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| Complete List of Authors: | Shirani, Mahboube; University of Jiroft, Chemistry<br>Akbari, Ali; University of Jiroft, Chemistry<br>Hassani, Mohsen; Najafabad Branch, Islamic Azad University, Department of Mechanical Engineering |
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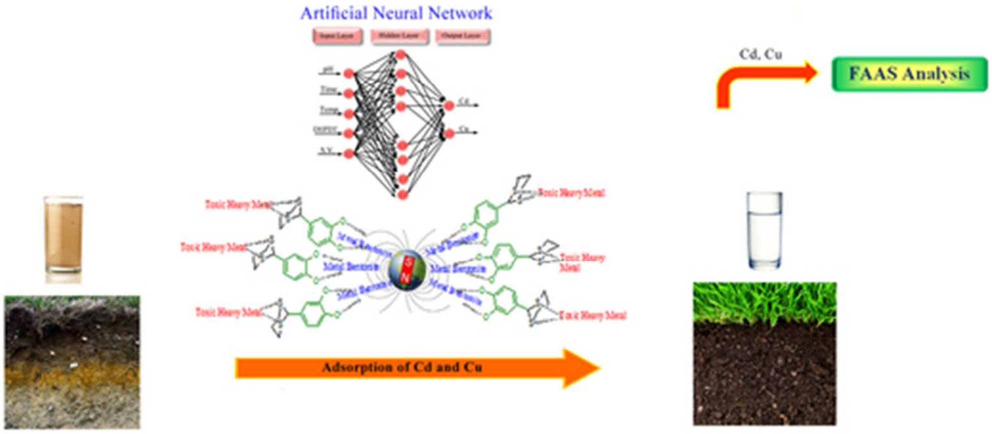

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# Adsorption of cadmium (II) and copper (II) onto magnetic organozeolite modified with 2-(3,4-Dihydroxyphenyl)-1,3-dithiane from soil and water samples by flame atomic absorption spectrometry using artificial neutral network

Mahboube Shirani[a], Ali Akbari[a], Mohsen Hassani[b]

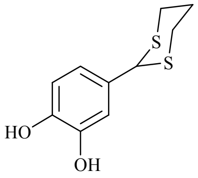
## Abstract

In this study the adsorbent, magnetic zeolite modified by 2-(3,4-Dihydroxyphenyl)-1,3-dithiane as an easy separable sorbent, was synthesized for simultaneous removal of two toxic heavy metals of cadmium and copper from soil and water samples. The synthetized magnetic sorbent was characterized by SEM, and XRD. The magnetic property of sorbent was identified by VSM method. The obtained saturation magnetization of 18.4 emu $g^{-1}$ showed facile separation of magnetic modified zeolite after adsorption process. The effects of five dominant parameters of pH, temperature, time, amount of sorbent and sample solution volume on the adsorption process were investigated. The optimum conditions of 6, 25 °C, 9 min, 40 mg and 40 mL were acquired for pH, temperature, time, amount of sorbent and sample solution volume respectively. The maximum experimentally achieved adsorption percent of 98.2 ± 2.5, 97.5 ± 2.8 were obtained under optimum conditions which showed the high adsorption potential of the proposed sorbent. The experimental data were found to be properly fitted to the Langmuir and Freundlich model which indicated that the sorption took place on a heterogeneous material. The sorption capacities of 178.5711 and 181.8182 (mg $g^{-1}$) were achieved for cadmium and copper respectively from sorption isotherms. A three-layer artificial neural network model with 8 neurons and tan-sigmoid function at hidden layer and a linear transfer function (purelin) at output layer were develop to predict simultaneous removal of cadmium and copper. The results indicated that the proposed artificial neural network model could perfectly predict the process with mean square error (MSE) of 0.037. The optimization procedure showed a close interaction between the experimental and predicted values.

Keywords: 2-(3,4-Dihydroxyphenyl)-1,3-dithiane, Adsorption, Magnetic Organozeolite, Heavy metal, Flame atomic absorption spectrometry, Artificial neural network

## 1. Introduction

Heavy metals removal from various matrixes especially soil, ground and underground water is a serious concern for scientists. Therefore this important challenge has been in the centre of attention in recent years due to the environmental matters and their deadly effects on human life and all living organisms.[1, 2] Cadmium is categorized as one of the deadliest heavy metals for human being which directly affects the liver, kidneys, lungs, the immune system even in trace concentrations. Accumulation of copper in body can lead to the livers dysfunction and nervous system problems.[3] Consequently, many separation techniques have been presented to extract heavy metals (i.e. Cd, Cu, As, Hg, Pb, etc.) from various matrixes such as water and soil in order to avert environmental contamination. Among those, adsorption techniques have been attractively and widely used due to their simplicity and facile accessibility. Therefore, various studies were reported to introduce high loading capacity materials with significant efficiency of heavy metals adsorption from the media.[4-6] Different materials such as silica gel,[7] aerobic granules,[8] zeolite[9] and clay[10] have been reported to obtain the interest aim of heavy metals removal. In order to increase the heavy metals removal efficiency, modification of sorbent surface by different materials such as surfactants,[11] thiols[12, 13] was reported. Among all proposed sorbents, zeolite has been widely applied to avoid the release of heavy metals into the environment.[14] Zeolite is noticeably applied for adsorption of environmental contamination due to its structure which consists of one $Al^{3+}$ octahedral sheet placed between two $Si^{4+}$ tetrahedral sheets.[15] Effective adsorbents are prepared by modifying the surface of various substrates with a surface functionalization of thiol groups. These modified sorbents effectively adsorb toxic soft metal ions such as $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$ and $Cd^{2+}$ by binding to the thiol ligands.[16-18] 2-(3,4-Dihydroxyphenyl)-1,3-dithiane (DHPDT) (Scheme 1) is one of the efficient sulfide group chelating agents for binding with heavy metals in various matrixes. Immobilization of DHPDT on the surface of the heterogeneous sorbents, such as zeolite, could increase the adsorption capacity of the sorbent. This new hybrid organic–inorganic material may be a good alternative for separation and preconcentration of heavy metal ions. However, few research studies have focused on the interactions of heavy metals with the surface of zeolite modified by sulfide group.



**Scheme 1.** Molecular structure of 2-(3,4-Dihydroxyphenyl)-1,3-dithiane (DHPDT)

One of the main problems in adsorption techniques is separation of the adsorbent from the solution. Mostly due to the dispersion of the adsorbent in the solution during the adsorption process the separation of solid adsorbent becomes exhausting and time consuming. Moreover, in some cases even centrifuging of the solution fails to complete separation of the solid dispersed particles of the sorbent. Recently, the synthesis of magnetic adsorbents such as magnetic organozeolites has opened a new horizon regarding this area due to the fast and easy separation. Magnetic sorbents such as zeolites are used for removal of environmental pollutants.[19, 20] This facile low cost separation of magnetic sorbent by a simple magnet is pleasant in separation science especially in industrial applications. Artificial neural network (ANN) is a simple model of human brain, consists of certain number of processing units called neurons. An ANN is a parallel processing network that has particular performance characteristics in common with biological neural networks in both linear and non-linear systems.[21] It is one of the most applicable models for nonlinear analysis. The role of ANN is determining the complex nonlinear relationships between parameters and prediction of output variables. ANN is widely applied for heavy metals determination processes.[22-24] In the present study, magnetic DHPDT-Zeolite was synthetized and applied for the simultaneous removal of cadmium and copper. The influential parameters of pH, temperature, time, the amount of sorbent and sample volume were investigated. The adsorption isotherms of the prepared sorbent were studied. The ability and potential of the proposed method was considered in soil and water samples. An artificial neural network model was developed to predict the behaviour of simultaneous removal of cadmium and copper in the proposed process under various conditions.

## 2. Materials and methods

### 2.1. Reagents

The materials were purchased from Sigma–Aldrich and Merck and were used without any additional purification. DHPDT was synthesized and characterized by FT-IR, $^1$H-NMR, $^{13}$C-NMR and the comparison of physical properties was done with those reported in the literature. The standard stock solutions of cadmium (1000 mg L$^{-1}$) and copper (II) (1000 mg L$^{-1}$) were prepared by dissolving appropriate amount of Cd $(NO_3)_2 \cdot 4H_2O$ (Merck), Cu $(NO_3)_2$ (Merck) in 1% nitric acid solution. Standard solutions of cadmium and copper were prepared daily by dilution of stock solutions. Deionized water was used for preparation of all solutions.

### 2.2. Instrumentation

The cadmium and copper determination was carried out on a Buck Scientific atomic absorption spectrometer (Model 210 VGP, USA) with the hollow cathode lamps at wavelengths of 228.8 nm and 324.8 nm for cadmium and copper respectively using air-acetylene flame. The operating conditions were set as recommended by manufacturer. The single line flow injection system consisting of peristaltic pump (Osmatic, MS-REGLO/8-100, Switzerland), and rotary injection valve (Redone, CA, USA) with a loop of 100 µL capacity was used for effective control of the amount of sample and reproducibility of the measurements. The absorbance time response was monitored on an x-t chart recorder (L-250) and quantitative analysis was based on measurement of the peak height of transient signals. The pH measurements were carried out with a Met Rohm pH meter (model 691, Switzerland). Ultrasonic bath (Sonora digital, DT255H, and Germany) and oven (Universal model UF 55, Germany) both were used for magnetic organozeolite preparation. IKA overhead stirrer (model RW 28 digital Package, Germany) with glass stirrer was utilized to stir the magnetic sorbent sample solution during adsorption process. A vibration–sample magnetometer (Magnates Dogfight Caver Co.) was used to characterize the magnetic properties of synthetized magnetic organozeolite. FT-IR spectra were run on a Broker, Equinox 55 spectrometer using the conventional ATR method.

### 2.3. Sample preparation

The samples were selected from the areas which had the probability to heavy metals pollution due to the industrial pollution released in those parts.

### 2.3.1. Water samples preparation

Water samples were filtered to remove any suspended contamination and then were used for analysis.

### 2.3. 2. Soil sample preparation

Soil samples were prepared for analysis according to the proposed procedure.[25] Briefly, the collected soil samples (250 g) were dried at 105 °C and grounded by a 200-mesh sieve to obtain a homogenized sample. 1 g of homogenized sample were dissolved in 15 mL aqua regia and dried subsequently. 5 mL of $HNO_3$ (2 M) was added to the residue and then filtered. The filtrate was evaporated to 5 mL. After dilution to 5 ml with deionized water, the analytical procedure was done and determined by FI-FAAS.

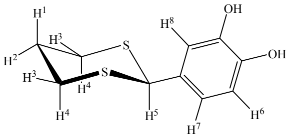
### 2.4. Preparation of 2-(3,4-Dihydroxyphenyl)-1,3-dithiane (DHPDT)

A mixture of 2, 3-dihydroxy benzaldehyde (10 mmol), 1, 3-ethanedithiol (12 mmol) and 37% $BF_3.SiO_2$ (0.3 g) was grounded in a pestle at an ambient temperature. The progress of reaction was monitored by TLC. After the completion of the reaction, the products were dissolved in ethanol, filtered, and the solvent was evaporated. The obtained solid was recrystallized in chloroform (yield= 91%). The $^1$H-NMR of DHPDT was described based on the Scheme 2. The values of $^{13}$C-NMR were shown on the structure of DHPDT in Scheme 3.

The spectroscopic data of IR, $^1$H-NMR, and $^{13}$C-NMR as bellow:

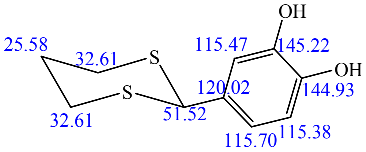
FT- IR: ν max (KBr) = 3479, 3306, 2929, 2891, 1622, 1607, 1620, 1454, 1428, 1408, 1352, 1299, 1275, 1248, 1183, 1112, 961, 907, 873, 816, 797, 763, 706, 677, 582, 436 cm$^{-1}$.

$^1$H-NMR (500 MHz, $CDCl_3$/DMSO) δ= 1.88 (m, 1 H, $H^1$), 2.13 (m, 1 H, $H^2$), 2.87 (m, 2 H, $H^3$), 3.03 (m, 2 H, $H^4$), 5.05 (s, 1 H, $H^5$), 6.82 (d, J = 8.15 Hz, 1 H, $H^6$), 6.84 (dd, J = 8.15 Hz and J = 1.86 Hz, 1 H, $H^7$), 7.14 (d, J =1.86 Hz, 1 H, $H^8$) ppm.



**Scheme 2.** The structure of hydrogen bond of DHPDT

$^{13}$C-NMR (125 MHz, $CDCl_3$/DMSO) δ= 25.58, 32.61, 51.52, 115.47, 115.38, 115.70, 120.02, 11.44, 144.93, 145.22 ppm.



**Scheme 3.** The values of $^{13}$C-NMR on the chemical structure of DHPDT

### 2.5 Preparation of magnetic zeolite

Magnetic zeolite was prepared according to the proposed procedure.[19] Meanwhile, the mixture of NaY zeolite in 100 mL of ammonia solution (1 M) was deoxygenated (solution A). The solution of $FeCl_3.6H_2O$ (1M) and $FeCl_2.4H_2O$ (2 M in HCl 2 M) was deoxygenated too (solution B). Then the two solutions were mixed under nitrogen atmosphere by ultrasonic treatment. The solution was washed with oxygen-free deionized water for several times. Finally, the obtained magnetic zeolite was dried at 50 °C in the oven.

### 2.6. Preparation of magnetic DHPDT-Zeolite

Magnetic organozeolite was prepared by mixing 5 g magnetic zeolite with 50 mL methanol and then 10 mL NaOH 10% was added and the solution was stirred by overhead stirrer. Then 1 g DHPDT was added to the mixture. The mixture was stirred for 4 h at 25 ºC. The obtained magnetic sorbent was separated from the solution using an external magnet. The magnetic organozeolite was washed with deionized water and dried in oven at 60 ºC for 12.

### 2.7. Adsorption process of $Cu^{2+}$ and $Cd^{2+}$

The pH of 10 mL sample solution containing 10 mg $L^{-1}$ of $Cu^{2+}$ and $Cd^{2+}$ was adjusted at 6 by adding 0.1 mol $L^{-1}$ nitric acid or sodium hydroxide. 40 mg NaY Zeolite or magnetic DHPDT-Zeolite was added to the solution. The mixture was stirred for 9 min by an overhead stirrer at room temperature. Then the magnetic sorbent was separated by a magnet and the upper aqueous phase containing the residual cadmium and copper in the solution was used for determining by flow injection- flame atomic adsorption spectrometry (FI-AAS). The uptake of adsorbate mathematically can be stated as follows (Eq.1):[26]

$$Q_i = (C_i - C_e)/ S \qquad (1)$$

$Q_i$: the adsorbate concentration adsorbed at the equilibrium (mg of adsorbate /g of adsorbent)

$C_i$: The initial dye concentration in the solution (mg $L^{-1}$)

$C_e$: Equilibrium concentration or final dye concentration (mg $L^{-1}$)

S: Dosage concentration which is obtained as following (Eq. 2)

$$S = m/v \qquad (2)$$

Where m is the adsorbent mass (g) and v is the volume of adsorbate solution (L).

Finally the percentage of adsorbate removal can be expressed and calculated according to the following equation (Eq. 3):

$$\text{Percent of adsorption (\%)} = (C_i) /C0\times 100 \qquad (3)$$

### 2.8. Artificial neural network

In this study, Neural Network Toolbox Version 6.0.4 of MATLAB® R2010 a mathematical software was utilized to predict the process. A three-layer ANN with tan-sigmoid and purline function was used for hidden and output layers as transfer functions respectively. Equation (4) shows the tan-sigmoid transfer function[27]:

$$F(x) =1/ (1+\exp (-x)) \qquad (4)$$

Feed forward back propagation (FFBP) was used as training algorithm in this artificial neural network. For FFBP, the final calculated outputs are compared with the experimentally obtained outputs, and the errors are calculated. These errors are then propagated backwards and used for adjusting the weights of each of the neurons. The process of using the experimental outputs to minimize the mean squared error is iteratively called as training network. The weights of the trained network are stored, and can be used later for estimating the outputs of a different set of inputs. The input variables of pH, DHPDTO amount, time, temperature, sample volume were considered through the process. Twenty nine experimental points were employed to feed the model. The data set was derived to training and test sets which contained 24 and 5 data points respectively. According to the Eq. (5), all data points were normalized in the range of [-0.9, 0.9] due to applying tan-sigmoid transfer function as follows:

$$X_{norm}=1.8 (X-X_{min})/ (X_{max}- X_{min}) - 0.9 \qquad (5)$$

Where X is variable, $X_{min}$ , $X_{max}$ are minimum and maximum values respectively.

## 3. Results and discussion

### 3.1. Characterization of NaY Zeolite and magnetic DHPDT-Zeolite

The SEM images of magnetic NaY Zeolite and magnetic DHPDT-Zeolite are shown in Fig. 1. The VSM analysis (Vibrating Sample Magnetometer) was applied to prove the magnetic properties and the required force to move magnetic organo-modified zeolite from solution. The magnetic curve in Fig. 2 shows appropriate super paramagnetic property of magnetic organo-modified zeolite due to no hysteresis loop and no eminence existence. While the magnetic organo-modified zeolite was exposed to an external magnetic field reserves no magnetization and redisposed after magnetic field removal. The saturation magnetization of 18.4 emu $g^{-1}$ at 298 K was observed which indicated the easy attraction of magnetic organo-modified zeolite by permanent magnet. The XRD pattern of zeolite, magnetic zeolite, and magnetic organozeolite was shown in Fig. 3.

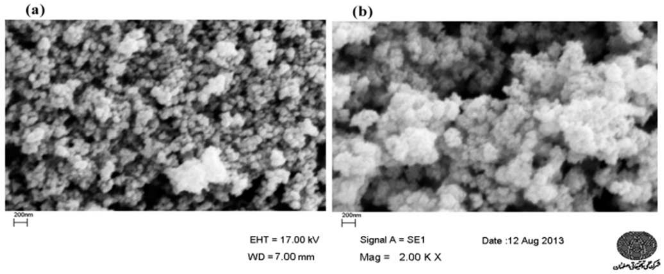


**Fig.1.** The SEM images of a) NaY Zeolite and b) Magnetic DHPDT-Zeolite

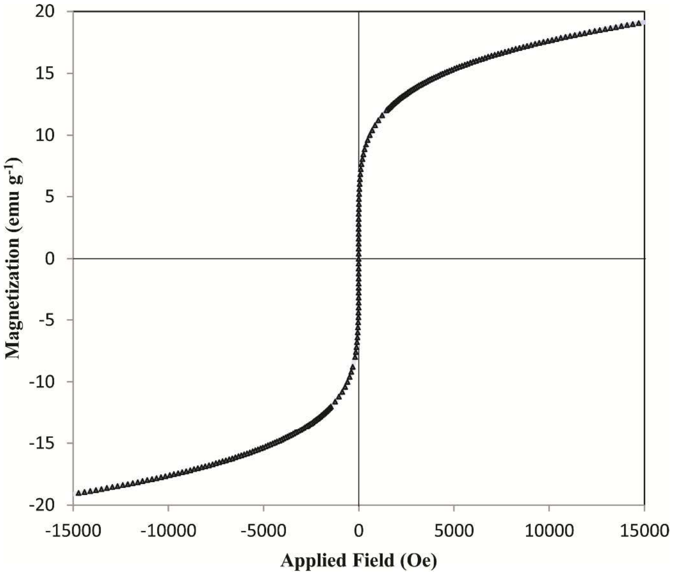


**Fig. 2.** The hysteresis loops of magnetic organo-modified zeolite

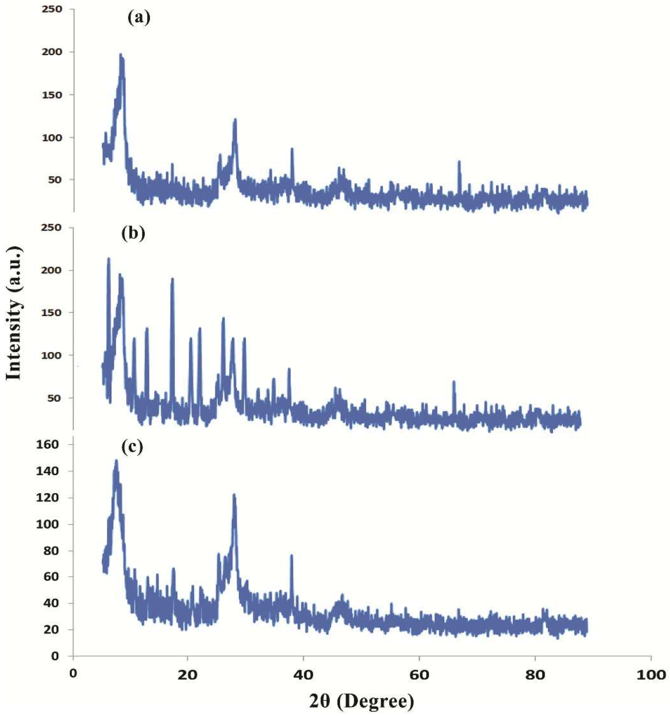


**Fig. 3.** The XRD pattern of zeolite (a), magnetic zeolite (b), and magnetic organozeolite (c)

### 3.2. ANN Modelling

The input variables of trained ANN are pH, temperature, time, amount of sorbent, sample solution and the outputs are removal efficiencies of cadmium and copper. Table 1 indicates the ranges of these parameters. Topology of ANN is illustrated in Fig.4. which shows the number of layers, neurons of each layer and their interconnects. The regression analysis between experimental data and predicted data by ANN showed $R^2$ value of 0.9999 for both cadmium and copper which indicated good agreements between predicted and experimental responses. The aim of ANN training is to obtain the best weights with minimum values of prediction error.

**Table 1**

The ranges of influential parameters in adsorption process for ANN

| Parameters | Ranges |
|---|---|
| pH | [3- 8] |
| DHPDTO | [10- 80] |
| Time (min) | [3- 15] |
| Temperature (°C) | [25- 55] |
| Sample Volume (mL) | [5- 60] |

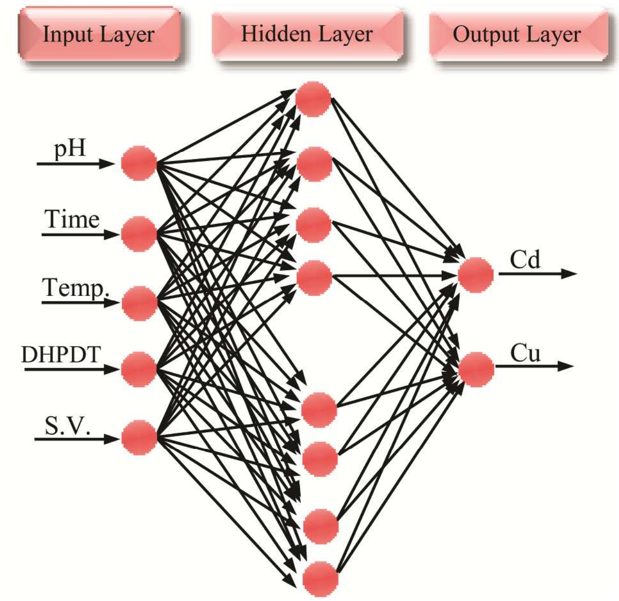


**Fig.4.** Optimized topology of artificial neural network

Minimum prediction error was obtained by changing the number of neurons in hidden layer, transfer functions and repetition of training step. In order to find the best number of neurons in hidden layer, various topologies were studied. Fig. 5 shows the error of each topology by changing the number of neurons in hidden layer. It can be seen that artificial neural network with 8 neurons in hidden layer has the minimum value of mean square error (MSE).The equation of MSE function is as follows:

$$\mathrm{MSE} = \frac{1}{N}\sum_{i=1}^{N}\left(Y_{pre} - Y_{ex}\right)^2 \qquad (6)$$

Where $Y_{ex}$ is the experimental output, $Y_{pre}$ is the network output and N is the number of data points. [28] The most competent experimental model provides the minimum MSE.

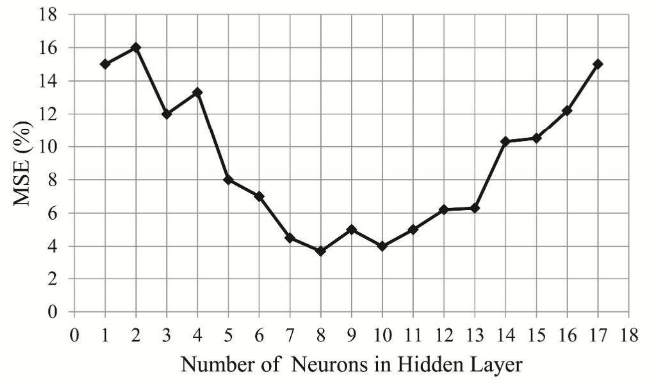


**Fig.5.** The mean square error based on variation of neurons in hidden layer

The accuracy of ANN was examined by using test data set and the absolute percentage error (APE) values for both analytes were shown in Table 2. The values of mean absolute percentage error (MAPE) were acquired 0.87 % and 0.82 % for cadmium and copper respectively which reveal high accuracy of the model for process.

**Table 2**
Comparative results of the experiment and predicted values by ANN for test data set

| Factors | | | | | | Cd | | | Cu | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | pH | Time (min) | Temp (°C) | DHPDTO ( mg) | S.V. (mL) | Exp. | ANN | APE (%) | Exp. | ANN | APE (%) |
| 1 | 5 | 9 | 25 | 50 | 10 | 97 | 96.2 | 0.82 | 96.3 | 95.5 | 0.83 |
| 2 | 6 | 9 | 25 | 30 | 10 | 92.5 | 91.7 | 0.86 | 89.6 | 88.8 | 0.89 |
| 3 | 6 | 9 | 35 | 40 | 10 | 95.3 | 94.4 | 0.94 | 94.5 | 93.7 | 0.85 |
| 4 | 6 | 12 | 25 | 40 | 10 | 98.1 | 97.3 | 0.82 | 97.3 | 96.6 | 0.72 |
| 5 | 6 | 7 | 25 | 40 | 40 | 98.1 | 97.2 | 0.92 | 98.1 | 97.3 | 0.82 |
| | | | | | | MAPE (%) | | 0.87 | | | 0.82 |

### 3.3. Effect of initial pH

Acidity or basicity of the aqueous medium plays an important role in the adsorption process. Therefore, the pH of the solution was investigated in the range of 3-8. As the results show in Fig. 6 (a), the adsorption efficiencies were maximum in the pH range of 5-6. The decrease in adsorption of interested metal ions at low pH is owing to the competition of hydrogen ion with analyses for occupation of the active sites on the surface of the sorbent. Also the sorbent surface is protonated and cannot adsorb metal ions. And at high pH ranges the adsorption efficiencies decrease to the formation of metal hydroxides in the solution which reduce the concentration of metal ions on the surface of the sorbent. Therefore pH of 6 was selected for subsequent studies.

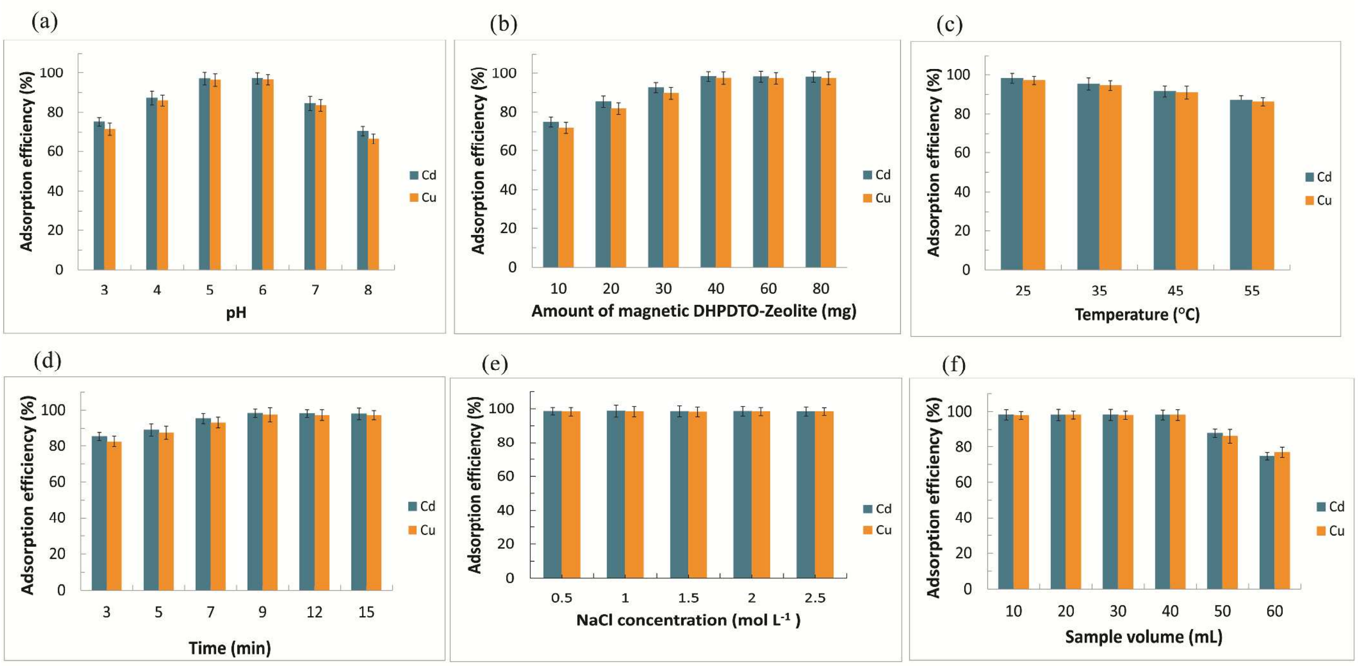


**Fig.6.** The effect of pH (a), amount of magnetic DHPDT-Zeolite (b), temperature (c), time (d), NaCl concentration (e), and sample volume (mL) (f) on the adsorption efficiencies.

### 3.4. The effect of amount of sorbent

The amount of synthetized magnetic organo-zeolite was studied in the range of 10-80 mg. According to the obtained results in Fig. 6 (b), as the amount of sorbent increases the adsorption efficiencies will increase consequently due to the enhancement of active and vacant sites for metal ions occupation and more contact surface between the metal ions which lead to more adsorption on the sorbent. From 10 to 40 mg an increasing trend was observed and from 40 to 80 mg the adsorption efficiencies are nearly constant for both ions. Therefore the sorbent amount of 40 mg was chosen for further studies.

### 3.5. The effect of temperature

One of the most influential factors in all separation procedures especially adsorption processes is temperature. The effect of temperature was studied in the range of 25-55 °C. As it is shown in Fig. 6 (c), along with increasing the temperature a very slight increase was observed in the process. It seems that at higher temperatures the mobility of ions in the solution increases and the ions adsorption on the sorbent is endothermic and by increasing the temperature the adsorption efficiency and the percent of metal ions removal will increase. Since at higher temperatures the adsorption efficiency had no significant difference, therefore the ambient temperature of 25 °C was selected for further studies.

### 3.6. The effect of time

Adsorption time is another factor which can noticeably influence the percent of metal ions removal due to acquiring the equilibrium between aqueous solution and adsorption process. Therefore the adsorption time was investigated from 3-15 min. According to the results in Fig. 6 (d), it can be concluded that the more the contact time is the more complete the adsorption will be. The percent of metal ions removal from 3-15 min increased and after that no change was observed in the adsorption efficiency. Hence the optimum time of 9 min was considered for simultaneous removal of cadmium and copper.

### 3.7. The effect of ionic strength

The effect of ionic strength of the sample solution was investigated to consider the performance and potential of the proposed process in saline matrixes. Therefore, different concentrations of NaCl in the range of 0.5- 2.5 mol $L^{-1}$ were added to the sample solution. The obtained results in Fig. 6 (e) indicated that salt has no significant effect on adsorption percent of the interest analytes. Hence, the proposed process can be successfully applied for adsorption of cadmium and copper in the saline matrixes like sea water and soil.

### 3.8. Sample volume

In order to investigate the potential of the proposed method for separation of cadmium and copper in large sample volumes, the effect of the sample volume was studied in the range of 10-60 mL. The results in Fig. 6 (f) indicated that from 10-40 mL the recoveries are quantitative and up to 40 mL the recoveries decrease.

### 3.9. Adsorption isotherm study

The adsorption isotherms indicate the partition of adsorbate molecules between the liquid sample solution and solid sorbent in the adsorption process. In other words the adsorption isotherms clarify the relationship between the adsorbent and adsorb ate at a specific temperature. Therefore, to evaluate the adsorption isotherm of the proposed method, the common isotherms of Langmuir and Freundlich were studied at different concentrations in the range of 50-1000 mg $L^{-1}$ at optimum conditions. Langmuir isotherm has a rational basis and implies the monolayer adsorption on a homogenous adsorbent. As a site is occupied by an iron, no further molecule can be adsorbed at that site.[27] The Langmuir equation is as follows [20]:

$$C_e / Q_e = 1/ (Q_m b) + C_e / Q_m \qquad (8)$$

Where $Q_m$ is the saturation adsorption capacity (mg $g^{-1}$) and b the constant related to the free energy of adsorption were obtained from the slope and the intercept of equation. The plots of $Q_i$ versus $C_e$, and $C_e/Q_e$ versus $C_e$ are shown in Fig. 6 for $Cd^{2+}$ and $Cu^{2+}$. The favourability of $Cd^{2+}$ and $Cu^{2+}$ adsorption onto the DHPDT-Zeolite can be assessed by dimensionless constant called separation factor, $R_L$ (Eq. 9).

$$R_L = 1/ (1+bC_0) \qquad (9)$$

In this equation $C_0$ (mg $g^{-1}$) is the highest initial ions concentration in adsorption isotherm studies. The value of $R_L$ implies the unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), and irreversible ($R_L = 0$) type of the adsorption isotherm. As the results show in Table 3, the values of $R_L$ for two ions are $0<R_L<1$ which are favourable for adsorption isotherm.[19, 29]

The Freundlich isotherm is an empirical equation which is commonly applied for many adsorption processes. The Freundlich isotherm was also considered for the process applying Eq. 10 as below:

$$Q_e = K_f C_e^{(1/n)} \qquad (10)$$

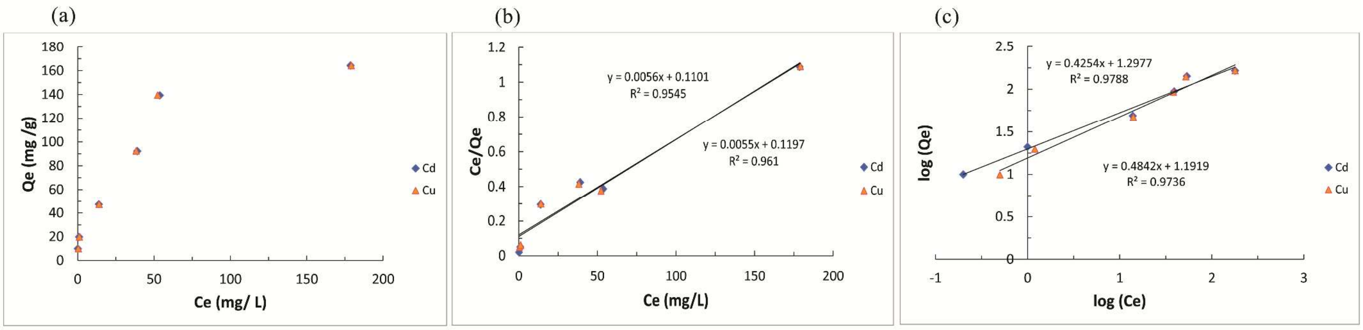
This can be linearized as following:

$$\text{Log } Q_e = \log K_f + 1/n \log C_e \qquad (11)$$

Where the $K_f$ is Freundlich constant related to the adsorbent capacity, and n is the constant indicative to the intensity of the adsorption process. The values of the constant n and $K_f$ were calculated from the slope and the intercepts of equation and shown in Table 3. The Langmuir and Freundlich isotherm plots are shown in Fig. 7**.** The Freundlich intensity constants of $Cd^{2+}$ and $Cu^{2+}$ were as n>1 which show the significant adsorption of $Cd^{2+}$ and $Cu^{2+}$ in the proposed procedure even at high ions concentration. The adsorption isotherms were also considered for magnetic NaY zeolite. As the results show for both Cu and Cd, higher K values were observed for magnetic DHPDT- Zeolite than magnetic NaY Zeolite. The diagrams showed models were fitted to the data of adsorption of copper and cadmium highly correlated. As it is obvious Langmuir isotherm plots were obtained by mean correlation coefficient of 0.9610 and 0.9545 for Cu and Cd respectively. Also Freundlich isotherm was satisfactorily to describe the adsorption of copper and cadmium by both adsorbents.

**Table 3**
Isotherm parameters for adsorption of cadmium and copper onto the magnetic DHPDT-Zeolite and magnetic NaY Zeolite at the optimum conditions

| Ion | Langmuir isotherm | | | | Freundlich isotherm | | | |
|---|---|---|---|---|---|---|---|---|
| | $Q_{max}$ (mg $g^{-1}$) | b (L $mg^{-1}$) | $R^2$ | $R_L$ | $K_f$ | 1/n | N | $R^2$ |
| Magnetic DHPDT-Zeolite | | | | | | | | |
| $Cd^{2+}$ | 178.5710 | 0.0509 | 0.9545 | 0.0193 | 19.847 | 0.425 | 2.351 | 0.9788 |
| $Cu^{2+}$ | 181.8182 | 0.0459 | 0.9610 | 0.0213 | 15.556 | 0.484 | 2.065 | 0.9736 |
| Magnetic NaY Zeolite | | | | | | | | |
| $Cd^{2+}$ | 108.6960 | 0.005 | 0.9802 | 0.2018 | 2.3313 | 0.578 | 2.294 | 0.9561 |
| $Cu^{2+}$ | 107.5269 | 0.006 | 0.9848 | 0.1814 | 1.9006 | 0.621 | 1.961 | 0.9608 |


Magnetic DHPDT-Zeolite

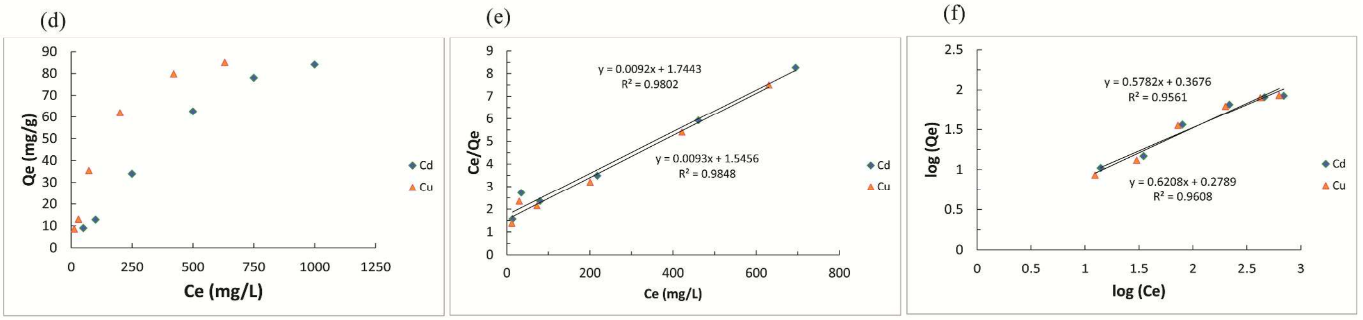

Magnetic NaY Zeolite

**Fig. 7.** The Langmuir and Freundlich isotherm plots obtained at optimum conditions for cadmium, and copper: (a), (b) The Langmuir isotherm plots, (c) The Freundlich isotherm plots for Magnetic DHPDT-Zeolite, and (d), (e) The Langmuir isotherm plots, (f) The Freundlich isotherm plots for Magnetic NaY Zeolite.

### 3.10. Desorption of magnetic organo-zeolite

The reusability of the sorbent is one of the most considerable parameters which indicate the potential of the adsorption process. Therefore, in order to regenerate the sorbent, the used polluted sorbent was desorbed in 0.1 M solution of $HNO_3$. The sorbent was contacted with the acid solution for 30 min at room temperature. This process was done for three times. Each time the concentrations of cadmium and copper were determined by atomic absorption spectrometry to ensure that there were no residual metal ions in the sorbent. Then the sorbent was rinsed by deionized water several times to remove any remaining contamination in sorbent.

### 3.11. Regeneration

The regenerated sorbent was reused from 1 to 6 in adsorption processes. The obtained results showed that the adsorption efficiency is constant till three times and after that a decreasing trend was observed.

## 4. Analysis of real sample

The proposed method was applied to tap water, river water, sea water, and two soil samples. Reliability of the method was investigated either by spiking the sample or comparing the results with data obtained by ETAAS analysis. The results are shown in Table 4.

## 5. Comparison with other studies

In order to evaluate the potential and efficiency of adsorption of cadmium and copper with magnetic DHPDT-Zeolite in water and soil samples, the proposed process was compared with other studies. As the results show in Table 5, the time of the proposed method is much shorter (9 min) and the amount of sorbent is significantly lower (0.04 g) than other previous studies which is an indicative potential for the novel magnetic DHPDT-Zeolite. Moreover, the sorption capacities of sorbent for simultaneous removal of cadmium and copper are much higher at optimum conditions of the process. Consequently, the proposed process could potently apply for simultaneous removal of cadmium and copper comparing to other studies.

**Table 4**

Removal and separation of cadmium and copper from real samples for 10 mL of sample at optimum conditions

| Sample | Concentration of Cd and Cu ( mg $L^{-1}$) | Added Cd and Cu ( mg $L^{-1}$) | Found Cd and Cu * ( mg $L^{-1}$) | Relative recovery (%) |
|---|---|---|---|---|

| | Cd | Cu | Cd | Cu | Cd | Cu | Cd | Cu |
|---|---|---|---|---|---|---|---|---|
| Tap water [a] | n.d [b] | n.d | 10.0 | 10.0 | 9.84 ± 2.1 | 9.8 ± 2.4 | 98.4 | 98.0 |
| River water[c] | n.d. | n.d. | 10.0 | 10.0 | 9.8 ± 2.5 | 9.9 ± 3.2 | 98.0 | 99.0 |
| sea water [d] | 0.1** | 0.8** | 10.0 | 10.0 | 10.3 ± 2.3 | 10.5 ± 2.9 | 102.0 | 97.0 |
| Soil[e] | 1.1 | 4.5 | 10.0 | 10.0 | 11.2 ± 1.5 | 13.9 ± 2.8 | 101.0 | 94.0 |
| Soil[f] | 0.9 | 2.8 | 10.0 | 10.0 | 10.7 ± 1.8 | 12.5 ± 2.2 | 98.0 | 97.0 |

*For three replicates (n=3)
** Determined by Electrothermal atomic absorption spectrometry
[a] Tap water from Isfahan
[b] Not Detected
[c] River water from Halil Roud River in Jiroft
[d] from Persian Gulf
[e] Obtained from farm in Lenjan, Isfahan
[d] Obtained from farm in Gavart, Isfahan

**Table 5**
Comparison of the proposed method with other adsorption processes for adsorption of cadmium and copper

| Sorbent | Time (min) | | Sorbent mass (g) | | Sorption capacity (mg g$^{-1}$) | | Adsorption (%) | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | Cd | Cu | Cd | Cu | Cd | Cu | Cd | Cu | |
| MZ- DHPDT [a] | 9 | 9 | 0.04 | 0.04 | 178.5711 | 181.8182 | 98.2 | 97.5 | This study |
| MWCNT [b] | 15 | 15 | 0.25 | 0.25 | - | - | 13.85 | 84.98 | [30] |
| Bamboo charcoal | 360 | - | 1.5 | - | 18.06 | - | 96 | - | [31] |
| Areca[c] | 60 | 60 | 1 | 1 | 1.12 | 2.84 | 97.75 | 96.46 | [32] |
| Iranian natural zeolite | 24 | 24 | 1 | 0.5 | 4.01 | 4.7 | 30 | 90 | [33] |
| Fly ash | 60 | 60 | 2 | 2 | 3.7 | 13..2 | 100 | 100 | [34] |

[a] Magnetic zeolite modified by 2-(3,4-Dihydroxyphenyl)-1,3-dithiane (MZ- DHPDT)
[b] Multi-walled carbon nanotube
[c] A food waste

## 6. Conclusions

The easy-separable Magnetic DHPDT-Zeolite was synthesized and applied for simultaneous removal of cadmium and copper from aqueous solution. The optimum conditions of 6, 25 °C, 7 min, 40 mg, and 40 mL were achieved for pH, temperature, time, amount of sorbent, and sample volume were acquired respectively. The maximum experimentally achieved adsorption percent of 99.2 ± 0.3, 98.5 ± 0.2 were obtained under optimum conditions which showed the high adsorption potential of the proposed sorbent. The adsorption isotherms studies showed favorable fitting of the process in Langmuir and Freundlich isotherms. The applied ANN model could successfully predict the process with mean square error (MSE) of 0.037. Moreover, the proposed sorbent of magnetic DHPDT-Zeolite utilized in this study can be properly applied in industrial scale due to low-cost sorbent, easy separation, and high percent of ion removal. Also, magnetic DHPDT-Zeolite can be used for adsorption of other heavy metals in future studies.

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## Notes and references

[a] Department of Chemistry, Faculty of Science, University of Jiroft, Jiroft, P. O. Box 8767161167, Iran. Tel.: +98 3443260061; fax: +98 3443260065. E-mail: shirani.mahboubeh@gmail.com
[b] Department of Mechanical Engineering, Najafabad Branch, Islamic Azad University, Isfahan, Iran

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