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COMPARING ADSORPTION ACTIVITY of RAW SEPIOLITE AND CTAB MODIFIED SEPIOLITE: KINETIC AND ADSORPTION STUDY FOR REMOVAL of Hg^{+2}

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Abstract

In our study adsorption of Hg^{+2} ions from water solutions on Sepiolite (Sep) and Modified Sepiolite (MSep) with cationic surfactants namely cetyl trimethyl ammonium bromide CTAB was investigated. Different parameters were used to investigate such as contact time, pH and adsorbent dosage. The adsorption capacity of MSep and Sep was examined. Both particles were characterized with FTIR spectrum. According to the our results the equilibrium adsorption data corresponded to the Langmuir isotherm and q_{max} was 54,7 mg/g and 104,1 mg/g for Sep and MSep respectively. Kinetic parameters showed that pseudo-second-order adsorption kinetic model was the best model than the pseudo-first-order. MSep is more active adsorbent than Sep and it can be the best alternative adsorbent for removing of heavy metal from industrial waste water. In addition MSep can be used as adsorbent for removal of nonpolar toxic organic molecules, because sepiolite surface can be converted from hydrophilic form to hydrophobic form by CTAB resulting in increased the adsorption capacity.

Keywords: Mercury Removal, Clay, sepiolite

Introduction

Environmental contamination pollution caused by hydrocarbons is unavoidable problem due to the increasing demand for oil and oil products (Khan *et al.*, 2013). In addition heavy metal pollution is growing problem in many countries. It comes from domestic and industrial waste (Chand *et al.*, 2015). Heavy metal ions for example Pb^{+2}, Cd^{+2}, Hg^{+2} are discharged into the environment from industrial sector such as ceramics, pulp, lead smelters (Karthik *et al.*, 2015). Mercury adversely affect human and ecosystem health and it may be natural or anthropogenic origin (Santos *et al.*, 2015). If this metal entered the human body from food chain or water pollution, it caused serious illness, like cancer, central nervous system, damage to brain (Xiong *et al.*, 2011). Mercury is a global pollutant when it's physical and chemical properties is considering and even it is the potential hazard even at low concentrations due to its accumulation in food chain. The best-known characteristic of mercury is its strong absorption into biological tissue (Arshadi, 2015). Membrane separation, ion exchange and adsorption methods have been investigated to remove Hg^{+2} ions. But some of them, because of some concern, like low mechanical and thermal stability have inhibited applications while heavy metals are removed from industrial water (Bidhendi *et al.*, 2014). In the past decade, adsorption process is the most commonly performed method to remove Hg^{+2} ions (Gan *et al.*, 2012) and for this, researchers use the most known adsorbents such as activated carbons, inorganic oxide, natural adsorbents, clays and clay minerals. Natural adsorbents have been used in a wide range for removal of toxic ions from waters and probably it is optimal alternative adsorbents for studies in these days (Abollino *et al.*, 2008). ''Raw sepiolite is a hydrous magnesium silicate. Its molecular formula is $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4.8H_2O$ for the half-unit cell. The morphologies of sepiolite are fibrous morphology and intra crystalline channels. This clay is used in many industrial fields due to its molecular sized channels and large specific surface area (more 200 m^2/g)'' (Karaoğlu *et al.*, 2013**)**. Sepiolite surface is hydrophilic because they are very strong hydrated inorganic cations in the presence of water (Yılmaz *et al.*, 2007). The adsorption capacity of sepiolite is enhanced by modification with cationic surfactant because sepiolite surface is negative charges (Li et al., 1998). In addition to, clay minerals can be grafted to a hydrophobic surface by inlet the long chain molecules into the interlayer of surface (Wang and Wang; 2008).

In this study, CTAB modified sepiolite was synthesized. Some parameters like pH, adsorbent dosage, and contact time were investigated for sorption of Hg^{+2} ions from water solution using Sep and MSep at the same time kinetic and isotherm model were also investigated.

Materials and Methods

Materials

Sepiolit was found in Turkey and it was used without further purification. CTAB were purchased from Aldrich. Other chemicals were analytical purity and were prepared with deionized water.

Preparation of CTAB modified Sepiolite

The modified Sepiolite was synthesied by following procedure. 2g CTAB was dissolved at 60°C in 150 ml water acidified to pH=3 with 0,1N HCl solution. Above this solution was added into the Sepiolite (5 g). The mixture was stirred at 60°C for 24 h and then filtered and washed several times with deionized water. Modified Sepiolite (MSep) was dried in oven at 60°C for 18 h.

Adsorption Studies

Adsorption studies were conducted 50 ml of Hg^{+2} solution of 300ppm. The effect of initial concentration was carried out 0,1g adsorbent, solution pH 4 and 50 ml of Hg^{+2} solutions 50ppm, 100ppm, 150ppm, 300ppm respectively. After adsorption, amount of Hg^{+2} q_e (mg/g), was calculated at below equation.

$$q_e = \frac{(Co - C_e).V}{m} \tag{1}$$

Where q_e is the adsorption capacity (in mg Hg^{+2} per g of adsorbent), C_o is the initial concentration of Hg^{+2} (mgL^{-1}), C_e is the equilibrium concentration of Hg^{+2}(mgL^{-1}), V is the volume of Hg^{+2} solution and m is the amount of adsorbent. Removal percentage of Hg^{+2} given below equation

$$\mathrm{Re}\,moval.(\%) = \frac{(\mathrm{C_o} - \mathrm{C_e})}{\mathrm{C_o}} x100 \tag{2}$$

We determined the amount of Hg^{+2} in residue solutions after adsorption with flame atomic absorption spectroscopy (FAAS) with GBC Avanta model and it was monitored at 253.7 nm wavelength.

Results and Discussion

Characterization of Sep and MSep

FTIR analysis

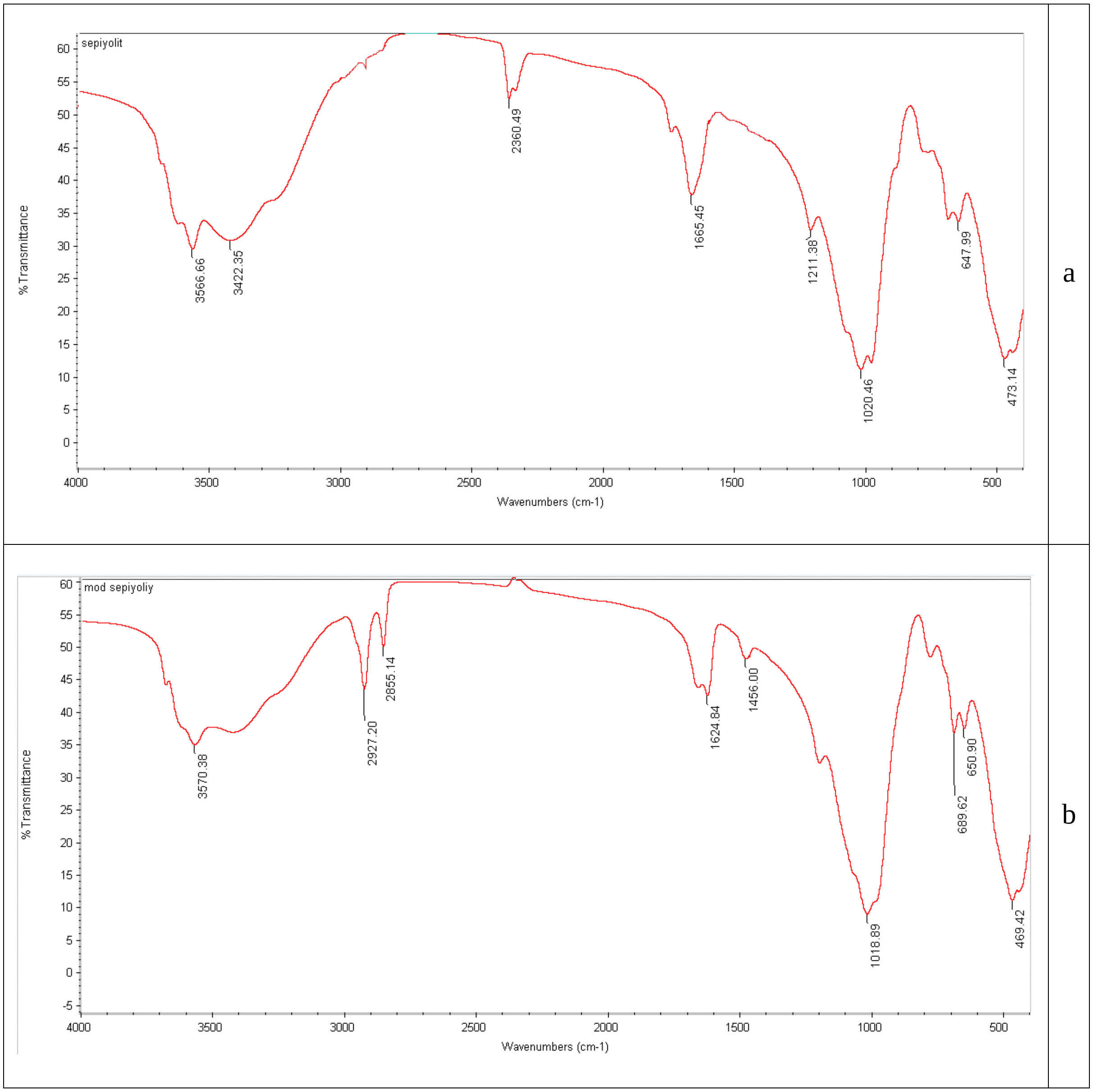

Fig.1. FTIR spectra of Sep(a) and MSep(b)

Figure 1 shows us FTIR spectrum of Sep and MSep. According to FTIR spectrum, the bands at 3566 cm^{-1}, 3422 cm^{-1} for Sep (Fig 1a) and band at 3570 cm^{-1} (Fig 1b) for MSep belong to the asymmetric and symmetric vibration of water (Ongen *et al.*, 2012). The band at 1211 cm^{-1} is attributed to the lattice vibrations of Si-O. The bands at 1018 cm^{-1} and 1020 cm^{-1} are Si-

O-Si vibrations. Si-O-Mg octahedral-tetrahedral linkage for MSep and Sep is 469 cm^{-1} and 473 cm^{-1} respectively. The bands at 650 cm^{-1} and at 647 cm^{-1} are Mg-OH bending vibration (Ongen *et al.,* 2012 and Eren *et al.,* 2010).

We observed the new absorption peaks at 2927 cm^{-1} and 2855 cm^{-1} for MSep (Fig.1b). These values belong to asymmetric and symmetric vibrations of C-H groups. The band at 1456 cm^{-1} is attributed to C-N bending vibrations (Fig 1b). This value means that there are chemical bonds between sepiolite layer and CTAB by intercalation (Gan *et al.,* 2012 and Huang *et al,.* 2007).

Effect of pH

Solution pH is an important parameter in the adsorption process. The adsorption efficiency of Sep and MSep were carried out at 300 mg/L of initial Hg^{+2} concentration and pH range 2,0-10,0. The effect of pH on the adsorption of Hg^{+2} was shown in Fig 2. It was clear that MSep was the better effective for removal of Hg^{+2} than Sep at nearly at the same pH. We observed that removal of Hg^{+2} ions was increased at pH range 2-6 after that removal percentage decreased significantly as the pH increased from 6 to 10. In general the removal of Hg^{+2} depends on to the formation of mercury hydroxide species for example $Hg(OH)^+$ or $Hg(OH)_2$ at pH above 6 (Arshadi;2010). This result can be based on to the occupying of the active sites by hydrogen ions and at low pH it restricted Hg^{+2} ions because of repulsive force (Karaoğlu *et al.,* 2013). When the pH level increased, there was probably for the positive metal ions to be attracted to negatively charge adsorbent surface resulting in the increase of adsorption capacity. In this case weak Wan Der Walls forces appeared which hydrogen bonds between MSep and OH^- ions in solution medium. These OH^- ions chelated with Hg^{+2} ions resulting in increase on sorption capacity. In addition, excessive OH^- ions used in adjusting the pH was more available around the active site of the adsorbent therefor the percentage of the Hg^{+2} on adsorbent surface decreased (Gutti *et al*., 2015).

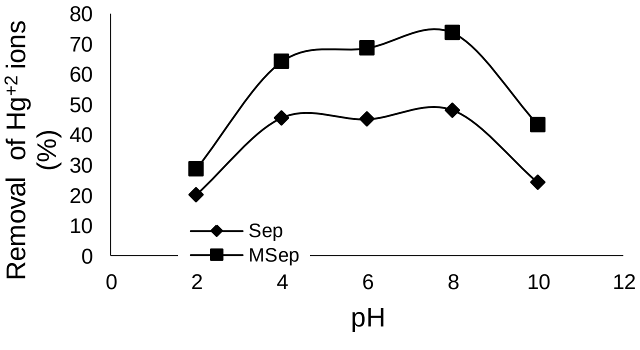

Figure 2: Influence of pH on Hg^{+2} adsorption by Sep and MSep (Hg^{+2}concentration 300 mg/L;contact time 60 min;adsorbent dosage 0,1g/50ml)

Effect of Adsorbent Dosage

The effect of amount of adsorbent on removal of Hg^{+2} ions is shown in Fig. 3. When the amount of adsorbent increased the sorption percentage of Hg^{+2} increased for Sep from 29.28 to 36,42% and for MSep from 39.21 to 73.17%. This can be attributed to the presence of alkyl chains in the interlayer or on the surface of Sep. After adding of 0.1 g adsorbent, there was no change for adsorption of Hg^{+2} ions onto Sep and Msep surface. The maximum adsorption dosage was found at about 0.1 g adsorbent. At low adsorbent dosage the dispersion stability of MSep and Sep is better which can speed up the oncoming of Hg^{+2} ions to adsorbent surface. In contrast, at higher adsorbent dosage the collision can increase between the adsorbent particles in this case it revealed particle aggregation causing a decrease in the total surface area that affect the adsorption capacity of the adsorbent. Thus 0.1 g adsorbent dosage was used for all sorption experimental (Arshadi, 2012).

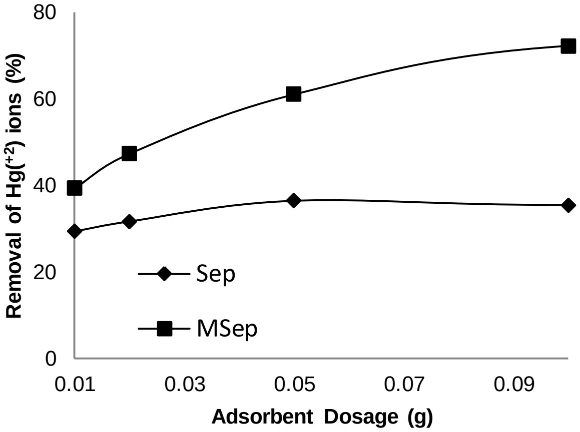

Figure 3: Influence of adsorbent dosage on Hg^{+2} adsorption by Sep and MSep (Hg^{+2}concentration 300 mg/L; contact time 60 min; pH:6,15)

Effect of Contact Time

Fig 4 shows the contact time effect on adsorption process. We observed that the adsorption process reached to equilibrium at the end of 30 minutes, after this time there was no change in the removal of Hg^{+2} ions for Sep and MSep. We observed that adsorption rates initially rapid and then slowed. The equilibrium time of Hg^{+2} ions onto Sep and MSep were 30 min and adsorption capacity (q_{max}) was 57.47 mg/g for Sep and 104.1mg/g for MSep respectively.

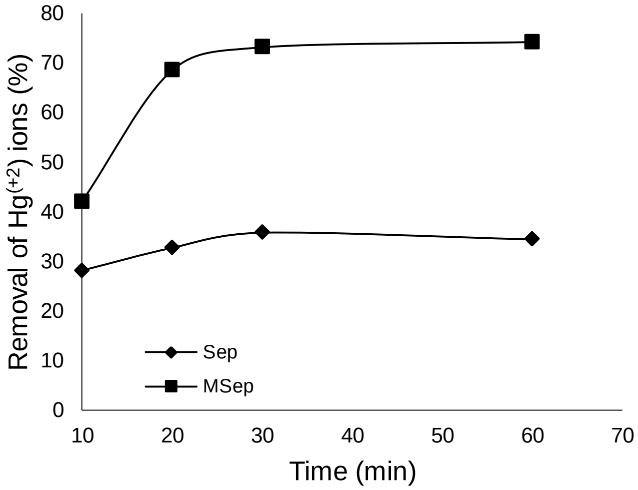

Figure 4: Influence of contact time on Hg^{+2} adsorption by Sep and MSep (Hg^{+2}concentration 300 mg/L; adsorbent dosage 0,1g/50ml; pH:6,1)

Sorption mechanism

Modified natural adsorbents because of nontoxic and highly adsorption capacity play an important role for removal of heavy metals. In this study, we hypothesized that the sorption mechanism of MSep was attributed to the hydrogen bonds which were created between CTAB and Sepiolite surface because of OH, O and H_2O atoms, ions or molecules in the Sepiolite structure. More hydrogen bonds caused more branched OH and H_2O molecules that caused chelating onto Sepiolite surface. In this case Hg^{+2} ions can chelate with H_2O as a $[Hg(H_2O)_4]^{2+}$ or with OH as a $HgOH^+$ in adsorption medium resulting in adsorption capacity.

Sorption isotherms

In order to explain, the adsorption mechanisms of Sep and MSep on removal of Hg^{+2} ions were evaluated using Langmuir and Freundlich models (Langmuir;1916). Initial concentrations of Hg^{+2} ions were varied (50-300mg/L) and adsorbent dosage 0.1g, contact time 60 min.

The Langmuir equation refers to the monolayer adsorption of adsorbate onto adsorbent surface. The bonding to adsorption sites may be physical or chemical but it must be significantly strong to prevent replacement of adsorbed molecules along the surface. This model also presumes that adsorbed molecules in neighboring regions do not react to each other (Erdem *et al.*, 2009). Langmuir adsorption model can be expressed as follows

$$q_e = \frac{q_m K C_e}{1 + K C_e} \qquad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \qquad (4)$$

Where q_e is the equilibrium of Hg^{+2} concentration on adsorbent (mgg^{-1}), K the affinity constant (Lmg^{-1}), q_m the maximum amount of adsorption (mgg^{-1}), and C_e is the solution concentration at equilibrium (mgL^{-1}). q_m and K values can be calculated by plotting C_e/q_e versus C_e. Fig 5 represents the Langmuir isotherm for MSep and Sep and the values of the Langmuir constants q_m, and K and the correlation coefficient R^2 were given. Langmuir isotherm model showed a good agreement correlation both Sep (R^2 0.96) and MSep (R^2 0.99). This expressed that the surface of the Msep was covered by a monolayer of Hg^{+2} ions and adsorption mechanism occurred by chelation between MSep and Hg^{+2}. Langmuir isotherm model is more appropriate when the R^2 values are compared. Table 1 shows the characteristic parameters of sorption process of Hg^{+2} ions on Sep and MSep. The Langmuir adsorption isotherm can be also explained by equilibrium parameters (R_L) as calculated below:

$$R_L = \frac{1}{1 + KCo} \qquad (5)$$

Where K is the Langmuir constant, C_o is initial concentration of Hg^{+2} ions and R_L is equilibrium parameter. R_L Value supports the Langmuir isotherm and favorable when between 0-1. Our results revealed that R_L values were between 0-1 both MSep and Sep and it favoured adsorption process (Table 1).

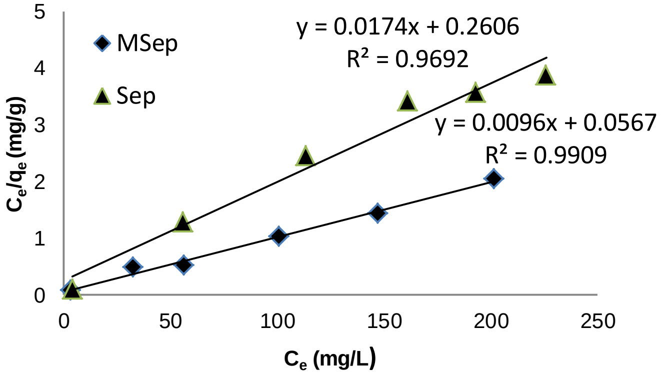

Fig 5: Langmuir adsorption isotherms for the adsorption of Hg^{+2} ions onto the Sep and MSep

Table1. The characteristic parameters of sorption process of Hg^{+2} ions on Sep and MSep

Adsorbents	Langmuir isotherm				Freundlich isotherm
	q_m (mg/g)	K(L/mg)	R^2	R_L	R^2
Sep	57,47	0,067	0,96	0,05	0,83
Msep	104,16	0,169	0,99	0,02	0,31

Adsorption Kinetics

The expression of adsorption kinetics described the solute adsorption relation. We examined Pseudo-first-order and Pseudo-second-order kinetic model. For this, two Hg^{+2} solution of 50mg/L was prepared 0.1 g Sep and 0.1 g MSep were added respectively then mixed 60 min and Hg^{+2} concentration was calculated according to equation 5 every 10 minutes.

The pseudo-first-order equation can be formulated as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2,303} \tag{6}$$

Where q_e and q_t are the adsorption capacity at equilibrium and at the contact time t(mg/g) and k_1 pseudo-first-order rate constant (1/min). Where correlation coefficient (R^2) of Sep and MSep were found 0.61 and 0.83 respectively.

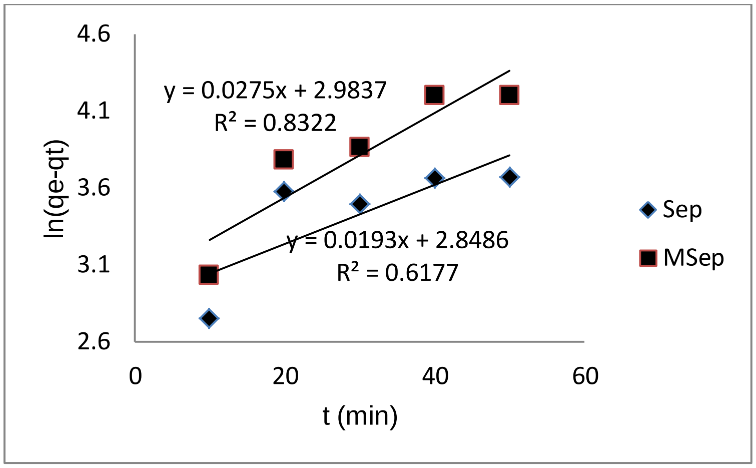

Fig.6. The pseudo-first-order kinetics for the adsorption Hg^{+2}

Pseudo-second-order model indicates chemisorption of the adsorbate. This model can be expressed as;

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

When we examined the Table 2; the correlation coefficients of pseudo-second-order kinetic model was 0.99 and 1 for Sep and MSep respectively.

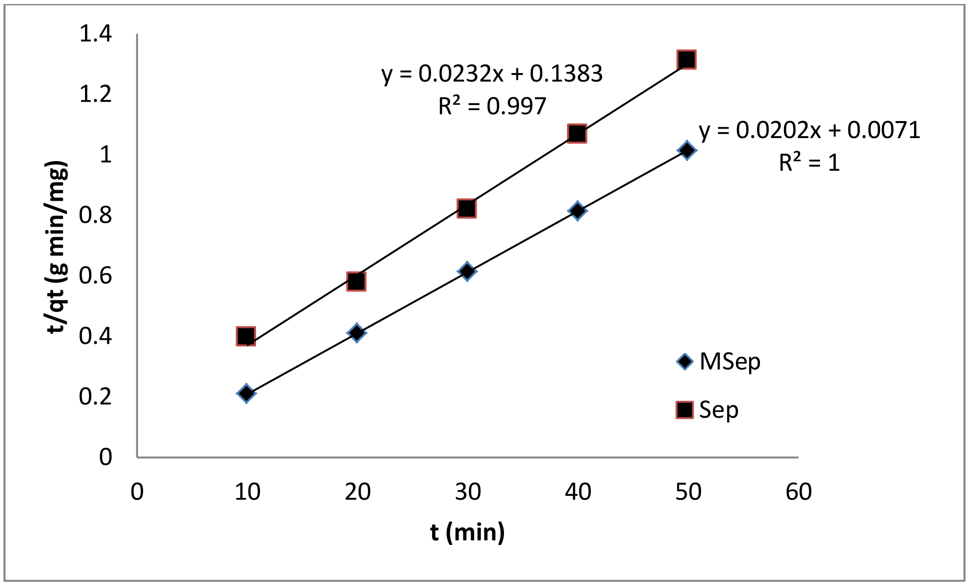

Fig.7. The pseudo-second-order kinetics for the adsorption Hg^{+2}

Table 2: The kinetic parameter constants for the adsorption of Hg^{+2} on Sep and MSep

			Pseudo-first-order			Pseudo-second-order		
	C_o (mg/L)	*qe* (exp)	k_1 (1/min)	*qe* (cal) (mg/g)	R^2	k_2 (1/min)	*qe* (cal) (mg/g)	R^2
Sep	50	38,5	0,0193	17,3	0,61	0,0039	43,1	0,99
Msep	50	49,2	0,0275	19,7	0,83	0,0575	49,5	1

According to our results Langmuir isotherm was closer to 1 as compared to the Freunlich isotherm. When we compared the calculated values of q_{eq} for both models it was found that the q_{eq} obtained by pseudo-second-order model was very close to the experimental value for Msep. In addition R^2 values indicate that this model was more appropriate than pseudo-first-order model. From these results it can be expressed that the adsorption process of Hg^{+2} onto Sep and MSep followed pseudo-second-order kinetic model. Based on this model the rate limiting step can be chemical sorption process either by sharing of electrons or by exchanging of electrons between MSep, Sep and Hg^{+2} ions (Gan *et al.*, 2012). In addition chemical modification of Sepiolite can be used different contaminants for example organic substances having a hydrophobic or hydrophilic surface because the surface of sepiolite can be converted from hydrophobic to hydrophilic or vice versa.

Conclusion

In this study, a new material CTAB modified sepiolite (Msep) was prepared and its adsorption capacity was investigated comparing with raw sepiolite. Our results showed that Msep has an effective material for sorption of Hg^{+2} ions. It can be used as an adsorbent in waste water treatment. The experimental results were suitable to the Langmuir isotherm and pseudo-second-order kinetic model. In addition MSep can be used as adsorbent for removal of nonpolar toxic organic molecules, because sepiolite surface can be converted from hydrophilic form to hydrophobic form by CTAB.

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