

Adsorption of Cadmium Ions onto Zeolite-A prepared from Egyptian Kaolin using Microwave Technique

Alaa Fahmy¹, Magdy A. Wassel², Hassan A. Shehata³, H. F. Youssef⁴, Ahmed S. Elzaref⁵

^{1, 2, 3, 5} Chemistry Department, Faculty of Science, Al-Azhar University, 11884 Cairo, Egypt

⁴ Inorganic Chemical Industries and Mineral Resources Division, National Research Centre (NRC), Giza, Egypt

Abstract: Zeolite-A has been prepared from Egyptian kaolin to remove divalent cadmium ion from wastewater. The synthesized zeolite was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A batch technique was employed as a function of temperatures, contact time and pH of the solution. Zeolite-A morphology was observed by SEM analysis, and it showed well-defined crystals slightly different sized crystals of the same cubic shape. Results revealed that the optimum conditions of the adsorption process are: zeolite dose= 0.25g in 25 mL of Cd(II) with contact time of 140 min, 333 K and pH 7.5. Two equations, namely pseudo-first order and pseudo-second order have been used to determine the kinetics of removal process. The collected kinetic data showed that pseudo-second order equations controls the adsorption. Chemisorption process and Langmuir isotherm proved best fitting to the experimental data. The adsorption mechanism was based on cation exchanges of Cd²⁺ ions present in wastewater and the available Na⁺ ion.

Keywords: Zeolite-A, Adsorption, Water treatment, Cadmium ions

1. Introduction

The development of chemical processes has clearly affected our universe over the last few centuries. For instance, water resources have been impurities by several trace elements such as Cd(II), Cu(II), Pb(II), Cr(III), Zn(II), and Fe(II) produced as residues from different chemical industries [1].

The removal of heavy metals (Pb, Zn, Cd, etc.) from contaminated water/wastewater has been received great attention, because of the adverse impact on the health and the natural environment [2]. Various techniques such as reduction and precipitation, coagulation, lime softening, adsorption, ion exchange and reverse osmosis were used for the removal of different pollutants from wastewater [3]. However, adsorption process onto solid substrate is preferred because of its high efficiency, easy handling, and cost-effectiveness [3]. Activated carbon, activated alumina, clays and Zeolites are among the most industrially used as adsorbents. The preference of using Zeolites, especially the synthetic forms, in the field of cation recognition and heavy element removal is due to their pore size uniformity and selectivity [4]. Zeolite-A is the universal type of synthetic Zeolite in the area of detergent and water softening, due to its large ion exchange capacity, mechanical strength and particular crystal shape. Besides, it is environmentally safe with almost zero loading of harmful effect on the environment [5]. The term "Molecular sieves" is applied for the manufactured Zeolite types, owing to their shape selective nature, which is a reflection of their three-dimensional well-controlled porous framework skeleton. Their structure contains specific uniform sets of channels and cavities of molecular dimensions and free contact with the external medium. The presence of charge compensation cations within the porosity of the inorganic frameworks gives

to these materials ionic exchange and catalytic properties, which are widely used in the industry [4]. Moreover, the hydrophobic (zeosil, SiO₂) or hydrophilic (aluminosilicates) nature of the inorganic framework make these solids useful as specific adsorbents for organic molecules in the gas or liquid phase [6].

However, synthetic Zeolites are preferred for the industrial applications, such as adsorption, catalysis and ion exchanging, than their natural counter parts due to more uniform pore sizes, relative ease of manufacture, low costs and can be tailored to specific shape and size needs. The pore size ranges of some synthetic molecular sieves are 3.5-4.5 Å for LTA (Z-A) Zeolite, 4.5-6.0 Å for ZSM-5 and 6.0-8.0 Å for Zeolite X and Y [7]. Adsorption is a special characteristic of Zeolites which is usually ion exchange occur into the pore openings of the ion exchanger and active side on the surface. The amount of metal ion to be adsorbed is strongly affected by nature and concentration of the metal ion, pH, and metal solubility, presence of competing and complexing ions [8].

Zeolites are generally prepared under hydro-thermal procedure [9] starting from a gel whose basic constituents are silicon, aluminum, mineralizing agent (hydroxide ion or fluoride media), and an organic template. The first artificial Zeolite was synthesized according to the sequences observed in nature and this synthesis has been constantly improved in order to obtain new structures, shape and size properties [10]. The introduction of microwaves during the hydrothermal synthesis of ceramic powders, gels and metal powders leads to increase the kinetics by over an order of magnitude [11,12]. The advantage of using microwave heating in Zeolite synthesis is attributed to the reduction of crystallization time compared to the conventional hydrothermal method owing to the relatively fast dissolution

Volume 5 Issue 7, July 2016

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

of the gel and uniform heating of the synthesis mixture leading to a more abundant nucleation [13].

A new solid phase (synthetic zeolites type Na-LTA, Ca-LTA, Na-FAU and Ca-FAU) extraction technique was developed based on the removal of metal ions from water samples including Pb(II), Ni(II), Cd(II) and Co(II) and determine its concentration by FAAS. The conditions for quantitative, elution and FAAS determinations were studied by using 0.02 g of Zeolite can be used in more than 200 experiments of adsorption/elution cycles after washing with ultrapure water without any loss in its adsorption behavior. The adsorption mechanism in acidic medium is based on interactions between acidic active sites of Zeolite and different metal ions. The degrees of interactions are highly independent because the systems are different for each metal ion [14].

Zeolite obtained from coal fly ash is an inexpensive and effective adsorbent for the removal of cadmium from wastewater. Javadian et al. [15] reported that a specific type of zeolite, synthesized from coal fly ash, was used to adsorb Cd(II) ions from aqueous solution. They found the optimum conditions of the adsorption process: zeolite dose= 0.08 g in 25 mL of Cd(II) with contact time of 7 h and pH 5. Four equations, namely Weber Morris, Pseudo-first order, Pseudo-second order and Elovich have been used in order to determine the kinetics of removal process. The collected kinetic data showed that pseudo-second order equations controlled the adsorption process. According to the adsorption isotherm studies, the Langmuir isotherm was proved to be the best fit for experimental data. Furthermore, maximum adsorption has been found at pH= 6, 40 °C and an adsorbent dosage of 2 g/100 mL by Das et al. [16]. The change in the surface morphology of Zeolite was observed from the SEM images. The adsorption data fit well in both the Langmuir and Freundlich adsorption isotherms which indicate ion exchange mechanism.

In summary, this method is simple, accurate, economical, and environmentally friendly and can be applied for water softening. In the present work, synthetic Zeolite-A, prepared from Egyptian kaolin (for economic value), will be used for the adsorption of Cd(II) ions from aqueous solutions as water treatment application. A batch technique will be employed as a function of temperatures, contact time and pH values of the solution. Moreover, the equilibrium process will be described by the Langmuir and Freundlich isotherm models.

2. Experimental

2.1 Materials and methods

2.1.1 Adsorbate

Cadmium chloride salt (Molar mass=183.32 g/mol, purity=99%) was used for preparing a synthetic solution containing 0.008M. These solutions were prepared by dissolving a weighed quantity of the respective chloride salt in De-ionized H₂O (ultrahigh purity water, resistivity > 18 MΩ/cm, Millipore). Acetic acid and ammonium hydroxide

solution were used to adjust the initial pH values in the range from 6.0 to 7.5. It should be noted that chloride anions are not forming precipitates or complexes at the test conditions, all reagents were BDH grade or products and considered inert. It is assumed that the impact of adjusting the initial solution pH with acetic acid and ammonium hydroxide solutions in terms of changing the chemistry of the solution is not significant [17,18].

2.1.2 Adsorbent

Zeolite-A has a cubic structure with LTA-type (Na₁₂Al₁₂Si₁₂O₄₈) formula and an aperture of 4x4 Å [4]. The starting materials for Zeolite-A synthesis are sodium hydroxide pellets (NaOH) of analyzed A.C.S. reagent with the composition of 98.6 % NaOH + 0.4 % Chloride (Baker, SG403INT, Sanford, ME, USA); refined Egyptian kaolin is supplied by Middle East Mining Investments Company (MEMCO). The mineralogical and chemical composition of the used kaolin is shown in Table 1.

Table 1: Chemical and mineralogical analysis of the used kaolin

Chemical composition of kaolin		Mineralogical composition	
Oxides	Conc. (W %)	Mineral	(%)
SiO ₂	50.00	Kaolinite	56.0
Al ₂ O ₃	30.31	Quartz	38.5
TiO ₂	1.65	Anatase	5.5
Fe ₂ O ₃	4.61		
MgO	0.20		
CaO+Na ₂ O+K ₂ O+MnO	0.96		
L.O. I	12.27		

2.2 Methods

The supplied kaolin is a calcined and Fe-refined product with Al₂O₇Si₂.2H₂O, CAS-Nr: 1318-74-7. Although, the delivered material is actually a metakaolinite, its storage and handling can alter its composition, thus a re-calcination at 1023K for 2h was necessary to insure its amorphous nature and get rid of the probable adsorbed water on its surfaces. The metakaolinite is then reacted with NaOH on stirring and heated at 353K for 2 h using microwave irradiation [13]. The Microwave instrument (MARS Extraction and Digestion system, Model XP-1500, CEM Corp., Matthews, NC) was used. The synthesis materials were collected, washed several times with distilled water to remove the excess alkali content, and finally dried in an electric oven at 353K overnight.

2.3 Characterization Methods

The chemical composition (in wt %) of the starting refined kaolin is obtained by X-ray fluorescence technique using XRF instrument model AXIOS, WD-XRF sequential spectrometer (Panalytical, 2005). Meanwhile, the mineral constituents of the calcined metakaolinite and prepared Zeolite was investigated by X-ray diffraction method; using BRUKUR D8 ADVANCE with secondary monochromatic beam Cu Kα radiation at KV = 40 and mA = 40. The obtained zeolitic materials were scanned for identifying their microstructures using SEM model Philips XL30 attached

with EDX unit, using an accelerating voltage of 30 K.V. with a magnification of 10x up to 400,000x, and resolution for wavelength (3.5 nm)

2.4 Concentration of cadmium ions (Cd²⁺)

For testing the cation exchange property for Zeolite, 25 ml of synthetic solutions containing different initial concentrations of Cd²⁺ were added to 0.25g of Zeolite. The test is set for wide range of temperature ranging from 303 to 333K during batch testing at constant period of time (140 min). After testing, the metal ion concentrations left in the liquid phase to determine the final cadmium concentrations using an atomic absorption spectroscopy (AAS vario® 6, Analytic Jena).

The adsorbed amount of Cd(II) ions q_t (mg . g⁻¹), per unit weight at time (t), was calculated from the mass balance equation as shown in Eq.(1) [1,19]:

$$q_t = \frac{C_0 - C_t}{M} V \quad (1)$$

Where C_0 : the initial concentration of Cd(II) (mg . L⁻¹), C_t : the concentration at time t, V: the volume of solution (L) and M: the mass (g) of Zeolite-A.

3. Results and Discussion

3.1 XRD for the prepared Zeolite-A from refined Egyptian kaolin

The X-ray pattern of Zeolite-A was obtained from the metakaolinite [when reacted with 3.0 M NaOH and heated under microwave conditions at 353K for 2h]. The position and intensity of the recorded peaks are in good agreement with JCPDS data of the reference Card # 39-0222 of Zeolite-A composition (Z-A formula from chart) shown in Figure 1a. The XRD results reflect the well-developed Zeolite product of sharp and strong peaks of high intensity. Only one crystalline phase of Zeolite-A was achieved. From an economic point of view it is a main advantage as it is a fast process which requires cheap materials, and which opens even more space for applications which demand it in large quantities.

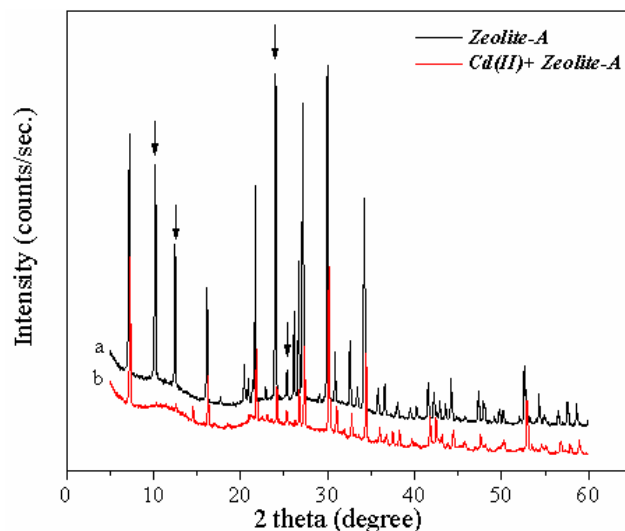


Figure 1: XRD for the prepared Zeolite-A from refined Egyptian kaolin before (a) and after (b) adsorption of Cd(II) ions

However, some changes in the structure of Zeolite- A were observed after dipping in aqueous solutions containing Cd(II) ions (Figure 1b). It means something happened in the structure of Zeolite-A. According to the published papers [20-22], it was expected that ion-exchange will be the main sorption mechanism of cadmium ions onto Zeolite-A, where mainly Na⁺ ions will be replaced by cadmium ions. SEM connected with EDX was used to confirm this hypothesis.

3.2 SEM and Microanalysis of Zeolite-A

Figure 2 (a and b) and (c and d) show the SEM micrographs and chemical microanalysis (EDX) of the prepared Zeolite-A crystals before and after the adsorption process, respectively. The characteristic Zeolite-A cubic crystals of relatively uniform size of up to 5µm are likely spread all over the scanned area before (Figure 2a) and after

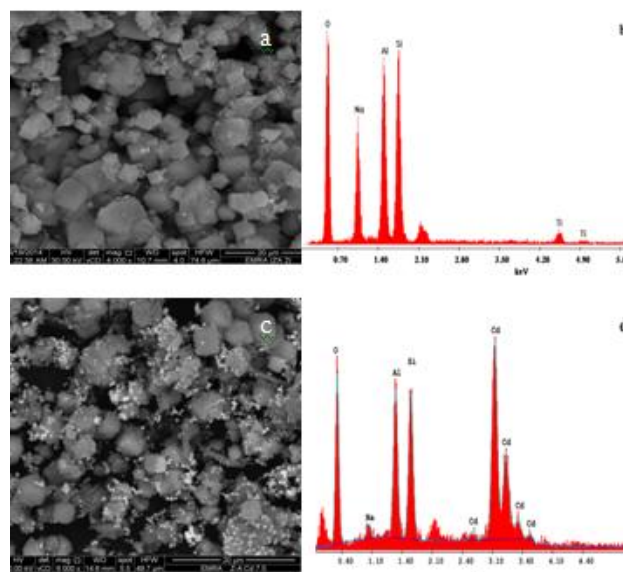


Figure 2 (c): Adsorption Process

Figure 2: SEM of the prepared Zeolite-A before and after adsorption, a, c where EDX of Zeolite-A before and after adsorption reveals in b, d, respectively

Meanwhile, Figures 2b and d implies the corresponding microanalysis of the zeolitic product where the Cd⁺² ions are showing up in the chemical composition of crystals after the adsorption process (Figure 2d). It has to be pointed out that cadmium may have been retained both to outer surfaces and to the network of pores forming complexes inner micro-structure of zeolitic materials. The expected replacement of sodium ions by cadmium is evident and was confirmed by EDX spectra analysis, where significant decrease of sodium peak after cadmium sorption was observed (Figure 2d).

During the ion-exchange process, cadmium ions not moved only through the pores of the zeolite, but also through channels of the lattice, and they had to replace exchangeable cation (mainly sodium) [23]. It should be noted that the diffusion was faster through the pores and was limited when ions moved through the smaller diameter channels. Therefore, the cadmium uptake could mainly be related to the ion-exchange reactions in the microporous minerals of zeolite samples. Thus, the adsorption on the surface of the minerals also plays an important role. The SEM data witnessed an intensive backing of crystals, which agrees well with the XRD results of having well crystalline product [18]. In addition, preservation of the cubic morphology of the crystals after the exchanging process indicates the stability of the Zeolite-A structure was established (Figure 2c).

Table 2: Adsorption of Cd⁺² on Zeolite-A surface at different pH values

Elements	Z-A W%	Adsorption (%)		
		pH= 6.0 W%	pH=6.5 W%	pH=7.5 W%
OK	40.75	37.97	34.33	32.48
NaK	14.15	02.52	02.13	01.69
AlK	19.22	16.94	12.42	10.68
SiK	22.90	17.49	12.51	10.50
TiK	02.98	----	-----	-----
CdL	00.00	25.08	38.61	44.65
Total	100.0	100.0	100.0	100.0

Table 2 shows the performance of Zeolite-A for adsorbing the cadmium ions from its prepared solutions at different pH values. The obtained results reveal a successive increase in the weight % of Cd⁺² contents in the exchanged samples from 0.0 to 44.65, at the expenses of Na⁺ contents which reduced from 14.15 to 1.69 W%. This result confirms the efficiency of Zeolite-A to remove Cd⁺² ions from heavy polluted water.

3.3 The role of initial pH values on the removal of Cd (II) ions

The aqueous solution pH seems to be an important factor for controlling the adsorption mechanism and cadmium ions removal on aluminosilicates [24]. As shown in Figure 3 the adsorption of Cd(II) ions was increased with increasing the pH values from 6 to 7.5 at wide range of temperatures (303 to 333K).

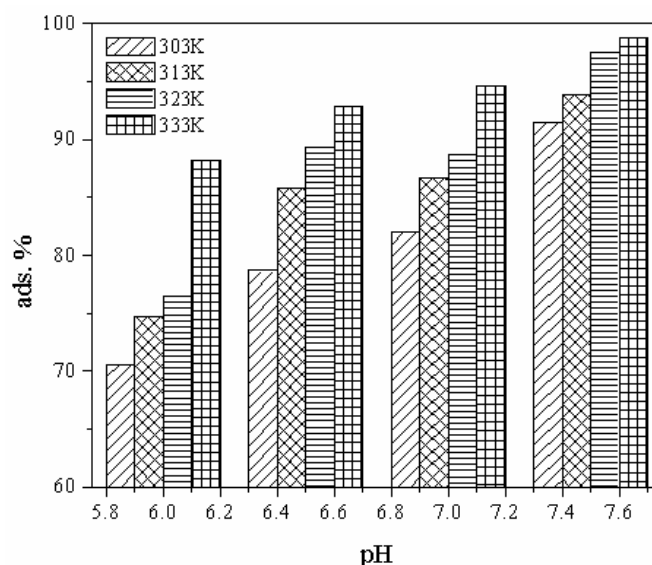


Figure 3: Adsorption behavior independence on pH and temperature values

The pH change the ionization degree of Cd (II) ions (the initial concentration of Cd(II) = 8.0 mmol/L) and the surface property of Zeolite-A [25]. Chemically, heavy metal ions Cd (II) may form complexes with inorganic legends such as OH⁻. The extent of the complex formation is varied with pH values, the ionic composition and the particular metal concerned. However, metal ions have a significant impact on the removal efficiency of Zeolites and the selectivity of metal ion by Zeolites was also influenced by the character of the metal complex that predominates at a particular pH value. As known, Zeolite has hydroxyl groups which exist on the surface (Si-OH and Al-OH), therefore, degree of ionization depends on the pH values, and the acid/base reaction occurring between the hydroxyl group on the surface with Cd(II) ions from solution [26].

3.4 Effect of contact time and temperatures

Figure (4) represent the result of the effect of contact time on the removal efficiency of Cd (II) ions using Zeolite-A with respect to the temperature. The adsorption rate was observed as rapid in the first 20 min, followed by a gradual increase with time until equilibrium adsorption in the range of (90 - 140 min).

The fast adsorption at the initial stage was probably due to the interaction between Cd(II) ions (adsorbate) in the solution and active sites those available on the Zeolite-A (adsorbent) surface take place. The equilibrium of adsorption occur when all active sites on the surface of Zeolite-A were blocked by Cd(II) ions from solution [27].

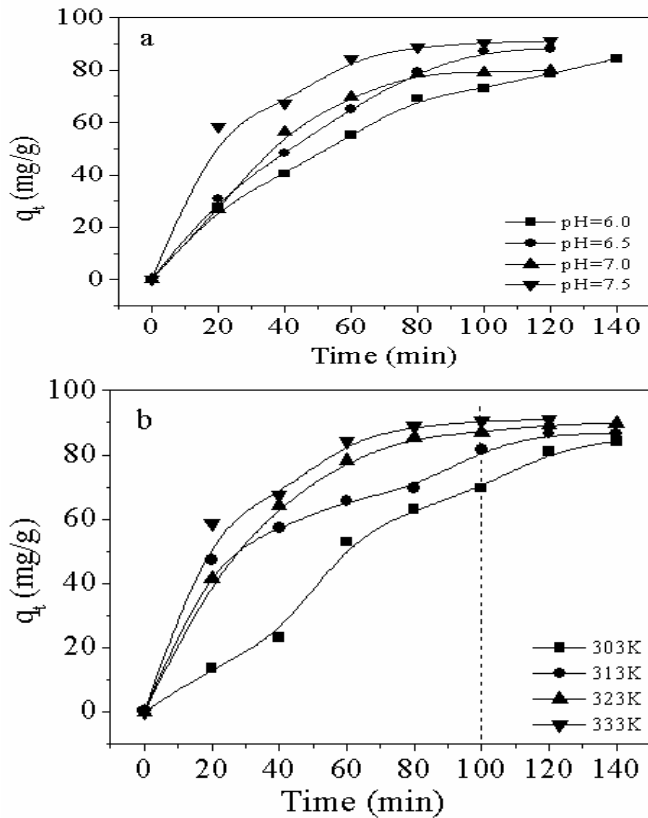


Figure 4: The amount of Cd(II) ions were adsorbed onto Zeolite-A independence on pH (at 333K) (a) and temperatures (pH=7.5) (b) values

3.5 Adsorption isotherm

The adsorption isotherms are very important for describing the adsorption mechanism of metal ions on the adsorbent. In this study, two important isotherm models Langmuir and Freundlich were discussed. For Langmuir adsorption isotherm models, the monolayer coverage of the adsorption surfaces and assumes that adsorption occurs on a structurally homogeneous adsorbent and the activity for all the adsorption sites was identical. The Freundlich expression is an empirical equation based on a heterogeneous surface [27]. The general form of Langmuir and Freundlich isotherm was assigned as:

$$C_e/q_e = (1/k_L q_m) + (C_e/q_m) \quad \text{(Langmuir) (2)}$$

$$\ln q_e = \ln k_f + 1/n \ln C_e \quad \text{(Freundlich) (3)}$$

Where q_e (mg/g) is the adsorbed amount of metal ions per 1 gm of adsorbent, C_e (mg/L) is the equilibrium concentration of metal ions in the solution, q_m is the monolayer adsorption capacity (mg/g), K_L is the Langmuir constant related to the adsorption intensity, K_f is the constants of Freundlich isotherm. The magnitude of the n indicates the adsorption process is favorable because $0 < n < 1$ [28].

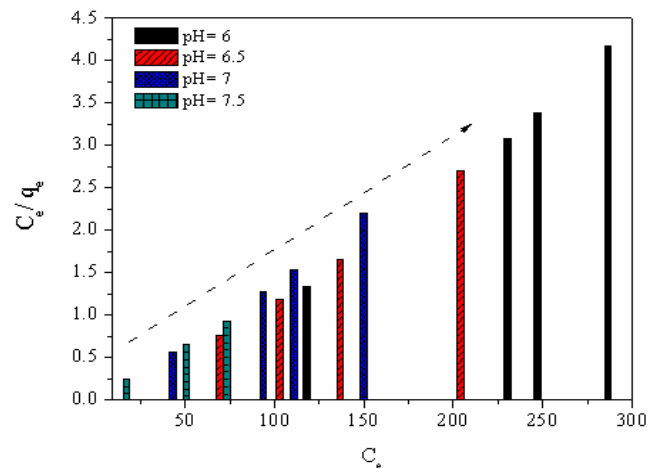


Figure 5: Langmuir plot for adsorption of Cd(II) ions onto Zeolite-A with different pH values

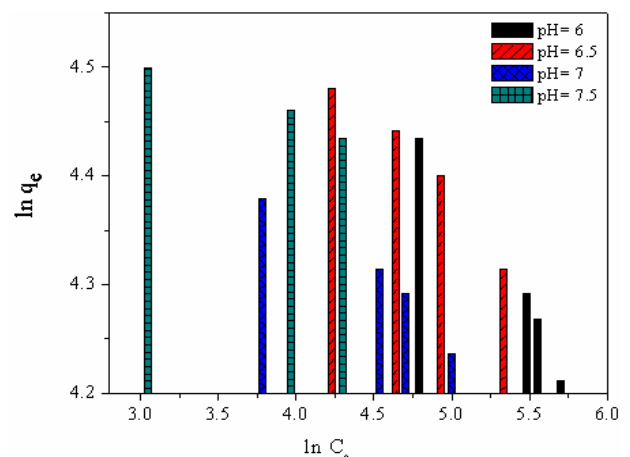


Figure 6: Freundlich plot for adsorption of Cd(II) ions onto Zeolite-A with different pH values

Table 3: Constants of isotherm models

pH	Langmuir			Freundlich		
	V_m	K_L	R^2	n	K_f	R^2
6.0	60.57	0.03	0.9942	-4.32	252.58	0.9741

6.5	69.06	0.06	0.9964	-6.65	168.14	0.9439
7.0	65.66	0.10	0.9965	-8.90	123.21	0.9361
7.5	83.33	0.72	0.9995	-25.73	100.66	0.9210

The data were obtained with Langmuir and Freundlich parameters for the removal of Cd (II) ions were presented in Table 3. The values of $n > 1$ indicating that the adsorption of Cd(II) onto the adsorbent was unfavorable at the studied conditions. In this work, it was observed that results fitted better with the Langmuir in terms of the correlation factor (R^2) value than Freundlich model, recording (0.994, 0.996, 0.996, 0.999) for the adsorption Cd (II) for pH: 6, 6.5, 7.0 and 7.5, respectively (Table 3). Therefore, the nature of metal ions adsorption on the adsorbent is more compatible with Langmuir isotherm model [27,29].

3.6 Kinetic Models

As discussed before, the adsorption of the Cd (II) ions onto Zeolite-A as a function of contact time was investigated and data were given in (Figure 2). Adsorption was very fast in the first view minutes and then slowed considerably as the reaction approached equilibrium. To design an appropriate adsorption process, one should have sufficient information about the rate at which adsorption occurs. Thus, the rate of constants for the adsorption of Cd (II) ions from aqueous solution onto Zeolite-A were determined (Figs.7, 8) using the pseudo first order and pseudo second order equations (Eqs. 4, 5). The second order model gave the best description of the rate of reaction between adsorbate and adsorbent [30].

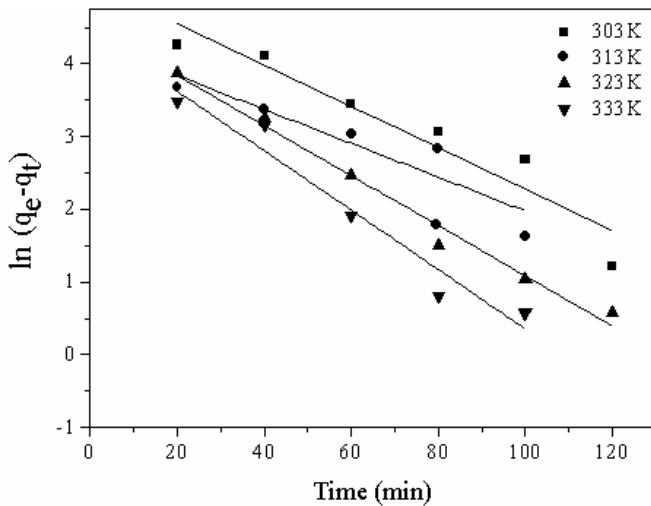


Figure 7: Concentration of Cd ions vs. the time of adsorption process onto Zeolite-A at pH = 7.5 with respect to the temperatures for pseudo first order

3.6.1 Pseudo first order equation

$$\ln (q_e - q_t) = \ln q_{e1} - k_1 t \quad (4)$$

Where q_e and q_t (mg/g) are the concentration of metal ions in the adsorbent at equilibrium and at time t , respectively and k_1 is the pseudo first-order rate constant (min^{-1}).

3.6.2 Pseudo second order equation:

$$(t/q_t) = (1/k_2 q_e^2) + (1/q_e)t \quad (5)$$

Where k_2 is the rate constant of pseudo second-order equation.

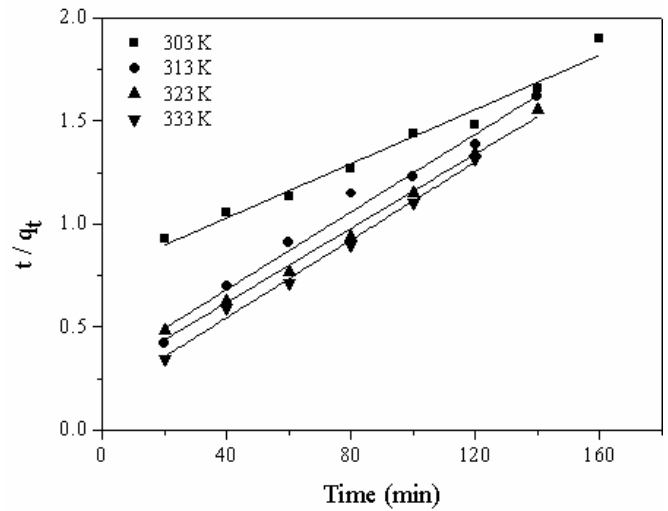


Figure 8: Concentration of Cd ions vs. the time of adsorption process onto Zeolite-A at pH = 7.5 with respect to the temperatures for pseudo second order

According to the data were obtained (Table 4), the values of the rate constant ' k_2 ' were increased with increasing temperatures. The correlation coefficient R^2 has an extremely high value (>0.99), and the theoretical q_e values agreeing well with the experimental one. These results suggest that the pseudo second -order adsorption mechanism was predominant and that the overall rate constant of each ion appears to be controlled by the chemisorption process [30].

Table 4: parameters for pseudo first and second order kinetic model

T (K)	Pseudo first order			Pseudo second order		
	K_1	q_{e1}	R^2	q_e	$K_2 \times 10^{-3}$	R^2
303	0.028	167.602	0.888	152.439	0.10	0.976
313	0.023	73.806	0.829	106.157	0.29	0.979
323	0.043	136.458	0.968	110.987	0.31	0.992
333	0.052	134.208	0.958	106.044	0.53	0.992

4. Conclusion

In the present work, synthetic Zeolite-A was prepared from Egyptian kaolin. Obtained zeolitic materials were applied as sorbents to remove Cd^{+2} ions as a model of toxic heavy metals from water solutions. Results showed that the removal of metal ions by the Zeolite-A was dependent on the system employed and was mainly dependent on the initial pH values of solutions. The pseudo second order model gave the best description of the rate of reaction between adsorbate and adsorbent. However, it was demonstrated that a Zeolite-A can interact with water efficiently to remove Cd (II) from the solution, due the hydrophilic characteristics of the Zeolite-A. In addition, due the Zeolite-A characteristics, this type of materials presents the possibility to obtain a self-supported sorbent, in the membrane form or as thin film in different surfaces.

References

- [1] N. A. Miranda, S. E. Baltazar, A. Garcia, D. M. Lira, P. Sepulveda, M. A. Rubio, D. Altbira, "Nanoscale zero valent supported by Zeolite and Montmorillonite: Template effect of the removal of lead ion from an aqueous solution", *J Hazard Mater.*, 301, pp. 371-380, 2016.
- [2] Q. Zhang, B. Pan, B. Pan, W. Zhang, K. Jia, Q. Zhang, *Environ Sci Technol.* 42, pp. 4140, 2008.
- [3] H. Merrikhpour, M. Jalali, Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite, *Clean Techn Environ Policy*, 15, pp.303, 2013.
- [4] H. S. Ibrahim, T. S. Jamil, E. Z. Hegazy, Application of zeolite prepared from Egyptian kaolin for the removal of heavy metals: II. Isotherm models, *J Hazard Mater.*, 182 pp. 842–847, 2010.
- [5] L. Ayele, J. P. Pariente, Y. Chebude, I. Diaz, , *Microporous Mesoporous Mater.*, 215, pp. 29, 2015.
- [6] J. Cejka, H. van Bekkum, Zeolites and ordered mesoporous materials: progress and prospects; *Studies in Surface Science and Catalysis* 157, pp. 13-40, 2005.
- [7] H. F. Youssef, W. H. Hegazy, H. H. Abo-almaged, G. T. El-Bassyouni, *Bioinorganic Chemistry and Applications*, 2015, pp. 12, 2015.
- [8] S. Hashemian, S. H. Hosseini, H. Salehifar, K. Salari, *Am J Analyt Chem.*, 4, pp. 123, 2013.
- [9] D. Nibou, S. Amokrane, H. Mekatel, N. Lebaili, *Phys Proc.*, 2, pp. 1433, 2009.
- [10] H. v. Bekkum, E.M. Flanigen, P.A. Jacobs, J.C. Jansen, *Introduction to Zeolite Science and Practice*, *Studies in Surface Science and Catalysis*, 137, pp. 1-1062, 2001.
- [11] S. Komarneni, M. C. D'Arrigo, C. Leonelli, G. C. Pellacani, H. Katsuki, *J Am Ceram Soc.*, 81 (11), pp. 3041, 1998.
- [12] M. Park, S. Komarneni, *Microporous Mesoporous Mater.* 20, pp. 39, 1998.
- [13] H. F. Youssef, D. M. Ibrahim, S. Komarneni, *Microporous Mesoporous Mater.*, 115, pp. 527, 2008.
- [14] Y. P. Pena, W. Rondon, *Am J Analytic Chem.*, 4, pp. 387, 2013.
- [15] H. Javadian, F. Ghorbani, H. Tayebi, S. M. H. Asl, *Arab J Chem.*, 8, pp. 837, 2015.
- [16] G. Das, N. C. Pradhan, G. M. Madhu, H. S. Preetham, *J Mater Environ Sci.*, 4 (3), pp. 410, 2013.
- [17] M. V. Mier, R. L. Callejas, R. Gehr, B. E. J. Cisneros, P. J. J. Alvarez, *Water Res.*, 35, pp. 373-378, 2001.
- [18] M. Majdan, S. Pikus, M. Kowalska-Ternes, A. Gladysz-Plaska, P. Staszczuk, L. Fuks, H. Skrzypek, *J Colloid Interface Sci.*, 262, pp. 321, 2003.
- [19] S. A. Sadeek, N. A. Negm, H. H. Hefni, M. M. Abdel Wahab, *Int J Biol Macromol.*, 81, pp. 400 2015.
- [20] H. Merrikhpour, M. Jalali, *Clean Technol Environ Policy*, 15, pp. 303, 2013.
- [21] M. Sprynskyy, B. Buszewski, A. P. Terzyk, J. Namiesnik, "Study of the selection mechanism of heavy metal (Pb⁺², Cu⁺², Ni⁺², and Cd⁺²) adsorption on clinoptilolite", *J Colloid Interface Sci.*, 304, pp. 21, 2006.
- [22] L. Remenarova, M. Pipiska, E. Florkova, M. Hornik, M. Rozloznik, J. Augustin, *Clean Techn Environ Policy*, 16, pp. 1551, 2014.
- [23] A. Saravanan, V. Brindha, S. Krishnan, *J Adv Bioinf.*, 2, pp. 193, 2011.
- [24] D. Nibou, S. Khemaissia, S. Amokrane, M. Barkat, S. Chegrouche, A. Mellah, *Chem Eng J.*, 172, pp. 296, 2011.
- [25] P. K. Corner, M. W. Munthali, E. Johan, N. Matsue, *Am J Analyt Chem.*, 5, pp. 395, 2014.
- [26] C. Covarrubias, R. Arriagada, J. Yanez, R. Garcia, M. Angelica, S. D. Barros, P. Arroyo, E. F. Sousa-Aguiar, *J Chem Technol Biotechnol.*, 80, pp. 899, 2005.
- [27] S. Mehdizadeh, S. Sadjadi, S. J. Ahmadi, M. Outokesh, *J Environm Health Sci Eng.*, 12, pp. 7, 2014.
- [28] N. Daneshvar, D. Salari, S. Aber, "Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake", *J Hazard Mater.*, 94, pp. 49-61, 2002.
- [29] M. A. Wassel, H. A. Shehata, A. Fahmy, A. Sh. Elzaref, *Middle East Journal of Applied Sciences*, 5, pp. 297, 2015.
- [30] S. Lim, A. Lee, *Environ Sci Pollut Res Int.*, 13, pp. 10144, 2015.