

Removal of Hexavalent Chromium from Aqueous Solution using Magnetic Sepiolite Nano-composite as an Adsorbent

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ABSTRACT

Magnetic nano-composite (MNCs) samples were prepared by co-precipitation method and characterized by XRD, SEM, nitrogen adsorption–desorption. The prepared MNCs evaluated for removal of hexavalent chromium Cr(VI) from its solutions. The adsorption experiments performed by batch method and the effects of solution pH, Cr(VI) concentration and contact time were studied. The adsorption capacity of the MNCs was affected significantly by pH of the Cr(VI) solution and based on the degree of magnetite. The results showed that the adsorption of Cr(VI) decreased with the increase of pH. The highest removal efficiency was achieved with the composite having the highest content of magnetite. The optimum contact time for maximum adsorption capacity was determined to be 480 min. The obtained adsorption data analyzed by the Langmuir, Freundlich and Sips isotherm models. The equilibrium data fitted well to the Sips model at a solution pH value of 2.0. The kinetic study showed the adsorption process followed pseudo-second-order kinetic. The prepared nano-composite materials can be used to remove Cr(VI) from water and industrial wastewater.

Keywords: Magnetic nano-composites, sepiolite, chromium (VI), adsorption, modeling and kinetics.

1 Introduction

Hexavalent chromium Cr(VI) is a highly toxic element release from various industrial applications such as plating of metals, magnetic tapes, pigments, leather tanning, wood preserving, paints, electrical and electronics' equipment manufactures and catalyst production [1]. In natural waters, Cr(VI) is also presented due to erosion of chromium deposits found in rocks and soils. The concentration of chromium in drinking-water should be less than 1 $\mu\text{g}/\text{dm}^3$ [2]. Repeated exposure to hexavalent chromium compounds can cause damage to the nose, inflammation of the lungs, allergic reactions in the skin, kidney damage and cancer of the lung [3].

Several treatment technologies have been developed to remove chromium from water and wastewater [4]. The common methods include chemical precipitation, ion exchange, membrane separation, ultrafiltration, flotation, electrocoagulation, solvent extraction, reduction, reverse osmosis, dialysis/electrodialysis, adsorption/filtration, flocculation, chelation [3]. Among these methods, adsorption is considered as a promising process for the removal of different ions such as Cr(VI) due to its low cost and high ions selectivity.

In recent years, magnetic nano-composites (MNCs) displayed considerable attention as adsorbent materials to remove undesired chemical components from industrial wastewaters and the magnetic materials can be separated conveniently from aqueous solutions. Several MNC materials have been investigated for removing of chemical pollutants from wastewater such as magnetite/sepiolite for removal of atrazine, Co^{2+} and Cd^{2+} [5,6,7]. Other types of MNCs for example, magnetite/zeolite-X [8], diatomite-supported/magnetite nanoparticles [9], montmorillonite-supported magnetite nanoparticles [10], magnetic activated carbon composites [11] and magnetic chitosan composites [12] for the removal of Cr(VI). Sepiolite is a hydrated magnesium silicate with the ideal formula of $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$ which characterized by its fibrous morphology and intracrystalline channels [13]. Due to high specific surface area and nano-sized channels of the magnetite sepiolite particles, it can be dispersed into its structure [7].

The aim of this study was to investigate the adsorption of Cr(VI) ions on pure magnetite, and magnetite/sepiolite nano-composites. The effects of solution pH, Cr(VI) concentration and contact time on the adsorption capacity of Cr(VI) are evaluated. The achieved experimental results of Cr(VI) removal were analyzed by adsorption isotherms and kinetics models.

2 Experimental Procedure

2.1 Materials and Methods

The natural sepiolite (SEP) obtained from Andrići (Serbia). The reagent grade chemicals, such as NaOH, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ were used without any further purification.

2.2 Preparation of Sepiolite-magnetite Nano-composites and Pure Magnetite

The sepiolite-magnetite nano-composite (MSEP) and pure magnetite (Fe_3O_4) were prepared by the co-precipitation method according to procedures described in previous study [7]. The details are: magnetic sepiolite composites were synthesized by adding 5 g of sepiolite into 1 M NaOH solution and the mixture stirred for 30 min under nitrogen atmosphere. Exactly 4.51 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.306 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with Fe(II)/Fe(III) molar ratio of 1:2 were dissolved in 100 cm^3 of deoxygenated deionized water by bubbling N_2 gas then kept at 60 °C in water bath under nitrogen atmosphere. The sepiolite and NaOH suspension was added into the Fe(II)/Fe(III) solution and the mixture was aged for 2 h at 60 °C. The produced solid materials separated and washed three times with deoxygenated deionized water and then with ethanol. The powder dried in vacuum oven at 60 °C until constant mass. Three types of MSEP (MSEP 1, MSEP 2 and MSEP 3) are synthesized using different weights of both $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (see Table 1).

Pure magnetite particles were synthesized by dissolving 4.51 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.306 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 cm^3 of deoxygenated deionized water by N_2 gas. The solution was kept under nitrogen atmosphere in a water bath at 60 °C followed by drop wise adding of a desired concentration of NaOH solution (25 %). The formed black mixture aged at 60 °C for 2 h. The obtained solid material was separated and washed several times with deionized and deoxygenated water and then with ethanol and dried at 60 °C under vacuum until constant weight.

Table 1: Masses of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ salts for the composites preparation and assessment of the magnetization

Sample	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (g)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (g)	Magnetization
MSEP 1	2.31	4.51	Yes
MSEP 2	3.46	6.77	
MSEP 3	1.15	2.25	

2.3 Characterization of the Adsorbents

X-ray diffraction (XRD) analysis of the samples was carried out by ITAL STRUCTURES APD2000 diffractometer using Cu KR radiation in the 2θ angle range from 3° to 50° with a 0.02° step. The specific surface area (S_{BET}), volume of the mesopores and micropores and the pore size distribution of the samples were calculated from the nitrogen adsorption–desorption isotherms using a Micrometrics ASAP 2020 apparatus. Furthermore, the morphology of the samples was examined by a Tescan MIRA3 field emission gun scanning electron microscope (FESEM).

2.4 Adsorption Experiments

Adsorption of Cr(VI) ions from water by the produced pure magnetite and sepiolite-magnetite nano-composites materials is investigated by batch method at room temperature (25 ± 1 °C). The general method used for this study is described as follows: 20 cm^3 of chromium solution was placed in 50 cm^3 reagent bottle and pH of solution adjusted to a desired value. A constant amount of adsorbent (0.02 g) was added to the solution and shaken for certain contact time. The pH of solutions before and after adsorption measured by using a pH meter (Ino Lab WTW series pH 720) and the initial and final concentrations of Cr(VI) ions were determined by using atomic absorption spectrometer (AAS) (Perkin Elmer 730). The effects of different pH value (2.0 to 5.0), ion concentration (10, 20, 30, 40, 50 mg/dm^3) and contact time (0.5 to 24 h) on Cr(VI) ions adsorption capacity are investigated. The equilibrium adsorption capacity (q_e) was calculated by using the following equation [13]:

$$q_e = \frac{C_i - C_e}{m} \cdot V \quad (1)$$

where C_i and C_e are the initial and the equilibrium concentrations of Cr(VI) (mg/dm^3), respectively, m is the mass of the adsorbent (g), and V is the volume of the solution (dm^3).

The quantity of Cr(VI) ions adsorbed after period of time t (q_t) was calculated according to the following equation [13]:

$$q_t = \frac{C_i - C_t}{m} \cdot V \quad (2)$$

where C_i is the concentration of Cr(VI) after period of time t .

2.5 Adsorption Isotherms

The adsorption isotherms play an important role in understanding the mechanism of adsorption process (adsorbate-adsorbent interaction) as well as to estimate the maximum capacity of an adsorbent. Langmuir, Freundlich and Sips isotherm models has been selected to analyze the obtained results from initial chromate concentration at pH 2.0 ± 0.1 . The adsorption isotherms constants were determined by non-linear regression analysis using the OriginPro 8.5. The experimental adsorption kinetic data was fitted with pseudo first-order and pseudo-second-order models.

2.5.1 Langmuir model

Langmuir adsorption isotherm assumed that the adsorption takes place at specific localized sites (homogeneous sites) on the surface of adsorbent and adsorption is complete when a monolayer is formed [14]. The nonlinear form Langmuir isotherm is described by the following equation [14]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir constant related to the energy of adsorption (dm^3/mg).

2.5.2 Freundlich model

In Freundlich model, the adsorbate form multilayer on surface of the adsorbent with non-uniform distribution of adsorption energies over the heterogeneous surface of adsorbent [15], which may include chemisorption if active sites are strong followed by physisorption [16]. Freundlich isotherm model is expressed by the following equation:

$$q_e = K_f C_e^{1/n} \quad (4)$$

where K_f is the Freundlich constant related to the adsorption capacity ($\text{mg}^{(1-1/n)} \text{dm}^{3/n}/\text{g}$) and n is the dimensionless adsorption intensity parameter.

2.5.3 Sips model

Sips isotherm is a combined form of Langmuir and Freundlich models [17]. When C_e approaches at low value, the Sips isotherm effectively reduces to Freundlich, which can be employed to describe the system's heterogeneity, while at high C_e it predicts the Langmuir monolayer adsorption characteristic and it implies a homogeneous adsorption process. The Sips isotherm model is described by the following mathematical equation:

$$q_e = \frac{q_m K_a \cdot (C_e^{n_s})}{1 + K_a \cdot (C_e^{n_s})} \quad (5)$$

where K_a is the Sips equilibrium constant $(\text{dm}^3/\text{mg})^{n_s}$ and n_s is the index of heterogeneity.

2.6 Kinetics Study

The effect of contact time on adsorption of Cr(VI) on MSEP 2 adsorbent were studied by changing the time from 0.5 to 24 h using solutions of 40 mg/dm³ concentration at pH 2.0±0.1. Pseudo-first order and pseudo-second order models are widely used to examine the adsorption kinetics data to describing the adsorption mechanism [18,19]. The pseudo-first-order and pseudo-second-order models were fitted to the kinetics of Cr(VI) ions adsorbed onto MSEP 2 data. The linearized mathematical pseudo 1st order model is expressed by the following equation [18]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

where q_e is adsorption capacity at equilibrium in mg/g, q_t is the adsorption capacity at time t in mg/g and k_1 is the first order rate constant (min^{-1}). By plotting $\log(q_e - q_t)$ versus t , a straight line should be obtained with a slope of $-k_1$ and y-intercept of $\log q_e$. The adsorption is more inclined towards physisorption if the pseudo 1st order model best fits the adsorption kinetic data. The pseudo-second-order kinetic equation is given by the subsequent equation [19]:

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

where: k_2 is the rate constant of the pseudo second order model in unit of $\text{g}/(\text{mg} \cdot \text{min})$. If the experimental data fits to pseudo 2nd order model then the adsorption's mechanism is chemisorption controlled.

3 Results and Discussion

The produced adsorbent composites are characterized by XRD patterns, SEM images and textural parameters of MSEP 2 and MSEP 3. In our previous reported work [7], the XRD patterns of SEP and Fe₃O₄ are reported. That reported data is used in this work for the comparison. The XRD patterns of the MSEP 2 and MSEP 3 composite samples are shown in Figure 1. Diffraction characteristic peaks of SEP were seen in these samples and the main diffraction peak of Fe₃O₄ is observed at 2θ of $\sim 35.5^\circ$ partially overlapped with the sepiolite peak at $2\theta \sim 35^\circ$ [7]. However, taking into account that the most intensive magnetite peak is hardly noticeable in the pattern of the MSEP 3 sample, probably because of the low quantity of magnetite in the sample. The sample with higher content of magnetite (MSEP 2) showed a wide peak which indicated the presence of small crystallites as a result of the formation of high number of nuclei at high concentration of Fe(II) and Fe(III).

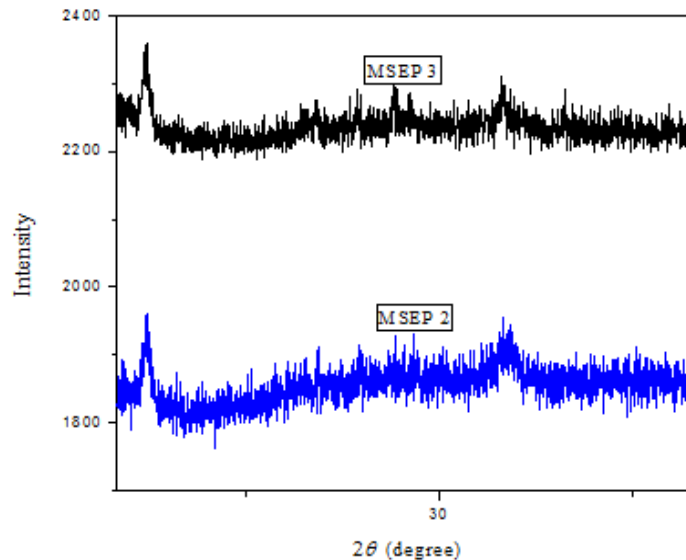


Figure 1: The XRD patterns of MSEP 2 and MSEP 3 composites.

The SEM images of the samples MSEP 2 and MSEP 3 are presented in Figure 2. Both MSEP 2 (Figure 2a) and MSEP 3 (Figure 2b) composite samples showed similar surface morphologies to the surface morphology of the sample MSEP 1 as reported in our previous work [7]. The SEM images of the samples are clearly showed the single and aggregates of magnetic particles along with the sepiolite fibers. Furthermore, the samples MSEP 2 and MSEP 3 had different content of magnetite but the differences in morphologies were insignificant (Figures 2 a and b).

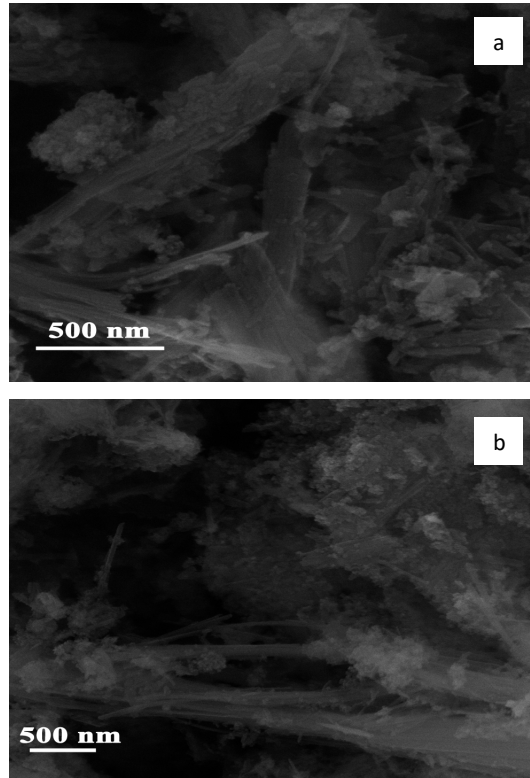


Figure 2: SEM images of (a) MSEP 2 and (b) MSEP 3.

The textural parameters of both MSEP 2 and MSEP 3 composites are shown in Table 2 while textural parameters of Fe_3O_4 and SEP are reported previously [7]. It can be seen from the Table 2, that the values of the specific surface area of the composites are between the values of pure compounds of Fe_3O_4 and SEP. The mesopore volume of the composites is slightly higher than SEP and the micropore volume is lower than of SEP. This may be due to the coating of SEP surfaces by Fe_3O_4 which obstructs some of the main micropore channels of SEP and the formation of new mesopores between Fe_3O_4 particles in the composites. The specific surface area, volume of mesopores and volume of micropores of MSEP 3 composite are slightly higher than MSEP 2 composite. It is obvious that the higher quantity of iron salts lead to lower S_{BET} , V_{micro} and V_{meso} , due to the higher magnetite content and aggregation.

Table 2: The textural parameters of MSEP 2 and MSEP 3 composite samples.

Sample	Specific Surface Area S_{BET} (m^2/g)	Micropore Volume V_{micro} (cm^3/g)	Mesopore Volume V_{meso} (cm^3/g)	Maximum Pore Diameter D_{max} (nm)	Mean Pore Diameter D_{mean} (nm)
MSEP 2	182.6	0.059	0.354	3.7	7.9
MSEP 3	215.1	0.081	0.498	4.0	10.6

3.1 Effect of Solution pH

The pH plays major role in the adsorption process because it affects the solution chemistry of adsorbate and surface charge of adsorbent. The influence of initial pH of solution on the adsorption capacity of Cr(VI) from different solution concentrations for the sample MSEP 1 was studied and the results presented in Figure 3. The results showed that the adsorption capacity sharply decreases when the increase of pH value above pH 2. Therefore, pH 2.0 has been considered as the optimum pH for further Cr(VI) adsorption experiments. General, Cr(VI) is present in solution as anions, CrO_4^{2-} , $HCrO_4^-$ or $Cr_2O_7^{2-}$, depending on its concentration and solution pH. In acidic solution, $HCrO_4^-$ exists at low concentrations, and $Cr_2O_7^{2-}$ and $HCrO_7^-$ exist in solutions of high concentration, whereas CrO_4^{2-} becomes dominant species at $pH \geq 7$. For wide range of pH values, the surface charge of natural sepiolite is negative, therefore adsorption of Cr(VI) anions on sepiolite was negligible [20]. The decrease in the adsorption capacity with pH value could be attributed to the increasing in the negative charges of the adsorbent surface [9,10, 21].

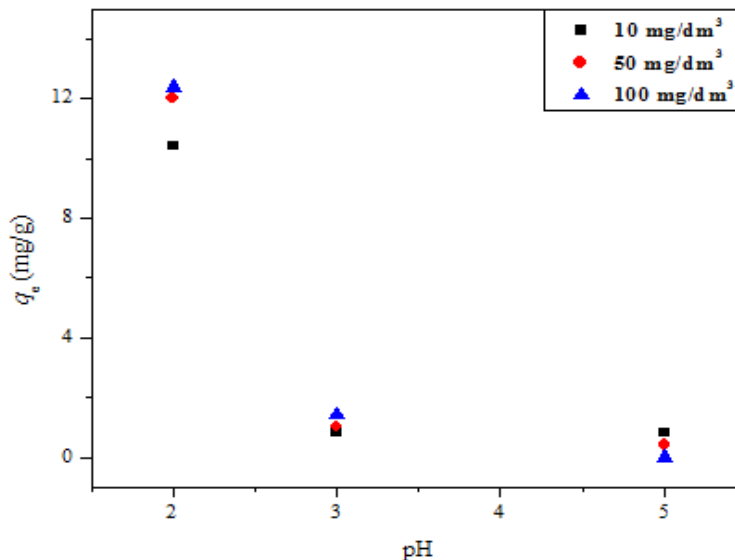


Figure 3: The effect of the initial pH on Cr(VI) adsorption by sample MSEP 1 for the initial Cr(VI) concentrations of 10, 50 and 100 mg/dm³.

3.2 Effect of Cr(VI) Concentration

Figure 4 presents the relationship between the maximum adsorption capacity of Cr(VI) ions on Fe₃O₄, MSEP 1, MSEP 2 and MSEP 3 and the concentration of Cr(VI) solution. It is very clear that the maximum adsorption capacities of the different adsorbents have similar trends with different values. The maximum capacity of Cr(VI) ions (17.3 mg/g) on pure magnetite is higher than the other adsorbent materials (MNCs). Furthermore, the sample with higher content of magnetite MSEP 2 displays highest capacity of 15.6 mg/g than MSEP 1 (11.8 mg/g) and lower content of magnetite MSEP 3 (9.0 mg/g). It is obvious that the content of magnetite is the major factor controlled the adsorption capacity due to the limit capacity of the sepiolite [20]. The adsorption capacity of the sample MSEP 2 is less than the pure magnetite by about 10%, while the theoretical content of magnetite in this sample was 36.5 weight percentages. It

can be concluded that the presence of sepiolite in composites has improved the adsorption properties of the magnetite.

According to the literature [22], Cr(VI) can be adsorbed onto magnetite and magnetite composites by formation of inner and outer sphere complexes. In addition, the possible mechanism is also the reduction of Cr(VI) by magnetite to Cr(III) ions, which can be adsorbed on the surface of the adsorbent or precipitate as $\text{Cr}(\text{OH})_3$ or Cr_2O_3 . The precipitation is more likely at higher pH values, but reduction of Cr(VI) at higher pH values is difficult to take place. It can be supposed that the main mechanism of chromate adsorption on magnetite and magnetite composites is the electrostatic interactions of chromate ions and protonated surface functional groups (formation of outer-sphere complexes).

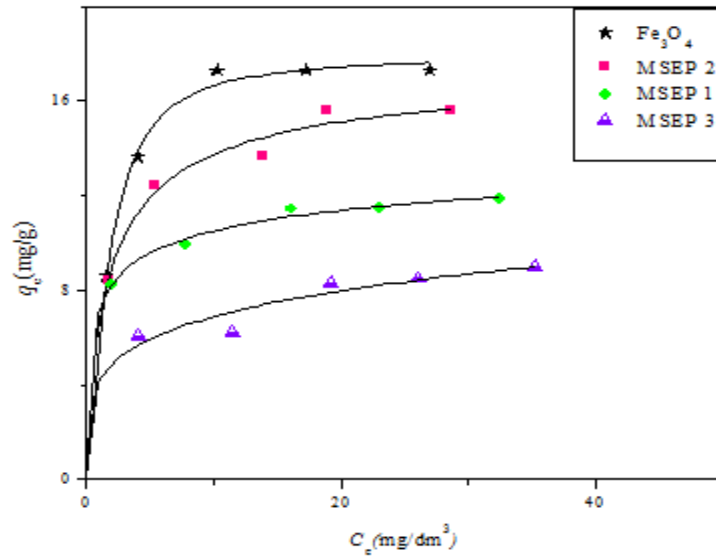


Figure 4: Adsorption isotherms for Cr(VI) onto Fe_3O_4 and the MNCs (adsorbent dosage = 0.02 g/20 cm³, pH 2.0±0.1).

3.3 Adsorption Isotherm Study

The adsorption isotherms constants are summarized in Table 3. The correlation coefficients (R^2) of the fitted data of the studied isotherm models proved that the Sips model showed the highest R^2 (0.998) and is the best model to explain the adsorption behavior of Cr(VI) for all the samples. Both Langmuir and Freundlich isotherm models were also fitted the results well. Sips isotherm is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm while at high concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. According to the suitability of Sips model for the chromium adsorption, it can be supposed that the ions adsorbed on the heterogeneous surface of the adsorbents until the monolayer is formed.

The maximum adsorption capacities (q_m) and K_L parameter calculated by Langmuir model are found in the following order MSEP 1 > MSEP 2 > Fe₃O₄ > MSEP 3. The high values of K_L due to strong interactions between Cr(VI) ions and surface of the samples [17]. The Freundlich constant K_f is indicator of the adsorption capacity, while n is a adsorption intensity parameter (the strength of adsorption bonds is high when n is high) [17]. Moreover, the calculated maximum adsorption capacities by Sips model were slightly higher than that obtained by Langmuir model. Sips constant (K_a) is indicator of strength bond between the Cr(VI) ions and active sites on the surface of samples [17]. The decrease in K_a values is in the order of MSEP 1 > MSEP 2 > Fe₃O₄ > MSEP 3. The value of n_s in Sips model for a homogeneous material is 1 but it is less than one for heterogeneous materials [13]. Finally, the correlation coefficient (R^2) of isotherm models has very high value for all samples (near to the unity as shown in Table 3), which indicated that theoretical values (q_m) are in good agreement with experimental values ($q_{e,exp}$).

Table 3: Langmuir, Freundlich and Sips isotherms constants and coefficients of correlation (R^2) for the adsorption of Cr(VI) onto the Fe₃O₄ and the magnetic composites at pH 2.0 ± 0.1

Sample	Adsorption model									
	Langmuir			Freundlich			Sips			
	q_m (mg/g)	K_L (dm ³ /mg)	R^2	K_f (mg ^(1-1/n) dm ^{3/n} /g)	$1/n$	R^2	q_m (mg/g)	K_a (dm ³ /mg) ⁿ	n_s	R^2
MSEP 1	11.91	1.087	0.994	7.668	0.131	0.997	12.43	0.827	0.359	0.998
MSEP 2	16.31	0.608	0.992	8.209	0.203	0.987	17.79	0.621	0.738	0.994
MSEP 3	9.26	0.364	0.963	4.237	0.211	0.981	9.83	0.022	0.219	0.981
Fe ₃ O ₄	17.82	0.579	0.993	9.503	0.206	0.958	17.96	0.481	1.419	0.997

3.4 Adsorption Kinetics Study

To study the effect of contact time on adsorption capacity of Cr(VI) ions, the sample with the highest adsorption capacity has been selected (MSEP 2). The adsorption capacity as a function of contact time is presented in Figure 5. The adsorption process required relative long time to reach the equilibrium. The optimum contact time for maximum adsorption capacity was determined to be about 480 min in which the chromium ions formed outer-sphere complexes and concentrated near the charged surface with weak bonds. All steps of adsorption process which are external film diffusion, internal particle diffusion and adsorption step need long time to be completed. The overall rate of adsorption is controlled by the slowest step, which is film diffusion or pore diffusion.

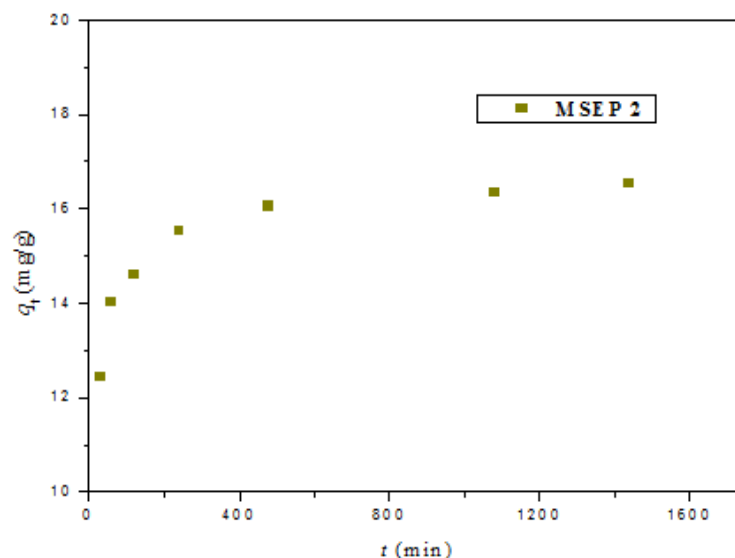


Figure 5: The effects of adsorption time on the adsorbed quantity of Cr(VI) at $pHi = 2.0 \pm 0.1$ onto MSEP 2, (Cr(VI) concentration was 40 mg/dm^3).

In order to evaluate the adsorption kinetics of Cr(VI) on MSEP 2, the conventional kinetic models, pseudo-first and pseudo-second order models, were applied to analyze the experimental data. The adsorption kinetics constants, obtained by linear fitting and correlation coefficients (R^2) are summarized in Table 4. The correlation coefficients suggest that the adsorption kinetic data was fitted much better to pseudo-second order rate equation than by pseudo-first order equation. The R^2 value for the pseudo-first order model is 0.858 while for pseudo-second model is close to 1. Moreover, the value of equilibrium adsorption capacity (q_e) of 16.66 mg/g calculated by pseudo-second mode was close to the experimental maximum capacity (16.53 mg/g). These results illustrated that the rate-limiting step in Cr(VI) is a chemisorption which involve valency forces through sharing or exchanging of electrons between adsorbent and adsorbate.

Table 4: The kinetic parameters and correlation coefficients for the adsorption of Cr(VI) onto the MSEP 2 composite.

Adsorbent	Pseudo-first order model			Pseudo-second order model		
	k_1 (min^{-1})	q_e (mg/g)	R^2	q_e (mg/g)	k_2 (g/mg·min)	R^2
MSEP 2	$2.30 \cdot 10^{-3}$	1.53	0.858	16.66	0.074	0.999

4 Conclusions

In this study, natural sepiolite (SEP) was used to synthesize the magnetic nano-composites (MNCs) for the removal of Cr(VI) ions from solution. The adsorption capacity of the sepiolite for Cr(VI) was very low and magnetite sepiolite improved the Cr(VI) adsorption capacity. Adsorption capacity of composites decreased when pH of the solution increased. The optimum pH value of the Cr(VI) solution for the maximum adsorption of Cr(VI) onto MNCs, was 2.0 under the experimental conditions. The magnetic nano-composite sample (MSEP 2) showed the highest adsorption capacity among other prepared MNCs samples. The optimum contact time for maximum adsorption capacity was 480 min. Adsorption isotherm models study of Cr(VI) onto the prepared nano-composites showed the best fitted data with the Sips model and suggested the adsorption onto all adsorbents occurred via chemisorption mechanisms. Pseudo-second order model has given the good fitting of the data and suggested the rate-limiting step mechanism.

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