

RESEARCH PAPER

Adsorption of Cd, Co, and Zn from multi-ionic solutions onto Iranian sepiolite isotherms

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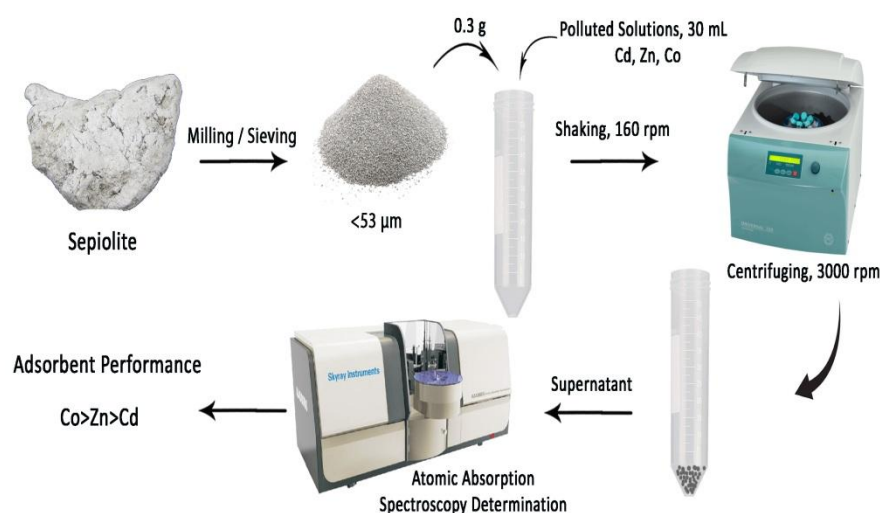
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Highlights

- Heavy metals removal from waste water especially from industrial waste waters is an important way for environmental protection.
- One of the cost-effective ways for heavy metals removal from polluted waters and aqueous solutions is using of clays such as sepiolite which has high potential for heavy metals adsorption.
- Heat pre-treatment on clays can increase their capacity to heavy metals adsorption.
- Cd, Co, and Zn adsorptions by sepiolite in aqueous solutions at different pH values can be investigated through some of common isothermal models including Freundlich and Langmuir.

Graphical Abstract



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Abstract

Nowadays, removal of heavy-metal contaminants from industrial waste waters is one of the most important environmental polemics which necessarily requires a solution. Clays, because of their low cost and unique chemical and structural properties have been widely used to remove heavy metals from aqueous solutions. In this investigation, sepiolite mineral was obtained from a mine near Fariman Township, Khorasan, Iran. The mineral samples used in this study were powdered with sizes less than 0.05 mm ($<53 \mu\text{m}$). Batch tests were conducted to investigate the adsorption behavior of Cd (II), Zn (II), and Co (II) by natural and heat pre-treated sepiolites at 150 and 250 °C in initial slurry concentrations of (60, 120, 180, 240, 360, 480, and 540 g/L). Langmuir and Freundlich isotherm models were investigated to illustrate the adsorption of heavy metals by natural and heat pre-treated sepiolites from aqueous solutions in two different pH values: 4 and 5. It was determined that the experimental data were more fitted to the Langmuir model ($R^2 \approx 0.99$) and it was observed that cobalt ions were more adsorbed than zinc and cadmium in the order of adsorbing regularity: $\text{Co} > \text{Zn} > \text{Cd}$. In this study, the quantities of released Mg^{2+} from the mineral structures were also investigated. In addition, changes in pH values in final solutions were investigated at the end of the experiments.

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1. Introduction

Heavy metals contamination is one of the environmental problems worldwide which has aroused considerable public concern and jeopardizes human and environmental health (Liang et al., 2011; Wang et al., 2007). There are so many ways by which heavy metals enter into the environment to cause contamination, such as: discharging of industrial wastewater, battery manufacturing, welding industries, municipal industrials, chemical pharmaceuticals, electroplating, mining operations, fertilizer, dyestuffs, and many others (Kocaoba and Akyuz, 2005). Nowadays, removal of heavy-metal contaminants from industrial waste waters is a major environmental issue (Doğan et al., 2008). The most widely used techniques employed in removing of heavy metals from waste waters include: chemical reactions (Chen et al., 2011; Foo and Hameed, 2010), solvent extraction (Silva et al., 2005), coagulation-flocculation (Amuda et al., 2006), reverse osmosis (Hyung and Kim, 2006), electrochemical techniques (Vasudevan and Lakshmi, 2011), biological process (Gauri et al., 2011), sedimentation (Bürger et al., 2000), filtration (Fu and Wang, 2011), membrane processes (Mortaheb et al., 2009), adsorption and ion exchange etc, (Dwivedi et al., 2008; Eren et al., 2010a; Lazarević et al., 2007). One of the best methods which are readily available and more economical for removing heavy metals from waste waters is adsorption (Eren et al., 2010b). Nowadays, the use of natural materials for removing heavy metals is gaining considerable importance (Kassae et al., 2011). As compared to different adsorptive materials, clays because of their low cost and unique chemical and structural properties such as high surface area, negatively charged layers, and abundance in the environment, are widely used to remove heavy metals from aqueous solutions (Álvarez-Ayuso and García-Sánchez, 2007; Jiang et al., 2009).

Natural sepiolite mineral which belongs to phyllo-silicate clay family is a fibrous hydrated magnesium silicate, with a half unit cell formula of $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$. It has fine micro-porous channels with dimensions of 0.37×1.06 nm. Typically, the fiber size is variable, but $800 \times 25 \times 4$ nm has been suggested as an average. Its structure is similar to 2:1 tri-octahedral clays with a central magnesium ion surrounded by two tetrahedral silicate sheets. Discontinuity of external silica sheets and their inversion gives a structure with tunnels and blocks. All corners of the inner blocks are connected to the adjacent blocks but some corners in the outer blocks are silica atoms bounded to hydroxyl groups (Si-OH) known as silanol group. This eccentric structure causes the penetration and connection of organic and inorganic molecules into the mineral structures which makes sepiolite an importance adsorptive material in industrial activities. Sepiolite reserves are mainly found in Turkey, Vallecas of Spain, Madagascar and Tanzania (Lazarević et al., 2007; Tekin et al., 2006). Recent studies confirm the ability of sepiolite to significantly adsorb heavy metals in waste waters and remove toxic pollutants from the environment (Lazarević et al., 2007; Brigatti et al., 2000; Donat, 2009). For our study, the sepiolite mineral was obtained from the mine near Fariman Town ship, Khorasan-Iran.

Accordingly, the present investigation evaluates the effect of pH on the pattern of absorption of zinc, cobalt and cadmium as well as the effect of pH on the absorption capacity of powdered natural and pre-heated sepiolite samples, with a particle size of less than $53 \mu\text{m}$. Towards this end, the effect of initial heavy metal concentrations in polluted solutions were investigated to detect the adsorption capacities of natural and heat pretreated sepiolites for each of the experimental elements and measure the ability of heat treated mineral in comparison with natural sepiolite. On the other hand, we aimed to compare the application of isothermal models (Freundlich and Langmuir) in the adsorption process and distinguish selective adsorption of the following toxic heavy metals: Cd (II), Co (II), and Zn (II) ions. In addition, desorption of magnesium from the mineral structure to suspensions and changes in pH value of the final suspensions were investigated. Finally, we investigated the relationship between structural magnesium released into the solutions and changes in their pH values.

2. Materials and Methods

2.1. Preparation of adsorbent

The mineral samples used in this study were sepiolite samples powdered by using the electrical mash after which they were milled with the ball-mill and sieved to obtain particles with sizes less than 0.05mm ($<53 \mu\text{m}$).

The adsorbents used in this study were prepared in two temperature pretreatments; one sample as natural mineral at room temperature (22.5 ± 0.2 °C). By determining the size of adsorbents, the amount needed to act as a modified adsorbent for removing heavy metals were placed in the kiln for 4 hours at 150 and 250 °C to remove the zeolitic water bound in the mineral structure and increase the mineral's specific surface area. Then the lacuna of the kiln was cooled at room temperature and the samples were extracted and kept in a desiccator containing pure CaCl_2 to prevent the possible adsorption of atmospheric moisture by the surfaces of the heat-treated (modified) and natural sepiolites.

2.2. Chemicals

Absorbent surface of the powdered minerals with particle sizes less than 0.05 mm were saturated with Ca^{2+} to prepare them for adsorption experiments. In fact Ca^{2+} ions exchanges with the other cationic forms at the absorptive surface of sepiolite samples. For saturating action, CaCl_2 solution of 0.5 M was made by using CaCl_2 from Merck, Dramsladt Germany. 55.45 g of CaCl_2 , was dissolved in one liter of de-ionized water to make a solution with 0.5 M concentration. The powdered samples were saturated to obtain suspensions of 5 g mineral + 25 ml CaCl_2 0.5 M. placed in tubes and centrifuged at 350 rpm for 30 min. After centrifugation, at 3000 rpm for 10 min, EC value of limpid solutions was measured to obtain a permanent value. Finally, the saturated samples in the tubes were placed in an oven for 72 hours at 75 °C to be dried completely. After drying, flouring was done to obtain particles of 0.05 mm ($< 53 \mu\text{m}$).

2.2.1. Making polluted solutions

Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by activated carbon Adsorbent isotherm experiment was used to study the mineral sample's ability for absorbing heavy metals and which of the heavy metals; Cd, Zn or Co, would be adsorbed more by the mineral sample. Polluted multi component solutions used in this study contained $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ obtained from BDH (England) and CoCl_2 and ZnCl_2 from Merck Dramsladt, Germany. ppm standard solutions were obtained from each of the studied heavy metals and then the final polluted solution was prepared at arbitrary concentrations of 60, 120, 180, 240, 360, 480 and 540 ppm of Cd, Zn and Co. For example, the 60 ppm polluted solutions contained 20 ppm of Cd, 20 ppm of Zn and 20 ppm of Co). After preparing the polluted solutions, 0.2 N each of HCl and NaOH were used for regularizing the solutions at pH values of 4 and 5.

2.3. Experimental methods

2.3.1. Batch experiments

To investigate the absorption of heavy metals on natural and modified sepiolite samples and the effect of reaction influences among these heavy metals in the adsorption process with respect to volume ratio of (1:100) by weight, 0.3 gr experimental minerals with 30 mL of solution at different concentrations was mixed in polyethylene containers. Then adsorption isotherms of these elements and their effects on competitive adsorption were determined. These experiments were carried out in three repetitions to ensure that the final output is reliable.

Batch tests were conducted to investigate the adsorption behavior of Cd (II), Zn (II), and Co (II) with seven different initial slurry concentrations (i.e., 60, 120, 180, 240, 360, 480, and 540 g/L). The sample tubes were then put into a shaker machine which was rotated at 160 rpm. The reaction temperature was maintained constant at 22.5 ± 0.2 °C (room temperature) and the reaction duration was 48 hours. Afterwards, the slurries were centrifuged at a speed of 3000 rpm for 10 minutes to obtain the supernatants. Atomic absorption spectroscopy (AAS) was then used to determine equilibrium concentrations of Cd (II), Zn (II), and Co (II). The heavy metals removal efficiency (R) was calculated by dividing the difference between the initial concentration, C_0 and the equilibrium concentration, C_e separately for each of the experimental elements. Mg/L : $(R (\%) = [(C_0 - C_e)/C_0] \times 100)$. Blank tests were also conducted as parallel tests to obtain an average value for equipment

adsorption to evaluate the adsorption of the heavy metals, on the inner surface of the tubes and on the pores of the filter papers used (Eren and Gumus, 2011; Ghassabzadeh et al., 2010; Murugesan et al., 2011).

2.4. Adsorption isotherms

For quantitative description of the adsorption process, adsorption isotherms (at constant temperature), show the amount of heavy metal adsorbed by natural and heat pre-treated sepiolite samples. The equilibrium heavy metal concentrations measured in the slurry solutions after the adsorption equilibrium was completed in 48 hours by shaking and centrifugation. Langmuir and the Freundlich equations are among the commonly used isothermal models used to describe adsorption process (Jeppu and Clement, 2012; Lasheen et al., 2012).

2.4.1. Langmuir isotherm model

The adsorption data of cadmium, cobalt and zinc ions were correlated with the Langmuir model. Sorption data were interpreted in terms of Langmuir equation (Kocaoba and Akyuz, 2005). The physical and mathematical explanations and interpretation of the monolayer adsorption isotherms measured on homogeneous surfaces begun with an isothermic model in 1916. This theory is based on the dynamic character of adsorption. In equilibrium condition, the number of adsorbed/desorbed molecules at unit time and at unit surface is equal. Langmuir's theory does not take the lateral interactions and horizontal mobility of the adsorbed molecules into account (Doğan et al., 2008). The well-known expression of the Langmuir model is given by equation 1:

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

And the linear form of this equation is in form of equation 2:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_m} + \frac{C_e}{q_m} \quad (2)$$

where C_e is the equilibrium concentration of heavy metals solution (mg/L), q_e the equilibrium capacity of cadmium, cobalt and zinc on the adsorbent (mg/g), q_m the monolayer adsorption capacity of the adsorbent (mg/g), and b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption (Sdiri et al., 2011; Wang et al., 2007).

2.4.2. Freundlich isotherm model

The Freundlich equation is an empirical isothermic model which is based on sorption onto a heterogeneous surface and is given as equation 3:

$$q_e = K_f \cdot C_e^{\frac{1}{n}} \quad (3)$$

And the linear form of Freundlich isotherm is given as equation 4:

$$\log q_e = \log K_f + n \cdot \log C_e \quad (4)$$

In this equation, K_f and n are the Freundlich constants for the system which are indicators of adsorption capacity and intensity, respectively (Al-Futaisi et al., 2007; Sdiri et al., 2011). Coefficients of Langmuir equation, q_m and b are calculated from the slopes and intercepts of the straight plot lines of (C_e/q_e) versus C_e . While the values of K_f and n in Freundlich model could be calculated from the plots of $\log C_e$ against $\log q_e$ (Sdiri et al., 2011).

3. Results and Discussion

3.1. Electron microscopy

To observe the morphology, texture, size and the individual particles of clay minerals, electron microscopy is very effective (Lazarević et al., 2012). Selected TEM images of Iranian sepiolite are shown in Fig. 1 (a, b). It is clearly shown that all of the sepiolite samples used were powdered in arbitrary particle sizes.

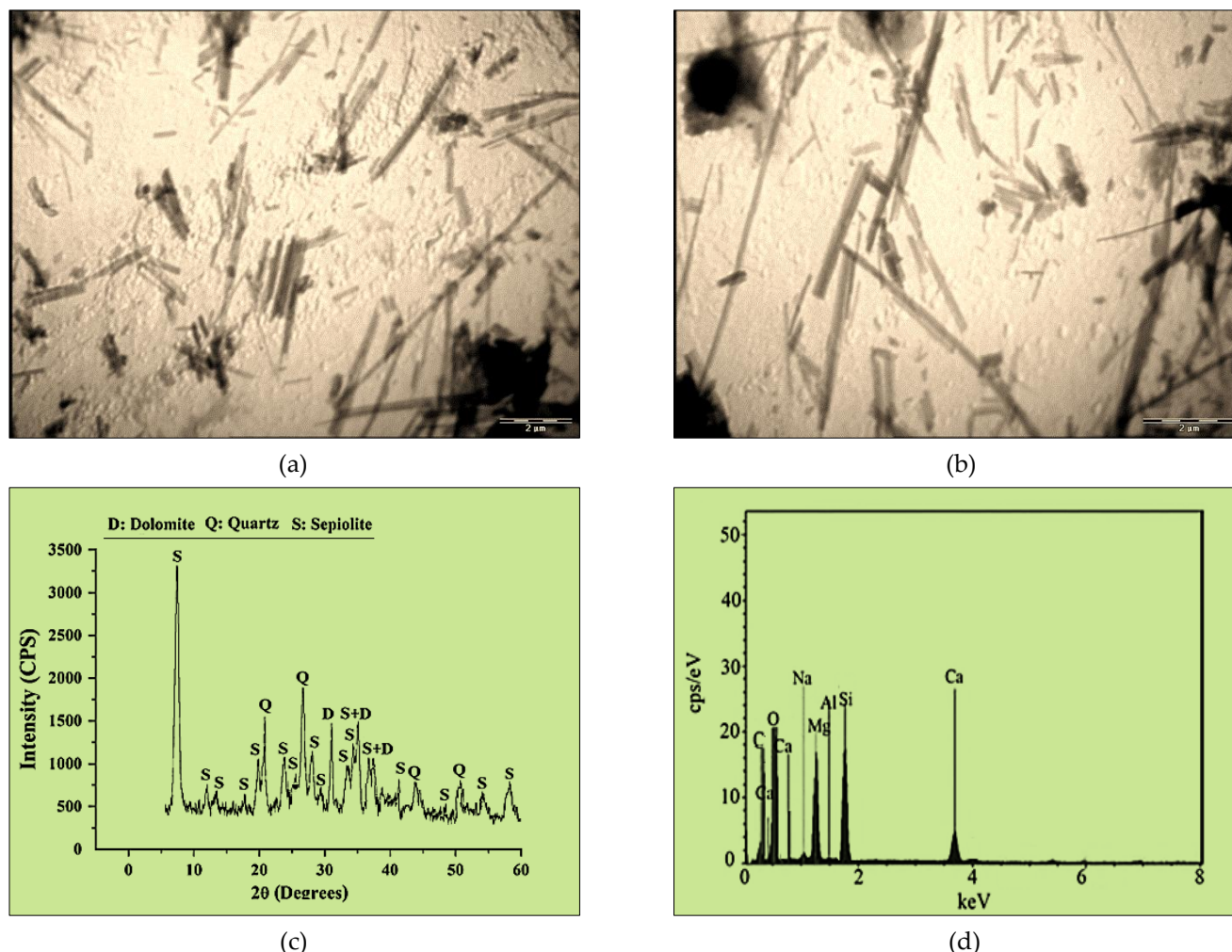


Fig. 1. (a) and (b): TEM images, (c): XRD pattern, and (d): EDAX spectrum of applied sepiolite.

3.2. Adsorption isotherms

Isothermal adsorption experiments of cadmium, cobalt and zinc on natural and heat pre-treated sepiolite in multi component solutions with concentration conditions of 60, 120, 180, 240, 360, 480, and 540 ppm at pH values of 4 and 5 were investigated. In this study, the Langmuir and Freundlich isotherm models were applied to interpret the adsorption process of heavy metals for which the results are as follows.

3.2.1. Comparisons of isotherm models

The Langmuir and the Freundlich isotherm models were investigated to illustrate the adsorption of heavy metals (Cd^{2+} , Co^{2+} and Zn^{2+}) by natural and heat pre-treated sepiolites from aqueous solutions at two pH values of 4 and 5. As seen in Tables 1 and 2 comparing the results between these isotherm models in our study, it is determined that the experimental data were more fitted with the Langmuir model ($R^2 \approx 0.99$) than the Freundlich model at both pH values and all the mineral samples. Based on this theory (Langmuir isotherm model), it could be determined that the adsorption process of the experimental heavy metals was like a mono layer adsorbing and the adsorption energy for all of cationic forms on adsorbing surfaces was same. There were also no interactions between ions, atoms and molecules during the adsorption process. Similar results were

given by (Lazarević et al., 2012), as they reported that the equilibrium sorption data of Co²⁺ on Fe-sepiolite was adequately described by the Langmuir isotherm equation (Lazarević et al., 2012). Although processing data with the Freundlich isotherm model showed that the coefficient adsorption of mineral (K_f) for each sepiolite samples increased by exerting heat on the minerals from which it was determined that the heat pre-treating could increase the adsorption capacity of sepiolite.

Table 1. Adsorption coefficients of Cd²⁺, Co²⁺, and Zn²⁺ ions onto different natural and heat pre-treated sepiolites: comparisons between the Langmuir and Freundlich models at solutions with the pH value of 4.

Model		Langmuir			Freundlich		
adsorbent		Natural sepiolite					
Element	Coefficients	b (L/mg)	q _m (mg/g)	R ²	n	K _f ((mg/g)(L/mg) ^{1/n})	R ²
Cd		0.1005	3.968	0.996	3.623	1.039	0.672
Co		0.131	8.475	0.998	2.710	1.758	0.925
Zn		0.097	8.403	0.990	2.915	1.702	0.857
adsorbent		150 °C heat pre-treated sepiolite					
Element	Coefficients	b (L/mg)	q _m (mg/g)	R ²	n	K _f ((mg/g)(L/mg) ^{1/n})	R ²
Cd		0.055	5.347	0.989	0.416	2.193	0.830
Co		0.134	9.174	0.998	2.841	1.954	0.948
Zn		0.106	9.260	0.993	2.809	1.832	0.878
adsorbent		250 °C heat pre-treated sepiolite					
Element	Coefficients	b (L/mg)	q _m (mg/g)	R ²	n	K _f ((mg/g)(L/mg) ^{1/n})	R ²
Cd		0.081	5.682	0.993	3.134	1.210	0.804
Co		0.106	11.764	0.989	2.544	2.089	0.983
Zn		0.131	10.204	0.991	2.865	2.203	0.855

Table 2. Adsorption coefficients of Cd²⁺, Co²⁺, and Zn²⁺ ions onto different natural and heat pre-treated sepiolites: comparisons between the Langmuir and Freundlich models at solutions with the pH value of 5.

Model		Langmuir			Freundlich		
adsorbent		Natural sepiolite					
Element	Coefficients	b (L/mg)	q _m (mg/g)	R ²	n	K _f ((mg/g)(L/mg) ^{1/n})	R ²
Cd		0.157	3.184	0.998	6.410	1.439	0.973
Co		0.339	17.241	0.993	2.070	4.102	0.870
Zn		0.313	5.181	0.999	4.673	1.990	0.707
adsorbent		150 °C heat pre-treated sepiolite					
Element	Coefficients	b (L/mg)	q _m (mg/g)	R ²	n	K _f ((mg/g)(L/mg) ^{1/n})	R ²
Cd		0.056	4.524	0.963	4.367	1.262	0.928
Co		0.457	16.949	0.993	2.188	4.472	0.872
Zn		0.320	5.650	0.999	4.273	2.037	0.730
adsorbent		250 °C heat pre-treated sepiolite					
Element	Coefficients	b (L/mg)	q _m (mg/g)	R ²	n	K _f ((mg/g)(L/mg) ^{1/n})	R ²
Cd		0.088	4.629	0.979	5.076	1.618	0.923
Co		0.568	17.241	0.992	2.174	5.284	0.818
Zn		0.223	6.756	0.999	3.663	2.037	0.783

According to the quantities of (K_f) shown in Tables 1 and 2, it indicates that the samples heat treated at 250 °C efficiently adsorbed heavy metals than the 150 °C heat pre-treated samples. Therefore the 150 °C heated minerals adsorbed more quantities than the naturally used sepiolite. In comparing the adsorption intensity coefficient (n) for experimental heavy metals, more quantities were obtained respectively for Cd, Zn and Co and it is well known that the quantity of (n) in the Freundlich model has a converse relationship with adsorption. Therefore, these results could describe the ability of heavy metals to adsorb natural and modified minerals.

When the value of $1/n$ is less than 1 ($1/n < 1$), results indicate that adsorption capacity at lower equilibrium concentrations are slightly suppressed. The Freundlich isotherm model could not yield any authentic information about the adsorption mechanism, but was applicable on heterogeneous solid surfaces as non-specific adsorption (Kocaoba, 2009). Many other studies showed that Langmuir and Freundlich isothermal models corresponded well with the adsorption of heavy metals (Bektaş et al., 2004; Karahan et al., 2006; Kilislioglu and Aras, 2010; Wang et al., 2007).

3.3. Effect of heat pre-treating

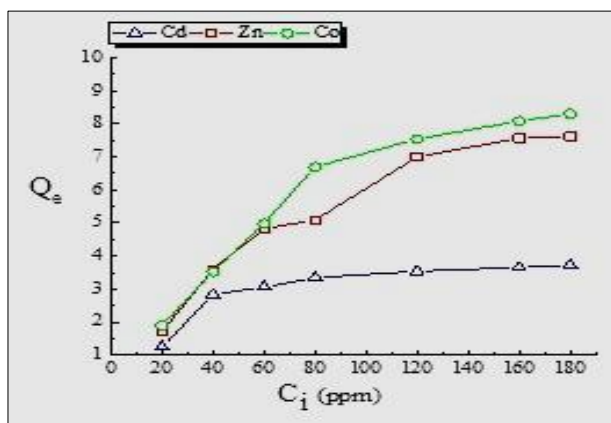
In this study, the effect of heat pre-treatment on sepiolite was investigated to determine how heats change its adsorption capacity. As seen in Tables 1 and 2, the coefficients of q_m and K_f shows the heavy metals adsorbed on sepiolite samples by the Langmuir and Freundlich equations, respectively. The amounts of heavy metals adsorbed by heat pre-treated samples were more than the amounts adsorbed by natural sepiolite samples. At similar solution concentration and pH values, adsorption capacity of the samples heated at 250 °C was more than the 150 °C heated minerals. Thus, the natural sepiolite has the least ability for heavy metal adsorption compared to the heated minerals. During the heating of sepiolite, zeolitic water will be removed from the mineral's structure and also, the surface area of mineral will be increased. Due to these kinds of structural changes, the cation exchangeable sites increased. Doğan et al., in two separate studies (2008 and 2009) showed that by increasing the heat on sepiolite, the ability of heavy metals adsorption was enhanced (Doğan et al., 2008; Doğan et al., 2009). Frost and Ding, reported that by increasing the heat until around 300 °C and due to the removal of zeolitic and coordinated waters from sepiolite structure, the adsorption capacity of the mineral was increased (Frost and Ding, 2003). Fig. 3 (i, ii and iii) shows the effects of heat pre-treating on heavy metals adsorption by sepiolite using the Duncan test at 1% level.

3.4. Effect of initial concentrations

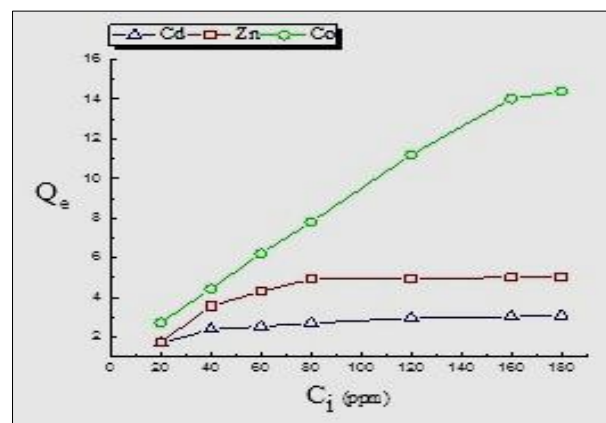
Fig. 2 (a to f) shows that an increase in the amounts of adsorbed heavy metals by natural and heat pre-treated sepiolite samples occurred with increasing the concentrations of the initial solution. The unit adsorption of Cd (II), Zn (II), and Co (II) on the experimental minerals shows a gradual ascending trend and eventually achieved a maximum adsorption amount with an increase in equilibrium solute concentration after 2880 minutes. Decreases in the equilibrium solution were observed with an increase in initial concentrations. A similar linear with higher slopes was observed in low initial solution concentrations range which might be result due to the high adsorption capacity of sepiolite earlier in the adsorption process (Fig. 2). The equilibrium in which adsorption occurred in final solutions differed for each of the experimental heavy metals because the ability of sepiolite to adsorb these cationic forms is different. Similarly, the same equilibrium solution concentrations were observed for the two pretreated sepiolite samples. An increase in the quantity of heavy metals adsorption by heat pre-treated minerals could be explained by the possible adsorption centers during the heating process. Therefore, it was concluded that the affinity of the surfaces to cationic forms or surface irregularities might cause increases in the number of active sites after heating the minerals.

The differences in the solution equilibrium concentrations achieved by removing zeolitic water and increasing specific surface area of sepiolite was due to heating the mineral and becomes significant by increasing heat pre-treating temperature. Sepiolite active surface centers are of three types and consist of (i) SiOH (silanol groups), (ii) water molecules (zeolitic water), and (iii) oxygen atoms. Distribution of these active sites within the sepiolite makes a heterogeneous surface. The coordinated water molecules are the most effective adsorption sites; therefore the adsorption occurs by replacement with coordinated water and hydrogen bonding to water molecules. The surface properties of sepiolite which determines the degree of crystallinity relates to the content of SiOH groups distributed on the surface of this mineral. Hence the active centers distribution and crystal imperfections exist within the mineral (Balci, 2004). The higher quantities of heavy metals adsorption occurred in the high solution concentrations in the three mineral samples at the equilibrium conditions. Increase

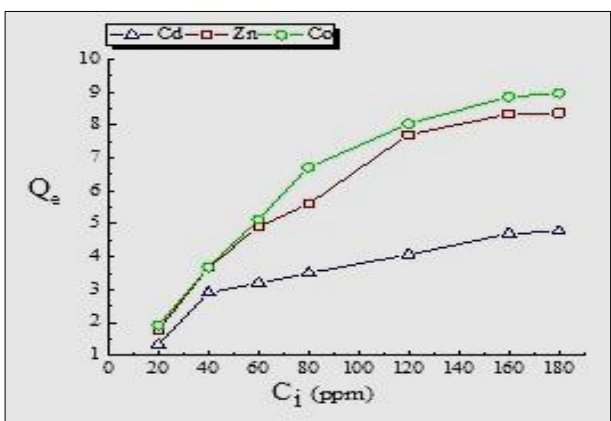
in initial solution concentrations leads to decreases in the removal capacity of all used minerals. Such that for final cationic solution concentrations, the concentration value of cobalt were less than Zn and Cd under equilibrium conditions and this result were repeated for all using minerals (150 and 250 °C heat pre-treated sepiolites) at both pH values. Therefore, according to the reduced concentrations of experimental heavy metals, it was shown that cobalt was more adsorbed than zinc and cadmium in this order of adsorbing regularity: $Co > Zn > Cd$.



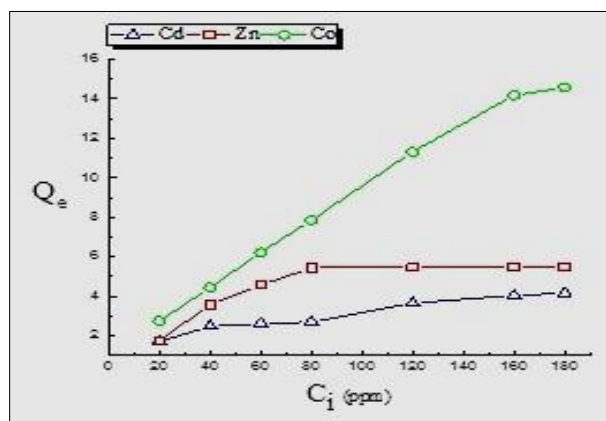
(a): Natural sepiolite in solution with pH 4 values.



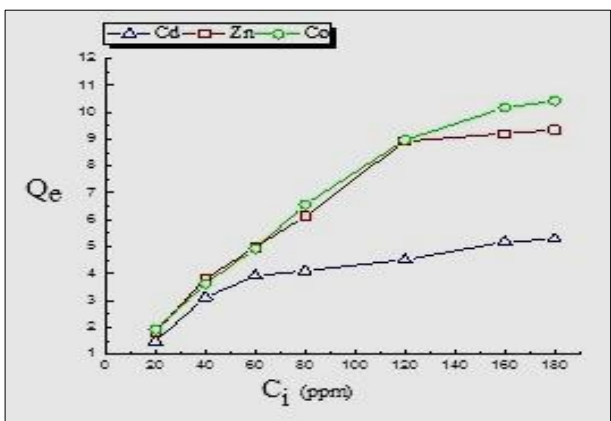
(b): Natural sepiolite in solution with pH 5 values.



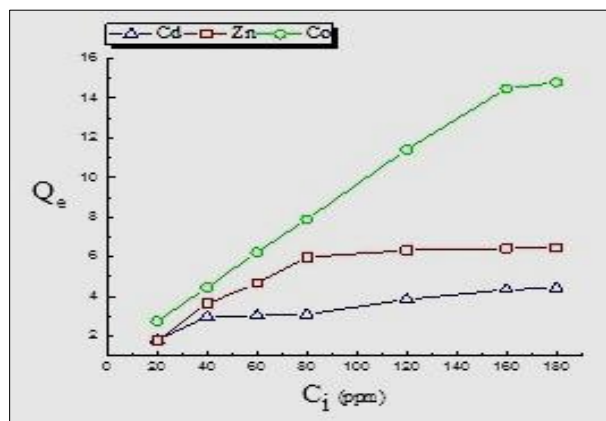
(c): heat pretreated sepiolite at 150 °C in solution with pH 4 values.



(d): heat pretreated sepiolite at 150 °C in solution with pH 5 values.

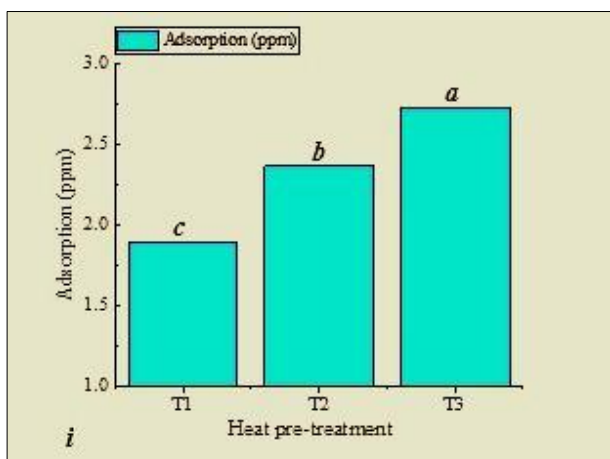


(e): heat pretreated sepiolite at 250 °C in solution with pH 4 values.

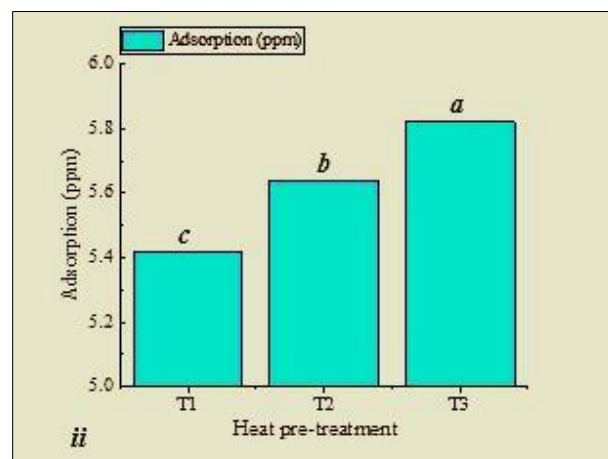


(f): heat pretreated sepiolite at 250 °C in solution with pH 5 values

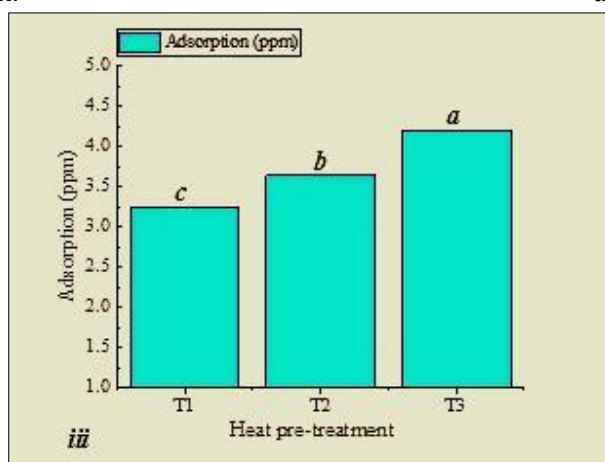
Fig. 2. Heavy metals Adsorption of natural and heat pretreated sepiolites at different pH values.



i: The effects of heat pre-treatment on cadmium adsorption.



ii: The effects of heat pre-treatment on cobalt adsorption.

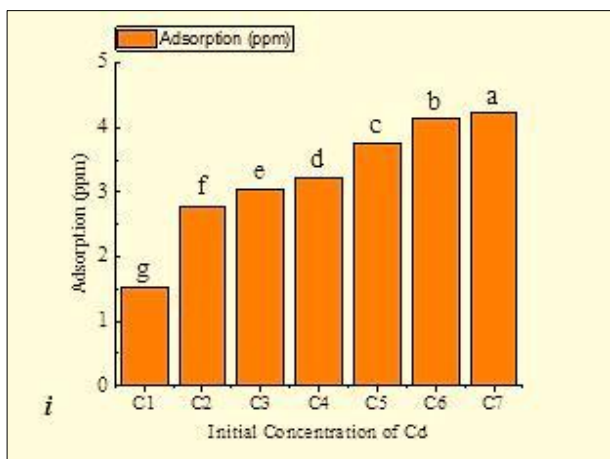


iii: The effects of heat pre-treatment on zinc adsorption.

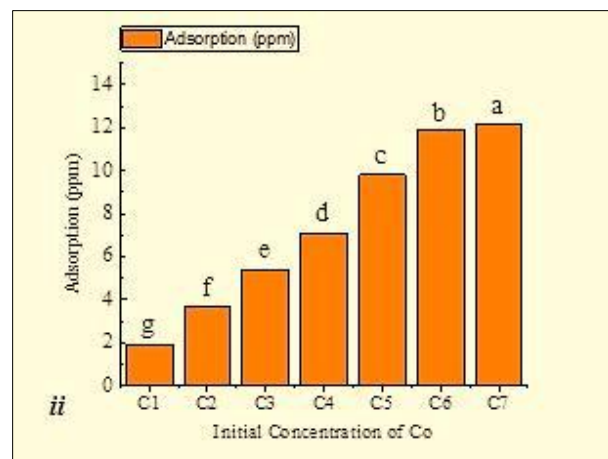
Fig. 3. Effects of heat pre-treatment on heavy metal adsorption by sepiolite.

T1: Without heat pre-treatment, T2: 150 °C heat pre-treatment, T3: 250 °C heat pre-treatment.

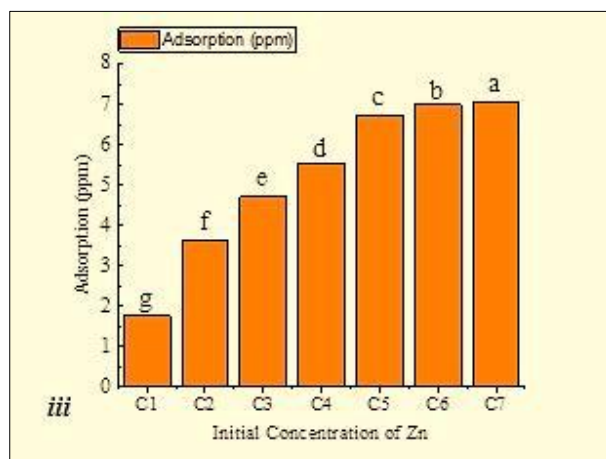
At the early stages (points) of the adsorption process, the exchangeable sites and the adsorption surfaces of minerals are prepared to adsorb heavy metals. As seen in these shapes, Cobalt ions were more adsorbed by natural and heat pre-treated sepiolite samples as the ionic forms of this element could be fitted more than the active centers of zinc and cadmium ions. Fig. 4 (i, ii and iii) shows the effects of initial concentrations of heavy metals adsorption.



i: The effects of initial concentration on cadmium adsorption.



ii: The effects of initial concentration on cobalt adsorption.



iii: The effects of initial concentration on zinc adsorption.

Fig. 4. Effects of initial concentration on heavy metal adsorption by sepiolite.

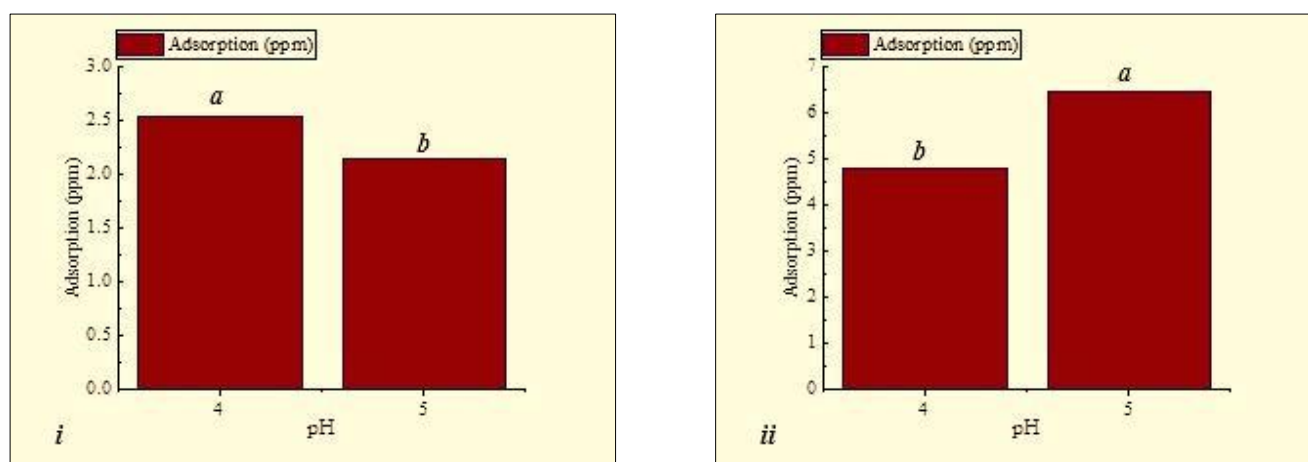
C1: 20 ppm, C2: 40 ppm, C3: 60 ppm, C4: 80 ppm, C5: 120 ppm, C6: 160 ppm, C7: 180 ppm.

3.5. Effect of pH

Incorporation of metallic ions onto sepiolite adsorptive surface groups is extremely dependent on pH value. Therefore, the pH value of aqueous solutions is an important parameter in the adsorption process. As seen in Fig. 2 (a to f), the yields of (n) and (qm) quantities from Freundlich and Langmuir isotherm equations shows that the amounts of cobalt adsorbed by natural and both heat pre-treated sepiolites increased and the amounts of adsorbed cadmium and zinc decreased by increasing the solutions pH value from 4 to 5. For example, comparing qm quantities between Table 1 and 2, quantities of qm for cobalt ions at pH value of 4 (8.475) increased (17.241) at pH value of 5 and the quantities of qm for cadmium and zinc decreased respectively (from 3.986 to 3.184 and 8.403 to 5.181). Furthermore by increasing the solutions pH value, the coefficient of (n) decreased for cobalt and increased for cadmium and zinc adsorption by natural and heated sepiolite samples. In lower pH values (acidic pH values), the silanol groups (Si-OH) which exists at surfaces of sepiolite caused the production of positive charge hence these groups have less ability to adsorb heavy metals and it leads to low quantity of Co(II) on the adsorbent. The fact that Co adsorption increases with increasing solution pH value may be attributed to a decrease in competitive protons in the cationic species to occupy the adsorptive sites on the natural and heated sepiolites samples to enhance the electrostatic attraction between cationic forms in solutions and adsorptive surfaces on minerals. Similar results were reported by (Wang et al., 2007) where they showed that the adsorption of Cd (II) on palygorskite, increased with increase in pH. This is because at lower pH, the silanol groups (Si-OH) which exists on surfaces of palygorskite creates a positive charge (Si-OH²⁺) and this mineral has less ability to adsorb cadmium, and increasing pH, caused a decrease in competition between protons and cationic species to adsorb on palygorskite. However, in the present study, multi component solutions of heavy metals were investigated. The decrease in zinc and cadmium adsorbed increased with the solution's pH value and could be attributed to competition between cobalt, zinc and cadmium to incorporate with the active centers of the experimental minerals. The cobalt ions due to their small sizes could bond to the inner structures of sepiolite samples more than zinc and cadmium. Furthermore, statistical analyses of the effect of pH were done to clarify how the changes in pH could affect the adsorption process Fig. 5 (i, ii and iii).

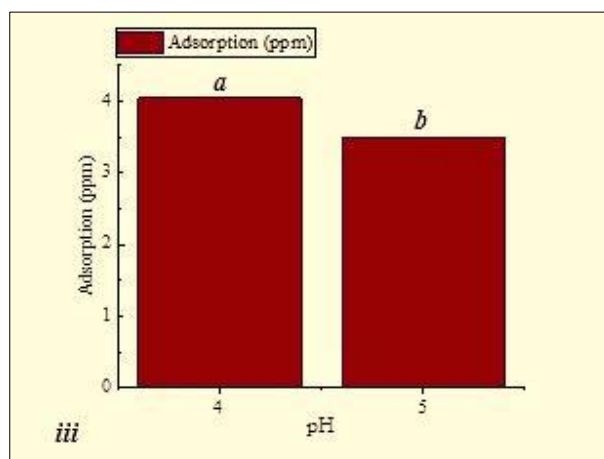
In this study the quantities of Mg²⁺ released from the mineral structures of the solutions has been investigated. Also, changes in pH values in the final solutions were investigated at the end of experiments. Atomic adsorption was used to measure magnesium in solutions and this determined that the quantities of released Mg²⁺ from natural minerals structures at both experimental pH solutions were more than all heated samples and on the other hand, released magnesium from the minerals structure heated at 150 °C were more than the released quantities of this element in 250 °C heated samples. These results show the occurrence cation exchange between experimental heavy metals with the structural Mg²⁺. In fact, both the adsorption and ionic

exchange of Cd (II), Zn (II), and Co (II) with magnesium ions, during the isothermal experiments occurred. The reason for quantity differences in magnesium released from natural and heat pre-treated sepiolites structures was due to an increase in surface area and the adsorption ability of heated samples than natural ones.



i: The effects of initial solution pH values on cadmium adsorption.

ii: The effects of initial solution pH values on cobalt adsorption.

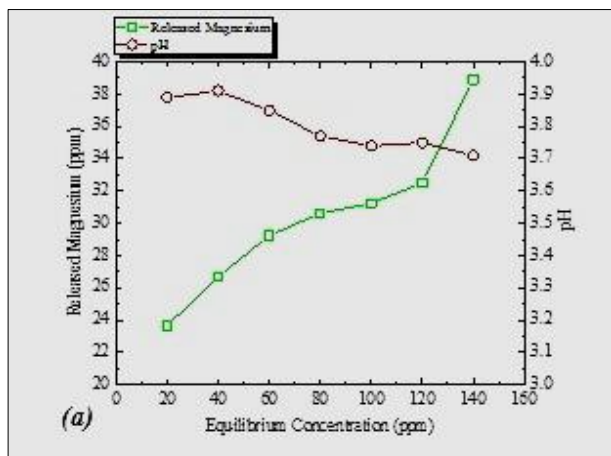


iii: The effects of initial solution pH values on zinc adsorption.

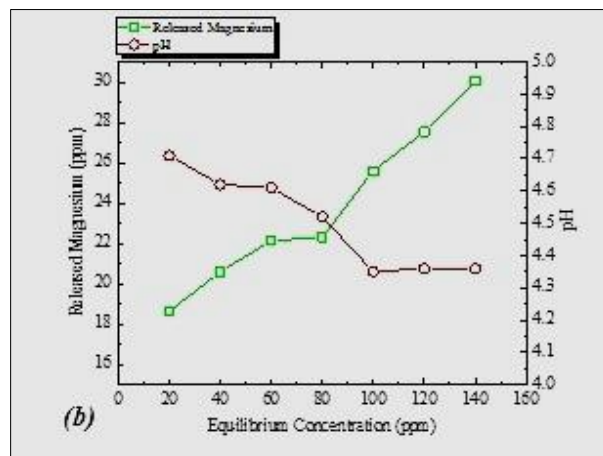
Fig. 5. Effects of solution pH value on heavy metal adsorption by sepiolite.

The magnesium at the edges of the octahedral sheets in the 250 °C heated sepiolite samples was due to zeolitic water and increasing surface area was less in 150 °C heated and the natural samples. Therefore, the magnesium in edges of octahedral sheets in the natural sepiolite, were more exchanged with cationic ions in experimental solutions. (Lazarević et al., 2007) reported that acid treatment on sepiolite caused leaching in the magnesium ions from octahedral sheets and exchanged with lead ions in solutions. (Miura et al., 2012) reported that fibrous morphology of sepiolite degradation was observed for all thermal, acid and base treatments. After these kinds of treatments, the smaller fibers were found in samples treated in high-temperature or long-term treatment and acid treatment caused an increase in surface area of sepiolite (Miura et al., 2012). Changes in pH values and the leached magnesium via equilibrium of heavy metal concentrations are shown in Fig. 6 (a to f). As seen in these figures, at low equilibrium concentrations, acidic content of experimental solutions, freedom effect of solute ions and high adsorption ability of sepiolite lead to release high quantity of Mg^{2+} to the solutions and these ions take contractions with (OH^-) in solutions which decreased the pH values in the final solutions. Then increasing heavy metal concentrations in the initial solutions, decreasing pH values and increasing the released magnesium to the solutions occurred smoothly. When the increasing of heavy metal concentrations continued

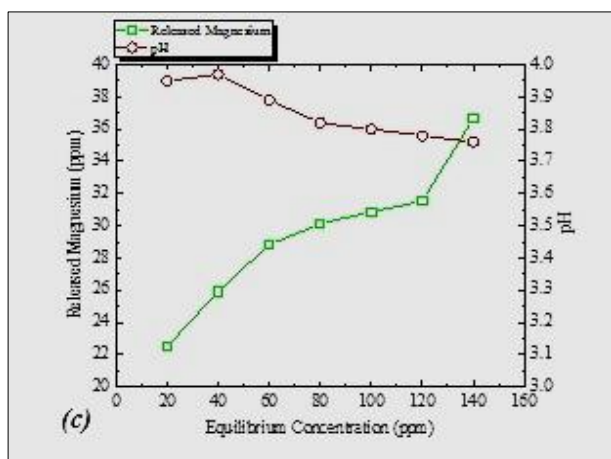
due to the exchangeable effect of magnesium with cationic metals, releasing Mg^{2+} to the solutions and decreasing pH values were observed in high ratio than in low equilibrium concentration.



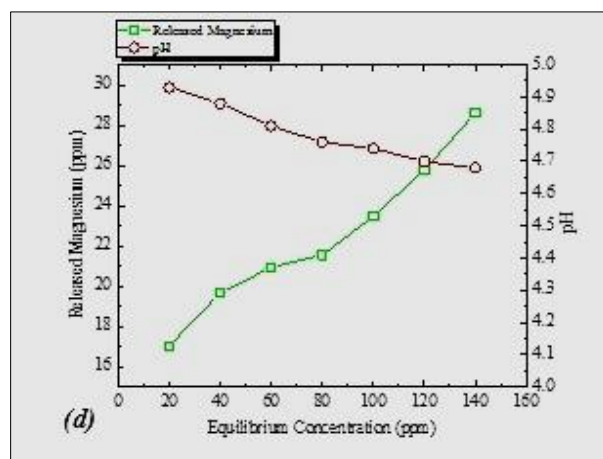
(a): Natural sepiolite in solution with pH 4 values.



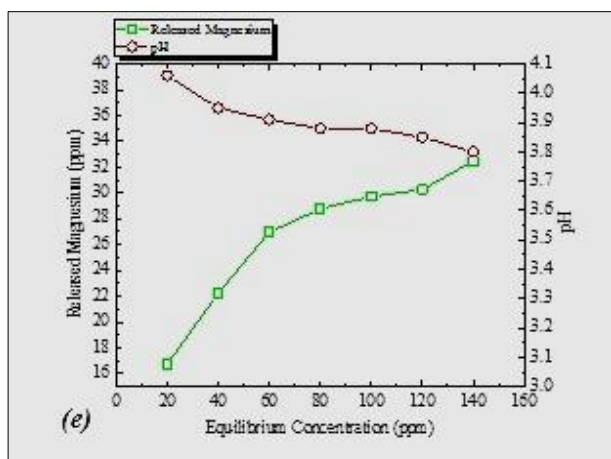
(b): Natural sepiolite in solution with pH 5 values.



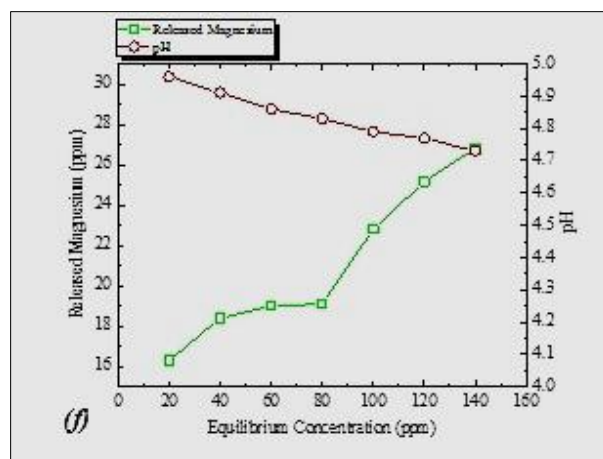
(c): heat pretreated sepiolite at 150 °C in solution with pH 4 values.



(d): heat pretreated sepiolite at 150 °C in solution with pH 5 values.



(e): Heat pretreated sepiolite at 250 °C in solution with pH 4 values.



(f): Heat pretreated sepiolite at 250 °C in solution with pH 5 values.

Fig. 6. Magnesium released from natural and heat pretreated sepiolite at initial solution pH values of 4 and 5, and changes in final pH values of the solutions.

3.6. Statistical analysis

In this investigation, the effects of heat pre-treatment, pollutant concentrations and solutions pH value in adsorption isotherm tests of heavy metals by sepiolite minerals were significant at 1% level. Analysis of variance showed that the adsorption isotherms in the interaction experiments: (heat pre-treatment and concentration), (heat pretreatment and pH), (concentration and pH) and interactions (heat-pretreatment, concentration and pH) for Cd (II), Zn (II), and Co (II) was significant at the 1% level. Statistical and variance analyses of resulted data were done by using of SAS-9.1 and MSTHATC. Furthermore the SPSS-16.2 program was used to compare statistical results. After all, it was determined that both SPSS-16.2 (SAS-9.1) and MSTHATC showed the same results in analysis of data. In Table 3, analysis effects of variance in different treatments on adsorption isotherms (Qt) by using SAS-9.1 and MSTHATC are shown. Although the statistical analysis of adsorption the isotherms of cadmium, cobalt and zinc with SPSS-16.2 are shown in Tables 4, 5, and 6 respectively. As seen, comparisons between results of Table 3 and Tables 4, 5, and 6, the significance, df and other analytical results were similar for each of the experimental heavy metals and for different treatments.

Table 3. The effects of analysis of variance in different treatments on adsorption isotherms (Qt).

Source	df	Mean squares			F value		
		Cd	Co	Zn	Cd	Co	Zn
T	2	6.93**	4.41**	8.52**	3533.71**	3109.27**	4572.35**
Ci	6	15.77**	289.59**	70.81**	8040.80**	203994**	38002.7**
pH	1	7.59**	238.93**	46.98**	3871.18**	168311**	25215.3**
T * Ci	12	0.46**	0.73**	0.78**	238.64**	517.19**	423.10**
T * pH	2	0.07**	2.10**	0.06**	37.56**	1484.52**	33.26**
Ci * pH	6	0.75**	33.38**	7.82**	383.27**	23519.6**	4199.38**
T * Ci * pH	12	0.02**	0.36**	0.02**	13.35**	26.24**	14.65**
Error	84	0.001	0.001	0.001			
Coefficient of variation		1.36	0.50	0.83	1.36	0.50	0.83

* Significance at 5% level and ** significance at 1% level. T: Heat pre-treatment, Ci: Initial concentration.

Table 4. The effects of analysis of variance in different treatments on adsorption isotherms of Cd.

Dependent variable: Qi						
Source	Type III sum of squares	df	Mean square	F value	Significance	
Corrected model	126.704 ^a	41	3.090	1.575E3	0.000	
Intercept	1332.032	1	1332.032	6.789E5	0.000	
T	13.866	2	6.933	3.534E3	0.000	
Ci	94.652	6	15.775	8.041E3	0.000	
pH	7.595	1	7.595	3.871E3	0.000	
T * Ci	5.618	12	0.468	238.637	0.000	
Ci * pH	4.512	6	0.752	383.268	0.000	
T * pH	0.147	2	0.074	37.563	0.000	
T * Ci * pH	0.314	12	0.026	13.348	0.000	
Error	0.165	84	0.002			
Total	1458.900	126				
Corrected total	126.868	125				

a. R Squared =0 .999 (Adjusted R Squared = 0.998)

Table 5. The effects of analysis of variance in different treatments on adsorption isotherms of Co.

Dependent Variable: Q_t					
Source	Type III sum of squares	df	Mean square	F value	Significance
Corrected model	2203.099 ^a	41	53.734	3.785E4	0.000
Intercept	6946.958	1	6946.958	4.894E6	0.000
T	8.828	2	4.414	3.109E3	0.000
Ci	1737.545	6	289.591	2.040E5	0.000
pH	238.936	1	238.936	1.683E5	0.000
T * Ci	8.810	12	0.734	517.188	0.000
Ci * pH	200.332	6	33.389	2.352E4	0.000
T * pH	4.215	2	2.107	1.485E3	0.000
T * Ci * pH	4.433	12	0.369	260.241	0.000
Error	0.119	84	0.001		
Total	9150.176	126			
Corrected total	2203.218	125			

a. R Squared = 1.000 (Adjusted R Squared = 1.000).

Table 6. The effects of analysis of variance in different treatments on adsorption isotherms of Zn.

Dependent Variable: Q_t					
Source	Type iii sum of squares	df	Mean square	F value	Significance
Corrected model	545.802 ^a	41	13.312	7.144E3	0.000
Intercept	3407.625	1	3407.625	1.829E6	0.000
T	17.041	2	8.521	4.572E3	0.000
Ci	424.906	6	70.818	3.800E4	0.000
pH	46.989	1	46.989	2.522E4	0.000
T * Ci	9.461	12	0.788	423.097	0.000
Ci * pH	46.953	6	7.826	4.199E3	0.000
T * pH	0.124	2	0.062	33.263	0.000
T * Ci * pH	0.328	12	0.027	14.652	0.000
Error	0.157	84	0.002		
Total	3953.583	126			
Corrected Total	545.959	125			

a. R Squared = 1.000 (Adjusted R Squared = 1.000).

Conclusion

Results of this investigation showed that sepiolite mineral at different heat pre-treatments and different solution concentrations showed variable adsorption behavior for each heavy metal ions which existed in suspensions. According to the explanations above, natural sepiolite has a lesser ability for adsorbing heavy metals than the two other mineral samples heated at 150 and 250 °C. Also, the quantity of adsorbed experimental heavy metals by the heated mineral samples increased with increasing concentrations of these cationic forms in solution suspensions, there as on being the loss of zeolitic water from the mineral structure which then enhances the minerals' surface area. Results of the study showed that the adsorption quantities of cobalt ions at all solution concentrations, heat treatments and both experimental pH values were more than zinc and cadmium adsorptions. Furthermore, it was observed that structural magnesium leached to the solutions which determined that some of the adsorbed heavy metals were exchanged by magnesium in the octahedral sheets of sepiolite, while the released magnesium from natural mineral was more than in the heated ones.

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