



## Removal of Dimethyl Phthalate from Aqueous Solution by Synthetic Modified Nano Zeolite Using Cu<sub>2</sub>O Nanoparticles

H. Esfandian<sup>\*a</sup>, E. Yousefi<sup>b</sup>, M. Sharifzadeh baei<sup>c</sup>

<sup>a</sup> Faculty of Chemical Engineering, Gas and Petroleum, Semnan University, Semnan, Iran.

<sup>b</sup> Department of Chemical Engineering, Mazandaran University of Science and Technology, Babol, Iran.

<sup>c</sup> Department of chemical engineering, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran.

### PAPER INFO

#### Paper history:

Received 22 May 2016

Received in revised form 19 August 2016

Accepted 25 August 2016

#### Keywords:

Dimethyl phthalate

Zeolite

Nanoparticles,

Isotherm

Thermodynamic

### ABSTRACT

In this paper, a novel nano crystalline sodalite was synthesized and characterized by XRF, XRD, SEM and FTIR analysis. Cu<sub>2</sub>O nanoparticles (30-60 nm) were loaded on nano zeolite bed and utilized as an adsorbent to remove dimethyl phthalate. The SEM-EDX of modified zeolite indicates that the amount of copper loading on the zeolite was 4.5 wt%. Modified nano zeolite was used as an effective adsorbent for removal of dimethyl phthalate from aqueous solutions in batch method. Results showed that Cu<sub>2</sub>O nanoparticles have a significant effect on the dimethyl phthalate sorption (adsorption rates were 92.98% with 10, 0.4g and 55min of pH, adsorbent dose and contact time, respectively for modified zeolite). The kinetic studies showed that the dimethyl phthalate sorption process was well described by the pseudo second order kinetic model. Also, Langmuir isotherm provided the best fit to the equilibrium data with maximum adsorption capacity of 20.41 mg/g for modified zeolite. Experiments showed increase of temperature has a positive effect on the dimethyl phthalate sorption process by nano zeolite. Thermodynamic parameters showed that the sorption of dimethyl phthalate onto zeolite was feasible, spontaneous and endothermic under studied conditions.

doi: 10.5829/idosi.ije.2016.29.09.c03

## 1. INTRODUCTION

At present, one of the important of persistent organic pollutants (POPs), which could harmful for both the environment and the human health, and might also be carcinogenic is existence of Phthalate esters (PAEs) in soils, ground water and surface water [1]. PAEs as prevalent environmental pollutants are widely used as a component of solvents, flotation reagents, repellents, and in the production of cosmetics, lubricants, textiles and other products. The short-chained esters such as dimethyl phthalate (DMP), is widespread in the environment because of its common usage and its refractory biodegradability. DMP has been detected in diverse environmental samples such as fresh waters, marine waters, soil and sediments. Also, DMP can be bioconcentrated and biomagnified in the aquatic food

chain. Potential sources by which DMP may enter the aquatic environment are mainly release of wastewater from production and processing activities, and the release from usage and disposal of materials containing phthalate esters [2]. Thus, because of its ecological toxicity and hazard, DMP has been designated as a priority-controlled organic pollutants by EPA and other European countries [3].

Zeolites make up a favorable class of advanced crystalline microporous inorganic materials with amazing properties which make them ideal for applications such as the molecular sieving, ion-exchange and shape-selective catalytic processes [4]. They have strongly organized microporous channel systems and high surface areas that is advantageous by comparison with the other classical support materials that hold particular interest for the adsorbent [5, 6]. Sodalite is considered one of the most typical artificial zeolites that is regarded as a traditional zeolite primarily produced by the hydrothermal crystallization method

\*Corresponding Author's Email: [hossein.esfandian@gmail.com](mailto:hossein.esfandian@gmail.com) (H. Esfandian)

[7]. It comes with a small pore size (2.8 Å) and high ion exchange capacity. Also, it attracted a lot of attention in industry and is employed in applications such as optical material [8], hydrogen storage [9] and catalyst support [10]. To remove phthalate, various methods such as treatment via adsorption [11], membrane filtration [12], Biological treatment [13] and ion exchange treatment [14] were utilized. Each method has its pros and cons. Among the others, the adsorption process provides one of the most efficient physical methods for the elimination of pollutants from the environment because the technique uses readily available equipments that are energy efficient and easy to use. Therefore, it provides a cost-effective treatment [15-17]. Many factors such as dimethyl phthalate concentration, adsorbent amount, temperature, pH, etc have some effect on adsorption process by adsorbent and the type of adsorbent is of great importance [18].

In Zhang et al [1], a modified zeolite was used for the elimination of dimethyl phthalate from aqueous solutions and the effect of various parameters such as the function of initial dimethyl phthalate concentration, the solution pH, contact time, amount of dosage and temperature on the removal of dimethyl phthalate was studied. In another research, the possibility of using carbon nanotubes for the sorptive elimination of dimethyl phthalate from aqueous solutions using batch method was examined [11]. To remove dimethyl phthalate from from aqueous phase, hydrophilic hyper-cross-linked polymer resin NDA-702 was utilized as sorbent and the effect of various operating variables on the sorption of dimethyl phthalate onto sorbent and also the equilibrium kinetic and isotherm of this sorption process were studied [19]. In this study, synthetic sodalite zeolite adsorbent was prepared and the adsorption of dimethyl phthalate from aqueous solution was studied. The effects of various operational parameters such as initial pH, adsorbent dosage, contact time, initial dimethyl phthalate concentration and temperature are also studied on the elimination of dimethyl phthalate during the batch adsorption experiments. Some isotherm, kinetic and thermodynamic models were used to evaluate the sorption process and this led to a better understanding of the adsorption characteristics.

## 2. MATHEMATICAL MODEL

### 2. 1. Reagents and Chemicals

The two formulations, i.e. Sodium metasilicate ( $\text{Na}_2\text{O}_3\text{Si}\cdot 5\text{H}_2\text{O}$ ) and sodium aluminate that are of analytical reagent grade were provided by Merck Co. The dimethyl phthalate was obtained from Merck. The sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and sodium hydroxide ( $\text{NaOH}$ ) were obtained from Merck.

### 2. 2. Instrumentation

In this study, X-ray diffraction (XRD) patterns were used with a GBC MMA diffractometer equipped with  $\text{CuK}\alpha$  radiation. Scans were compiled in the angular range of  $5^\circ$  to  $70^\circ$ . To study the sodalite zeolite surface, the Scanning Electron Microscope (SEM) model S3400, Hitachi, Japan was used. Using a sputter coater, the sample was coated with gold and palladium. It contained conductive materials to improve the image quality. The coating thickness and the density were 30.00 nm and  $19.32 \text{ g/cm}^3$ , respectively. Energy dispersive X-ray (EDX) spectra were recorded on an EDX Genesis XM2 attached to SEM. The sodalite infrared spectra (IR) were provided by FTIR Spectrometer (Shimadzu 4100) in order to form the sodalite functional groups. Using a spectrometer and KBr pellets, spectra were collected. In each case, using mortar and pestle, 1.0 mg of dried sodalite and 100 mg of KBr are homogenized and later pressed into a transparent tablet at  $200 \text{ kgf/cm}^2$  for 5 min. The pellets characterization is done using a FTIR spectrometer in the transmittance (%) mode with a scan resolution of  $4 \text{ cm}^{-1}$  in the range of  $4200\text{--}500 \text{ cm}^{-1}$ .

### 2. 3. Batch Adsorption Experiments

To study the effect of various parameters (pH, adsorbent dosage, initial concentration and contact time), tests were carried out on the sorption of dimethyl phthalate. These tests were performed according to the batch method at room temperature. The second purpose of doing the aforementioned tests was to determine the optimum conditions for the maximum elimination of the dimethyl phthalate. Isotherm, kinetics and thermodynamics of adsorption were also studied in this paper. The adsorption tests were performed in magnetic mixer. Through the dilution of 1 g/L stock solutions, 100 mL of the dimethyl phthalate solution was prepared for each adsorption test. Using the diluted solution of sulfuric acid or sodium hydroxide, the initial pH was adjusted to variable values. The suspension was filtered at the end of the predetermined time intervals and the filtrate was analyzed for any residual dimethyl phthalate. Each experiment was conducted two times with the purpose of observing the reproducibility and the mean value used for each set of values. The clear liquid phases that are obtained during these experiments were diluted to reach an appropriate concentration range for the elemental analysis using the Gas chromatography-mass spectrometry (GC-MS, 7890A-5975C, Agilent, USA). The experimental error was below 4%. The efficiency of dimethyl phthalate and/or the percent removal was obtained as follows:

$$\% \text{Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where,  $C_i$  is the initial concentration (mg/L) and  $C_f$  is the final concentration (mg/L);  $q$  is the adsorption capacity that indicates the amount of ions adsorbed per a specific

amount of adsorbent (mg/g). The sorption capacity at time  $t$  was calculated as follows:

$$q_t = (C_i - C_t) \times \frac{V}{m} \quad (2)$$

where,  $q_t$  is the amount of adsorbed dimethyl phthalate at time  $t$  (mg/g);  $V$  is the solution volume (L);  $C_i$  the initial concentration and  $C_t$  indicates the concentration at time  $t$  (mg/L); and  $m$  is the adsorbent weight (g).

The adsorption capacity at state of equilibrium,  $q_e$ , was given as the following (Equation (3)):

$$q_t = (C_i - C_e) \times \frac{V}{m} \quad (3)$$

where,  $C_e$  (mg/L) is the concentration of dimethyl phthalate at equilibrium.

**2. 4. Synthesis of Sodalite Zeolite** Sodalite nano zeolite was provided by hydrothermal crystallization method using sodium metasilicate ( $\text{Na}_2\text{O}_3\text{Si}\cdot 5\text{H}_2\text{O}$ ) and sodium aluminate ( $\text{NaAlO}_2$ ) as a silica and aluminum sources, respectively. In a standard synthesis, solution A was prepared by dissolving 18.235 g  $\text{Na}_2\text{O}_3\text{Si}\cdot 5\text{H}_2\text{O}$  (43 %  $\text{H}_2\text{O}$ , 29 %  $\text{Na}_2\text{O}$ , 28 %  $\text{SiO}_2$ ) in 8 cc double distilled water at 80 °C. Also, solution B was prepared by dissolving 3.097 g NaOH in 12 cc double distilled water. The solution was used for solving 1.837 g of  $\text{NaAlO}_2$ . Then, solution A was added to solution B drop wise under vigorous stirring and was kept there for 1 h under stirring before hydrothermicity is achieved. The molar composition of the above reactants was as follows: 1.0  $\text{Al}_2\text{O}_3$ :3.8  $\text{SiO}_2$ :2.1  $\text{Na}_2\text{O}$ :50  $\text{H}_2\text{O}$ . Subsequently, the above gel was transferred to Teflon-lined stainless steel autoclaves and heated at 100 °C for 20 h under static condition. At the end of the process, the product was separated via centrifuge (5,000 rpm), washed several times with double distilled water until the pH value of the solution was about 8.0 and dried overnight at 80 °C.

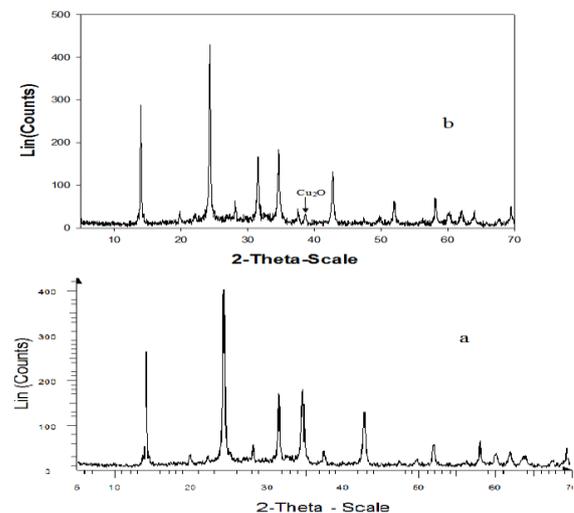
**2. 5. Synthesis of Cu Modified Sodalite** Through the grains draining in a dispersed suspension of nanoparticles, nanoparticles coating on zeolite grains was carried out. Typically, 0.1gr Copper oxide ( $\text{Cu}_2\text{O}$ ) with a particle size of 30-60 nm was spilled into an Erlenmeyer flask containing 10 mL distilled water and later sonicated a few minutes to make a uniform suspension. Then, 2 gr sodalite zeolite was added to the flasks and shook moderately for two hours. Ultimately, the flasks contents were dried slowly at 80°C for ten hours. The added value of nanoparticles was 4.5 wt% of zeolite [20, 21].

### 3.RESULT AND DISCUSSION

#### 3. 1. Characterization of Nano Sodalite Zeolite

The characterization of synthesized sodalite zeolites was

done using XRD, SEM, Energy dispersive X-ray (EDX) and FTIR. Figure 1(a-b) shows the XRD powder pattern of synthesized sodalite and Cu modified sodalite. The crystallization products matched sodalite characteristic peaks which were all given by Treacy and Higgins [22, 23] indicating a successful synthesis of sodalite nanozeolite with good crystallinity and Cu modified sodalite exhibits a  $\text{Cu}_2\text{O}$  phase which can be assigned at  $2\theta = 38.5^\circ$ . This result is fitted with previous works [7, 24]. Figure 2 shows the morphology of synthesized zeolite. It can be seen from the figure that the morphology of synthesized sodalite zeolite has a spherical structure and its mono dispersed particle size equals 30-60 nm. Figure 3 presents the elemental analysis of Cu modified analcime by means of energy dispersive X-ray (EDX). The presence of Cu peaks in EDX spectrum was explained in detail and the amounts of elements were given in Table 1. The modified sodalite structure has come under scrutiny by means of the FTIR technique and is shown in Figure 4. The band located at  $736.7 \text{ cm}^{-1}$  matching the vibration of Al-O fragment and the strong broad band at  $985.4 \text{ cm}^{-1}$  are related to the T-O band ( $T = \text{silica or aluminum}$ ) and its sharpness is indicative of an appropriate crystallization of the modified zeolitic product [25]. The peak at  $1658.5 \text{ cm}^{-1}$  is related to the bending vibration of free water. The strong broad band at  $3400\text{-}3700 \text{ cm}^{-1}$  (centered at  $3459.7 \text{ cm}^{-1}$ ) indicates the stretching of water molecules adsorbed on OH groups [26-28]. The appearance of a new absorption peak at  $437 \text{ cm}^{-1}$  is the result of the formation of single four-membered ring of sodalite unit [22]. Comparison of Figures 4(a) and (b) shows that the structure of adsorbent did not changed before and after adsorption. So, this means that the adsorption phenomena in this case is physical adsorption.



**Figure 1.** X-ray diffraction of synthesized sodalite zeolite a- zeolite b- modified zeolite .

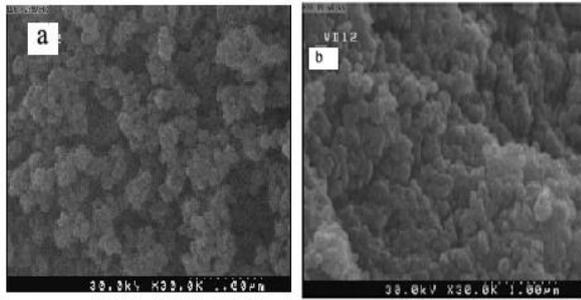


Figure 2. Scanning electron micrographs (SEM) image of modified sodalite zeolite a- zeolite b- modified zeolite

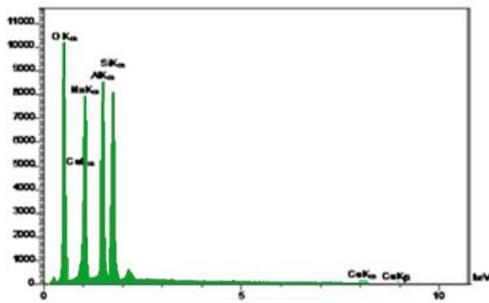


Figure 3. The EDX spectrum for Copper modified sodalite

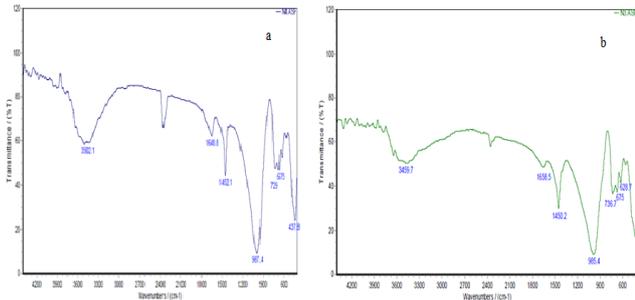


Figure 4. FTIR spectrum of modified sodalite zeolite (a) before adsorption (b) after adsorption

TABLE 1. Amounts of the elements obtained by EDX analysis

Element	Wt. %
O	49.22
Na	17.08
Al	14.55
Si	14.85
Cu	4.3

**3. 2. Effect of pH on Dimethyl Phthalate Sorption**

The pH of the solution has a significant impact on the uptake of dimethyl phthalate, since it determines the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate. Experiments

were carried out with 100 mL of a 50 mg/L dimethyl phthalate solution containing 0.4 g of the sorbent at different pHs in the range of 3–12 at 20 °C to study the effect of initial pH on the efficiency of the removal (Figure 5). As can be seen from figure 5, increasing the pH leads to an increase in the dimethyl phthalate adsorption amount. This increase gradually reached a maximum value sharply at pH 10 and then it remained constant over a wide pH region. It can be deduced that an increase in the aqueous solution pH leads to an increase in the negative charge density of the adsorbent. Thus, the uptake of the diazinon might be ascribed to increasing negative charge on the adsorbent surface (i.e., zeolite) [29, 30]. All future sorption experiments in this research were conducted at initial pH value of 10.0.

**3. 3. Effect of Contact Time**

The effect of contact time on the sorption of dimethyl phthalate was studied by sodalite zeolite (0.4 g in 100 mL) were with initial dimethyl phthalate concentration of 50 mg/L, pH 10 and temperature of 20 °C (Figure 6). It is clear that the amount of dimethyl phthalate sorption is increased by every increase in contact time. Under the above conditions, Figure 6 shows that the adsorption amount reaches the maximum value after 55 min and a subsequent little change of sorption occurs (i.e, remains constant thereafter).

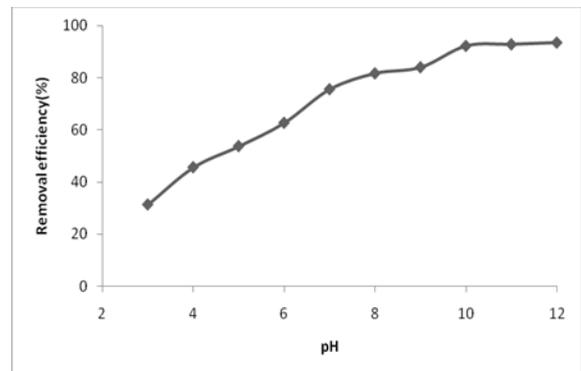


Figure 5. The effect of pH on the removal efficiency

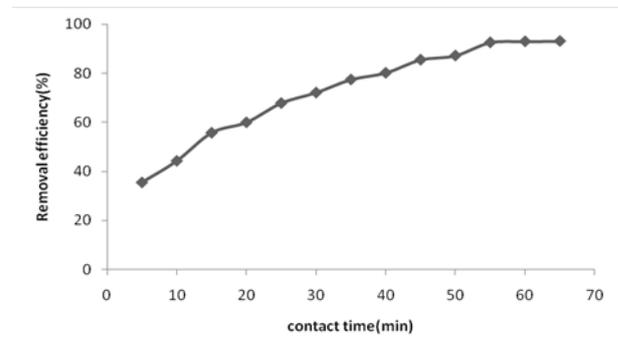


Figure 6. The effect of contact time on the removal

**3. 4. Kinetics of Sorption** Most of all adsorption processes in various solid phases depend on the time element. Knowledge of the kinetics of these processes is important to understand the dynamic interactions of dimethyl phthalate with modified zeolite and predict the rate of adsorption with time [31]. Some kinetic models, i.e Morris– Weber, Lagergren and pseudo second order models were used for their validity with the experimental adsorption data for the adsorption of dimethyl phthalate onto modified zeolite. These models were supposed to offer no mass transfer (both external and internal external) resistance to the overall adsorption process. A study was conducted on the adsorption kinetics and the findings suggest that these rates along with the solute uptake rate control the residence time of adsorbate uptake at the solid–solution interface including the diffusion process [32, 33]. The kinetic data of dimethyl phthalate sorption onto modified zeolite was used in Morris–Weber Equation (4) to examine the change in the concentration of sorbate onto sorbent with contact time [34]:

$$q_t = K_{id}(t)^{0.5} + C \tag{4}$$

where,  $q_t$  is the sorbed concentration of dimethyl phthalate at time ‘t’. The Morris-weber transport ( $K_{id}$ ) rate constant value is calculated from the slope of the linear plot of this graph ( $K_{id} = 1.358 \text{ min}^{-1}$ ) with a correlation factor of 0.993.

In Lagergren [35, 36], a pseudo-first-order equation was suggested for the sorption of liquid/solid system based on solid capacity. It is assumed in this equation that the rate of change of sorbate uptake with time is proportionate to the difference in the saturation concentration and the amount of solid uptake with time. The Lagergren equation is mostly used in liquid phase sorption. The general equation is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K}{2.303}\right) t \tag{5}$$

where,  $q_e$  is the sorbed concentration at equilibrium and  $K$  is the first order rate constant. The linear plot of  $\log(q_e - q_t)$  against time ‘t’ reveals the applicability of the above equation for dimethyl phthalate sorption onto the modified sodalite zeolite. The rate constant  $K = 0.0725 \text{ min}^{-1}$  was calculated from the slope of the straight line using the correlation factor of 0.8225.

The sorption of dimethyl phthalate onto modified zeolite following pseudo-second-order kinetics is expressed as Equation (6):

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e} \tag{6}$$

where,  $q_t$  denotes the amount of dimethyl phthalate adsorbed at time t and  $q_e$  shows that amount at equilibrium ( $\text{mg.g}^{-1}$ ). Also,  $k_2$  ( $\text{g.mg}^{-1}\text{min}^{-1}$ ) is the pseudo-second-order rate constant for the adsorption process. The rate constant  $K = 20.0382$  ( $\text{g.mg}^{-1}\text{min}^{-1}$ )

was calculated from the slope of the straight line using the correlation factor of 0.9954.

The kinetic data showed that the adsorption process was controlled by pseudo-second-order equation. Based on the above assumption, the dimethyl phthalate uptake process occurs due to chemisorptions. The fact that the rate-limiting step might be chemisorptions involving valence forces through sharing or exchanging of electrons between adsorbent and adsorbate forms the assumption of pseudo-second order kinetic model. The dimethyl phthalate molecules behavior in system is strongly dependent upon the concentration and the properties of otherspecies, pH of the solution, physical and chemical properties of both the adsorbent and adsorbate. The adsorption kinetics form and its related coefficients in the system were influenced by both the interaction and competition effects among the dimethyl phthalate [37]. The parameters of kinetic models are presented in Table 2.

**3. 5. Effect of Adsorbent Dosage** The effect of zeolite dose was studied at the dose between 0.05 g and 0.5 g in 100 mL aqueous solution. The experiments were performed at 20°C, pH 10, contact time 55 min and the initial dimethyl phthalate concentration of 50 mg/L. It was found out that increasing the zeolite dose increases the amount of adsorbed dimethyl phthalate (Figure 10). The increase in the adsorption efficiency with the increase in the adsorbent amount can be explained by the fact that as the adsorbent amount increases, the number of active sites that are available for the metal ions increase accordingly, but after passing the adsorbent optimum amount, the solution reaches an equilibrium and the increase in the adsorbent amount will have little effect on the adsorption efficiency. Another reason may be the particle interaction such as aggregation which results from high adsorbent dose.

**TABLE 2.** Kinetic constants for dimethyl phthalate adsorption

Morris-Weber equation	$K_{id}(\text{min}^{-1})$	$R^2$	
	1.358	0.993	
Pseudo-first order kinetic model	$K(\text{min}^{-1})$	$q_e(\text{mg/g})$	$R^2$
	0.0725	17.94	0.8225
Pseudo- second order kinetic model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$k_2(\text{g.mg}^{-1}.\text{min}^{-1})$	$q_e(\text{mg/g})$
	$\frac{t}{q_t} \text{ VS } t$		$R^2$
	20.0382	14.55	0.9954

Such aggregation would lead to a decrease in the total surface area of the adsorbent and an increase in diffusional path length [29, 38]. In order to fit different isotherm models, i.e., Langmuir, Freundlich and Dubinin-Randkovich (D-R), the data of Figure 7 were used.

**3. 6. The Isotherm Model** The assumption that every adsorption site is equal and independent of adjacent sites occupation or lack of occupation is the ground on which the adsorption isotherm is based [39]. The relationship between dimethyl phthalate concentration in solution can be easily understood from the presence of isotherms and the amount of dimethyl phthalate sorbed on a specific sorbent at a constant temperature.

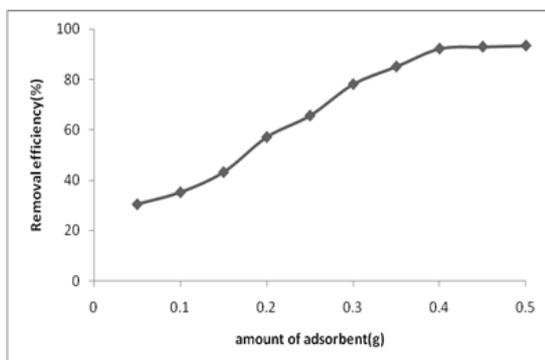
**3. 6. 1. The Langmuir Isotherm Model** In this model, the assumption is that the adsorption occurs in a monolayer and the adsorption sites located on the surface of the adsorbent is uniform and all of them have the same absorbing capacity. This isotherm model is often suggested in the form of the Equation (7) [40]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where,  $q_e$  denotes the dimethyl phthalate adsorbed per specific amount of adsorbent;  $C_e$  is the concentration of the dimethyl phthalate solution (mg/ L) at equilibrium and  $q_m$ , indicates the maximum amount of adsorption dimethyl phthalate (mg g<sup>-1</sup>). The rearrangement of the Langmuir equation leads which are presented in Table 3. Regarding the dimensionless constant separation factor or equilibrium parameter  $R_L$  the basic features and practicality of the Langmuir isotherm are defined as the following Equation (8) [41]:

$$R_L = \frac{1}{1 + K_L C_i} \quad (8)$$

where,  $K_L$  is the Langmuir constant and  $C_i$  the initial concentration of dimethyl phthalate. The desired value of absorption is specified somewhere between 0 and 1.



**Figure 7.** The effect of amount of adsorbent on the removal efficiency

**3. 6. 2. The Freundlich Isotherm Model** The Langmuir isotherm is based on the assumption that the enthalpy of adsorption is independent of the amount adsorbed while the empirical Freundlich equation is based on sorption on heterogeneous surface that can be obtained assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. Based on sorption on heterogeneous surface, the Freundlich equation is completely empirical and is expressed by Equation (9) [41]:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (9)$$

where,  $K_F$  and  $(1/n)$  are the Freundlich constants corresponding to the adsorption capacity and adsorption intensity, respectively. The equilibrium constants evaluated from the intercept and the slope of the linear plot of  $\log q_e$  versus  $\log C_e$  based on the experimental data. In logarithmic terms, the Freundlich equation can be linearized as the following Equation (10) to determine the Freundlich constants:

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log C_e \quad (10)$$

The slope and the intercept are related to  $(1/n)$  and  $K_F$ , respectively. It was found out that the plot of  $\log q_e$  vs.  $\log C_e$  gives a straight line. Results are given in Table 3.

**3. 6. 3. The Dubinin-Radushkevich Isotherm Model**

To determine the nature of the adsorption process namely physisorption and/or chemisorption, the Dubinin-Radushkevich (D-R) [42-44] isotherm was used. The linear form of this model is given as the following equation:

$$\ln(q_e) = \ln(q_m) - \beta \varepsilon^2 \quad (11)$$

where,  $q_e$  is the amount of dimethyl phthalate adsorbed per unit dosage of the adsorbent (mg/g);  $q_m$  denotes the monolayer capacity;  $\beta$  indicates the activity coefficient related to the mean sorption energy and finally  $\varepsilon$  is the Polanyi potential expressed as:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (12)$$

The  $\beta$ ,  $q_m$  values were determined by the slope and intercept of the linear plot using the plots of  $\ln q_e$  versus  $\varepsilon^2$ . Table 3 presents the statistical results together with the isotherm constants. Results suggest that the dimethyl phthalate adsorption by zeolite can be matched using the Langmuir equation. Also, the D-R equation suggests there is a considerable correlation factor. It can be understood from the D-R isotherm that the heterogeneity of energies is close to the adsorbent surface. The quantity is related to the mean sorption energy,  $E$ , which is the free energy for the transfer of 1 mole of dimethyl phthalate from the infinity to the surface of the adsorbent [45]. The following equation

shows how the mean free energy of adsorption ( $E$ , kJ/mol) is calculated [42, 46]:

$$E = (2\beta)^{-0.5} \tag{13}$$

It is clear that we can use the  $E$  magnitude to estimate the adsorption type. If this value goes below 8 kJ/mol, the adsorption type is expressed by the physical adsorption and between 8 and 16 kJ/mol the adsorption type can be explained by ion exchange. In this study, the  $E$  values were below 8 kJ/mol. This reveals that the adsorption of dimethyl phthalate onto modified zeolite was in fact a physical adsorption [47, 48].

### 3. 7. Effect of Temperature on the Adsorption of dimethyl phthalate

The adsorption studies were conducted at 25–45 °C, pH 10 and an adsorbent dosage of 0.4g in a 100 mL solution to examine the thermodynamics of adsorption. The equilibrium contact time for adsorption was kept constant at 55 min. The adsorption percentage increased with the rise in temperature from 25 to 45 °C. Results suggested that the adsorption process has an endothermic nature. Table 4 explains the effect of temperature on the removal efficiency. To determine the changes in Gibbs free energy ( $\Delta G$ ), heat of adsorption ( $\Delta H$ ) and entropy ( $\Delta S$ ) of the adsorption of dimethyl phthalate from aqueous solutions, the table 4 data were used.

### 3. 8. Effect of Temperature on Thermodynamics Parameter on Adsorption of Dimethyl Phthalate

Different thermodynamic parameters such as the enthalpy change  $\Delta H$ , free energy change  $\Delta G$  and

**TABLE 3.** Isotherm constants for dimethyl phthalate adsorption

Langmuir equation		
$K_l$	$q_m(\text{mg/g})$	$R^2$
0.1654	20.4082	0.9516
Freundlinch parameter		
$K$	$n$	$R^2$
8.6179	5.6818	0.7464
D-R parameter		
$q_m(\text{mg/g})$	$\beta$	$R^2$
14.2008	0.000001	0.9328

**TABLE 4.** The effect of temperature on the removal efficiency.

Temperature (°C)	Removal efficiency of dimethyl phthalate (%)
25	92.75
35	93.79
45	94.65

entropy change  $\Delta S$  were calculated using the Equations (14)-(16) in order to study the thermodynamics of adsorption of dimethyl phthalate on zeolite. Table 5 presents these parameters values. Using the following equations, the thermodynamic parameters  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for dimethyl phthalate on zeolite system were calculated as follows:

$$K_c = \frac{F_e}{1-F_e} \tag{14}$$

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{15}$$

$$\Delta G = -RT \ln K_c \tag{16}$$

where,  $F_e$  is the fraction of dimethyl phthalate sorbed at equilibrium. The values of these parameters are given in Table 5. It shows that the enthalpy change  $\Delta H$  is positive (endothermic) because of the increase in adsorption on successive increase in temperature. The negative  $\Delta G$  values revealed that the nature of sorption is thermodynamically feasible and spontaneous. The positive value of  $\Delta S$  indicates the increased randomness at the solid–solution interface during the fixation of the ion on the active sites of the sorbent.

### 3. 9. Comparison of the Adsorption Capacity of Various Sorbents

To have a better understanding of the adsorption capacity of modified zeolite, the values of the maximum removal obtained for dimethyl phthalate uptake with various types of sorbents are presented in Table 6. The experimental data collected from the present investigations are corresponding to the reported values. As seen in Table 6, the adsorption capacity of modified zeolite is higher than that of Chitosan, Chitosan beads cross-linked by 2-O-formylmethyl- $\alpha$ -cyclodextrin and N,N-dimethylformamide and Magnetic polyvinyl alcohol.

**TABLE 5.** Thermodynamic parameter for adsorption of dimethyl phthalate on modified zeolite

$\Delta H(\frac{Kj}{mol})$	$\Delta S(\frac{Kj}{mol.k})$	T(°C)	$\Delta G(\frac{Kj}{mol})$	$R^2$
8.6872	0.0506	25	-6.3151	0.969
		35	-6.9517	
		45	-7.596	

**TABLE 6.** Comparison of removal efficiency of different methods on DMP elimination

Sample	Sorbent material	qm(mg/g)	Reference
1	Modified zeolite	20.41	This work
2	Chitosan	0.009	[19]
3	Chitosan beads cross-linked by 2-O-formylmethyl- $\alpha$ -cyclodextrin and N,N-dimethylformamide	2.76	[20]
4	Magnetic polyvinyl alcohol	4.22	[21]
5	Carbon nanotubes	23.5	[22]

#### 4. CONCLUSION

Nano sodalite zeolite crystals can be successfully synthesized in an alkaline solution. Results suggested that the modified zeolite have considerable potential for removal of dimethyl phthalate from aqueous solutions. Results showed that Cu<sub>2</sub>O nanoparticles loaded on the zeolite have a significant effect on the dimethyl phthalate removal processing. Modified zeolite with Cu<sub>2</sub>O nanoparticles showed considerable potential in the removal of heavy metals, color and anions from industrial wastewater. The conditions of sorption are as follows: a sorbent dose of 0.4 g in 100 ml of solution, contact time of 55 min and a pH 10. Later, it was observed that the experimental data are in best agreement with the pseudo second order kinetic model related to the dimethyl phthalate adsorption reaction on the modified zeolite. This shows that the rate-limiting step in this process is the chemical adsorption reaction that includes the exchange of electrons between the adsorbate and adsorbent. The results obtained from this study were given by the theoretical Langmuir that the adsorption occurs in a monolayer and the absorption sites located on the surface of the adsorbent is uniform and all of them have the same absorbing capacity in this chemical process. Thermodynamic studies are indicative of a negative  $\Delta G$  and positive  $\Delta S$  and  $\Delta H$ . Results showed that the sorption has an endothermic nature. The negative  $\Delta G$  values suggested that the sorption has a thermodynamically feasible and spontaneous nature. The positive value of  $\Delta S$  indicate that there is an increased randomness at the solid-solution interface during the fixation of the ion on the sites of the sorbent.

#### 5. REFERENCES

- Zhang, P., Zhu, G., Ren, B., Zhang, Y. and Luo, W., "Adsorption characteristics of dimethyl phthalate by modified zeolite", *Journal of Chemical & Pharmaceutical Research*, Vol. 6, No., (2014).
- Ding, X., An, T., Li, G., Chen, J., Sheng, G., Fu, J. and Zhao, J., "Photocatalytic degradation of dimethyl phthalate ester using novel hydrophobic TiO<sub>2</sub> pillared montmorillonite photocatalyst", *Research on Chemical Intermediates*, Vol. 34, No. 1, (2008), 67-83.
- Keith, L. and Telliard, W., "Es&t special report: Priority pollutants: Ia perspective view", *Environmental Science & Technology*, Vol. 13, No. 4, (1979), 416-423.
- Cejka, J., Corma, A. and Zones, S., "Zeolites and catalysis: Synthesis, reactions and applications, John Wiley & Sons, (2010).
- Hassaninejad-Darzi, S.K. and Rahimnejad, M., "Electrocatalytic oxidation of methanol by ZSM-5 nanozeolite-modified carbon paste electrode in alkaline medium", *Journal of the Iranian Chemical Society*, Vol. 11, No. 4, (2014), 1047-1056.
- Li, L., Li, W., Sun, C. and Li, L., "Fabrication of carbon paste electrode containing 1: 12 phosphomolybdic anions encapsulated in modified mesoporous molecular sieve MCM-41 and its electrochemistry", *Electroanalysis*, Vol. 14, No. 5, (2002), 368-375.
- Felsche, J., Luger, S. and Baerlocher, C., "Crystal structures of the hydro-sodalite Na<sub>6</sub> [AlSiO<sub>4</sub>]<sub>6</sub> 8H<sub>2</sub>O and of the anhydrous sodalite Na<sub>6</sub> [AlSiO<sub>4</sub>]<sub>6</sub>", *Zeolites*, Vol. 6, No. 5, (1986), 367-372.
- Kalantari, N., Vaezi, M.J., Yadollahi, M., Babaluo, A.A., Bayati, B. and Kazemzadeh, A., "Synthesis of nanostructure hydroxy sodalite composite membranes via hydrothermal method: Support surface modification and synthesis method effects", *Asia-Pacific Journal of Chemical Engineering*, Vol. 10, No. 1, (2015), 45-55.
- Buhl, J.-C., Gesing, T.M. and Ruscher, C., "Synthesis, crystal structure and thermal stability of tetrahydroborate sodalite Na<sub>8</sub> [AlSiO<sub>4</sub>]<sub>6</sub> (BH<sub>4</sub>)<sub>2</sub>", *Microporous and Mesoporous Materials*, Vol. 80, No. 1, (2005), 57-63.
- Ogura, M., Morozumi, K., Elangovan, S., Tanada, H., Ando, H. and Okubo, T., "Potassium-doped sodalite: A tectoaluminosilicate for the catalytic material towards continuous combustion of carbonaceous matters", *Applied Catalysis B: Environmental*, Vol. 77, No. 3, (2008), 294-299.
- Wang, J., Wang, F., Yao, J., Wang, R., Yuan, H., Masakorala, K. and Choi, M.M., "Adsorption and desorption of dimethyl phthalate on carbon nanotubes in aqueous copper (ii) solution", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 417, No., (2013), 47-56.
- Cheng, A., Wang, L. and Wang, X., "Adsorption of Di-2-ethylhexyle phthalate onto nanofiltration membranes at filtering initial phase", *Membrane Science and Technology*, Vol. 4, (2012).
- Fang, H.H. and Zheng, H., "Adsorption of phthalates by activated sludge and its biopolymers", *Environmental Technology*, Vol. 25, No. 7, (2004), 757-761.
- Xu, Z., Zhang, W., Pan, B., Lv, L. and Jiang, Z., "Treatment of aqueous diethyl phthalate by adsorption using a functional polymer resin", *Environmental Technology*, Vol. 32, No. 2, (2011), 145-153.
- Kumar, A.J. and Namasivayam, C., "Uptake of endocrine disruptor bisphenol-a onto sulphuric acid activated carbon developed from biomass: Equilibrium and kinetic studies", *Sustainable Environment Research*, Vol. 24, No. 1, (2014).
- Secondes, M.F.N., Naddeo, V., Belgiorno, V. and Ballesteros, F., "Removal of emerging contaminants by simultaneous application of membrane ultrafiltration, activated carbon adsorption, and ultrasound irradiation", *Journal of Hazardous Materials*, Vol. 264, (2014), 342-349.
- Chang, C.-F., Chang, C.-Y. and Hsu, T.-L., "Preparation and adsorptive application of novel superparamagnetic zirconia material", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 327, No. 1, (2008), 64-70.
- Chang, C.-F., Chang, C.-Y. and Hsu, T.-L., "Removal of fluoride from aqueous solution with the superparamagnetic zirconia material", *Desalination*, Vol. 279, No. 1, (2011), 375-382.
- Zhang, W., Xu, Z., Pan, B., Lv, L., Zhang, Q., Zhang, Q., Du, W., Pan, B. and Zhang, Q., "Assessment on the removal of dimethyl phthalate from aqueous phase using a hydrophilic hyper-cross-linked polymer resin NDA-702", *Journal of Colloid and Interface Science*, Vol. 311, No. 2, (2007), 382-390.
- Rostami, R. and Jafari, A.J., "Application of an adsorptive-thermocatalytic process for BTX removal from polluted air flow", *Journal of Environmental Health Science and Engineering*, Vol. 12, No. 1, (2014).
- Hong, S.-S., Lee, G.-H. and Lee, G.-D., "Catalytic combustion of benzene over supported metal oxides catalysts", *Korean*

- Journal of Chemical Engineering*, Vol. 20, No. 3, (2003), 440-444.
22. Pourali, S. and Samadi-Maybodi, A., "Role of gel aging in template-free synthesis of micro and nano-crystalline sodalites", *Chemistry of Solid Materials*, Vol. 2, No. 1, (2015), 21-31.
  23. Azizi, S.N., Samadi-Maybodi, A., Fatemi, M.H. and Asemi, N., "Using taguchi experimental design to develop an optimized synthesis procedure of sodalite prepared by microwave and ultrasonic assisted aging", *Caspian Journal of Chemistry*, Vol. 2, No. 1, (2013), 1-7.
  24. Arieli, D., Vaughan, D. and Goldfarb, D., "New synthesis and insight into the structure of blue ultramarine pigments", *Journal of the American Chemical Society*, Vol. 126, No. 18, (2004), 5776-5788.
  25. Vadapalli, V.R., Gitari, W.M., Ellendt, A., Petrik, L.F. and Balfour, G., "Synthesis of zeolite-p from coal fly ash derivative and its utilisation in mine-water remediation", *South African Journal of Science*, Vol. 106, No. 5-6, (2010), 62-68.
  26. Ren, T.-Z., Yuan, Z.-Y. and Su, B.-L., "Surfactant-assisted preparation of hollow microspheres of mesoporous TiO<sub>2</sub>", *Chemical Physics Letters*, Vol. 374, No. 1, (2003), 170-175.
  27. Popescu, S.C., Thomson, S. and Howe, R.F., "Microspectroscopic studies of template interactions in alpo 4-5 and sapo-5 crystals", *Physical Chemistry Chemical Physics*, Vol. 3, No. 1, (2001), 111-118.
  28. Schnabel, K.-H., Finger, G., Kornatowski, J., Löffler, E., Peuker, C. and Pilz, W., "Decomposition of template in SAPO-5 and ALPO 4-5 molecular sieves studied by ir and raman spectroscopy", *Microporous Materials*, Vol. 11, No. 5, (1997), 293-302.
  29. Esfandian, H., Samadi-Maybodi, A., Parvini, M. and Khoshandam, B., "Development of a novel method for the removal of diazinon pesticide from aqueous solution and modeling by artificial neural networks (ANN)", *Journal of Industrial and Engineering Chemistry*, Vol. 35, (2016), 295-308.
  30. Moussavi, G., Hosseini, H. and Alahabadi, A., "The investigation of diazinon pesticide removal from contaminated water by adsorption onto NH<sub>4</sub>Cl-induced activated carbon", *Chemical Engineering Journal*, Vol. 214, No., (2013), 172-179.
  31. Mondal, P., Mohanty, B. and Majumder, C.B., "Removal of arsenic from simulated groundwater using GAC-Ca in batch reactor: Kinetics and equilibrium studies", *CLEAN-Soil, Air, Water*, Vol. 40, No. 5, (2012), 506-514.
  32. Metcalf, E., "Inc., wastewater engineering, treatment and reuse", *New York: McGraw-Hill*, (2003).
  33. Kazemi, S.Y., Hamidi, A.S. and Chaichi, M.J., "Kinetics study of selective removal of lead (ii) in an aqueous solution containing lead (ii), copper (ii) and cadmium (ii) across bulk liquid membrane", *Journal of the Iranian Chemical Society*, Vol. 10, No. 2, (2013), 283-288.
  34. Weber, W.J. and Morris, J.C., "Kinetics of adsorption on carbon from solution", *Journal of the Sanitary Engineering Division*, Vol. 89, No. 2, (1963), 31-60.
  35. Katal, R., Hasani, E., Farnam, M., Baei, M.S. and Ghayyem, M.A., "Charcoal ash as an adsorbent for Ni (ii) adsorption and its application for wastewater treatment", *Journal of Chemical & Engineering Data*, Vol. 57, No. 2, (2012), 374-383.
  36. Katal, R., Baei, M.S., Rahmati, H.T. and Esfandian, H., "Kinetic, isotherm and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk", *Journal of Industrial and Engineering Chemistry*, Vol. 18, No. 1, (2012), 295-302.
  37. Katal, R., Sefti, M.V., Jafari, M., Dehaghani, A.H.S., Sharifian, S. and Ghayyem, M.A., "Study effect of different parameters on the sulphate sorption onto nano alumina", *Journal of Industrial and Engineering Chemistry*, Vol. 18, No. 1, (2012), 230-236.
  38. Shukla, A., Zhang, Y.-H., Dubey, P., Margrave, J. and Shukla, S.S., "The role of sawdust in the removal of unwanted materials from water", *Journal of Hazardous Materials*, Vol. 95, No. 1, (2002), 137-152.
  39. Limousin, G., Gaudet, J.-P., Charlet, L., Szenknect, S., Barthes, V. and Krimissa, M., "Sorption isotherms: A review on physical bases, modeling and measurement", *Applied Geochemistry*, Vol. 22, No. 2, (2007), 249-275.
  40. Langmuir, I., "The adsorption of gases on plane surfaces of glass, mica and platinum", *Journal of the American Chemical Society*, Vol. 40, No. 9, (1918), 1361-1403.
  41. Freundlich, H., "Of the adsorption of gases. Section ii. Kinetics and energetics of gas adsorption. Introductory paper to section ii", *Transactions of the Faraday Society*, Vol. 28, No., (1932), 195-201.
  42. Dubinin, M. and Radushkevich, L., "Equation of the characteristic curve of activated charcoal", *Chem. Zentr*, Vol. 1, No. 1, (1947), 875.
  43. Anirudhan, T. and Suchithra, P., "Humic acid-immobilized polymer/bentonite composite as an adsorbent for the removal of copper (ii) ions from aqueous solutions and electroplating industry wastewater", *Journal of Industrial and Engineering Chemistry*, Vol. 16, No. 1, (2010), 130-139.
  44. Ghazy, S. and Ragab, A., "Removal of copper from water samples by sorption onto powdered limestone", *Indian Journal of Chemical and Technology*, Vol. 14, No. 2007, (2007), 507-514.
  45. Naiya, T., Bhattacharya, A. and Das, S., "Removal of Cd (ii) from aqueous solutions using clarified sludge", *Journal of Colloid and Interface Science*, Vol. 325, No. 1, (2008), 48-56.
  46. Ngah, W.W. and Fatinathan, S., "Adsorption characterization of Pb(ii) and CU (ii) ions onto chitosan-tripolyphosphate beads: Kinetic, equilibrium and thermodynamic studies", *Journal of Environmental Management*, Vol. 91, No. 4, (2010), 958-969.
  47. Chowdhury, S., Mishra, R., Kushwaha, P. and Saha, P., "Removal of safranin from aqueous solutions by naoh-treated rice husk: Thermodynamics, kinetics and isosteric heat of adsorption", *Asia-Pacific Journal of Chemical Engineering*, Vol. 7, No. 2, (2012), 236-249.
  48. Esfandian, H., Javadian, H., Parvini, M., Khoshandam, B. and Katal, R., "Batch and column removal of copper by modified brown algae sargassum bevanom from aqueous solution", *Asia-Pacific Journal of Chemical Engineering*, Vol. 8, No. 5, (2013), 665-678.
  49. Salim, C.J., Liu, H. and Kennedy, J.F., "Comparative study of the adsorption on chitosan beads of phthalate esters and their degradation products", *Carbohydrate Polymers*, Vol. 81, No. 3, (2010), 640-644.
  50. Chiou, M.-S. and Li, H.-Y., "Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads", *Journal of Hazardous Materials*, Vol. 93, No. 2, (2002), 233-248.
  51. Chang, C.-C., Tseng, J.-Y., Ji, D.-R., Chiu, C.-Y., Lu, D.-S., Chang, C.-Y., Yuan, M.-H., Chang, C.-F., Chiou, C.-S. and Chen, Y.-H., "Adsorption removal of environmental hormones of dimethyl phthalate using novel magnetic adsorbent", *The Scientific World Journal*, Vol. 2015, (2015).

## Removal of Dimethyl Phthalate from Aqueous Solution by Synthetic Modified Nano Zeolite Using $\text{Cu}_2\text{O}$ Nanoparticles

H. Esfandian<sup>a</sup>, E. Yousefi<sup>b</sup>, M. Sharifzadeh baei<sup>c</sup>

<sup>a</sup> Faculty of Chemical Engineering, Gas and Petroleum, Semnan University, Semnan, Iran.

<sup>b</sup> Department of Chemical Engineering, Mazandaran University of Science and Technology, Babol, Iran.

<sup>c</sup> Department of chemical engineering, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran.

### PAPER INFO

چکیده

#### Paper history:

Received 22 May 2016

Received in revised form 19 August 2016

Accepted 25 August 2016

#### Keywords:

Dimethyl phthalate

Zeolite

Nanoparticles,

Isotherm

Thermodynamic

در این مقاله، یک sodalite نانو کریستال جدید سنتز شد و با استفاده از تجزیه و تحلیل FTIR، XRD، XRF و SEM خصوصیت دهی شد. نانوذرات  $\text{Cu}_2\text{O}$  (۶۰-۳۰ نانومتر) در بستر نانو زئولیت بارگذاری شده و به عنوان جاذب برای حذف دی متیل فتالات استفاده شد. SEM-EDX زئولیت اصلاح شده نشان می دهد که میزان بارگذاری مس روی زئولیت ۴/۵ درصد وزنی بود. نانو زئولیت اصلاح شده به عنوان یک جاذب موثر برای حذف دی متیل فتالات از محلول های آبی در روش ناپیوسته استفاده شد. نتایج نشان داد که نانوذرات  $\text{Cu}_2\text{O}$  اثر قابل توجهی در جذب دی متیل فتالات (نرخ جذب ۹۲/۹۸ درصد با ۱۰، ۰/۴ گرم و ۵۵ دقیقه به ترتیب برای pH، مقدار جاذب و زمان تماس برای زئولیت اصلاح شده) داشت. مطالعات سینتیک نشان داد که فرایند جذب دی متیل فتالات به خوبی توسط مدل سینتیکی شبه درجه دوم توصیف شد. همچنین، ایزوترم لانگمیر بهترین تطابق داده های تعادلی با حداکثر ظرفیت جذب ۲۰/۴۱ میلی گرم / گرم برای زئولیت اصلاح شده ارائه داد. آزمایش ها نشان داد افزایش دما اثر مثبت بر فرایند جذب دی متیل فتالات توسط نانو زئولیت دارد. پارامترهای ترمودینامیکی نشان داد که جذب دی متیل فتالات بر روی زئولیت در شرایط مورد مطالعه امکان پذیر، خود به خود و گرماگیر بود.

doi: 10.5829/idosi.ije.2016.29.09c.03