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Removal of cadmium from industrial waste water by adsorption zeolite clinoptilolite

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ABSTRACT

Today, with the expansion of industry and industrial development, the risk of heavy metals pollution is more than before. With due attention to the increasing of environmental pollution by heavy metals, using appropriate methods is essential for removal of these elements from environment. In this study, the absorption of the Zeolite clinoptilolite was used to remove Cd^{+2} from industrial waste. For this purpose, the effect of pH parameters, contact time, adsorbent dosageand initialconcentrationof cadmium was studied on the removal of cadmium efficiency. The results showed that, the optimal pH, optimal contact time and optimal adsorbent dosage is equal to 4 and 15 minutes and 1 g/L respectively. The results of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich adsorption isotherms showed that Freundlich model is the best adapted model to the equilibriumexperimentdata for absorbent. According to the efficiency of natural zeolite clinoptilolite for removal of cadmium from industrial waste with an efficiency of 98% and also due to low cost, available and less environment effects of this absorbent than many of kinetics absorbent is proposed that industrial units use this kind of absorbent in waste water treatment.

KEY WORDS: REMOVAL, CADMIUM, CLINOPTILOLITE, INDUSTRIAL WASTEWATER

INTRODUCTION

The risk of environmental pollution, resulting from human activities has become a global concern (Alvarez-Ayuso, 2003).Heavy metals are also an important group of pollutants in the environment. Today, with the development of industry and technology the risk of heavy metals pollution has been created in the environment more than before (Inglezakis et al., 2004). Most of the heavy metals are very soluble at low concentration and they have theability to access to vital components of living things. In the nature, heavy metals are in the group of rate elements and generally have been formedless than one percent of the Earth's crust (Erdem et al., 2004). Removal of heavy metals from wastewater has become a major concern nowadays because of its ability to contaminate water bodies.

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Many processes have been proposed for removal of heavy metals, including chemical sedimentation, membrane filtration, ion exchange, reverse osmosis and adsorption by the activated carbon which is the most common of these methods (Buerge-Weirich et al., 2002). Researchers for the aim of environment protection are looking for appropriate solutions, scientific and economical to minimize the harmful effects of effluent. In this regard, the using of methods and materials that have minimal side effects are in top priority. Zeolite with extraordinary structure, high cation exchange capacity, keeping structure in high temperature, low cost and abundant distribution of it in the world has been caused to consider as a remover (Cecille and Toussaint, 1989, Bable et al., 2003, Rosales et al., 2012 and Kalantry et al 2014).

These minerals are used primarily in the high range in the industry as an adsorbent for removal of oil and metals (Inglezakis et al., 2004, Papaioannou et al., 2005). clinoptilolite is an inorganic and natural compound and safe, non toxic and harmless that using of that does not have sideeffects on the environment (Wu, 2008). In this study, with due regard to the previous studies for removing heavy metals from waste water and industrial water, it is tried to present best conditions to remove cadmium ion from simulated aqueous solution in the waste water by using of zeolite.

MATERIAL AND METHODS

In this study, zeolite was studied as adsorbent for the removal of cadmium ions from industries waste water to evaluate the effect of studied process of pH, contact time, concentration of cadmium, adsorbent mass and interferences effect. Utilizing Zeolitein this study was obtained from mines of Semnan in the central of Iran. pH meter system multi 340 I and shaker system FG model with regulating capability of round 50 to 600 was used for determining pH and for samples disorder respectively. The solution of centrifuge system centrion model was used to separate absorbent. This study was conducted non continuous in laboratory scale at temperature of 25°C and.

1) The Preparation of absorbent

Zeolite clinoptilolite samples were obtained from Semnan mines and they were used without any chemical modifications. At first, by using a sieve 1 & 3 mm, Particles absorbent have been grouped, and in different experimentation processes were used from these Particles in the size of 1-3 mm of absorbent.

2) Preparing an aqueous solution ofcadmium ion

At first, stock standard production was provided 1000 m/g per liter cadmium from sulfate cadmium ($CdSO_4.8H_2O$) and then standard solutions was made from it with concentrations1, 2.5, 5, 10.

3) The adsorption experiments stages

Experiments for determining the effects of pH on the adsorption process:

At this stages, cadmium solution was prepared with a concentration of 15mg per liter and its pH was regulate by 1 and 0.1 HCl and NaOH on the values of 4,5,6,7,8, and 9. Then Zeolite adsorbent was added with mass of 1g. The samples were analyzed for 120minutes on a shaker with speed of 180rpm and were centrifuged for 20minutes and finally the remaining cadmium concentration was measured by atomic absorption spectrometry. At first, the concentrations of 1, 2.5, 5, and 10 mg/l of cadmium was prepared from stock solution and after regulating pH, about 1 g of adsorbent was added to the samples. All of the laboratorial pipes settled on the shaker to shake and then after separating the solution from adsorbent with centrifuge, the remaining value of Cadmium was measured in the solution. After determining the optimal pH and concentration of cadmium, the effect of adsorption value was carried out for Zeolite clinopetilolite adsorbent in the masses of 0.1, 0.25, 0.5 and 1g in the solution and then the remaining concentration Cadmium was measured.

For determining the optimal time, 20 ml of Cadmium solution was prepared separately with concentration of 2.5 ppm at the optimal pH. The value of 1 g of adsorbent (optimal adsorbent) was added to the sample. Soluble were separately on the shaker in contact times of 5,10,15,20,30,60 minutes with absorbent with around 180rpm, and after separation of solution, the remaining concentration of cadmium ion was measured by using atomic absorption system.In order to evaluate the effect of other ions on cadmium on the zeolite, according to the analysis of industrial units `effluent, an simulation effluent was prepared and ions Cu^{+2}, Mg^{+2}, Zn, Ca^{+2}, Pb^{+2}, Cl^-, NH^{4+}, and sulfate was selected and studied as the experimental matrix.

In this study, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms models were used for modeling process of cadmium adsorption. Langmuir isotherm based on a uniform (homogenous) and monolayer of adsorb material with the same energy is on all the levels of the adsorbent. Freundlich isotherm unlike Langmuir is on the adsorbent, based on multilayer adsorption and heterogeneous adsorbent material. Temkin isothermal include one factor that shows clearly interactions between adsorbent and adsorb particles and Dubinin–Radushkevich model is more public than Langmuir, because in this model the monotonousness of adsorption sites is not needed (Crittenden et al., 2012, Naghizadeh, et al, 2011).

Freundlich isotherm model:

Equation 1 represents the mathematical model of Frendlich isotherm.

$$q = KC_e^{1/n} \quad (1)$$

$q=\frac{x}{m}$ Mass ratio of the solid phase which is the mass of adsorbent material, ratio to the mass of absorbent material.

C_e=Concentration in equilibrium

Kempirical constant (Freundlich equation coefficients)

Langmuir isotherm model:

The mathematical model of this isotherm, have been shown in Equation 2:

$$q = \frac{Bq_m C_e}{1+BC_e} \quad (2)$$

B and qm are empirical constants

Ce and q parameters are resemblance to Frendlich isotherm.

Temkin Isotherm:

The general from of Temkin isotherm is as follows:

$$q_e = \frac{RT}{b}\ln(AC_e)$$

By considering B=RT/B a linear form of Temkin isothermal will be as follow:

$$q_e = B\ln A + B\ln C_e$$

In this equation A in terms of mg/l is equivalent to bond constant associated with maximum energy, and b in terms of mol/J is Temkin isothermal constant, and b (no unit) constant is proportional to the heat of adsorption.

Dubinin Rudoshkevich isotherm model

$$\ln q_m = \ln q_e + K\varepsilon^2$$

In this equation:

qe is the amount of dissolved material that is on the adsorbent mass unit and qm is the capacity of absorption of adsorbent in per unit mass.

K is Dubinin–Radushkevich constant adsorption and ε is potential.

RESULTS

Clinoptilolite mineral analysis and mapping of x-ray diffraction of this mineral are presented in table1 and figure 1.

Table 1: Analysis of zeolite clinoptilolite

Composition	Percentage
SiO_2	61.91
Al_2O_3	11.02
Fe_2O_3	0.99
TiO_2	0.17
CaO	0.32
MgO	0.79
Na_2O	6.75
K_2O	2.47
P_2O_5	0.01
LOIa	14.34
Total	98.78

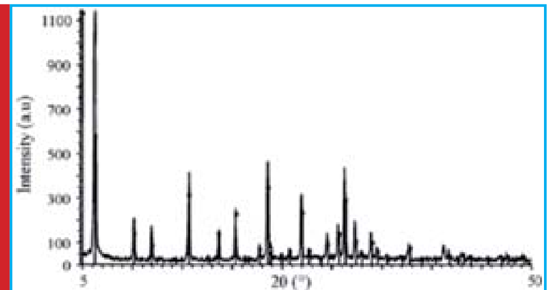

FIGURE 1. The radiation of X-ray related to the zeolite powder samples.

The effect of pH on cadmium adsorption:

The effect of pH solution on the adsorption of cadmium ions showed that the adsorptions process of the Zeolite have better conditions in acidic pHs and with the increasing of pH from 4 to 9 the value of removal is decreased and then by increasing of pH from 7 to 9 adsorption will increased. The presented results in figure 2 shows that the highest adsorption efficiency of cadmium was observed at pH=4.

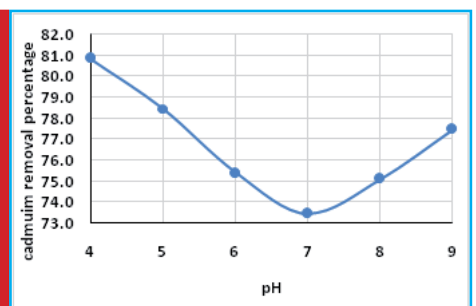

FIGURE 2. The effect of pH parameter on cadmium adsorption efficiency at temperature of 25°C and 15 minutes, the concentration of 1gr/L of adsorbent.

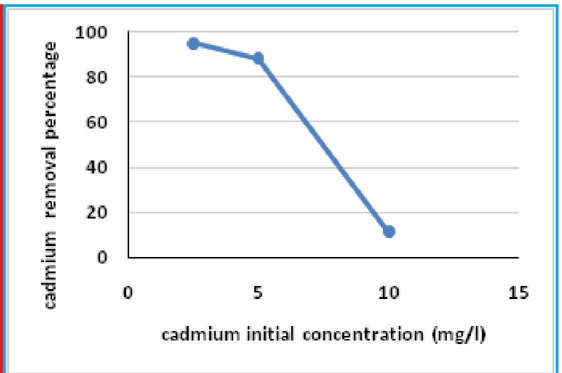

FIGURE 3. SThe effect of different concentration on removal efficiency inoptimal pH 4 at the temperature of 25ºC, in 15 minutes and concentration of 1 gr/L adsorbent.

Initial concentration effect on cadmium adsorbent

In figure 3, adsorption data have been shown in different initial concentrations of cadmium ion. As you can see the value of adsorption is at the highest by zeolite in concentration of 2.5 mg/l.

The effect of zeolite clinoptilolite adsorbent for the removal of cadmium

The results showed that, by increasing of 0.1 to 1g of adsorbent, the removal rate has increased from 32.70 to 92.77, which according to obtained result with the weight of 1g per liter is selected as optimal weight of adsorbent to absorb cadmium. (Figure 4).

The effect of time on the adsorption process.

Figure 5 shows the effect of time on the absorption process. At the initial times the rate of absorption is very high and by passing time, the removal rate has increased and after 15 minutes of contact time, the removal ratewill change with low slope.

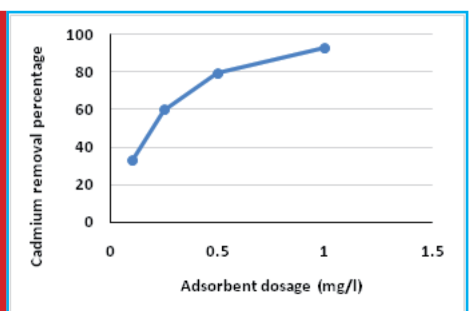

FIGURE 4. The effect of adsorbent value on the cadmium removal efficiency in optimal pH4, at temperature 25ºC,cadmium optimal concentration of 2.5 ppm in 15 minutes and 1 gr/L concentration of adsorbent.

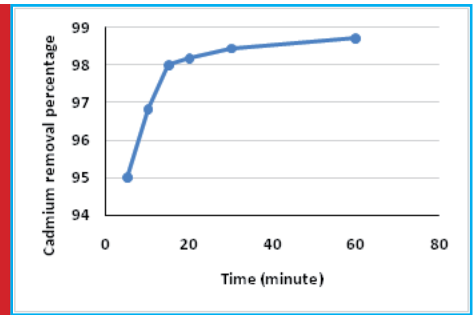

FIGURE 5. The effect of contact time changes on cadmium removal efficiency inoptimal pH (4), the concentration of 2.5 ppm cadmium at a temperature of 25ºC.

Interferences effect on the process of cadmium adsorption

The comparison of removal rate of cadmium in the terms of without interference ions and at the presence of interfering ions shows that at the presence of interference ions did not have significant impact on the process of removing cadmium by using zeolite clinoptilolit. The obtained results in this study correspond with the results of Motsi et al(2009). So that the removal of cadmium was 97% at the presence of while this amount for solutions without interfering ions was 98.1%.

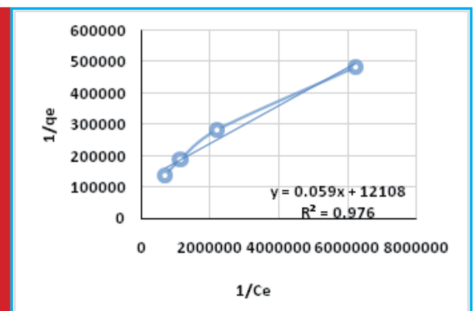

FIGURE 6. Langmuir isotherm curve for cadmium absorption in optimal condition.

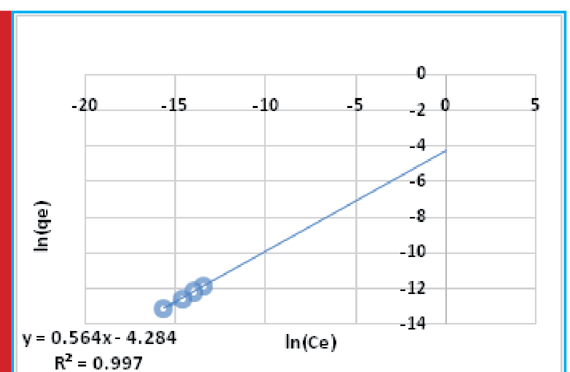

FIGURE 7. Freundlich isotherm curve for adsorption of cadmium in optimal condition.

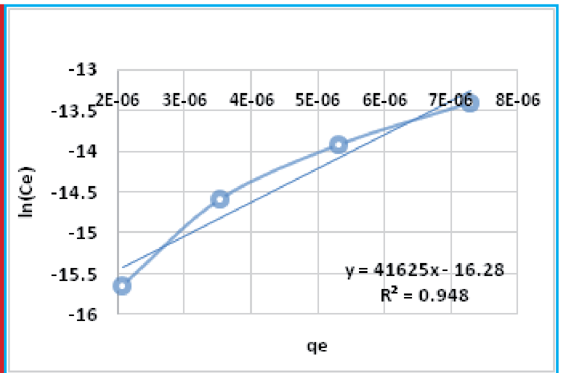

FIGURE 8. Temkin isotherm curve for cadmium adsorptionin optimal conditions.

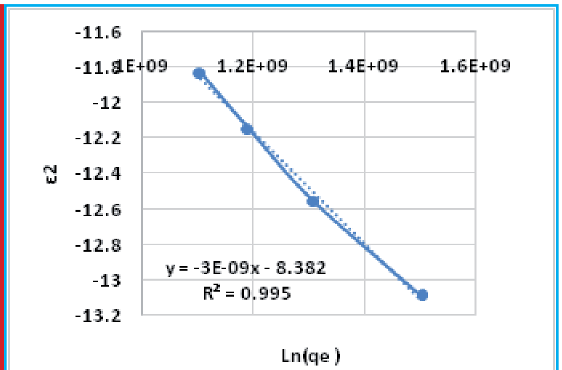

FIGURE 9. Dubinin–Radushkevich isotherm curve for cadmium adsorption in optimal condition.

The results of adsorption isotherms for zeolite clinoptilolite adsorbent.

The figures of 6, 7, 8, and 9 show the Langmuir, Freundlich, Temkin and **Dubinin–Radushkevich** isotherms for studied adsorbent respectively. According to the obtained results, it is observed that cadmium adsorption by zeolite clinptilolite from Freundlich model with a correlation coefficient R^2=0.998 have better efficiency than other isotherm models.

In Langmuir isotherm model, the coefficients of q_{max} and K_L will be calculated respectively through the slope and intercept of linear graph versus Ce.

In Freundlich isotherm model, we have constants of (n) and (K_f) that n is desirability of index in the adsorption process (densities) and K_f is the absorption capacity in terms of mg/g(1/mg)$^{1/n}$. In this model, the values of n less than 1, indicates poor absorption and the values of 1-2 and 2-10 represent optimal and average adsorption respectively.

In Temkin isotherm model, the amount of coefficients of B and K_t will be determined through slope and intercept linear graph q_e versus LnC_e respectively.

E Index is used for Radushkevich isotherm to evaluate the capability of using equation. This parameter provides information related to adsorption process mechanism (physical, chemical), in such a way that the values of E between 8 and 16 kJ/mol indicate that adsorption process has been follow a chemical mechanism and for values less than 8 kJ/mol, the mechanism had physical natural adsorption process (RezaeiKalantary et al., 2014).

DISCUSSION

The obtained results of initial pH effect of solution showed that the removal efficiency of cadmium by zeolite clinoptilolite, will be affected by the solution pH. In adsorption process, oH^- and H^+ are two determiners ions for surface charge. (Lu et al, 2009). Natural zeolite preferably tends to absorb H^+ ions from solution in comparison with heavy metals ions (Inglezakis et al., 2004). So by increasing of acidic conditions the adsorption of H^+ ions will increase from solution that includes the most efficiency for removing of cadmium, which its results correspond with the results of Moreno et al. (2001). In Low concentration of cadmium, specific surface and the sites ofadsorbent adsorption were more and cadmium ions are able to react to each other with available absorption opportunities on adsorbent surface and therefore the removal rate will increase. The removal efficiency of cadmium ions from solution has reverse relation by using of zeolite clinoptilolite with concentration more than 2.5 mg per liter and the results correspond with the results of Motsi et al (2009).

The study of balance time effect, showed that the removal of cadmium in contact time of 15 minutes have

Table 2: The results of adsorption isotherm coefficients for the removal of cadmium from aqueous by zeolite clinoptiolite.

Adsorbent	Freundlich			Langmuir		
	K(mg/g)(mg/l)^n	N	R^2	q_{max}(mg/g)	KL (L/mg)	R^2
Zeolite	0.013	1.77	0.998	16.73	4.93	0.976
	Dubinin–Radushkevich			Temkin		
	E(kJ/mol)	K	R^2	B	K	R^2
	12.91	109×3	0.995	2.27	5.14	0.949

maximum efficiency by zeolite clinoptilolite. The cause of high absorption rate in the initial moments of reaction is a large number of absorption active sites (Ghorai 2005). These results correspond with the results of Shawabkeh (2004).The results of adsorbent dosage effect on the adsorption process showed that, by increasing of adsorbent value, the value of cadmium absorption will be increased, that is because of increasing the number of levels at the available of adsorbent because of its increasing, which leads to an increasing in the level of contact and increasing in the free bonds on the level of adsorbent (Wajima et al., 2009; Ramdani et al., 2010).These obtained results correspond with the results of Shawabkeh, 2004 and Shamohammadi et al., 2008).

Rate and value of adsorption is subject to charge and mass of adsorbent. At all multipartite soluble concentrations, the amount of total absorb heavy metals ions increased in per unit mass of natural zeolite in comparison with the amount of absorbed article from partial solutions. This shows that the difference in the mechanism of surface absorption may include surface absorption per action. The obtained results correspond with Motsi et al (2009).In Freundlich model has been supposed that the adsorbed exit on heterogeneous surfaces will be occurred by adsorption on multi layers. By performed calculation it showsthat the value of R^2 is equal to 0.998 and n is equal to 1.77 and it indicates that this adsorption is optimal and the reaction follows from Freundlich equation. Also in this study, based on Radushkevich model E is equal to 12 kJ/mol (between 8 and 16 kJ/mol). So adsorption process is a chemical reaction. In a study that carried out by Motsi et al on the removal of Mn_2 by natural zeolite, also the obtained results by Wanga and Peng (2010) as well as the results of Mishra and Patel (2009) on the modified zeolite in aqueous environment, this process follows Freundlich model that corresponds with the results of the removal of cadmium zeolite clinoptilolite.

CONCLUSION

The results of this study shows that natural zeolite for removal of cadmium from industrial waste water under optimal conditions (times of 15 minutes, pH=4, adsorbent dosage of 1 g per liter and concentration of 2.5 ppm cadmium) has very good efficiency. The benefits of this natural, low cost, mineral article, is easy access to it. Moreover this absorbent is more advantageous than common absorbents such as activated carbon or operational procedures such as electro dialysis and exists in the numerous mines in Iran, including Semnan, Kerman and Azarbaijan.

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