimental Section

Reagents and stock solutions

Diclofenac and Ibuprofen were obtained from DarouPakhsh co. (Tehran, Iran). Methanol (HPLC grade) was purchased from Fluka (Buchs SG, Switzerland). All other chemical and solvents were of analytical reagent grade. Deionized water was purified by a Milli-Q system (Millipore, Bedford, USA). Stock solutions of Diclofenac and Ibuprofen (1000mgL⁻¹) were prepared in MeOH. Working solutions were prepared daily by dilution of the stock solutions with deionized water. All the solutions were protected from light throughout the experiments.

Instrumentation

All spectrophotometric measurements were carried out with a UUIKON-922 (Italy) double beam spectrophotometric equipped with 1 cm quartz matched microcell (with volume of 400μL). Measurements of pH were made with a Metrohm 632 pH-meter. PLS program was modeled using ParLeS v3.1 software.

UV/Vis spectrophotometric determination of Diclofenac and Ibuprofen by PLS calibration

To verify the governing Beer's law, several standard solutions in the concentration range of 0-100 mgL⁻¹ and 0-50 mgL⁻¹ for Diclofenac and Ibuprofen respectively were prepared. All dilutions were scanned in the wavelength range of 200-350 nm. Spectrum of Diclofenac (10mgL⁻¹) and Ibuprofen (5mgL⁻¹) has shown in Fig. 1. Diclofenac has λ_{max} of 222.6 nm while Ibuprofen has λ_{max} at 213.4 nm. Gained calibration coefficients, 0.992 and 0.991 is representative of good linear changes on concentration range of 0.2 – 70.0 mgL⁻¹ and 0.7 – 30.0 mgL⁻¹ for Diclofenac and Ibuprofen, respectively.

PLS method comprises two separate stages. In the first step, termed calibration, an empirical model is built, representing the relationship between the data generated from a set of reference samples and the respective concentrations of their component(s) of interest. This is followed by a second step called prediction, in which the calibration model is used to determine the concentration of the components in the unknowns from their spectral data.

A four-level factorial design was used to produce a calibration set of 16 samples (Table 1) and a three-level set was derived to produce a prediction set of 9 samples (Table 2). The UV absorption spectra were recorded over the wavelength range of 200–350 nm. The data points of the spectra were collected every 0.2 nm.

The predicted concentrations of the components (C_{pred}) in each sample were compared with the actual concentrations (C_{act}) in the prediction samples and the Root Mean Square Error (RMSE) was calculated for each method as follows:

$$RMSE = \sqrt{\frac{\sum (C_{pred} - C_{act})^2}{n}}$$

The prediction error of a single component in the mixture was calculated as the Relative Standard Error (R.S.E.) of the

$$\text{prediction concentration : } R.S.E.(%) = \sqrt{\frac{\sum_{j=1}^N (\hat{C}_j - C_j)^2}{\sum_{j=1}^N (C_j)^2}} \times 100$$





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where N is the number of samples, C_j the concentration of the component in the jth mixture and \hat{C} is the estimated concentration. The total prediction error of N samples is calculated as follows:

$$R.S.E.T (\%) = \sqrt{\frac{\sum_{i=1}^M \sum_{j=1}^N (\hat{C}_{ij} - C_{ij})^2}{\sum_{i=1}^M \sum_{j=1}^N (C_{ij})^2}} \times 100$$

The R.S.E.(%) of the predicted concentrations and other results are listed in Table 3.

HF-SLPME Procedure

Polypropylene hollow-fiber was cut into 1.5 cm segments and sonicated in acetone for 5 min to remove any possible contaminants. The fiber was then removed from the acetone and allowed to dry completely. Organic solvent was mixed with TiO₂ nanotubes and dispersed by sonification. Porous polypropylene fiber was immersed in the dispersed mixture until pores of the fiber was filled by capillary forces and sonification. Subsequently, 5.0 μL of dispersed TiO₂ nanotubes in 1-octanol (acceptor phase) was injected into the lumen of the hollow fiber with a syringe, after that the polypropylene tube sealed at both ends by iron pin as magnetic stoppers (iron pins; 1.5×0.6 mm). This fiber was placed into the sample solution containing Diclofenac and Ibuprofen (1.0mgL⁻¹ in HCl 1.0molL⁻¹) in an appropriate vial and it was operated as a pseudo- stir bar sorption. The samples were stirred at 800 rpm for 30 min. The analytes were trapped in the solid/organic solvent simultaneously. Thereafter the fiber was removed from the solution and the two stoppers were removed using a small forceps. Fiber segment was placed into the other clean vial containing 0.5mL of methanol. The fiber was stirred at 1000 rpm for 2min for analytes desorption. The UV absorption spectra were recorded over the wavelength range of 200–350 nm. The data points of the spectra were collected every 0.2 nm. Then, calculating both analytes' concentration by help of ParLes software and data gained from previous experiment (formed calibration set). All experiments were performed in triplicate, and the means of the results were used in the calculations.

RESULTS AND DISCUSSION

Optimization for the HF-SLPME

In order to reach the optimization of the HF-SLPME conditions, several parameters that influence the extraction efficiency were investigated. Various experimental parameters, such as donor phase volume, pH of the aqueous feed, extraction time, ionic strength (NaCl %) and stirring speed were optimized.

Membrane solvent selection

In this work, with respect to our previous research, 1-octanol has been selected as the organic solvent [Error! Bookmark not defined.] because it is consistent with polypropylene and is well established within the fiber pores. Moreover, TNTs' diameter is large enough to easily accommodate octanol molecules.

Effect of donor phase volume

Sample solution volume is one of important factors should be optimized. For this aim, extraction performed on 5, 10, 15, 20 and 25mL of sample. As one can see in Fig. 3, by increasing sample volume, the concentration of extracted



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analytes increase too; because more amount of analytes transform into hollow fiber. In the other hand by increasing amount of sample consumedly, mass transfer kinetics become weaker. In addition, the HF-SLMPE procedure is an equilibrium procedure. The amount of analytes that can be extracted depend on the partition coefficient of the analyte between the sample and the TNTs. This type of observation is common in many microextraction procedures. This could be due to the possible saturation of the TNT capacity for a large sample volume, or a longer extraction time is needed for a >10mL sample to reach equilibrium. Thus, 10.0 mL of donor solution was selected for subsequent experiments.

Effect of stirring of the sample solution

Since agitation of the sample permits the continuous exposure of extraction surface to fresh aqueous sample, the extraction efficiency could be enhanced by enhancing the stirring of the sample. As seen from Fig. 4, stirring improved microextraction efficiency. However, with extraction at 900rpm stirring rate, excessive air bubbles at the HF were generated. These adhered to the HF surface leading to poorer extraction precision. Therefore, on the basis of these observations the lower stirring rate 800rpm was selected.

Extraction time profile

The extraction time is a very important parameter in an HFLPME procedure because it influences the partition of the target analytes between the sample solution and the membrane (in the pores of the fiber) and, subsequently, between the organic solvent and acceptor phase. Different extraction times were tested and the corresponding results are provided in Fig. 5. Extractions were performed in periods of 10, 20, 30 and 40 min, while the other parameters remained the same. The experimental results indicate that the concentration of analytes were increased with increasing the extraction time to 30 min. Above 30 min there was no significant increase in the concentrations.

HCl concentration

The pH value plays an important role in this extraction method. A suitable pH can improve the extraction efficiency and reduce matrices interferences. Generally, for NSAIDs the donor phase should be strongly acidic in order to ensure that the analytes are not ionised and consequently reduce its solubility in the organic solution. Therefore, the pH of the sample solution (donor phase) was optimized. We used various concentrations (0.005–0.1 molL⁻¹) of HCl. For both compounds, concentrations increased with increasing HCl concentration up to 0.05 molL⁻¹. We used 0.05molL⁻¹ HCl for donor phase solution.

Effect of ionic strength

It is well known the beneficial effect of the ionic strength for the liquid microextraction of a wide variety of analytes. Therefore, its influence in the proposed procedure was evaluated by adding different amounts of sodium chloride to the samples in the range 0–15% w/v. The results demonstrated a slight improvement of the extraction for both compounds up to 5%w/v, however a decreasing was observed at concentrations higher than 5%w/v. This result may be explained as follows: the addition of a salt can reduce the amount of water available to dissolve analyte molecules due to the formation of hydration spheres around the ionic salt molecules which improved the extraction efficiency for the investigated compounds.



**Tahere Najafzadeh and Mohammad Reza Abedi****Evaluation of the Method Performance**

The characteristic data of the developed HF-SLPME method are summarized in Table 4. Measurements made under the optimum conditions, i.e., donor phase volume: 10.0 mL; stirring rate: 800 rpm; extraction time: 30 min.; HCl concentration: 0.05 molL⁻¹; and NaCl concentration, 5%, w/v. To check the accuracy of methods it is necessary to analyze statistics of numerical measurements. A decomposition features for one specific analyte is shown with some efficiency indexes. This indexes are described by some numerical value named efficiency numbers. Efficiency numbers that have analyzed in this study including: pre-concentration factor (PF), relative standard deviation (RSD %), limit of detection (LOD) and limit of quantitation (LOQ).

Real sample analysis

To demonstrate the practical applicability of this method, real water samples were analyzed using this technique. Drinking water from Quchan and Esfarayen water-supply network were spiked with 1.0 mgL⁻¹ of Diclofenac and Ibuprofen and extracted under optimal conditions. Method accuracy was determined by calculating the percent relative recovery (% R) as the ratio of the concentrations found in natural and distilled water samples spiked with the same amount of analytes, under the optimized conditions.

The relative recovery of the analytes from these real water samples were higher than 90% compared with that of spiked pure water. This indicates that the matrices effect does not have any significant effect on the extraction efficiency of this method. The relative recoveries for two types of water samples are presented in Table 5.

CONCLUSION

In this article, an initiative method based on Hollow Fiber supported Solid/Liquid Phase Microextraction (HF-SLPME) with an affordable and simple format; pseudostir bar device was used for extraction and determination of Non-steroidal Anti-inflammatory Drugs (NSAIDs) in water samples. The procedure offers a useful pre-concentration technique with acceptable accuracy and precision. In comparison with the other methods for determination of NSAIDs, many advantages can be achieved with this newly proposed method such as simplicity, sensitivity, and almost environmentally friendly. The operation is easy to handle because the receiving phase is protected by the polypropylene hollow fiber segment. TNTs are also compatible with the polypropylene fiber structure. In desorption stage, the pore structure of the polypropylene fiber allows rapid exit of the analytes from the sorbent in the enriched solvent. The disposable nature of the hollow fiber completely eliminates the possibility of sample carry over and guarantees high reproducibility. In addition, the small pore size prevents large molecules in matrix and unsolved particles in the donor solution from entering the acceptor phase, thus yielding very clean extract. In this technique valuable role of TNTs as solid sorbent combined with organic solvent extractor was very significant. Multivariate (PLS) method enable the quantitation of Diclofenac and Ibuprofen binary mixture with good accuracy and precision. All data proved that this method could be effectively applied to the analysis of NSAIDs in water samples.

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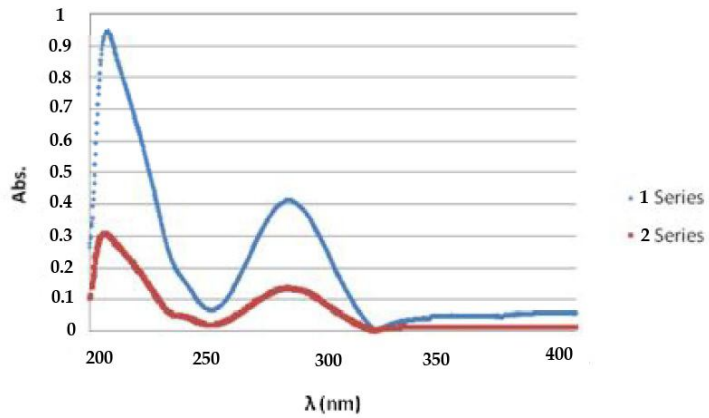


Figure 1. Spectrum of Diclofenac (10mgL⁻¹) and Ibuprofen (5mgL⁻¹)

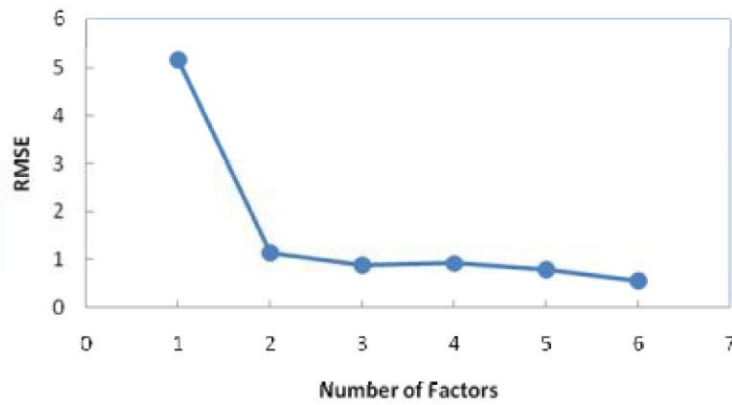


Figure 2. RMSE curve verses number of factors for Diclofenac and Ibuprofen

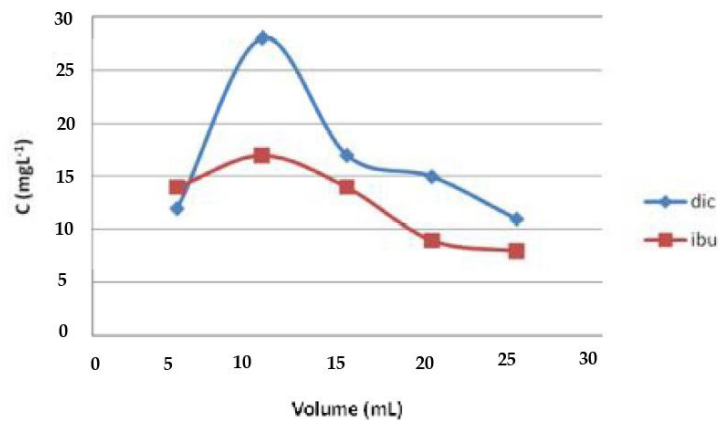


Figure 3. Effect of the donor phase volume on the method performance.





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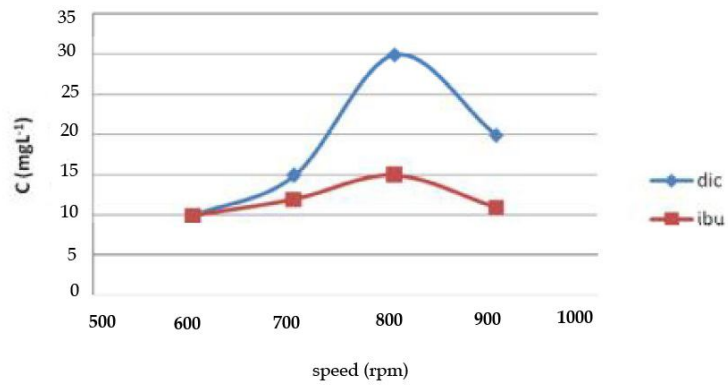


Figure 4. Effect of the stirring rate on the method performance.

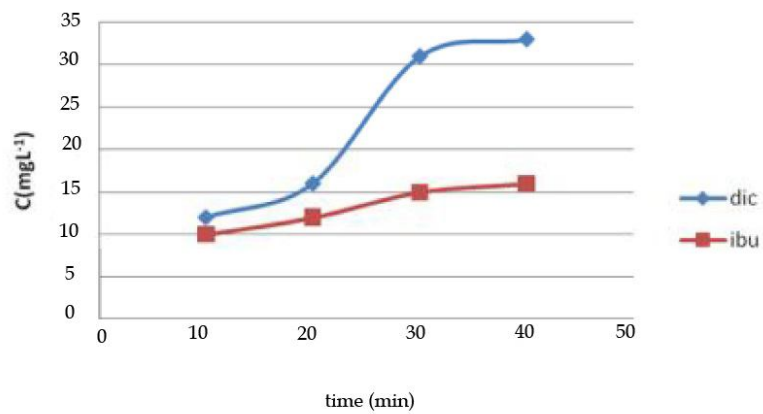


Figure 5. Effect of the extraction time on the method performance.

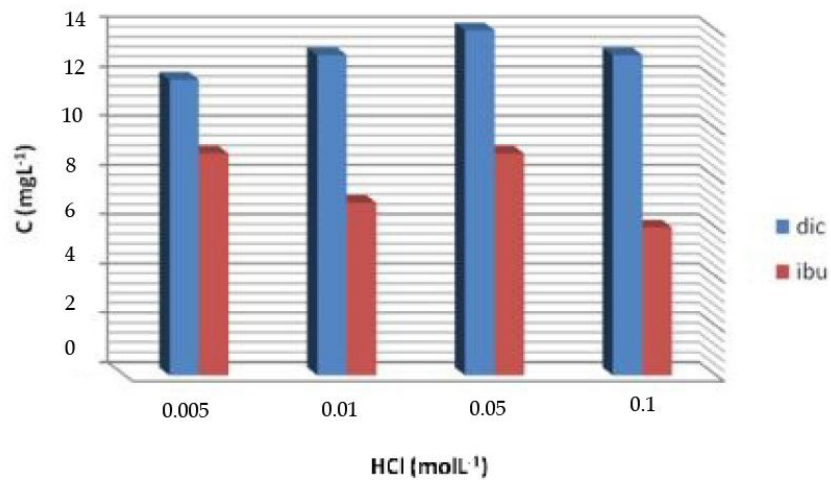


Figure 6. Effect of HCl concentration on the method performance





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Table 1. Calibration set composition

Sample	Concentration(mgL ⁻¹)	
	Ibuprofen	Diclofenac
C ₁	16.0	4.0
C ₂	0.0	12.0
C ₃	8.0	4.0
C ₄	8.0	8.0
C ₅	8.0	0.0
C ₆	8.0	12.0
C ₇	24.0	4.0
C ₈	0.0	0.0
C ₉	24.0	12.0
C ₁₀	24.0	8.0
C ₁₁	0.0	4.0
C ₁₂	24.0	0.0
C ₁₃	16.0	8.0
C ₁₄	16.0	12.0
C ₁₅	16.0	0.0
C ₁₆	0.0	8.0

Table 2. Prediction set composition

Sample	Concentration (mgL ⁻¹)	
	Ibuprofen	Diclofenac
P ₁	10.0	5.0
P ₂	20.0	10.0
P ₃	20.0	2.0
P ₄	4.0	5.0
P ₅	4.0	2.0
P ₆	20.0	5.0
P ₇	10.0	2.0
P ₈	4.0	10.0
P ₉	10.0	10.0

Table 3. Statistical parameters for PLS-1 analysis of Diclofenac and Ibuprofen

Parameter	Ibuprofen	Diclofenac
Optimum spectral range (nm)	200–350	200–350
Number of PLS Factors	3	3
R.S.E. (%)	3.7	5.1





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R.S.E. _T (%)	4.4	
Recovery (%)	98.7	101.5
Recovery _T (%)	100.1	

Table 4. Characteristic data of the established HF-SLPME-UV-PLS method for determination of Ibuprofen and Diclofenac

Analyte	LODs (mgL ⁻¹ , S/N=3) (n=7)	LOQs (mgL ⁻¹ , S/N=10) (n=5)	RSDs (%) (n=5)	PF (n=3)
Diclofenac	0.02	0.05	7.9	369
Ibuprofen	0.03	0.1	6.5	355

Table 5. Relative recovery of Ibuprofen and Diclofenac in real water samples by use of HF-SLPME-UV-PLS method

Sample	Ibuprofen	Diclofenac
Quchan drinking water	96	98
Esfarayen drinking water	94	95





Prediction of *Lactobacillus Acidophilus* in Concentrated Yoghurt by Artificial Neural Networks

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ABSTRACT

In recent years, using artificial neural networks (neural networks) has increased in many parts of food industry and artificial neural networks have been used to solve many problems of quality control. The aim of this study is to develop neural networks in order to evaluate the quality of probiotic yogurt. In this study, back propagation neural network with algorithm Levenberg–Marquardt was used as a model. Various parameters were considered including: pH, the percentage of prebiotic compound (inulin and oligo-fructose) and percentage of probiotic bacteria inoculation that are effective factors on *Lactobacillus acidophilus* survival. Performance of developed model was evaluated calculating the mean square error coefficient. Also, the sigmoid tangent stimulation function was used to optimize the model in pre-processing stage. The results show that sigmoid tangent stimulation function with 5 neurons in hidden layer on days 1, 7 and 14 respectively, had the most explain coefficients of 0.991, 0.985, 0.971 and mean square error (MSE) was 0.00054, 0.00065, 0.00081 and defined model has capacity of estimation accuracy for predicting survival capability of *Lactobacillus acidophilus* in three time period.

Key words: concentrated probiotic yoghurt, neural networks, *Lactobacillus acidophilus*





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INTRODUCTION

Probiotic dairy products are very important due to their large effects on people's health. Probiotic bacteria prevent the growth of harmful bacteria and have a positive effect on gastrointestinal tract through positive impact on beneficial intestinal flora. They also increase the food better digestion, enhance immune system function and increase sustainability of body, resist against spread and infection of disease. (Rasdary et al., 2008; Yeganezad et al., 2007). Probiotics also balance the intestine acidity through producing lactic acid, hydrogen peroxide and acetic acid and prevent the production and reproduction of pathogen bacteria. Some probiotics produce organic compounds called bacteriocin that is a natural antibiotic compound (Dao et al., 1997). Probiotic dairy consumption can be effective in preventing traveler's diarrhea and *Helicobacter pylori* infections of stomach. Yogurt can be a suitable environment for storage and transfer of probiotic bacteria in body due to specific physicochemical parameters (Barry et al., 2009; Dao et al., 1997). Starters used in probiotic yogurts include *Streptococcus thermophilus* and *Lactobacillus bulgaricus* and different strains of probiotic bacteria such as *Lactobacillus acidophilus*, *Bifidobacterium lactis* and *Bifidobacterium Bifidum* (Tarmaraj and Shah, 2003). Physicochemical parameters of yogurt such as pH, acidity, bacteria in yogurt, the storage temperature, oxygen, Incubation time and primary initiator can be effective on survival of probiotic bacteria during storage (Barry et al., 2009, Donker et al., 2007). In this study, the probiotic bacteria viability is reviewed during days 1, 7 and 14 after production and its value is predicted using neural network models. Artificial Neural Networks were introduced for the first time in 1943, but it was no use for a long time. Later, its usage entered a new phase with the advent of computers and propagation learning algorithm for feed forward networks in 1986 (Alborzi, 2004).

The neural network model is composed of a set of computational elements that is called neurons whose function is similar to biological neurons, these models are able to detect the intrinsic relationship between data without any prior knowledge of a problem or process in question, (Mahnaj, 2008).

Many researchers have used artificial neural networks in order to achieve desired objectives in food industry some of them includes: predicting microbial grow of food (Garsiya- Gimno et al., 2002), evaluating olive oil fraud (Gudakereh; 1992), predicting Persisting flour wheat in bakery (Harimoto et al., 1995), predicting the combined effect of temperature, pH and water activity on heat inactivity of bacteria (Lu and Nakaii, 2001), evaluating sensitive features of noodles (Tulbak et al., 2003), moisture as a function of thermal conductivity of food (Sablany Shyam and Shafior Rahman, 2003), predicting shelf life estimates of instant coffee drinks and sensory quality of instant coffee drinks (Samit Goyal, 2001). Examining various sources suggests that some researchers have proposed different models in order to predict the growth of probiotic bacteria that most of them have similar results. Kiwi Hardjo et al (2005) used RSM models in order to optimize and determine coefficients of *Bifido bacterium Langum* growth. Also, Sofo and Ikianji (2007) conducted a study entitled estimating the shelf life of yogurt using artificial intelligence model. In this research, physicochemical and microbial changes and yoghurt texture were evaluated during 1, 7 and 14 days of storage in order to determine the best shelf life. The data obtained by artificial intelligence model were used in order to determine the best retention time. Input data in this mathematical model included pH, aerobic bacteria count, yeast and mold and output data included the changes of yogurt retention time. Through this study, it was found that the results of mathematical model predictions are based on experimental work results.

Artificial neural networks are computational structures which are formed through biological nervous systems. Biological nervous system is appropriate for performing actions such as speech, vision, information retrieval, generalization and etc. The motivation for using artificial neural networks is availability of these abilities that biological nervous system is able to do so. There are several issues in the field of food that cannot be solved through physical modeling-based methods. In these modeling terms, artificial neural networks can be potential alternatives to physics- based models of food. Artificial neural networks are able to generalize data behavior without need to prior knowledge on parameters relationship. Data set may be provided through testing, simulating and resources.





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Application of artificial neural network modeling in foods is provided in different areas such as thermal conductivity modeling, estimating friction coefficient of in pipes and heat transfer coefficients. Interesting applications of artificial neural network modeling have been reported such as different food products reflectance spectrum analysis through chemometric. Artificial neural network modeling becomes a very promising tool in foods predictive modeling.

This study aimed to present a neural network model in order to predict the viability of probiotic bacteria in yogurt according to pH, primary, secondary and final acidity, syneresis, bacteria number of *Streptococcus thermophilus* and *Lactobacillus bulgaricus*, *Lactobacillus acidophilus* that factor R_2 is used at the end in order to correlate the results of experimental observations and the results of the neural network.

Data Selection

Concentrated Symbiotic yogurt sample (including *Lactobacillus acidophilus* bacteria, inulin and oligo-fructose fibers) was prepared according to formula presented in Table 1 and was tested on days 1, 7, 14 and 28 after production in terms of pH, syneresis and total count of probiotic bacteria.

Due to the fact that parameters of pH, syneresis and prebiotic compounds are effective on survival of probiotic bacteria, mentioned parameters are considered as input of model (independent variables) and prediction of total counts of probiotic bacteria is output of model (dependent variables).

Data cleansing and preparation

The second step is cleansing and preparation. In this step, data are removed that independent variables do not present due to incomplete information or are not calculated. Among independent selected variables, 12 variables were selected using conducted tests according to standard methods.

Data division using 10-Fold Cross-Validation

We need to divide data into two categories of education- validation and assessment data before entering data into models for this aim 10-Fold Cross-Validation method is used. In this method, data set (test set) is randomly divided into k equal parts so that there are 2 samples for study data in each section that are totally 20 treatments which are

selected randomly among 20 samples. K pairs of $\{x_i, y_i\}_{i=1}^K$ are extracted randomly where x_i is independent

variable and y_i is the dependent variable of i^{th} sample. In conducting first part of 10 parts, a part is used for evaluation and 9 remaining parts are used for learning data. Among 9 learning parts, 1 part is used for validation data and remaining is used for evaluation data. For example, in Figure 3, 10th piece is used as evaluation data and first piece is used as validation data and 2 to 9th pieces are used as training data for first conduction. In the second conduction, other part of 10 parts is used for evaluation and 9 remaining parts are used for training-validation. For example, according to Figure 3 in the second conduction, 9th piece is used as evaluation data and 2th piece as validation data and 1th and 3th to 8th and 10th pieces have been used as training data. 10 algorithms are conducted with the same procedure. Figure 3 shows the data segmentation in 10 iterations.

One error rate is calculated per iteration for learning and assessment data and finally, the average error rate obtained will be assigned as error rate of learning and assessment data.

Finally, the average error rate obtained will be assigned as error rate of learning and assessment data. The reason for using this method is that Error Rate is one of the criteria for evaluating a classifier/ regressor which includes different





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types, generally, comparing calculated error on learning data we cannot perform good judgment about ability of algorithms. The error rate on learning data is usually less than error rate on data which have not been seen in learning process. Based on this argument, we cannot use learning error for comparing two algorithms. This reason is that for more complex models, classifications that have usually more parameters will have more complex borders. The complex border will decrease error rate on learning data compared to simpler models. So, a set of data is required for test in addition to learning data sets. In the case of neural networks, we need a set of data as validation data in addition to learn and test data because of over-fitting phenomenon which is selected from learning data set (Over-fitting phenomenon is one of the biggest problems in learning process and one way to avoid that is to use validation data). Thus, each data set is divided into three independent subsets of learning data, validation data and test data. Learning data is used for model training; validation data is used for appropriateness of model parameters and prevent from over-fitting. Test data is used to calculate algorithms error rate (accuracy of model prediction) on data that has not seen. Conducting an algorithm is not sufficient for appropriateness of test. Algorithms usually tend to close the estimated error rate to actual error rate (errors that occur in the real world) and it is possible through implementing and evaluating learning and test processes repeatedly. So when a data set is provided, part of it is set aside for final test and others are used for validation and learning and again three sets are changed and the model is re-tested. One of the common ways to do this is called K-Fold Cross Validation.

Model evaluation and training process

The model is trained when the sample is divided into two categories of learning data (Education Accreditation) and evaluation data. The four evaluation criteria are used for evaluation of regression models including Mean Absolute Error (MAE), Mean Squared Error (MSE), Normalized Mean Square Error (NMSE), and Symmetric Mean Absolute Percentage Error (SMAPE) which are calculated using the following equations.

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - d_i)^2$$

$$NMSE = \frac{1}{n} \sum_{i=1}^n \frac{(y_i - d_i)^2}{\bar{y}\bar{d}}, \quad \bar{y} = \frac{1}{n} \sum_{i=1}^n y_i, \quad \bar{d} = \frac{1}{n} \sum_{i=1}^n d_i$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - d_i|$$

$$SMAPE = \frac{1}{n} \frac{\sum_{i=1}^n |d_i - y_i|}{\sum_{i=1}^n (d_i + y_i)}$$

Where y_i and d_i are actual total count (obtained from testing) and predicted total count (by algorithm for i^{th} sample) and n is the number of samples (in training or evaluation stage) and \bar{y} and \bar{d} are mean rate of real stock and mean rate of predicted stock, respectively. Among above errors, MSE is used more because it minimizes the mean error and the error variance from statistical standpoint. For this reason, it is interested for researchers in almost all researches.



**Mozhgan Nasiri Shahri et al.****MLP algorithm:**

The number of inputs, number of hidden layers and number of neurons in each hidden layer and totally, the internal structure of MLP neural network must be determined in order to apply training data to MLP neural network that in this study, back-propagation forward neural network 5-1 was chosen through trial and error that can be seen in Figure 4. Back-propagation algorithm of error is a descent gradient search algorithm that minimizes total mean square error between desired output and target output of neural networks.

This error is applied for back- propagation search guiding of error in weight and bias space. In back-propagation algorithm of error, output value is calculated at each stage and is compared with actual value and network weights are corrected according to obtained error. So that amount of resulting error is less than error rate in previous iteration. Each neuron in network includes a weighted sum of inputs that is filtered by sigmoid transfer function.

Using training data of network model, the model is stored after training to be used in evaluation stage.

The MATLAB software version 7 was used for modeling; designed network was Multilayer Perceptron (MLP). In this model 12 neurons were used in input layer including pH (days 1, 7, and 14), syneresis (days 1, 7 and 14), inulin percent (3 levels) and oligo-fructose percent (3 levels) and 1 neuron as output layer including total count of *Lactobacillus acidophilus* bacteria. Figure 4 shows the layered structure of this network.

RESULT AND DISCUSSION

Most studies show that viability of probiotic bacteria in dairy products over time is reduced. Changes in counts of yogurt probiotic bacteria can largely be effected by pre- and post-production conditions and these conditions are evaluated in physical, chemical and biological parameters. According to study results, decreasing pH in all samples within 21 days of maintaining will result in decreased trend in the number of *Lactobacillus acidophilus* bacteria. Despite the lower pH in samples with higher solid content, bacterial survival in sample with higher solid content was more during 21 days, so that the most survival was observed in yogurt with solid content of 20 and the lowest survival was observed in yogurt with solid content of 8.5. Higher glucose level of yogurt with higher solid content is one of the reasons and it can be concluded that factors other than pH are involved in reduction of bacteria living during maintenance. Reduction rate of yogurt with less solid content at the end of 21-day is a logarithmic cycle in a week and in yoghurts with high solid content is less than one logarithmic cycle. Reduction rate of bacteria living in solid material is regular while this regular reduction is seen less in second and third weeks. Ozer and Robinson (1999), in a study on milk solids effect on growth and activity of yogurt starter bacteria concluded that increased levels of milk solids from 16% to 23% strengthen *Lacto bacillus acidophilus* growth so that bacteria number in concentrated yogurt after 240 minutes of fermentation is more with 23% solids. They also observed that starters that grow in milk with higher solids have less reproduction time (15/1-23/1) hour compared to samples with less solid material (2/2 – 13/2) hour.

Yogurt syneresis gradually was decreased due to consolidation of casein gel during second and third weeks. The decline was significant in first, seventh and fourteenth days but sample syneresis was increased during maintenance of 14 to 21 days.

ALKadmany et al 2003, observed similar results in the case of negative effect of storage time on traditional yogurt syneresis. The syneresis of samples was reduced up to third week of maintenance and then it was increased. Time is a key factor in water gel networks, while decreased pH increases syneresis.



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Microbial count was performed to determine the growth rate of bacteria during incubation and shelf life.

Lactobacillus acidophilus bacteria were counted by direct counting. The results show that number of starter bacteria was decreased significantly after 7 and 14 days of first day. Probiotic bacteria must be alive for 10^7 (Log CFU / mL) in order to maintain their properties in food consumer body; in this study, despite the decrease in pH during storage of Lactobacillus acidophilus bacteria in most treatments in desired range. The desired properties of probiotic bacteria are created in consumers.

Some unreal data were added to training data set in order to enhance the training data set and increase the viability prediction in various times based on engineering insight and with regard to the range of parameters database input. MSE change results are given in Figure 3 that are obtained from data processing stages including training, validation and testing in order to predict changes of Lactobacillus acidophilus counts (viability) in output layer of defined neural network model where the lowest mean square error occurs during 10 periods of training with Lonberg-Marquardt algorithm that is selected as the optimal model.

After preprocessing step, many efforts were done in order to reduce the error function of network training through increasing the number of hidden layers and number of neurons and results showed that increasing the number of hidden layers (more than one hidden layer) did not significantly reduce the error function of networks but increasing numbers of neurons in hidden layers of both types of network reduced their error function further. Examining results present that increasing hidden layers from 1 to 5 will result in decreased square error rate and increased explanation coefficient while increasing hidden layers from 5 to 10 will result in increased square error rate and decreased explanation coefficient so the optimum network performance is with 5 hidden layers. Figure 4 (a, b and c) presents comparison of experimental data and predicted values of the best trained network with topologies of 1-5-12 in three days of 1, 7 and 14 graphically.

CONCLUSIONS

The results showed that this model is very powerful substitute for other traditional statistical models. In fact, the research findings showed that accuracy of model based on input data can have very good estimation of probiotic bacteria survival. In this paper, an advanced neural network model is given for prediction of probiotic bacteria survival in concentrated Symbiotic yogurt. Comparison results between neural network models and actual values shows that model can accurately predict Lactobacillus acidophilus growth. The proposed model can consider other factors affecting on Lactobacillus acidophilus growth. Although, models provided Lactobacillus acidophilus growth with high-precision, however, the accuracy of models can be increased through increasing empirical tests used for network input, in addition, using developed models, we can examine the effect of other parameters on yogurt quality.

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Table1.Used treatment for sample producing

Treatment	%inoculation	%Oligofroctose	% Inulin
1	0/5	0	3
2	0/3	1/5	1/5
3	0/5	0	0
4	0/5	3	0
5	0/1	1/5	1/5
6	0/5	3	3
7	0/5	1/5	1/5
8	0/3	1/5	1/5
9	0/3	1/5	0
10	0/3	1/5	1/5
11	0/3	1/5	1/5
12	0/3	3	1/5
13	0/3	0	1/5
14	0/1	3	3
15	0/3	1/5	1/5
16	0/3	1/5	1/5
17	0/1	0	0
18	0/1	0	3
19	0/1	3	0
20	0/3	1/5	3





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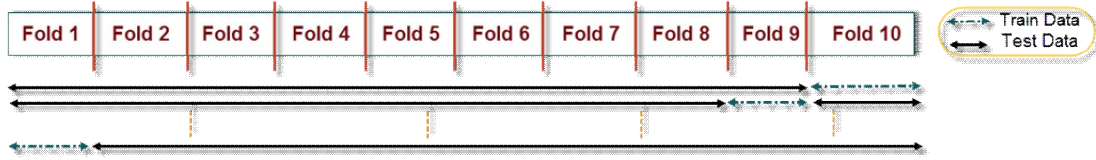


Figure1: Selection steps of learning and test data setwith k = 10.

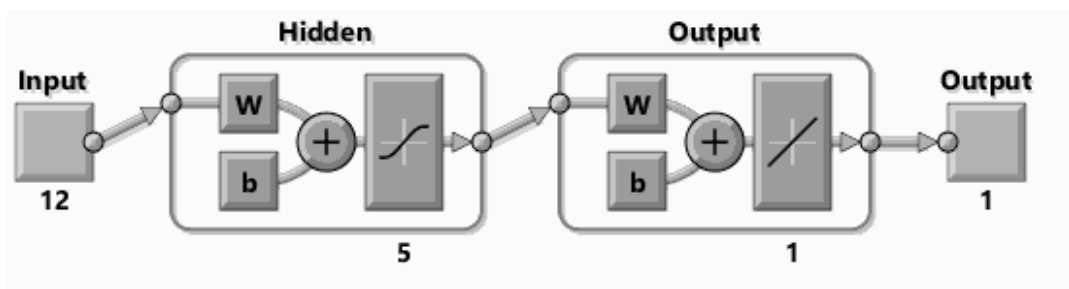


Fig 2. Suggested multi layer perceptron (MLP) neural network

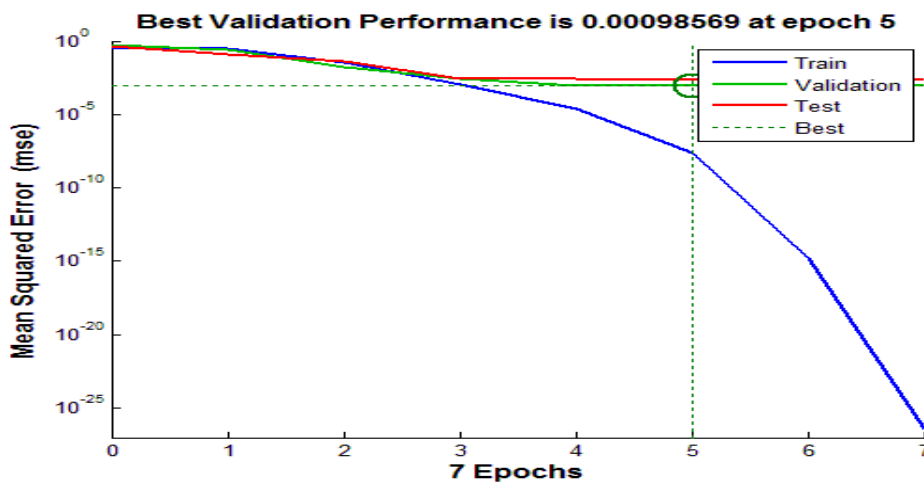
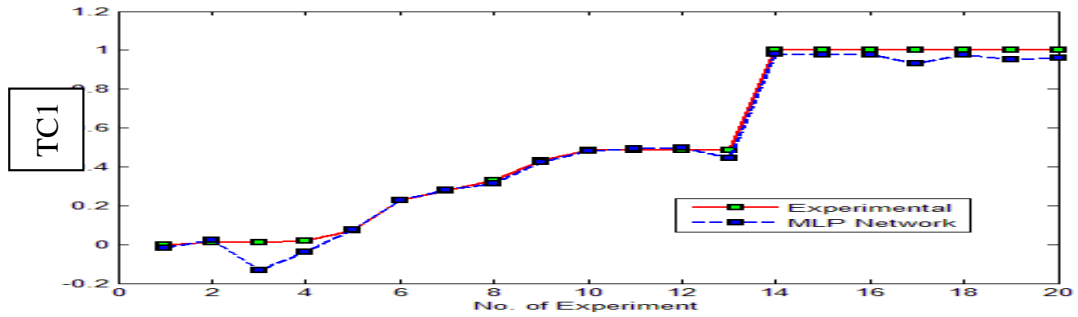


Fig 3. Best validation performance for MSE change results

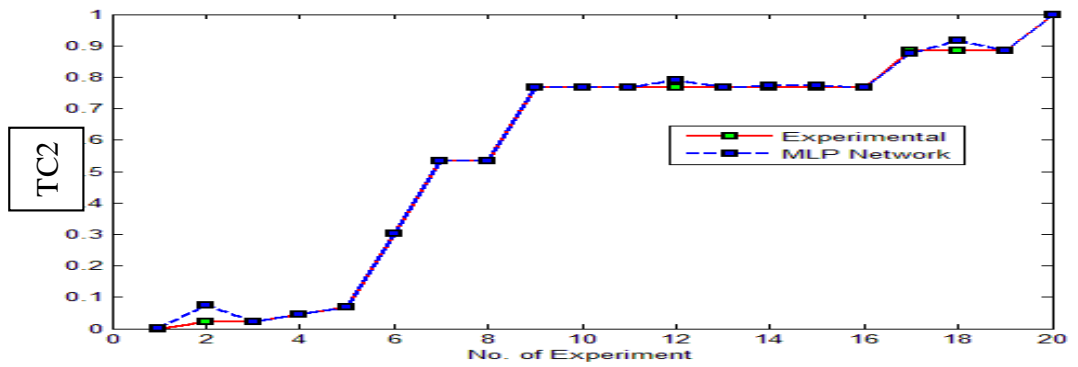




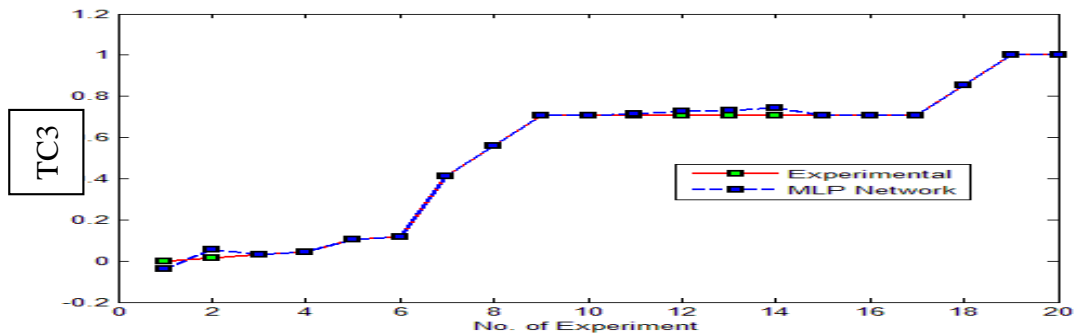
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(a)



(b)



(c)

Fig 4. Comparison between experimental data and predicted values (on the days 1(a), 7 (b) and 14 (c) after production)

