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Isotherms and kinetics of lead and cadmium uptake from the waste leachate by natural and modified clinoptilolite

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ABSTRACT

Aims: The purpose of this study is to investigate the feasibility of the absorption of lead and cadmium from the leachate, by natural zeolite clinoptilolite and improving the zeolite ability by a modified surface.

Materials and Methods: To examine the absorption ability of these two metals (lead and cadmium), the variables, such as, type of sorbent, sorbent concentration, and contact time were studied. Zeolite samples were analyzed by X-ray florescence, the spectrum of X-ray diffraction, and Brunauer-Emmett-Teller (BET).

Results: The absorption efficiency of the modified zeolites were increased from 4.2 and 5.3 percent to 71.6 and 75.2 percent for lead and cadmium, respectively. With increasing the surfactant concentration from 2 to 20 mmol/L, the absorption efficiency of modified zeolite for lead and cadmium was increased to 71 and 74%, respectively. The best isotherm model for lead adsorption was Freundlich model, with a determination coefficient equal to 0.99, and for cadmium it was Langmuir model with a determination coefficient equal to 0.99.

Conclusions: The modified zeolite with surfactant can be used as an appropriate adsorbent for the separation of heavy metals from waste Leachate. Lead and cadmium were absorbed in a single layer on the surface of the modified zeolite with surfactant, comparing different isoterm models, indicated that the capacity of the modified zeolite for lead adsorption was more than cadmium adsorption, but cadmium was absorbed with higher energy.

Key words: Adsorption, heavy metals, modified clinoptilolite, unmodified clinoptilolite

INTRODUCTION

Rapid population growth, development of technology, and increasing human consumption of food, has consequently led to an increase in waste generation. All these together are recently caused a tremendous crisis in human societies. Leachate result from the waste decomposition contains all types of biological and chemical materials that exist in the waste. Landfill leachate is one of the most contaminated of waste types, and has created excessive health and environmental concerns due to the widespread use of urban landfill for the final waste disposal. Some of the important environmental parameters in waste leachate are soluble heavy metals. The leachate characteristics depend on various factors, such as,

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waste composition, stabilization level of the waste, landfill site hydrology, waste moisture content, climate change, and age of landfill. Table 1 shows the leachate characteristics in a landfill site of Mehriz city (located 30 km from Yazd). This landfill is a sanitary landfill that has applied for the disposal of municipal and commercial solid wastes of Mehriz city. In order to prevent environmental contamination with heavy metals and consequently prevent their irreversible damage to the ecological systems and living creatures, especially human health, the water and wastewater containing excessive amounts of these pollutants should be treated prior to being excreted and discharged into the environment.[1,2] Different methods are used for the removal of heavy metals, in the wastewater treatment, such as, chemical precipitation methods, ion exchange, adsorption, and reverse osmosis.[3-5] The adsorption method, because of its high efficiency and simple usage, has been introduced as one of the most applicable methods.[6] Among the heavy metal removal methods, the ion exchange method using natural exchange substances, such as zeolites, are being considered, due to their low cost, natural inherent material availability, and their being environmental friendly.[7] Zeolites are hydrated forms of aluminum silicate crystals, which have alkaline metals and alkaline earth metal cations; one property of these compounds is that they have the capacity for cation exchange, reversible adsorption, and water disposal, without causing remarkable changes in their molecular structure.[8] Among the natural zeolites, clinoptilolite has been selected due to its higher selectivity toward cations, higher ion exchange capacity, higher resistance to environmental conditions, and more availability.[9,10] As the surface of natural zeolites is negatively charged, for anions removal, the zeolites' surface potential must be changed. The zeolites' surface can be modify by surfactants, such as quaternary ammonium. It can change the profile surface of zeolites and convert it to a suitable ion-exchange substance.[11] Surfactants can be form a very stable, organic coating layer on the external surface of the zeolite.

Modification of the zeolite with a cationic surfactant enhances the ability of the zeolite to attract anions (nitrate, phosphate, arsenate, chromate, etc.), nonpolar organic solutions, and aromatic hydrocarbon, more than an unmodified zeolite.[12] The modified natural zeolite by various agents has been tested as an adsorbent for organic and inorganic anions. The cationic surfactant that uptake on the external surface of a zeolite is confined by cationic exchange and hydrophobic interaction.[13] A modified zeolite with surfactants remains stable under different conditions of pH (acidic, neutral, and alkaline) on the zeolite surface and will not leave through the water, and it also retains its absorption property.[14] In this study, the removal efficiency of lead and cadmium metals on leachate samples that were obtained from landfill site of Mehriz city, has been examined, by both natural clinoptilolite which was modified by the hexadesyl trimethyl ammonium-bromide surfactant (HDTMA-Br) and unmodified (simple) clinoptilolite.

Table 1: Analysis of the chemical quality of Leachate samples taken from the landfill site of Mehriz city

Amount	Unit	Parameters
8343	mg/l	COD
509	-	pH
9654	mg/l	TSS
1098	mg/l	Cd^{2+}
1061	mg/l	Pb^{2+}
312	meq/l	Cl^-
713	meq/l	HCO_3^-
268	meq/l	Na^+
294	meq/l	Mg^{2+}
456	meq/l	Ca^{2+}

MATERIAL AND METHODS

Characteristics of the absorbent and surfactant

In this study, the zeolite of Mianeh city was used. In order to modify the zeolites surface, hexadecyl trimethyl ammonium-bromide (HDTMA-Br) was used. All materials used in this study were purchased from the Merck Company. The protocol of the modified zeolite production by the surfactant is presented in Figure 1.

Determination of zeolite characteristics

The internal cation exchange capacity (CEC) and external

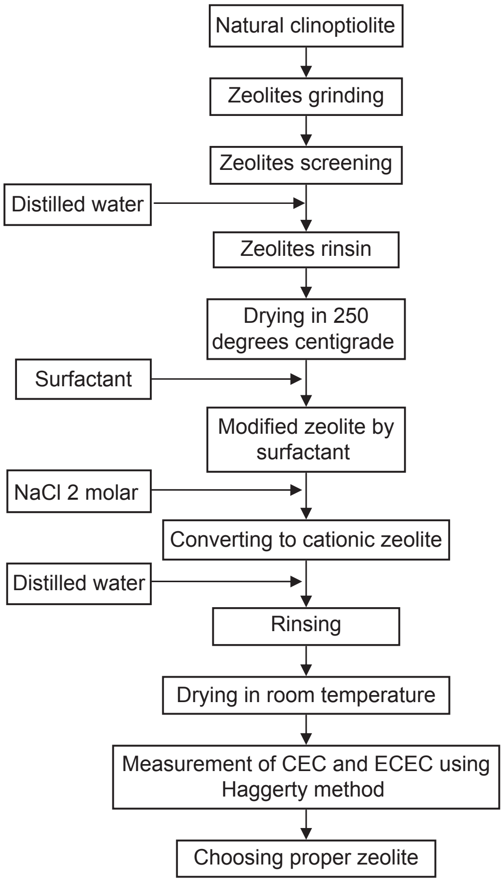

Figure 1: Protocol of modified zeolite preparation with surfactant (SMZS)

cation exchange capacity (ECEC) of the zeolites were measured by the Hagarty and Bowman method.[15]

Zeolite modification

At first, the zeolites was crushed and sieved with a laboratory sieve size 0.25 – 0.21 mm (60 to 70 mesh). After washing with distilled water for removing any adsorbed organic matter and drying, the zeolite was kept for 12 hours in a temperature of 250°C.[16] Next, the zeolite was converted to cationic zeolites according to the James and Prikryl method.[17] For zeolites being modified with surfactants, the critical micelle concentration (CMC) of the HDTMA surfactant was regarded to be equal to 1.8 mmol/L. Three concentrations were selected, 0.5 mmol/L was used as the concentration less than CMC, 2mmol/L was used as a concentration approximately equal to CMC, and 20 mmol/L was used as a concentration more than CMC.[18]

Heavy metal adsorption and their analysis

After the leachate samples were obtained from the Mehriz landfill site, the specimens were sent to the laboratory in 20 liter containers. After filtration and digestion of the samples, the initial concentrations of the lead and cadmium metals in the leachate samples were measured by a SPE cartridge, using a flame atomic absorption spectrometer, VARIAN model, after complexion with a specific ligand and as pre concentrate. Subsequently, 50 ml of the leachate sample and a control sample were placed in 100 ml containers, in contact with the modified zeolite (SMZs) and unmodified zeolite (NMZ), under different conditions of contact times (60, 120, 180, 240, 300, 360, 420, 480, 540, and 600 minutes), adsorbent dose of 5, 10, 20, and 40 g/L with an agitation speed of 150 rpm. Finally, after the desired contact time for passage of samples from the filter, the residual concentrations of the lead and cadmium metals were analyzed. Next, based on the results the absorbent dose and the optimum contact time were determined, All testing methods were based on "standard methods for examination of water and wastewater".[19]

RESULTS

The analysis of the chemical quality of the Leachate samples taken from the landfill site of Mehriz city is shown in Table 1.

Properties of different zeolites was summarized in Table 2. The zeolite had the highest CEC and ECEC, so for performing the adsorption tests, this zeolite was used. The zeolite was used in experiments such as: XRD (Shimadzu X-ray diffractometer XRD; model: XD-5A) [Figure 2] and (X-ray Florescence Oxford ED2000) [Table 3] and the surface area of the small and middle zeolites were analyzed with N_2 isotherm absorption by the BET method [Figure 3].

Table 4 shows types of modified zeolite and their acronyms signs.

Table 2: Type of zeolites and their properties

Types of zeolits	Mesh	CEC (Meq/g)	ECEC (Meq/g)
Moderate coarse zeolit	20–30	3.03	0.4782
Average zeolite	40–50	3.34	0.6213
Moderate fine zeolite	60–70	3.58	0.8464

Table 3: Results of the XRF test of zeolite

Compounds	Percent
SiO_2	63.1
Al_2O_3	12.6
CaO	4.03
K_2O	2.63
Na_2O	1.68
Fe_2O_3	1.67
MgO	1.12
TiO_2	0.23
P_2O_5	0.19
SrO	0.13
LOI*	12.3
Total	99.68

*Less on ignition

Table 4: Types of modified zeolite and their acronyms signs

Type of zeolite	Type of surfactant	Surfactant concentration (mmol/L)	Acronyms signs
Moderate fine zeolite	HDTMA-Br	0.5	SMZ#1
Moderate fine zeolite	HDTMA-Br	2	SMZ#2
Moderate fine zeolite	HDTMA-Br	20	SMZ#3
Moderate fine zeolite	-	-	NMZ

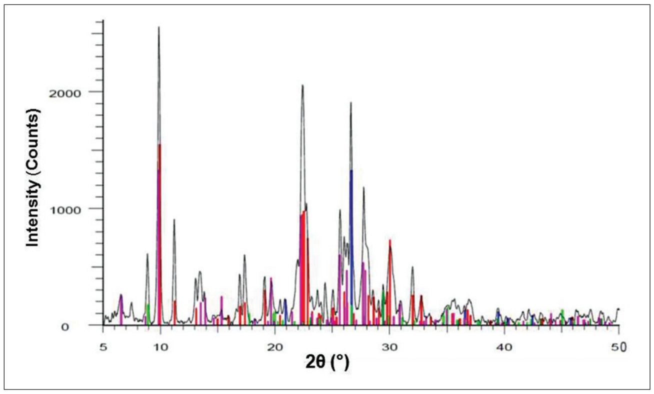

Figure 2: XRD spectra of clinoptilolite zeolite compared with the reference clinoptilolite

Different types of absorbent potentials in heavy metal adsorption

For evaluation of the efficiency of all type of modified zeolites, along with a sample of unmodified zeolite (NMZ) have been contacted in conditions that are listed in Section 3-2 (1 hour contact time and absorbent dose of: 5 g/l) and their results are presented in Figure 4. These results indicate that the best type of adsorbent is SMZ # 3, and the unmodified zeolite (NMZ) has less capacity than the modified zeolite. Also according to the results of the previous studies, with increasing concentrations of surfactant (CMC), approximately from 2 mmol/L to more than 20 mmol/L, the potential for contaminant uptake had increased with formation a surfactant double layer on the zeolite surface[20-22] — the results of this experiment fit the results of the previous studies in this case. As is shown in Figure 4, a unmodified zeolite has the lowest uptake in comparison to both types of heavy metals, and due to the misyl formation, this concentration has the lowest adsorption among all three types of zeolites. SMZ # 2 that had been modified with surfactant concentration is approximately equal to CMC. The SMZ # 3 that had been modified with a concentration more than that for CMC, by increasing the adsorption sites on its surface, had more adsorption capacity.

Effect of the adsorbent amount on lead and cadmium uptake

To investigation the effect of different adsorbent dose on heavy metal adsorption, the SMZ # 3 modified zeolite, which had the highest capacity in the previous experiment, was used, with four absorbents dose of 5, 10, 20, and 40 (g zeolite/L Leachate) in one hour contact time. Results of heavy metal uptake with dose of adsorbent was depicted in Figure 5. It was found that with increasing the adsorbent dose in contact with the leachate that naturally increased the available sites for adsorption, the adsorption efficiency of the heavy metals raised.

Cadmium and lead adsorption isotherm

For determination the adsorption isotherms, the SMZ # 3 zeolite was used as the best adsorbent, and the experiments were carried out at room temperature (21°C) with adsorbent dose of 5, 10, 20, and 40 (g zeolite/L leachate) in one hour contact time. For analyzing the data that was obtained from the adsorption process, the Freundlich, Langmuir, Temkin, and BET isotherms were used.[20-23] The results of isotherms calculation are listed in Table 5. Based on the isotherm calculation, the best absorption isotherm models for lead and cadmium were the Freundlich model with a correlation coefficient (R^2) of 0.978 and the Langmuir model with correlation coefficient (R^2) of 0.99, respectively. The charts of the Freundlich for lead and the Langmuir for cadmium are shown in Figure 6.

Effect of contact time on lead and cadmium uptake

For determination of the contact time effect on heavy metal adsorption from the leachate, SMZ # 3 was used as the best type of absorbent with optimal adsorbent to the solution ratio of 5 g/L. The test result showed that the metal uptake efficiency increased with an increase in exposure time, until it achieved the equilibrium contact time. For lead, the required time to achieve equilibrium was 420 to 480 minutes, while for cadmium adsorption, the time required to achieve equilibrium was longer, 540 to 600 minutes. Results of heavy metal adsorption and effect of different exposure time are presented in Figure 7.

Lead and cadmium adsorption kinetics

To determination the lead and cadmium adsorption kinetics, the modified zeolite of SMZ # 3, as the best adsorbent in the optimal absorbent tdose of 5 g/L, different contact times (one to six hours), and room temperature (21°C) were used. For analyzing the lead and cadmium absorption kinetics, the pseudo first order, pseudo second order, and Elovich were evaluated.[21,24] Based on the data of the uptake kinetics that

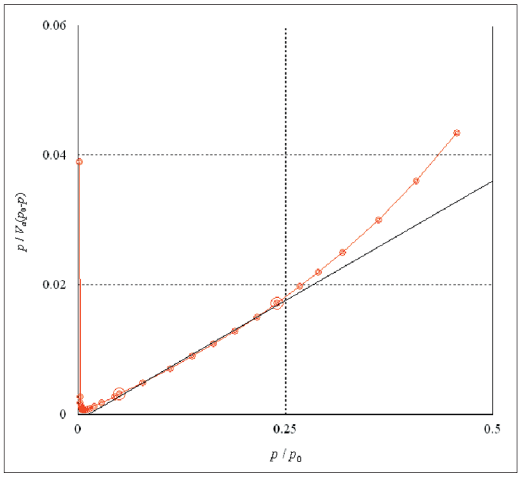

Figure 3: Chart of absorption and leave out of N_2 isotherms (BET)

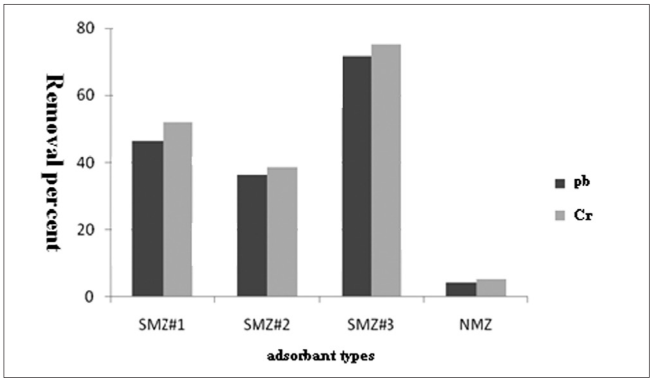

Figure 4: Potential of different absorbents in lead and cadmium adsorption

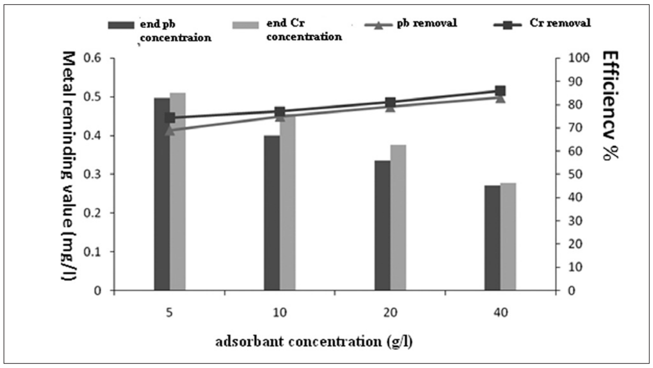

Figure 5: Effect of adsorbent dose on Lead and cadmium removal efficiency (1 h)

is presented in Table 6, the kinetics of the lead and cadmium uptake are in line to the pseudo second order kinetics, and the correlation coefficients (R^2) of lead and cadmium are 0.99 and 0.99, respectively. The diagram of the pseudo first order, pseudo second order and Elovich kinetic for lead and cadmium are given in Figure 8.

DISCUSSION

Based on the results of Figure 3, the Surfactant has a high potential to adsorb heavy metals from the landfill leachate, but in comparison to the modified zeolite, the neural zeolite does not have a great capacity for this purpose. Also, according to the previous studies, with increasing concentrations of the surfactant CMC, from 2 mmol/L to more than 20 mmol/L, the contaminant uptake capacity increased through the formation of a surfactant double layer on the zeolite surface.[11,25,26] Although, the heavy metals in the leachate are found in composition with other materials, these materials act as interfering agents in the adsorption process. Therefore, in Figure 4, the relationship between the adsorption efficiency and the increase in absorbent dose is nonlinear and interfering compounds prevent material from adsorbing on the adsorption sites.[25] Figure 6 shows that considering the chemical characteristic differences (concentration, composition, and size of ionic radius) and the interaction of two metals, cadmium and lead, in a non-homogeneous

Table 5: Results of lead and cadmium adsorption isotherms with SMZ#3 zeolite

Isoterm	Equation	R^2		Parameter	Value	
		Pb	Cd		Pb	Cd
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	0.99	0.95	K_f 1/n	1.38 3.01	1.31 3.14
Langmuir	$q_e = \frac{q_m K_a C_e}{1+K_a C_e}$	0.97	0.99	q_m K_a	0.06 0.54	0.08 0.66
Temkin	$q_e = \frac{RT}{b_T} Ln(A_T C_e)$	0.94	0.78	A_T b_T	0.42 0.31	0.48 0.37
BET	$q_e = \frac{K_B C_e Q_m}{(C_s - C_e)\left[1+(K_B-1)\left(\frac{C_e}{C_s}\right)\right]}$	0.91	0.99	Kb q_m	5.92 3.8	10.24 4.8

Table 6: Kinetic results for lead and cadmium uptake with SMZ # 3

Kinetic types	Equation	R^2		Parameter	Value	
		Pb	Cd		Pb	Cd
Pesudo first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	0.27	0.6	k_1 q_e	– 0.005 – 1.08	– 0.004 – 1.08
Pesudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	0.99	0.99	k_2 q_e	37.04 3.31	56.76 3.85
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	0.98	0.94	α β	52.63 53.26	55.55 41.82

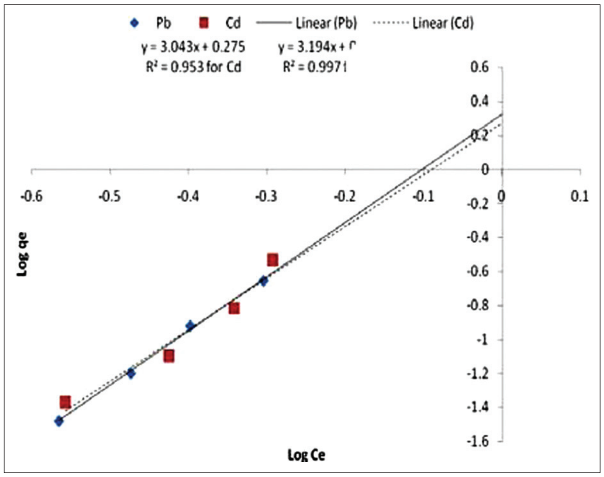

Figure 6a: Absorption isotherms of Freundlich

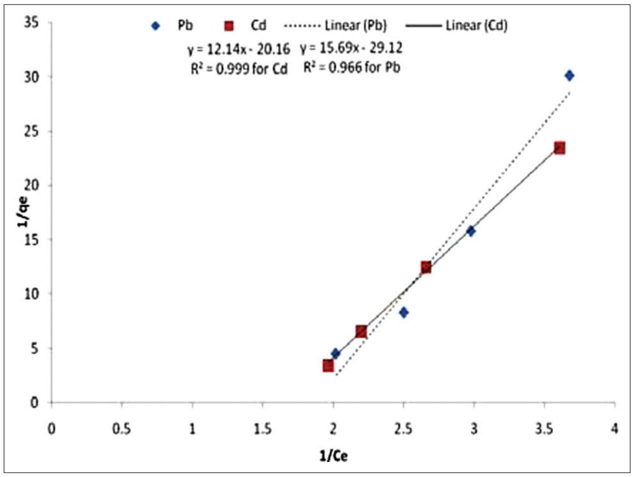

Figure 6b: Absorption isotherms of Langmuir

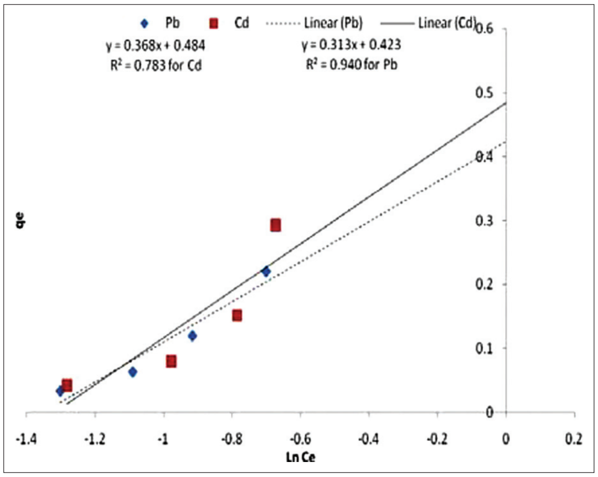

Figure 6c: Absorption isotherms of temkin

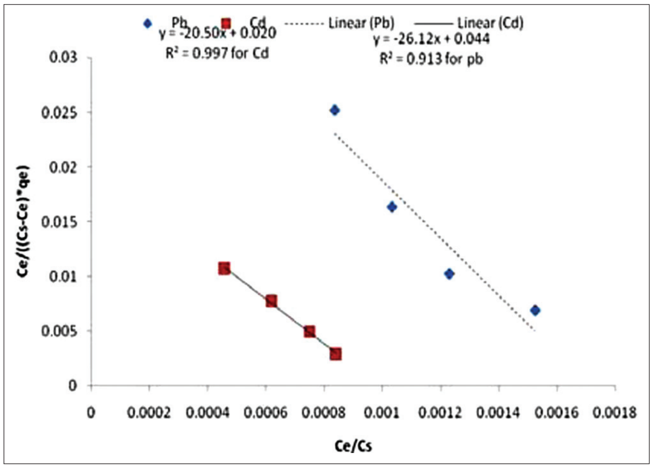

Figure 6d: Absorption isotherms of BET

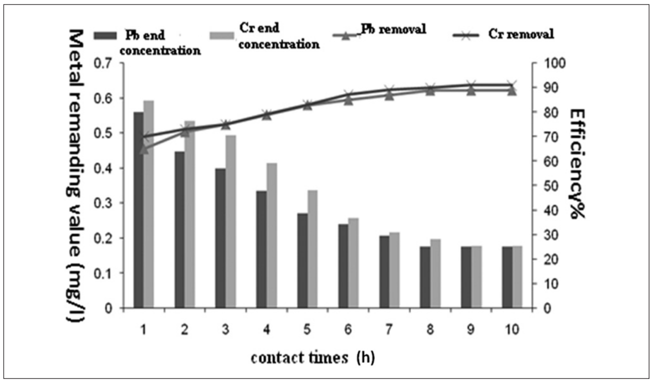

Figure 7: Lead and cadmium removal efficiency in different contact times

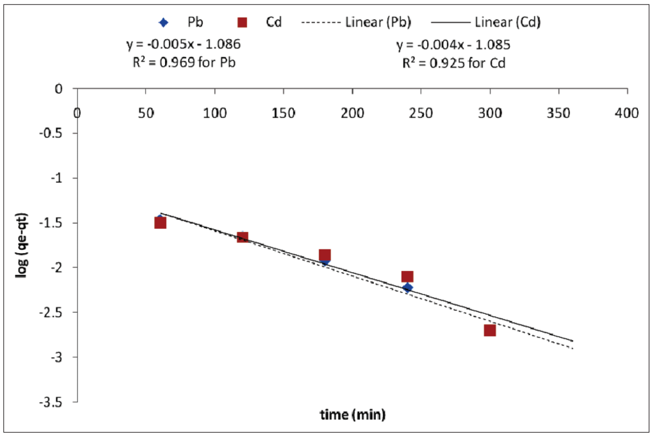

Figure 8a: Graphs of pseudo first order

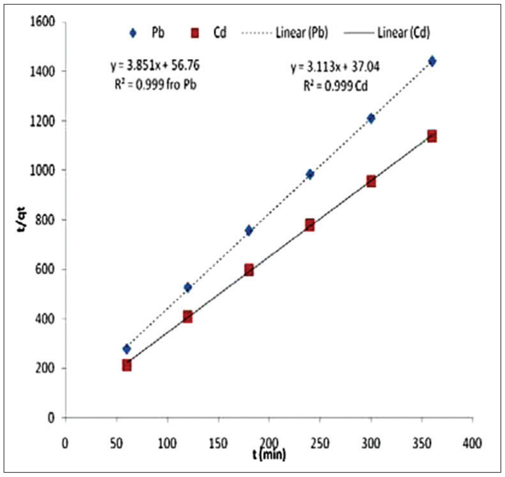

Figure 8b: Graphs of pseudo second order

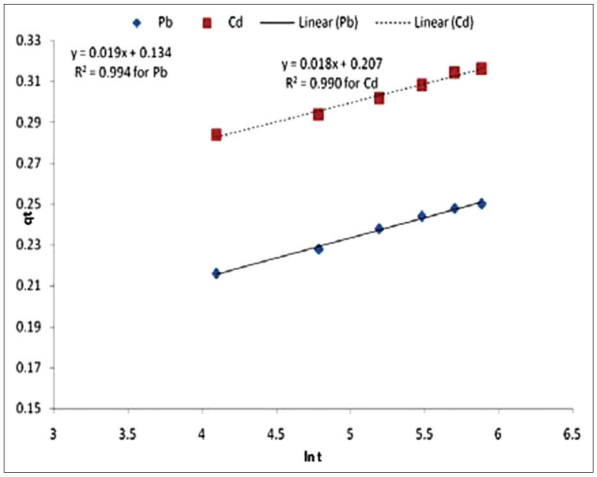

Figure 8c: Graphs of elovich kinetics for Lead and cadmium uptake

composition of waste leachate, the difference in adsorption efficiency and time of equilibrium between the two metals is inevitable. Based on Table 5, the lead and cadmium adsorption was fit the Freundlich and Langmuir isotherms. The Freundlich and Langmuir isotherms show a single-layer adsorption in comparison to the BET isotherm, which shows a two-layer adsorption,[27-29] it can be concluded that lead and cadmium uptake is done on a surfactant-modified zeolite as a single layer. Mehrasby *et al.* have also examined the adsorption of lead and cadmium on a modified banana peel and have achieved similar results.[30] In Table 5, the q_m values of the Langmuir and BET isotherms determine the required value of the metal ion for single- and two-layer uptakes, and determine that a greater amount of cadmium is required to complete the adsorption layers, therefore, the adsorption capacity of SMZ # 3 for cadmium is more than lead. The 1/n value in the Freundlich, and isotherms represents the energy of absorption and it is observed that SMZ # 3 adsorbs cadmium with higher energy than lead. Therefore, the results of both the Temkin and Freundlich isotherms show that SMZ # 3 adsorbs cadmium with the higher energy and capacity, and this is the reason for the higher adsorption efficiency of cadmium through SMZ # 3 in comparison to lead (from Table 6 and Figure 8). The adsorption rate and show that the adsorption rate of cadmium by modified zeolite was higher than the adsorption rate of lead. The experiment results of BET and N_2 adsorption show that the surface of the zeolite sample contains approximately 54 m^2/g. The results of XRD and XRF express that the zeolite sample used in this study is from the clinoptilolite zeolite type and this sample has a high CEC and ECEC (3.58 and 0.8474 Meq/g, respectively). As is observed in Figure 3, a unmodified zeolite has the lowest adsorption capacity for both types of heavy metals and is found in all three types of modified zeolites with surfactant SMZ # 2, which has an surfactant concentration approximately equal to modified CMC, which has the lowest uptake due to the formation of mysl in its concentration. SMZ # 3, which has been modified in a concentration more than the CMC concentration, has more capacity to absorb lead and cadmium, due to the increase in the adsorption sites on the zeolite surface. After SMZ # 3, the second appropriate adsorbate of the studied heavy metals is SMZ # 1. The results of this study show that the efficiency of lead and cadmium adsorption increase with an increase in contact time and adsorbent dose. In general, it can be concluded that cadmium adsorption by modified zeolite has a higher efficiency and energy in comparison to lead, and the adsorption capacity of modified zeolite with surfactant in lead uptake is more than cadmium. Lead and cadmium absorption follow the Freundlich and Langmuir isotherms, respectively, and the lead and cadmium uptake on modified zeolite is carried out in a single layer.

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