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Application of modified bentonite using sulfuric acid for the removal of hexavalent chromium from aqueous solutions

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Abstract

Background: Environmental contamination by chromium (Cr) has become an important issue due to its adverse effects on human health and environment. This study was done to evaluate the application of modified bentonite using sulfuric acid as an adsorbent in the removal of hexavalent Cr from aqueous solution.

Methods: Adsorbent features were determined using x-ray diffraction (XRD), fourier transformed infrared spectroscopy (FTIR) and scanning electron microscope (SEM) techniques. Thereafter, the effect of pH, contact time, adsorbent dosage and different concentrations of Cr was investigated. The experimental data was fitness in terms of kinetic and equilibrium adsorption processes.

Results: The maximum capacity (Qm) of Cr(VI) according to Langmuir model was obtained at 4.21 mg/g. The experimental data properly obeyed the Longmuir and pseudo-second-order models. The highest percentage of Cr(VI) adsorption was observed at pH = 3 and the process after 60 minutes reached the equilibrium state.

Conclusion: In Langmuir expression, the dimensionless constant separation term (RL) values for the adsorption of Cr onto the modified bentonite was in the range of 0-1, indicating that the adsorption is a favorable process and the modified bentonite has good potential in removing hexavalent Cr using sulfuric acid.

Keywords: Modified bentonite, Sulfuric acid, Adsorption, Hexavalent chromium, Aqueous solution

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Introduction

Environmental contamination by chromium (Cr) has become an important issue due to the potential hazard it poses to living organisms (1). The oxidation state of Cr includes 2 forms: Cr(VI) and Cr (III); of which Cr(VI) form is toxic to environment, due to its carcinogenicity, toxicity and high aqueous solubility (2,3). The maximum allowable discharge of Cr in aquatic environments is 0.05 mg/dm^3, whereas the total Cr should be less than 2.0 mg/dm^3 (4). Cr(VI) in concentrations more than 50 has irreversible effects on kidney and liver, and can cause skin and lung cancer, as well as allergic problems (5). For these reasons, researchers have used several methods, such as ion exchange, ultrafiltration, reverse osmosis, electrodialysis, chemical precipitation, evaporation, solvent extraction, membrane processes coagulation, flocculation, biological treatment and chemical oxidation to remove or reduce Cr (6).

The use of these methods are limited because of high cost, the need for chemical matters, waste disposal, low efficiency, high demand for energy, etc. (7-9). While, adsorption method is widely used to remove heavy metals, due to its simple design and easy operation, proper efficiency and low cost (10). In previous studies, different adsorbents have been used to remove Cr, including both organic and inorganic materials, such as granular activated carbon (GAC), powder activated carbon (PAC), mineral cartridge, biological and agricultural waste, hydrochloric acid (HCL), modified bentonite and natural bentonite (11-16). Despite the higher maximum adsorption capacity of PAC (49.6 mg/g), this adsorbent has some problems, such as its reusability and higher production costs (17). Thus, using adsorbents that have high efficiency in removing contaminants, in addition to having some benefits, such as inexpensiveness, availability, reusability and easy modification, can play important role in this field.

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The study of Slimane et al (18) showed that the bentonite has cost-effective recovery, and reusability without appreciable loss of performance. One way to establish the increase of mineral adsorbents, such as bentonite treated by acids, is using sulfuric acid. Results of Salem and Karimi (19) and Alemdaroglu et al (20) indicated that the treatment of bentonite using sulfuric acid changed its chemical properties, increased its specific surface area and surface acidity of the adsorbent. Since sulfuric acid is more effective than more acids such as HCL acid due to changes in the chemical properties of the adsorbent (21) and changes in the physicochemical properties of bentonite, such as crystallinity of its smectite, chemical composition, cation exchange capacity, adsorption capacity and selectivity, porosity, surface area, surface acidity, and catalytic power by acid modification (22), this study was undertaken to evaluate the application of modified bentonite using sulfuric acid in the removal of hexavalent Cr in aqueous solution.

Methods

Adsorbent preparation

At the beginning, bentonite granules, obtained from Zanjan region of Iran, were washed with distilled water, dried in an oven at 103°C for 6 hours and crushed and sieved through a 50 mesh sieve. Then, the adsorbent modification was conducted by adding 50 g of the bentonite to 500 mL of sulfuric acid solution (3M) and refluxing at 110°C under atmospheric pressure in a round bottomed flask equipped with a reflux condenser for 4 hours. The resulting bentonite suspension was then rapidly quenched by adding 500 mL ice cold water. The content was filtered, repeatedly washed with distilled water to remove any unspent acid and dried in an oven, calcined at 500°C for 1 hour (23). Finally, the prepared adsorbent was stored in an air tight container for future use.

Adsorbate

A stock solution of Cr(VI) (1000 mg/L) was prepared by dissolving certain amount of potassium dichromate ($K_2Cr_2O_7$) in deionized water and the considered concentrations (20-100 mg/L) were prepared by diluting the stock solution. The residual concentration of Cr(VI) was measured using a UV–VIS spectrophotometer (7400CE CECIL) at 540 nm by diphenylcarbazide method (17).

Characterization of the modified bentonite

The X-ray diffraction (XRD) (model Shimadzu XRD – 6000), fourier transformed infrared spectroscopy (FTIR) (model WQF-510), differential thermal analysis (DTA) and scanning electron microscope (SEM) (model Philips XL30) analysis were used for the characterization of acid treated bentonite. XRD was employed to determine the diffraction pattern of the natural and modified bentonite. SEM technique was used to analyze the surface morphology of the natural and modified bentonite. The functional groups of the modified bentonite were also determined using FTIR.

Batch adsorption experiments

To establish the experiments in batch condition, 100 mL Erlenmeyer flasks containing 20 mg/L Cr(VI) and a certain amounts of the adsorbent were used. All experiments were conducted at a constant rate of 220 rpm at 20±2°C. pH in the range of 3-10 was selected to determine its effect on adsorption efficiency. Herein, the pH of the solutions was adjusted using 0.1M HCL and/or 0.1M NaOH. Optimal contact time was obtained through 0.5 g/L adsorbent, 20 mg/L Cr(VI) and room temperature at optimum pH. The effects of adsorbent dosage and initial concentration of Cr(VI) were examined in the range of 0.1-2 g/L and 20-100 mg/L, respectively. All experiments were performed in triplicate and average values of the data were reported as the final results. The amount of Cr(VI) adsorbed onto the adsorbent was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where C_0 and C_e are the initial and equilibrium concentration of Cr(VI) (mg/L), respectively. V is the volume of the solution (L) and m is the weight of the modified bentonite (g).

Adsorption isotherm

Adsorption isotherm describes the equilibrium of the adsorption material at the surface of adsorbent (i.e., at the surface boundary). In this study, Langmuir and Freundlich isotherm models were used to predict the behavior of Cr(VI) adsorption onto the modified bentonite to production.

Langmuir Isotherm

The Langmuir equation is based on assumptions, which the maximum adsorption occurred due to a saturated mono-layer of adsorbate molecules on the adsorbent surface. Non-linear equation of Langmuir isotherm is as follows (7).

$$q_e = \frac{Q_m b C_e}{1 + b C_e}$$

Where q_e is the amount of adsorbed material at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), b is the affinity parameter or Langmuir constant (L/mg) and Q_m is the maximum adsorption capacity (mg/g).

Freundlich Isotherm

The Freundlich isotherm is based on multilayer adsorption on the heterogeneous surface of the adsorbent containing an unequal amount of energies. It is not limited to a monolayer adsorption, but also it is applied for multilayer adsorption. Non-linear equation of Freundlich isotherm is as follows (7).

$$q_e = K_f C_e^{1/n}$$

where K_f and n are the Freundlich constants related to the adsorption capacity and intensity, respectively.

Kinetics of adsorption

Chemical kinetics deals with the experimental conditions influencing the rate of a chemical reaction. Herein, two kinetic models including the pseudo-first-order and pseudo-second-order were used to analyze the experimental data and model the adsorption process (17).

Pseudo-first-order kinetic model

Non-linear and linear equations of pseudo-first-order kinetic are as follows (7):

$$\frac{dq_t}{d_t} = K_1\left(q_e - q_t\right)$$

$$log(1 - \frac{q_t}{q_e} = -\frac{k_1}{2.302}t$$

Where q_t is the amount of heavy metal adsorbed on the modified bentonite at a constant time (mg/g) and k_1 is the pseudo-first-order constant rate (min^{-1}).

Pseudo-second-order kinetic model

Non-linear and linear equations of pseudo-second-order kinetic are represented as:

$$\frac{dq}{dt} = k\left(q_e - q\right)^2$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$$

Where q_t and q_e are the concentration of heavy metals in t and equilibrium times (mg/g) and K_2 is the constant rate of pseudo-second-order kinetic (g mg^{-1} min^{-1}).

Results

Features of natural and modified bentonite in terms of morphology, size and surface were analyzed using SEM as shown in Figure 1A and 1B, respectively. One reflection was observed in region 2°<2θ<70° for the XRD pattern of the natural and modified bentonite. This corresponds to the 5.76° (2θ) value from which the interlamellar distance was found to be 15.33 A°. For the XRD pattern of the modified bentonite, the formation of a porous structure was observed by the shoulder appearing in region 2°<2θ<8° (Figure 2). The x-ray pattern of the modified bentonite sample indicated a slight shift in the position of d001 peak from 15.33 to 16.98 A, which was accompanied by a decrease in intensity (Table 1). Figure 3 shows the FTIR spectra of the modified bentonite fraction (KBr pellets with 1% bentonite). Figure 4A shows the effect of pH on Cr(VI) adsorption on the modified and natural bentonite. The maximum Cr(VI) removal occurred at acidic pH (Figure 4A). The effect of contact time on Cr(VI) adsorption was conducted under the following condition: 0.5 g/L solution of the adsorbent, optimal pH (pH = 3.0 ± 0.1) and initial concentration of 20 mg/L (Figure 4B). As shown in Figure 4B, Cr(VI) adsorption efficiency was sharply increased up to 45 minutes with increase in contact time, and then gradually reaches the equilibrium state at 60 minutes. Figure 5A and 5B shows the effect of different dosage and initial concentration of the modified and natural bentonite on efficiency removal and adsorption capacity under optimized conditions (pH = 3 and t = 45 minutes). As illustrated in Figure 5A, with increase in adsorbent dosage (modified bentonite) from 0.1 to 2 g/L, the removal efficiency of Cr(VI) increased from 16.85% to 94.8% for initial concentration of 20 mg/L, while the adsorption capacity decreased from 3.37 to 0.95 mg/g. But with increase in the initial concentration from 20 to 100 mg/L, the removal efficiency of Cr(VI) decreased from 73.4% to 32% for 0.6 g/L adsorbent, while the adsorption capacity increased from 2.44 to 5.38 mg/g. Table 2 shows that the calculated value of constants regarding the Langmuir and Freundlich isotherms for Cr(VI) adsorption on

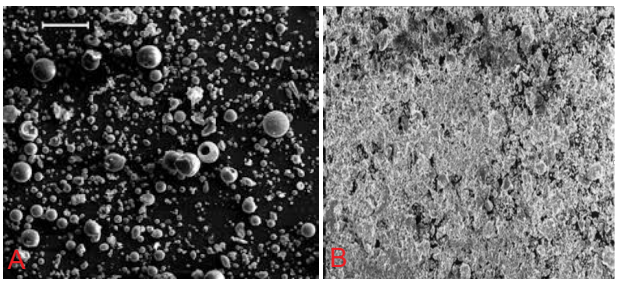

Figure 1. SEM microphotographs (Mag. 200X) of A) natural and B) treated bentonite with 3M sulfuric acid.

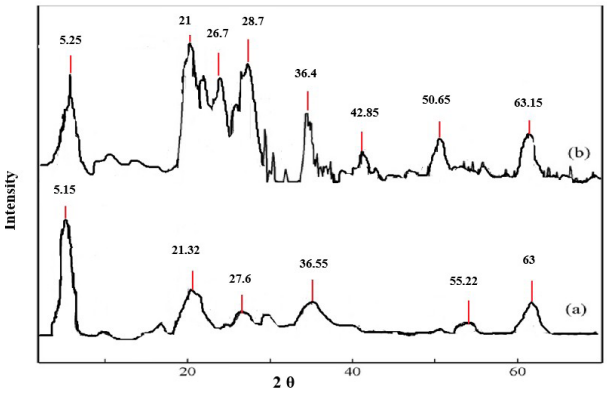

Figure 2. XRD patterns of the A) natural bentonite and B) modified bentonite.

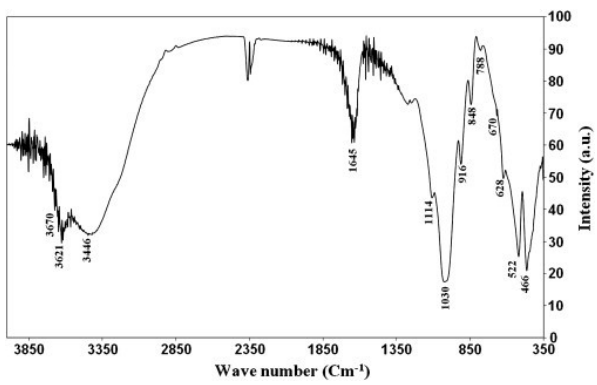

Figure 3. FTIR spectra of the modified bentonite fraction (KBr pellets with 1% bentonite).

Table 1. XRF analyses (chemical analyses) of natural and modified bentonite

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
Natural bentonite (%)	55.7	12.85	4.1	3.27	3.48	6.12	0.45
Modified bentonite (%)	65.33	11.74	3.24	2.96	1.87	2.54	0.38

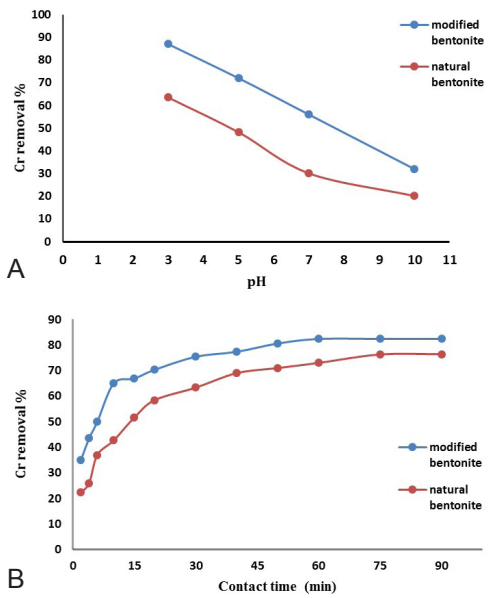

Figure 4. A) Effect of pH and B) contact time on the adsorption of Cr(VI) on the modified and natural bentonite (200 rpm agitation speed, 0.5 g/L adsorbent, 20 mg/L initial adsorbate, and 25 ± 1°C).

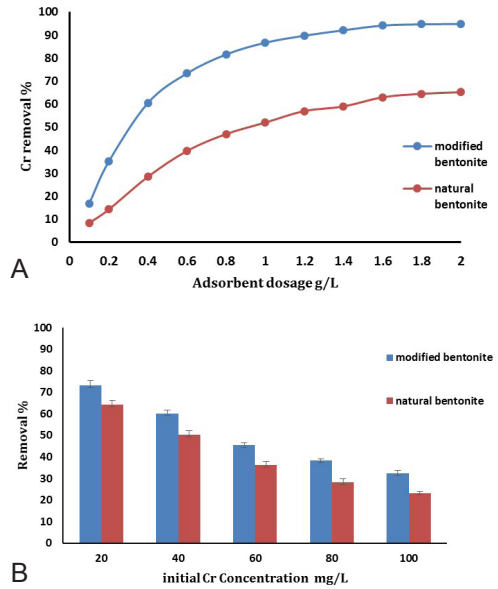

Figure 5. A) Effect of adsorbate dosage and B) initial Cr(VI) concentration on the removal efficiency of Cr(VI) using the modified and natural bentonite (200 rpm agitation speed, pH = 3, contact time = 45 minutes, and 25 ± 1°C).

Table 2. Parameters regarding the adsorption isotherm models for Cr(VI) adsorption on modified bentonite

Isotherm model	Parameters	
Langmuir	q_m (mg/g)	4.22
	K_L (L/mg)	0.286
	R_L	0.148
	R^2	0.992
Freundlich	K_f	10.54
	n	2.15
	R^2	0.974

Table 3. Parameters regarding the adsorption kinetic models of Cr(VI) on modified bentonite

Kinetic model	Parameters	
Pseudo first- order	$q_{e,cal}$ (mg/g)	1.297
	K_1 (min^{-1})	0.0023
	R^2	0.865
Pseudo-second-order	$q_{e,cal}$ (mg/g)	6.53
	K_2 (g/mg) (min^{-1})	0.022
	R^2	0.996

the modified bentonite at 25 ± 1°C. As shown in Table 2, the adsorption of Cr into the modified bentonite can be described by both Freundlich and Langmuir isotherms. But the correlation coefficient (R^2) of isotherms showed that the experimental data best obeyed the Langmuir isotherm model ($R^2 > 0.99$). Table 3 shows the obtained constants values of kinetic models of Cr (VI) adsorption on the modified bentonite with their corresponding regression coefficients. The obtained data indicated that the adsorption kinetics of Cr(VI) onto the modified bentonite is best described by pseudo-second-order model (Figure 6A and 6B). Also, the result showed that there is a significant difference between the modified and natural bentonite efficiency in removing Cr(VI) ($P < 0.05$). Table 4 shows a comparison between the adsorption capacities of various adsorbents for the removal of Cr(VI). The maximum uptake of Cr(VI) per mass unit of modified bentonite was found to be 4.22 mg/g based on the Langmuir model. Moreover, Table 4 shows that the modified bentonite has a proper adsorption capacity compared to many of the adsorbents.

Discussion

Adsorbent characteristics

It is clear that the dimension of particles markedly de-

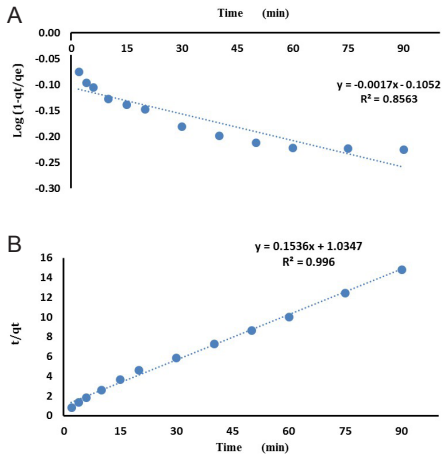

Figure 6. A) The pseudo-first-order and B) pseudo-second-order kinetics for adsorption of Cr(VI) on the modified bentonite.

creases due to modification by acid and cation exchange process (19). Additionally, in comparison with the natural bentonite, a porous and heterogeneous surface was observed for the modified bentonite. Hence, it can be concluded that modification of bentonite with sulfuric acid provides an external surface of porous with more reactive sites, which enhanced the adsorption capacity of bentonite. XRD results showed that the exception of Sio_2 after modification of the adsorbent by acid, other compounds of the adsorbent decreased, and as a result makes it possible to increase the ratio of silica to alumina (24). As result of Panda et al (23) showed that the treatment of kaolin clay by sulfuric acid caused the change of silica to alumina ratio (increased the Si/AL). The XRD pattern of the modified bentonite shows poor crystallinity, broad and less intense peaks as compared to the parent clay mineral due to the presence of layers activated with hydrogen ions, or an irregular stacking of the activated and non-activated layers and thus the structure of the resultant clay becomes amorphous to XRD (25). The FTIR pattern of the modified bentonite shows that some sharp peaks, located between 522 until 1065 cm^{-1} that indicated Si-O-Al bands (26). These sharp peaks are resulting increase of Si to Al ratio after acidic treatment (27). FTIR spectrum of adsorbent showed that peaks at 3632 and 3426 cm^{-1} are O–H stretching and H–O–H hydrogen-binding water. The peak of 1643 cm^{-1} is corresponded to H–O–H deformation (28). Band around 1030 cm^{-1} isdue to Si–O–Si and the peak observed at 783 cm^{-1} is due to Si–O stretching of quartz and silica. Peaks at 514 and 467 cm^{-1} can be attributed to Al–O–Si and Si–O–Si deformation, respectively (26).

Effect of pH

One of the important parameters which could have more effect on adsorption process is the solution pH (29). The maximum Cr(VI) removal occurred at acidic pH; this is attributed to the electrostatic attraction between the Cr(VI) anions and the adsorbent surface positive charges. CrO_7^{-2}, $HCrO_4^-$, $Cr_3O_{10}^{-2}$ and $Cr_4O_{13}^{-2}$ ions are the major species of Cr(VI) at acidic pH conditions, which can be easily adsorbed on the modified bentonite through the electrostatic attraction (3). Similar observation has been reported in the literature (2,17,30). But, decrease in Cr(VI) removal in alkaline conditions, can be due to the negative charges of the bentonite surface in alkali pH that makes electrostatic repulsion between Cr(VI) inions and the adsorbent (26,31). Hence, with increase of pH values, the adsorption efficiency was decreased. This can be explained by the fact that at higher values of pH, Cr is as CrO_4^- form that has repulsion state with SiO_2 which have been formed at high pH. But in lower pH, due to the high hydrated radius, $HCrO_4^-$ is absorbed by Si^{+3} in the most acidic pH (7). Because the pH_{ZPC} of the modified bentonite was obtained at 4.5, therefore, at pH values less than 4.5, the surface is positively charged and caused electrostatic attraction between CrO_7^{-2}, $HCrO_4^-$, $Cr_3O_{10}^{-2}$ and $Cr_4O_{13}^{-2}$ ions species of Cr(VI) and the adsorbent surface that resulted caused more removal of Cr(VI) in the solution (17,30). Herein, the maximum Cr(VI) adsorption (87%) was obtained at pH= 3; this pH was selected as the optimum. This result is in good agreement with previous studies (32).

Table 4. Maximum adsorption capacities (q_m) of Cr(VI) on the modified bentonite and other adsorbents documented in the literature

Adsorbent	Qm (mg/g)	Ref.
Single-walled carbon nanoTubes (SWCNTs)	44.64	(6)
Multi-walled carbon nanotubes (MWCNTs)	25.64	
Powdered scoria	2.828	(7)
Commercial iron powder	17.24	(39)
Potato peelings	3.28	(40)
Coffee polyphenol-formaldehyde/ acetaldehyde resins	19.34	(41)
Chemically activated carbon prepared from locally available waste of bamboo	59.23	(42)
Magnetic nanoparticles stabilized by tea-waste	24.9	(43)
Bentonite	4.68	(44)
Xanthan polymer B82	1.68	(45)
Granular ferric hydroxide	0.788	(46)
Hydrous stannic oxide	3.48	(47)
Neem leaf powder	7.43	(48)
Wheat bran	0.94	(49)
This study	4.22	-

Effect of contact time

Cr(VI) adsorption efficiency was sharply increased up to 45 minutes and then gradually reaches the equilibrium state at 60 minutes; increase in adsorption efficiency by increasing the contact time can be due to the existence of abundant vacant active sites in the adsorbent surface. However, with increase in contact time, the availability of Cr(VI) ions to the active sites on the adsorbent surface would be limited, which makes the adsorption efficiency to reduce (17). Some studies described similar phenomenon for Cr(VI) adsorption on the different adsorbents (33,34). For example, the result of the study of Moradi et al (7) showed that the adsorption of Cr by scoria reached

the equilibrium state at 60 minutes, while Tang et al (35) showed that the adsorption of Cr(VI) on nano-carbonate hydroxyl apatite reached the equilibrium state at 90 min and at different concentrations of Cr(VI).

Effect of adsorbent dosage

The removal efficiency of Cr(VI) increased from 16.85% to 94.8% for the initial concentration of 20 mg/L, while the adsorption capacity decreased from 3.37 to 0.95 mg/g. More availability of active sites on the modified bentonite can cause increase in the adsorption efficiency of Cr(VI) ions (7). Jung et al (8) reported that the removal efficiency of Cr(VI) was raised with increase in the adsorbent dosage. However, a decrease in the adsorption capacity with an increase in the adsorbent dosage is probably due to instauration of the active sites on the adsorbent surface during the adsorption process (17).

Effect of different chromium concentrations

With increase in the initial concentration of Cr(VI) from 20 to 100 mg/L, the removal percentage decreased from 86% to 14% (modified bentonite). Few active sites on the surface of the adsorbent seem to be the main reason for the aforementioned result (2,8). Also, the results showed that increase in the initial concentration of Cr(VI) have a positive impact on the adsorption capacity. This phenomenon may be attributed to the rise in the concentration gradient, which is similar to the findings by Cho et al (29) and Luo et al (2).

Adsorption isotherm

According to the result, adsorption of Cr into the modified bentonite can be described by both Freundlich and Langmuir isotherms; but the correlation coefficient (R^2) of the isotherms showed that the experimental data best obeyed the Langmuir isotherm model ($R^2 > 0.99$). This means that the Langmuir model can be proper to describe the experimental data. Based on this model, it was concluded that the active sites on the modified bentonite surface were distributed in homogeneous form, and monolayer adsorption manner was dominant in the adsorption of Cr(VI) (36). Najafpoor et al (6) reported that the isotherm data of Cr adsorption onto means of carbon nanotubes were obeyed by both Langmuir and Freundlich models, although the Langmuir isotherm was determined to be the most appropriate model.

The R_L value was between 0 and 1, which suggests that Cr(VI) ions have been desirably adsorbed on the modified bentonite (37). Similar results have also been reported by other researchers on the study of Cr(VI) adsorption on pumice and volcanic rock (5,29). The amount of adsorption intensity (1/n) between 0 and1 indicated that Cr adsorption on the used adsorbent was a favorable process (38).

Kinetics of adsorption

The obtained data indicated that the adsorption kinetics of Cr(VI) onto the modified bentonite is best described by pseudo-second-order model, which is in agreement with previous reports on Cr(VI) adsorption (17,50,51). Moreover, the adsorption capacity ($q_{e,cal}$) calculated from the pseudo-second-order model is best suited for the experimental data ($q_{e,exp}$).

Conclusion

Modified bentonite with sulfuric acid was used as an adsorbent to remove Cr(VI) from the aqueous solutions. The results indicated that the modification process has significant effect on the removal efficiency of Cr(VI). Acidic pH = 3 and contact time of 60 minutes were the optimum conditions for the adsorption process. Moreover, results showed that the experimental data are best obeyed by the Langmuir isotherm and pseudo-second-order kinetic models. Because the modified bentonite has appropriate efficiency in the Cr(VI) removal from the aqueous environment, it can be an appropriate alternative for heavy metals treatment from contaminated waters. However, bentonite is less efficient compare other adsorbents, such as activated carbon, but it is a proper alternative for the removal of contaminants in processes that need large quantities of adsorbents, because of its suitable characteristics, such as availability, inexpensive, reusability and proper ability in removing contaminants and by acidic modification of bentonite, its efficiency would be increasedmore, due to increase in the surface area.

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Ethical issues

Ethical issues (including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc.) have been completely observed by the authors.

Competing interests

The authors declared that they have no competing interest.

Authors' contributions

All authors contributed equally and participated to the data acquisition, analysis and interpretation. All authors critically reviewed, refined and approved the manuscript.

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