

Studies of Oxyanion Removal from Aqueous Solution Using Zeolite and HDTMA-Br Surface Modified Organo-Zeolite

Hutaf M. Baker^{1*}

¹Department of Chemistry, Faculty of Science, Al al-Bayt University, P.O.Box 130091, Mafraq 25113, Jordan.

Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Article Information

DOI: 10.9734/ACSJ/2016/22053

Editor(s):

(1) Anonymous.

Reviewers:

(1) Liudmila Novikova, Voronezh State University of Forestry and Technologies, Russia.

(2) Shiv Kumar Bharadwaj, Sabanci University, Istanbul, Turkey.

(3) Anonymous, Central University, New Delhi, India.

(4) Anonymous, G Pulla Reddy College of Engineering & Technology, India.

Complete Peer review History: <http://sciencedomain.org/review-history/12601>

Original Research Article

Received 15th September 2015

Accepted 18th November 2015

Published 9th December 2015

ABSTRACT

In the present study, the Jordanian zeolite was modified with cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br), and this organo-zeolite was used to remove the nitrate ion (oxyanion). Batch experiments were carried out using zeolite at different parameters; isotherms equilibrium models Langmuir, Freundlich, Dubinin-Radushkevich and Redlich-Peterson were investigated at different temperature values 25, 30, 35, 40 and 45°C. Redlich-Peterson, Freundlich and Dubinin-Radushkevich models showed that the experimental equilibrium data followed these models better than that of Langmuir model. The calculated energy using Dubinin-Radushkevich model was found to vary from 0.08 to 0.11 kJ mol⁻¹ which is less than 8 kJ mol⁻¹, this indicate a physisorption process. Zeolite and organo-zeolite were used as adsorbents for the investigation of the kinetic studies using column reactor. Kinetic models, a pseudo-second-order, intraparticle diffusion and Elovich were used to analyze the results. The calculated q_{max} values using second-order model for both organo-zeolite and zeolite are (1.720-2.074) and (0.916-1.274) respectively, the values of q_{max} for organo-zeolite are higher than that of zeolite. The normalized standard deviation (%SSE) showed a good agreement between the experimental capacity and the

*Corresponding author: E-mail: hutafb@aabu.edu.jo;

calculated one at different temperature values for both zeolite and the organo-zeolite. The intraparticle diffusion model showed deviation from linearity when zeolite is used and showed one line when the adsorbent is organo-zeolite. The calculated activation energies (E_a) in kJ/mol for both zeolite and the organo-zeolite, are 90.7 and 13.7 respectively, the value of the activation energy gives us evidence that the organo-zeolite is better than the zeolite as an adsorbent because it has lower activation energy than the zeolite.

Keywords: Batch; nitrate; surfactant; column; kinetics.

1. INTRODUCTION

Nitrate is a source of concern for environmental and human health. This contaminant enters surface and ground water from natural and synthetic fertilizers used in agriculture and aquaculture, municipal wastewater, and mineral processing. High nitrate levels in water can cause eutrophication, and elevated NO_3^- in drinking water can cause cyanosis and cancer of the alimentary canal, creating a potential public health risk. In infants, NO_3^- can cause methaemoglobinemia, commonly known as “blue baby syndrome”. Recent studies have found that NO_3^- can cause diabetes. Therefore, NO_3^- concentrations in drinking water are regulated in many areas, such as the United States (10 mg/L as N), Europe (50 mg/L as NO_3^-), and South Korea (10 mg/L as N). Nitrate contamination of drinking water is a widespread problem. It has long been known that levels of nitrates exceeding the 10 ppm (mg/L) (as N-nitrogen) limits are associated with certain health problems. Although high nitrogen concentrations in drinking water are found mainly in regions of intensive agricultural use.

Due to its stability and high solubility, NO_3^- is difficult to eliminate. Several physicochemical and biological processes have been investigated to remove NO_3^- from water and wastewater. Many biological processes are used in industrial plants, but they require specific bacteria, such as *Bacillus* or *Thiobacillus denitrificans*, to reduce NO_3^- into N_2 . Physical processes such as reverse osmosis, electrodialysis, adsorption, and ion-exchange can also remove NO_3^- . Adsorption is considered the simplest and most economical technology because the related sludge production and disposal issues are minimal compared with those of technologies. Adsorption is suitable even with adsorbate concentrations as low as 1 mg/L. many adsorbents were used for the removal of nitrate one of them zeolite [1-8]. Zeolites are hydrated aluminosilicate materials having cage-like structures with internal and external surface areas of up to several hundred square meters per gram and cation exchange

capacities of up to several milliequivalents per kilogram. At least 41 types of natural zeolites are known to exist, and many others have been synthesized. Both natural and synthetic zeolites are used in industry as adsorbents, soil modifiers, ion exchangers, and molecular sieves [9].

The modification of the Jordanian natural zeolite with cationic surfactant like hexadecyltrimethylammonium bromide (HDTMA-Br) can provide selectivity, with production of inexpensive adsorbent. Due to the quaternary ammonium compounds that are the surfactant consists of, the removal efficiency of zeolite will improved because of this modification. Surfactant modified zeolite with a positive charge will attract anionic contaminants like nitrates by electrostatic interactions [10,11].

The aim of this study is to investigate the removal of one of the oxyanions, nitrate ion, using Jordanian zeolite and its modified form which is treated with the cationic surfactant HDTMA-Br. Batch equilibrium and column experiments were done under the optimum conditions for this removal.

1.1 Adsorption Isotherms

Adsorption is actually a mechanism in which the forces of interaction between surface atoms and the adsorbate molecules are similar to Van der Waals forces that exist between all adjacent molecules. Adsorption is a process in which a soluble chemical (the adsorbate) is removed from a fluid (liquid or gas) by contact with a solid surface (the adsorbent) [12]. To know the mechanism of adsorption, adsorption isotherms models are applied. In this study, the equilibrium data were analyzed using the Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevich (DKR) isotherms expression.

1.1.1 Langmuir model

The Langmuir model assumes that uptake of adsorbate occurs on a homogenous surface by monolayer adsorption without any interaction

between adsorbed ions. The Langmuir linearized equation may be written as:

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

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), q_m (mg/g) is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites, K_L (L/mg) is the Langmuir constant related to the energy of adsorption [13,14].

1.1.2 Freundlich equation

To investigate the intensity of the removal of sorbate onto a heterogeneous surface of adsorbent Freundlich mathematical model is applied.

The expression of its linearized equation is commonly represented as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

Where C_e (mg/L) is the equilibrium concentration and q_e (mg/g) is the amount adsorbed metal ion per gram of the adsorbent. The constant n is the Freundlich equation exponent that represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface. K_F (L/g) is the Freundlich constant related to the adsorption capacity of the adsorbent. The Freundlich exponent, n , should have values lying in the range of 1 to 10 to be classified as favourable adsorption [13,14].

1.1.3 Redlich-Peterson model

Redlich–Peterson model is used as a compromise between Langmuir and Freundlich models, its linear equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{\alpha_{RP}}{K_{RP}} C_e^\beta \quad (3)$$

where K_{RP} (L/g), α_{RP} (L/mmol) and β are Redlich–Peterson constants. The value of β lies between 0 and 1, when β is equal to one then this equation becomes as linear equation and when it is equal to zero the Henry's law is equal to the

equation of Redlich [15,16]. The Redlich–Peterson isotherm constants can be predicted from the plot between C_e/q_e versus C_e^β . However, this is not possible as the linearized form of Redlich–Peterson isotherm equation contains three unknown parameters α_{RP} , K_{RP} and β . Therefore, a minimization procedure is adopted to maximize the coefficient of determination R^2 , between the theoretical data for q_e predicted from the linearized form of Redlich–Peterson isotherm equation and the experimental data.

1.1.4 Dubinin–Radushkevich model

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations also. This isotherm is temperature-dependent. And its equation is

$$\ln q_e = \ln(q_s) - K_{ad} \varepsilon^2 \quad (4)$$

Where q_e , q_s , K_{ad} , ε are q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g); q_s is the theoretical isotherm saturation capacity (mg/g); K_{ad} it is a constant related to the adsorption energy (mol^2/kJ^2). The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy; E is the mean energy of adsorption ($kJ mol^{-1}$) and can be calculated from this relationship.

$$E = \left[\frac{1}{\sqrt{2B_{DR}}} \right] \quad (5)$$

B_{DR} is denoted as the isotherm constant. ε , can be calculated as:

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (6)$$

Where R , T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration of the solution (mg/L), respectively [12,17]. The constants such as q_s , and K_{ad} were determined from the plotting $\ln q_e$ vs ε^2 using equation 4.

1.2 Adsorption Kinetics

Many kinetic models are used to examine the rate of the adsorption process and the potential rate-controlling step. In this work, column studies were done to obtain kinetic data. The kinetic models pseudo-second-order, intra-particle diffusion and Elovich are used to analyze these data using zeolite and the organo-zeolite.

1.2.1 Pseudo-second-order model

The linearized form for pseudo-second-order rate equation is expressed as follows

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where k_2 is the rate constant of pseudo-second-order sorption ($\text{g mg}^{-1}\text{min}^{-1}$), q and q_e are the amount of solute sorbed at a given time and at equilibrium time (mg.g^{-1}) respectively.

If the second order kinetic equation is applicable, then a plot of t/q against t of should give a linear relationship. The quantities q_e and k_2 can be determined from the slope and the intercept of the plot [13,18-20].

1.2.2 Intraparticle diffusion

The possibility of intra-particle diffusion resistance affecting adsorption was explored using the intra-particle diffusion model. The linear equation for the intra-particle diffusion model [13, 18-20] is expressed as

$$\log R = \log k_{id} + a \log(t) \quad (8)$$

Where: R is the percentage of nitrate adsorbed, t is the contact time, a is the gradient of the linear plots, and k_{id} is the intra-particle diffusion rate constant.

1.2.3 Elovich model

The Elovich equation is given by

$$q_t = \beta \ln(\delta) + \beta \ln t \quad (9)$$

Where: q_t is the adsorbed amount at time t , δ (mg/g min), and β (g/mg) are the equilibrium rate constants for the Elovich model.

A plot of q_t versus $\ln t$ results in a straight line, α and β can be obtained from the slope and intercept respectively [13,18-20].

2. EXPERIMENTAL

2.1 Materials

The zeolite was sourced from Jabal Arteen. This zeolite was washed with deionized distilled water to remove any unwanted material, the washing done by agitation; this step was done for several times to make sure of the removal of unwanted material. Then it was dried at 105°C for 8 hours. The dried sample was stored in screw bottles to be used later. The physical properties which are pH, % Moisture content, % Loss of mass ignition, Specific Surface area (SSA) and Porosity followed the procedure in [17] and chemical composition were investigated for Jordanian zeolite and shown in Tables 1 and 2. The scanning electron microscope (SEM) was done as shown in Figs. (1,2), and (3) is obtained using the X-ray diffraction (XRD). Some of this dry sample treated with surfactant which is hexadecyltrimethylammonium bromide (HDTMA-Br). All the samples were crushed and classified in different particle size in the range of ≤ 38 to $90-180 \mu\text{m}$.

2.2 Modification of Zeolite Surface Using Hexadecyltrimethylammonium Bromide (HDTMA-Br)

The modification of natural zeolite with HDTMA-Br was done based of the cation exchange capacity (CEC) which shown in Table (1). 41.6 mg of this surfactant added to one gram of zeolite. The resulted solution mixture was stirred over night using mechanical stirrer at room temperature. The heterogeneous mixture was settled down then the modified zeolite separated from the liquid layer using vacuum filtration. The separated solid washed several times with deionized distilled water to make sure that the Br^- ion was not detected using 0.1 M of AgNO_3 solution [10]. The obtained organo-zeolite dried at 105°C for several hours, then was classified in different particle size in the average range of ≤ 38 to $90-180 \mu\text{m}$. and stored in polyethylene screw bottles.

2.3 Preparation of the Standard Solutions

The standard solution of 1000 mgL^{-1} of nitrate was carried out by weighing the exact grams of this analytical grade of nitrate salt and dissolved in deionised distilled water; the HDTMA-Br was purchased from Sigma and used without further treatment. The other standard solutions were prepared from analytical grade salts which are dissolved in deionised distilled water.

2.4 Batch Study

Two steps were done to study the batch process. The first step is the determination of optimum conditions for the removal of nitrate; the second one is the studying of adsorption isotherms. Both steps were performed using the natural zeolite without treatment.

2.4.1 Optimum conditions

All of the experiments that were done to investigate the optimum conditions carried out with 0.1 g of zeolite mixed with 100 mL of synthetic nitrate then transfer to 250 mL screw Erlenmeyer flask to avoid evaporation; the flasks were placed in shaker water bath at 300 rpm. Different parameters were investigated: The contact time was studied from 5 to 1440 mints, the particle size was ranged from <38 to 90-180 μm , the pH values were ranged from 2 to 10, the temperature values were from 25 to 45°C, the adsorbent dosage which was applied over range 0.5-2.5 gram and the initial concentration of oxyanion was in the range of 10-90 ppm. By varying one of the parameters while keeping the others constant the batch experiments were done. The chosen optimum variables were used in the rest of the other experiments including adsorption isotherm and the kinetic studies. Finally, all mixture of solutions and adsorbents were filtered with membrane filter of 45 μm . The supernatants were kept for analysis of the residual of nitrate concentration by measuring the absorbance at 220 nm [21] by means of a UV-VIS spectrophotometer.

2.4.2 Adsorption isotherms

Equilibrium adsorption experiments were performed using various initial nitrate concentrations ranging from 10 to 90 mg L^{-1} at temperatures of 25, 30, 35, 40 and 45°C. All of the concentrations were contact to 0.1 g of zeolite in 100 mL of nitrate solution which are mixed separately in 250 mL screw flask. The flasks were shaken until reaching the equilibrium. The supernatants were separated from the sorbents then the final concentration was determined at 220 nm.

2.5 Kinetic Studies Using Column Reactor

All of the kinetic studies carried out using column reactors for both untreated zeolite and organo-zeolite separately; the same weight was used in the two columns. All the experiments done at

different temperatures ranging from 25°C to 45°C using jacket water bath to keep the temperature constant during collecting of the sample.

The columns used were made from glass, with 27 cm in length and 1.8 cm in diameter. Untreated and the modified zeolites were packed in separate columns. The weight of adsorbent added was 55 g; the volume of the nitrate solution was 1000 mL with concentration of 10 mg L^{-1} . Deionized water was passed through the column to clean it and to test the flow rate before packing of the adsorbents. The packing was wet one. The nitrate solution transferred to the columns in constant flow rate using peristaltic pump, the collecting flow rate was of 5 mL/min, and effluents collected from the columns at various time intervals ranged from 5 to 240 minutes, then analysed by measuring the absorbance at 220 nm.

Table 1. Some physical properties of the Jordanian zeolite

Property	Zeolite
Bulk density (g/cm^3)	0.8192
pH	8.79-9.14
% Moisture content	2.1
% Loss of mass ignition	0.79
Specific Surface area (SSA) (km^2/kg)	0.007
Porosity (%)	69.10

3. RESULTS AND DISCUSSION

3.1 Properties of Jordanian Zeolite

The results of the investigation of the properties of Jordanian zeolite are showed in Table (1), from this table the porosity and the SSA are found to be within the expected range, and the highest content of mineral in this "Natural" zeolite is for SiO_2 then for Al_2O_3 as shown in Table (2) and illustrated in Fig. 3, the phillipsite is the dominant mineral found in Jordanian zeolitic tuff [9] as can be seen at Fig. 3 and Table (3), that mean the ion-exchange process is easy to take place, also the scanning electron microscope (SEM) illustrated that this adsorbent has a lot of pores, which can be seen in Figs. 1 and 2.

3.2 Batch Study (Optimum Conditions)

3.2.1 Effect of contact time

It is an important parameter to study the nature of the adsorption, rate or equilibrium process

[14]. It was seen from Fig. (4, A) that the up take of nitrate is very rapid after nearly 15 minutes, after 1 hour of contact time no change in the adsorption capacity was observed, the equilibrium is achieved, this is because the sites of the zeolite are occupied by the molecules of this oxyanion after 15 minutes. The repulsion

between the interact oxyanion molecules with these in the aqueous phase is taking place for that there is no significant change in the rate of the removal of oxyanion. To ensure the complete up take of nitrate the contact time for all experiment was 240 minutes.

Table 2. Chemical composition (wt %) of Jordanian Zeolite

Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Fe ₂ O ₃
%	1.98	7.94	10.48	34.57	1.69	9.50	4.07	0.41	29.36

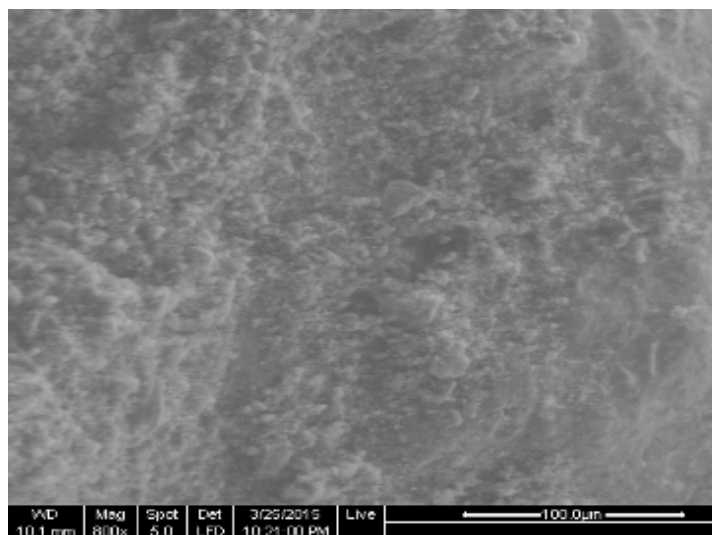


Fig. 1. SEM image of Jordanian zeolite from Jabal Arteen

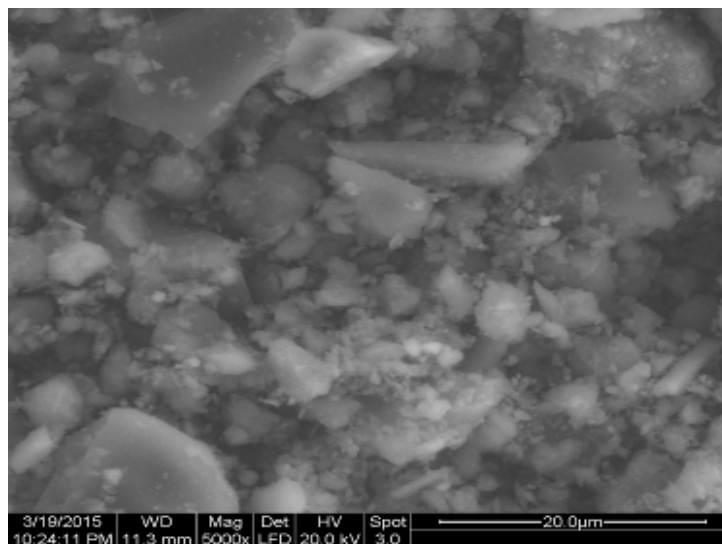


Fig. 2. SEM image of Jordanian zeolite from Jabal Arteen

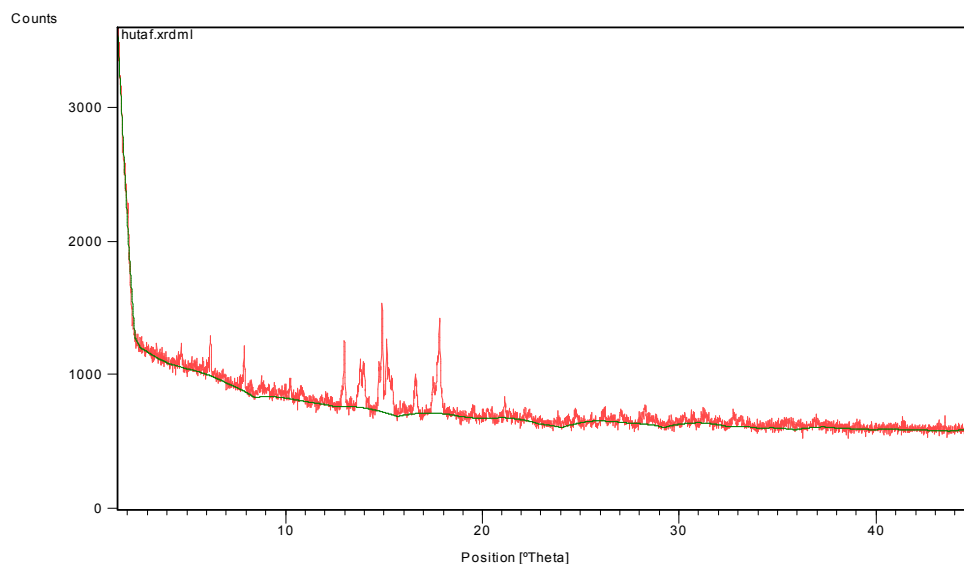


Fig. 3. XRD for Jordanian zeolite from Jabal Arteen

Table 3. X-ray diffraction (XRD)

Compound name	Chemical formula
Petedunnite	Ca Zn Si ₂ O ₆
Phillipsite	K Na Ca Fe Al Si O ₆ !39 H ₂ O
Augite, aluminian	Ca (Mg , Al , Fe) Si ₂ O ₆
Analcime	Na Al (Si O ₃) ₂ ! H ₂ O
Phillipsite	Ca Zn Si ₂ O ₆

3.2.2 Effect of particle size

The studying of the effected of the particle size was done using adsorbent particle sizes ranged from (<38 to 90-180) μm . Fig. (4, B) showed that the decrease in particle size increases the nitrate ion uptake, the maximum uptake of nitrate was observed when the particle size is <38 μm , slightly decreases in the removal was investigated when particle sizes of 38-63 and 63-75 μm are used. Small particle sizes which have bigger external surface area and exposed more active sites to nitrate molecules reduce the internal diffusion and mass transfer limitation for that the penetration of the adsorbate, because of this adsorption capability can be achieved [13]. The percentage of removal clearly decreased at bigger particle sizes (57-90 and 90-180 μm).

3.2.3 Effect of pH

The investigation of the effect of the pH was studied in the range of 2-10. Fig. (4, C) showed that the removal of the uptake of nitrate

increases by increasing the pH value and the maximum uptake (87.5%) was reached at pH equal to 5, then decreasing in adsorption capacity was observed in the range of 6-10 of the pH values, the removal at pH 10 is 77.9%, at high pH values the surface of zeolite becomes having negative charge because zeolite lost its positive surface charges, deactivation of the surface is occurred, for that oxyanion will be unable to interact with the surface because of the electrostatic repulsion [22]. The optimum pH that used in the all experiments is equal pH 5.

3.2.4 Effect of temperature

From Fig. (4, D) the study of the effect of temperature was investigated in the range of (25-45) $^{\circ}\text{C}$, this investigation showed that the removal of nitrate increases by increasing the temperature in the range of (25-40) $^{\circ}\text{C}$, this indicates that the removal of oxyanion is an endothermic process. The uptake of nitrate is almost constant at 35 and 40 $^{\circ}\text{C}$, reaction. At 45 $^{\circ}\text{C}$ decreasing in the adsorption capacity was noticed this may be because an exothermic reaction will take place at this temperature.

3.2.5 Effect of dose of adsorbent

The effect of the adsorbent dosage is investigated as shown in Fig. (4, E). The results showed that by increasing the adsorbent dosage the % removal increases, this is because the active sites of adsorbent will increased at

constant concentration of nitrate. At 2 and 2.5 grams of adsorbent the percentages of the removal of this oxyanion is almost constant this may due to the overlapping of active sites when the dosages increased [11,23]

3.2.6 Effect of initial nitrate concentration

Different initial concentrations of nitrate in the range of (10-90) ppm were contact with untreated zeolite. From Fig. (4, F) we can see that the adsorption capacity increased by increasing the initial concentration of this oxyanion. The molecules of water enhanced the mass transfer of nitrate ion by increasing its driving force between this hydrated ion and the surface of zeolite [24].

3.3 Adsorption Isotherms

3.3.1 Langmuir model

From the R^2 values which shown in Table 4, it can be seen that the Langmuir parameters at all experimental temperatures are fitted to this model and gave good description of the sorption process, the monolayer sorption was achieved. The q_{max} values increased by increasing the temperature, this indicates that the removal favored high temperature and the values of R_L constant, which refers to the shape of the isotherm and the feasibility of adsorption process as favourable, were calculated using equation 10 depending on the experimental temperatures

$$R_L = \frac{1}{1 + a_L C_o} \quad (10)$$

If the R_L value take the range $0 < R_L < 1$ then the sorption is favourable, all the calculated R_L values at the selected temperatures were in this range [22,25], it was found that this sorption process is favourable.

3.3.2 Freundlich model

The constants n and K_F are showed in Table (4), they were obtained from the slope and intercept respectively, the K_F values were increased by increasing temperature so the sorption capacity of zeolite increased, the values of n are between 1 and 10 for that the sorption is normal, favourable and efficient one at all temperatures, the n values are near to 1 and smaller than 10 then bigger heterogeneity is expected [23,25]. Because the R^2 values nearly the same of the R^2

of Langmuir model, the experimental results fitted this model like Langmuir one.

3.3.3 Redlich-Peterson model

The existing three constants that are in this model were obtained depending on the R^2 by maximizing it by error and trial. From Table (4) it was noticed that the K_R constants increased as the temperature increased, which followed the same trend of the constants of the Langmuir and Freundlich models for the adsorption capacity.

The higher $R^2 \geq 0.999$ showed that the experimental equilibrium data followed the Redlich-Peterson model. In this removal the Langmuir is a special case of Redlich-Peterson because the values of b_R constant at all temperature lied in the range of zero to unity "approaches to unity" [26].

3.3.4 Dubinin-Radushkevich model

Because the R^2 values are relatively high this model is fitting to the experimental equilibrium data. Table (4) showed the adsorption capacity of this removal which is q_s increased by increasing the temperature. The mechanism of adsorption is estimated by the magnitude of E . The calculated E was less than 8 kJ mol^{-1} at all temperatures, this means this process is physisorption, and the intra-particle diffusion is taking place [27].

3.4 Adsorption Kinetics

The results of the three kinetic models that are mentioned previously are for the zeolite and the organo-zeolite.

3.4.1 Pseudo-second-order model

The pseudo-second-order model was investigated for the zeolite and the organo-zeolite at different temperature values ranging from 25-45°C. By plotting t/qt versus t for both types of adsorbents straight lines were obtained as shown in Fig. (5), from this Figure the R^2 for the removal of this oxyanion using organo-zeolite is higher than that of zeolite; which indicated that this kinetic model is appropriate to this kind of removal and it is better when using modified zeolite. The investigation told us also that the adsorption capacity (q_e) using organo-zeolite is higher than using zeolite alone, because may be

the surfactant gives the adsorbent high ability to remove this oxyanion. The $q_{e,exp}$ values increase by increasing temperature for the two adsorbents and the K_2 increases in the range of temperature of 25-35°C then decreasing in the K_2 is noticed at 40 and 45°C. The two adsorbents have the same trend for the K_2 values.

temperatures for both zeolite and the organo-zeolite

$$SSE\% = \sqrt{\frac{\sum [(q_{e,exp} - q_{e,cal}) / q_{e,exp}]^2}{(n-1)}} \times 100 \quad (11)$$

By calculating the normalized standard deviation (%SSE) using equation (11) [13,25] which is the validity of this kinetic model, a good agreement between the experimental capacity and the calculated one was found at different

The calculated activation energies (E_a) 90.7 and 13.7 kJ/mol for both the zeolite and organo-zeolite, respectively showed that the organo-zeolite was better than the zeolite as an adsorbent due to its lower activation energy.

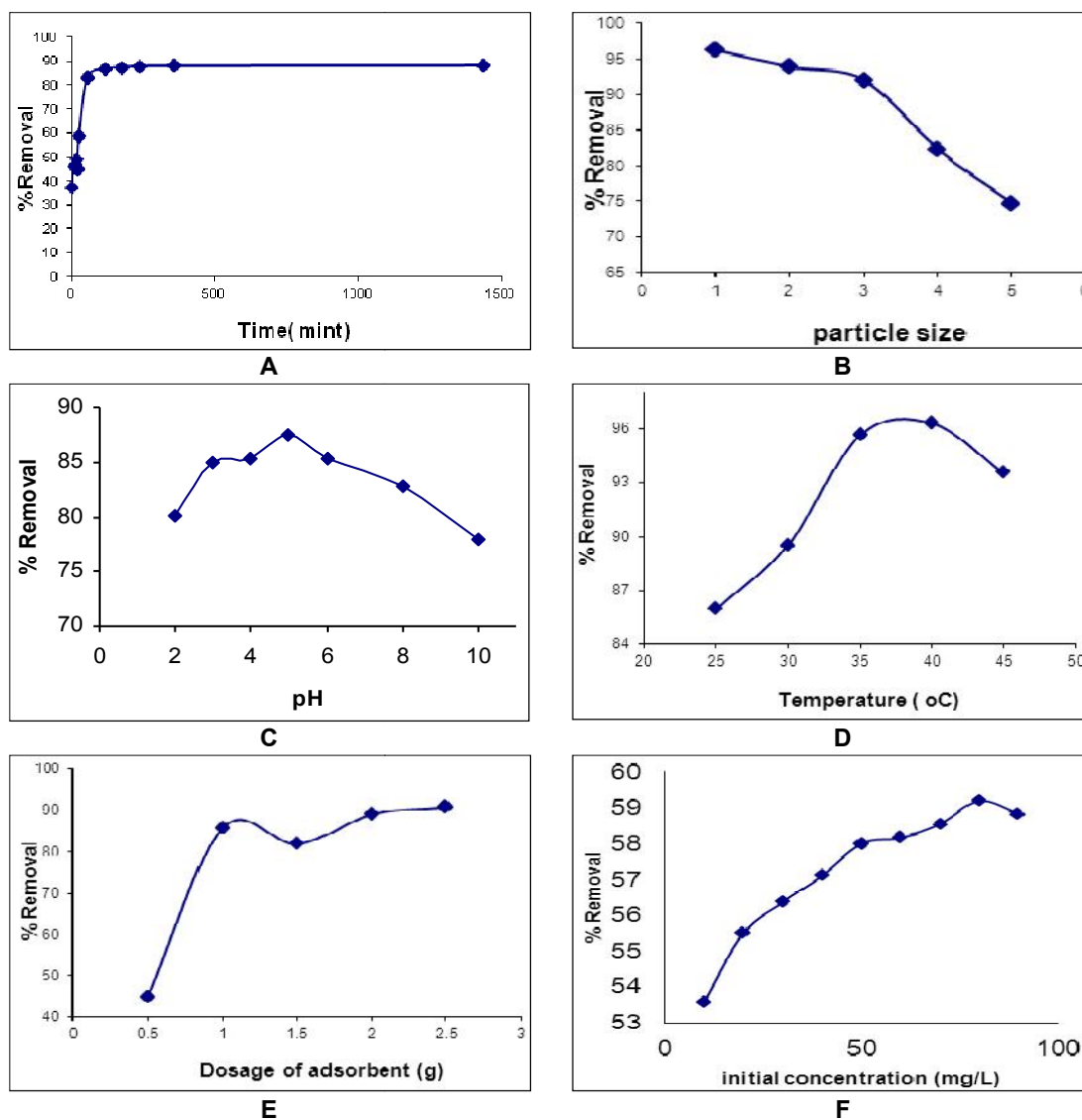


Fig. 4. Effect of different variables on the removal of nitrate ion using Jordanian Zeolite. A: Effect of contact time. B: Effect of particle size. C: Effect of pH. D: Effect of temperature. E: Effect of dose of adsorbent, F: Effect of initial concentration

3.4.2 Intra-particle diffusion model

It can be seen from the results which illustrated in Fig. (6) and shown in Table (6) That K_{id} which is related to the rate factor increased by increasing the temperature for both adsorbents. The correlation coefficients at all temperature values when using zeolite are less than the correlation coefficients when using organo-

zeolite. It seems that when the adsorbent is the zeolite a deviation from linearity is occurred as we can see from Fig. (6), two steps can be predicted, the first will toward the external surface the process will be the adsorption the second stage is the intra-particle diffusion one, the process will be adsorption but in gradual status. This indicates the intra-particle diffusion is the rate-controlling step.

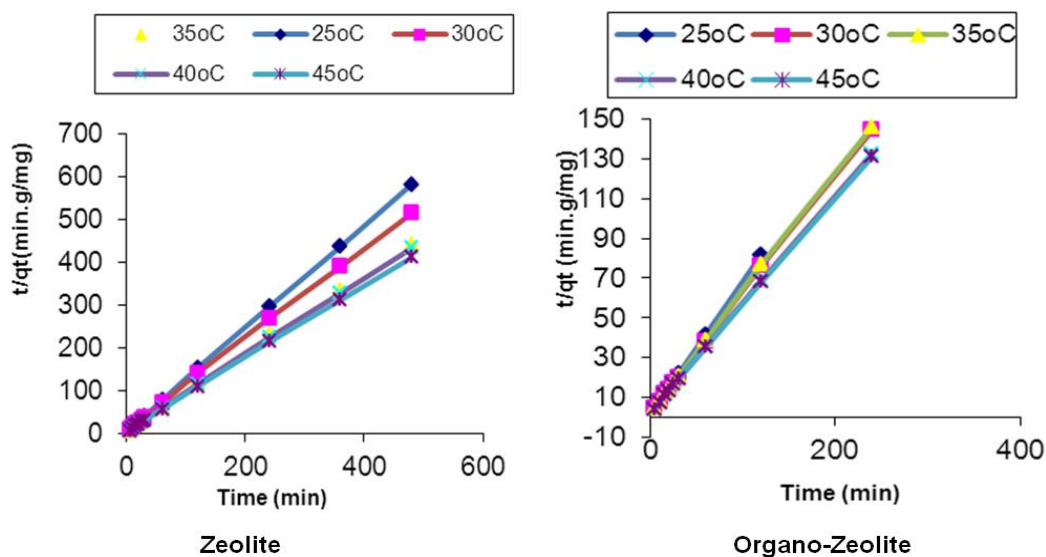


Fig. 5. Pseudo-second order model for the removal of nitrate ion aqueous solutions using column reactor: A-Zeolite. B-organo-Zeolite at various temperatures. Conditions: pH = 5, particle size <math><38 \mu\text{m}</math>, $C_o = 10$ ppm, adsorbent weight 55 gram and flow rate= 5 mL/minute

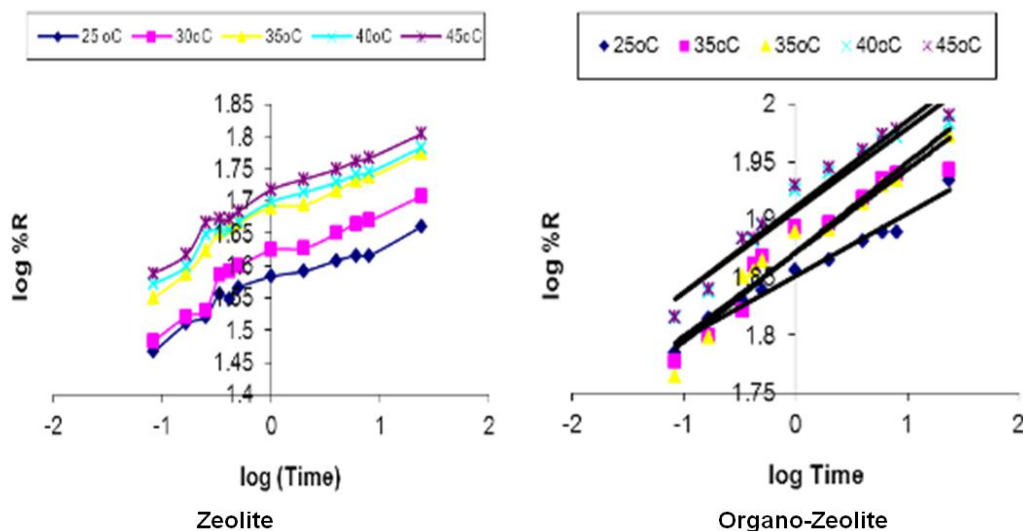


Fig. 6. Intra-particle diffusion kinetic model for the removal of nitrate ion aqueous using column reactor: A-Zeolite. B-organo-Zeolite at various temperatures. Conditions: pH = 5, particle size <math><38 \mu\text{m}</math>, $C_o = 10$ ppm, adsorbent weight 55 gram and flow rate= 5 mL/minute

Table 4. The Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevich coefficients for the adsorption of NO₃⁻¹ onto Zeolite

NO ₃ ⁻¹	Temp (°C)	Langmuir			Freundlich			Redlich-Peterson			Dubinin-Radushkevich			
		q _{max} (mg g ⁻¹)	a _L (L mg ⁻¹)	R ²	n	K _F (L g ⁻¹)	R ²	K _R	b _R	a _R	R ²	q _s (mg g ⁻¹)	E (kJ/mol)	R ²
Clay	25	30.2	0.04	0.9031	1.8	1.9	0.9210	19.3	0.92	1.02	0.9993	37.7	0.08	0.9311
	30	34.7	0.03	0.9412	1.6	2.0	0.9792	21.4	0.91	1.06	0.9990	42.2	0.11	0.9336
	35	42.4	0.05	0.9408	1.5	2.7	0.9701	22.7	0.94	1.06	0.9994	49.2	0.16	0.9038
	40	49.0	0.04	0.9497	1.7	3.4	0.9750	25.5	0.91	1.08	0.9991	59.7	0.22	0.9214
	45	58.1	0.04	0.9884	1.6	3.8	0.9821	25.7	0.91	1.09	0.9991	70.2	0.29	0.9840

Table 5. Pseudo- second order model for the removal of NO₃⁻¹ at various temperatures

q _{e,exp}	K ₂	R ²	q _{cal}	%SSE
25°C				
Clay	0.916	0.0418	0.918	0.0726
Organo-clay	1.720	0.0665	1.600	2.476805
30°C				
Clay	1.021	0.0624	1.020	0.0384
Organo-clay	1.899	0.1478	1.675603	3.921076
35°C				
Clay	1.191	0.0534	1.190	0.0373
Organo-clay	1.878	0.2179	1.599744	5.243921
40°C				
Clay	1.215	0.0535	1.213	0.0398
Organo-clay	2.048	0.1489	1.792757	4.41177
45°C				
Clay	1.274	0.0506	1.273	0.0291
Organo-clay	2.074	0.1145	1.856	3.916162

Table 6. Intra-particle diffusion model of the removal of NO₃⁻¹ at various temperatures at various temperatures

	25			30			35			40			45		
	k _{id}	α	R ²	k _{id}	α	R ²	k _{id}	α	R ²	k _{id}	α	R ²	k _{id}	α	R ²
Clay	36.6	0.07	0.9014	39.9	0.08	0.8887	46.4	0.08	0.9023	46.9	0.08	0.9275	49.9	0.08	0.9357
Organo- clay	70.7	0.06	0.9733	74.3	0.07	0.9216	74.4	0.08	0.9800	81.4	0.07	0.9657	82.3	0.06	0.9727

Table 7. Elovich kinetic model of the removal of NO_3^- at various temperatures

	Temperatures (°C)														
	25			30			35			40			45		
	β	δ	R^2	β	δ	R^2	β	δ	R^2	β	δ	R^2	β	δ	R^2
Clay	18.0	602.6	0.9761	14.8	203.91	0.9643	7.6	191.3	0.9566	11.6	118.4	0.9870	10.8	84.7	0.9712
Organo- clay	9.3	814.5	0.9700	7.1	103.3	0.9835	7.7	263.4	0.9782	6.9	196.1	0.9889	6.6	130.5	0.9939

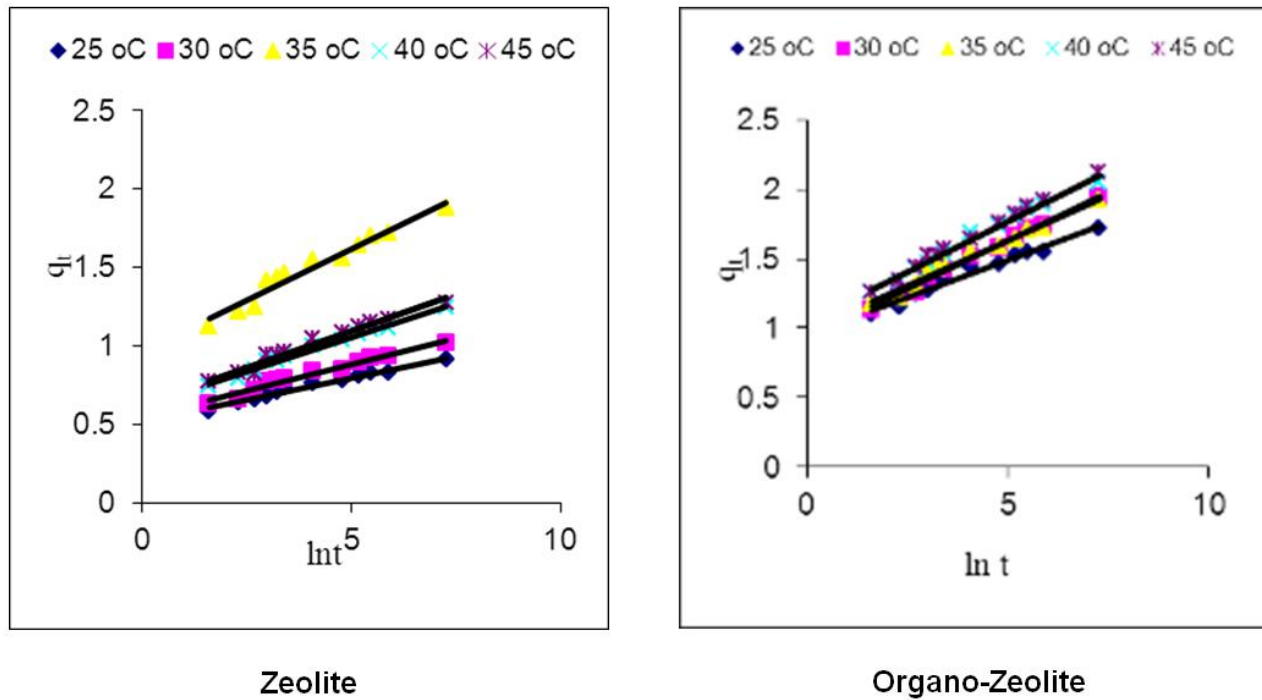


Fig. 7. Elovich kinetic model for the removal of nitrate ion aqueous using column reactor: A-Zeolite. B-organo-Zeolite at various temperatures. Conditions: pH = 5, particle size <math><38 \mu\text{m}</math>, $C_o = 10$ ppm, adsorbent weight 55 gram and flow rate= 5 mL/minute

When using the organo-zeolite the R^2 coefficients are relatively high without deviation from linearity as shown in Fig. (6) at all temperature values, this removal was achieved in one step only which is the at the surface of the adsorbent, this may due to the surfactant (HDTMA-Br) which has high affinity to interact with the nitrate ions [13,27].

3.4.3 Elovich model

From Fig. (7) and the results showed in Table (7), the linearity is observed for both zeolite and organo-zeolite at all temperature values. The initial adsorption rate which is δ decreases by increasing the temperature and the same trend occurs with the β constant. The obtained correlation coefficients for this model at all temperatures were relatively high > 0.9 ; this means this kind of removal is suitable for Elovich model [28].

4. CONCLUSION

- The Jordanian zeolite has the efficiency to work as an adsorbent because of its pores with high content of silica and it has high surface area.
- The modification of zeolite with the cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br) has higher ability for the removal of nitrate (oxyanion) from aqueous media than zeolite.
- The optimum pH for removal is 5 and the optimum equilibrium contact time is 240 minutes.
- The experimental equilibrium data followed Redlich-Peterson, Freundlich and Dubinin-Radushkevich models better than that of Langmuir model.
- The values of R_L are < 1 and > 0 which indicated that the sorption is favourable for nitrate ion using both kinds of zeolite.
- The calculated energy using Dubinin-Radushkevich model was less than 8 kJ mol^{-1} at all temperatures, physisorption, is taking place.
- The experimental values for q_{max} which obtained using pseudo-second-order kinetic model are higher for the organo-zeolite than that of the zeolite.
- The intraparticle diffusion model showed deviation of linearity when the used adsorbent is zeolite and showed one linear line when the adsorbent is organo-zeolite.
- Because the activation energies (E_a) for zeolite is higher than that of organo-zeolite,

respectively, the organo-zeolite is better than the zeolite as an adsorbent.

- The normalized standard deviation (%SSE) showed a good agreement between the experimental capacity and the calculated one at different temperatures for both zeolite and the organo-zeolite for pseudo-second-order model.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Prato T, Parent RG. Ionics, nitrate and nitrite removal from municipal drinking water supplies with electro dialysis reversal. GE Power & Water Water & Process Technologies. 1-5.
2. Khan MA, Ahn YT, Kumar M WL, Min B, Kim G, Cho DW, Park WB, Jeon BH, Separation Science and Technology. 2011;46:2575–2584.
3. Öztürk N, Bektaş TE. Nitrate removal from aqueous solution by adsorption onto various materials. Journal of Hazardous Materials B112. 2004;155–162.
4. Imran A, Gupta VK. Advances in Water Treatment by Adsorption Technology, Nature London1. 2006;2661-2667.
5. Imran A. The Quest for Active Carbon Adsorbent Substitutes: Inexpensive Adsorbents for Toxic Metal Ions Removal from Wastewater, Sepn. & Purfn. Rev. 2010;39:95-171.
6. Imran A. New generation adsorbents for water treatment. Chem. Revs. 2012;112: 5073-5091.
7. Imran A, Asim M, Khan T. A low cost adsorbents for removal of organic pollutants from wastewater. J. Environ. Manag. 2012;113:170-183.
8. Imran A. Water treatment by adsorption Columns: Evaluation at ground level. Sepn. & Purfn. Rev. 2014;43:175-205.
9. Baker HM, Massadeh AM, Younes H. A, natural Jordanian zeolite: Removal of heavy metal ions from water samples using column and batch methods. Journal of Environmental Monitoring and Assessment. 2009;157(1):319-330.
10. Aroke UO, El-Nafaty UA, Osha OA, Removal of oxyanion contaminants from wastewater by sorption onto HDTMA-Br surface modified Organo-Kaolinite.

- International Journal of Emerging Technology and Advanced Engineering. 2014;4(1):475-484.
11. Masukume M, Onyango MS, Aoyi O, Otieno F. Functionalised natural zeolite and its potential for treating drinking water containing excess amount of nitrate. Water SA. 2010;36(5):655-662.
 12. Itodo AU, Itodo HU. Sorption energies estimation using Dubinin-Radushkevich and temkin adsorption isotherms. Life Science Journal. 2010;7(4):31-39.
 13. Baker HM, Ghanem R. Study on removal behavior and separation efficiency of naturally occurring bentonite for sulfate from water by continuous column and batch methods. European Journal of Chemistry. 2015;6(1):12-20.
 14. Dawodu FA, Akpomie GK, Ogbu IC. Isotherm modeling on the equilibrium sorption of cadmium (II) from solution by agbani clay. International Journal of Multidisciplinary Sciences and Engineering. 2012;3(9):9-14.
 15. Baker HM. A study of the binding strength and thermodynamic aspects of cadmium and lead ions with natural silicate minerals in aqueous solutions. Desalination. 2009; 242:115-127.
 16. Brdar MM, Takači A.A, Šćiban MB, Rakić DZ. Isotherms for the adsorption of Cu(II) onto lignin – comparison of linear and non-linear methods. Hem. Ind. 2012;66(4): 497–503.
 17. Dada AO, Olalekan AP, Olatunya AM, Dada O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry (IOSR-JAC). 2012;3(1):38-45.
 18. Baker HM, Ghanem R. Evaluation of treated natural zeolite for the removal of o-chlorophenol from aqueous solution. Desalination. 2009;249(3):1265-1272.
 19. Baker HM, Fraij H. Principles of interaction of ammonium ion with natural Jordanian deposits: Analysis of Uptake Studies. Desalination. 2010;251(1-3):41-46.
 20. Baker HM. Evaluation of Jordanian treated natural zeolite for the uptake of p-nitrophenol from wastewater by continuous column method. Desalination and Water Treatment. 2014;52(16-18):3290-3300..
 21. Namasivayam C, Sangeetha D, Removal and recovery of nitrate from water by ZnCl₂ activated carbon coconut coir pith, an agricultural solid waste, Indian Journal of Chemical Technology. 2005;12:513-521.
 22. Bekele W, Faye G, Fernandez N, Removal of nitrate ion from aqueous solution by modified Ethiopian bentonite clay. IJRPC. 2014;4(1):192-201.
 23. Sivakumar S, Muthirulan P, Sundaram M. M. Adsorption kinetic and isotherm studies of Azure A on various activated carbons derived from agricultural wastes. Arabian Journal of Chemistry; 2014.
 24. Akosman C, Özdemir T. Adsorption dynamics and equilibrium studies of nitrate onto various soils. Fresenius Environmental Bulletin. 2010;19(10): 2246-2252.
 25. Samadi N, Hasanzadeh R, Rasad M. EA dsorption isotherms, kinetic, and desorption studies on removal of toxic metal ions from aqueous solutions by polymeric adsorbent. J. Appl. Polym. Sci. 2015;1-13.
 26. Shahmohammadi-Kalalagh Sh, Babazadeh H, Nazemi AH, Manshouri M. Isotherm and kinetic studies on adsorption of Pb, Zn and Cu by Kaolinite, Caspian J. Env. Sci. 2011;9(2):243-255.
 27. Al-Meshragi M, Ibrahim HG, Aboabboud MM. Equilibrium and kinetics of chromium adsorption on cement kiln dust. Proceedings of the World Congress on Engineering and Computer Science. 2008; 1-9.
 28. Ho YS, McKay G. Application of kinetic models to the sorption of copper(II) on to Peat. Adsorption Science & Technology. 2002;20(8):797-815.

© 2016 Baker; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://sciencedomain.org/review-history/12601>