

Hexavalent Chromium Adsorption onto Fire Clay

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Abstract

Cr (VI) as an extremely soluble and highly toxic ion is present in effluents of industries and imposes severe health-related problems. The current study aimed to provide information on Cr (VI) adsorption potential of fire clay as an abundant, cost-effective and untried material. Batch adsorption trials of Cr (VI) were performed to investigate the effects of pH, contact time, initial metal ion concentration and the adsorbent dosage. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used to evaluate the equilibrium data at 20°C and regression coefficients were derived. Moreover, adsorption kinetics was analyzed using the pseudo-first-order and the pseudo-second-order kinetic models. Maximum chromium removal was found at pH 2.0. A kinetic study yielded an optimum equilibrium time of 90 minutes with an adsorbent dose of 2.5 g/50 mL. Results suggested that the equilibrium adsorption described by the Freundlich model. The kinetic data of the sorption showed that the pseudo second-order equation was the more appropriate. The results of the study indicated that fire clay was not a suitable adsorbent for Cr (IV). Apart from relatively long equilibrium time, the efficiency was not satisfactory. Therefore, searching for better alternative and/or modify such adsorbent is necessary in this area.

Keywords: Fire Clay, Cr (VI) Adsorption, Isotherms, Kinetics

1. Introduction

Mining and metallurgical industries are associated with heavy metals containing wastewaters that are directly or indirectly discharged into the environment. Heavy metals are known to be toxic or carcinogenic (1). Chromium is one of the heavy metals present in effluents produced by the aerospace, electroplating, leather, mining, dyeing, fertilizer and photography industries. Cr (VI) exists as extremely soluble and highly toxic chromate ions (HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$) which can transfer freely in aqueous environments. Persistent exposure to Cr (VI) causes cancer in the digestive tract and lungs and may cause other health problems such as skin dermatitis, bronchitis, perforation of the nasal septum, severe diarrhea and hemorrhage (2). The recommended limit of Cr (VI) in potable water is 0.05 mg/L (3).

Therefore, effluents released by these industries should be removed before disposing to natural drainage systems. Several conventional techniques, including adsorption, electrochemical precipitation and reverse osmosis are used to treat effluents containing metal ions (4).

Nevertheless, these technologies have significant disadvantages, including incomplete or low Cr (VI) removal, high operating costs and investments, high consumptions of reagent and energy and generation of toxic secondary

pollutants, which are difficult to be disposed. Additionally, these processes are found ineffective to remove Cr (VI) at very low concentration in the range of 10 - 100 mg/L (5).

The adsorption technique is preferred to remove heavy metals since it is economically most satisfactory (6). Natural form of materials; for example, clay and geomaterials for adsorption of numerous environmental pollutants, particularly heavy metals attracted great attentions in recent years (7). Presently, several studies on the use of low-cost adsorbents are published. These studies recommend using clays as based barriers at the waste disposal area to protect the migration of hazardous contaminants (8). Clay minerals, due to their large surface area and high cation exchange capacity, are studied for potential applications as environmental remediation agents to remove heavy metals and organic contaminants from water (9).

Fire clay (FC) is a sedimentary material consisting of fine particles of aluminum hydro silicates with a layer structure, which is free from fluxes such as larger quantities of iron, alkaline earth, alkalis and excess silica. Its main constituents are minerals of the kaolin group (10). Therefore, the current study aimed to investigate possibility of FC for Cr (IV) adsorption from aqueous systems.

2. Materials and Methods

2.1. Preparation and Characterization of Fire Clay

The fire clay was procured from geology laboratory of Avicenna University of Hamedan, Iran. The clay then was powdered and sieved through 40 - 60 ASTM mesh, rinsed several times by deionized water to remove any pollutants from its surface and dried in oven at 105°C. Fourier transformed infrared (FTIR) analyses were conducted using a spectrometer (Bruker-VERTEX 70, Germany) at the wavelengths range of 400 - 4000 cm^{-1} using a KBr (Potassium Bromide) pellet technique pressure. X-ray powder diffraction (XRD) analysis was recorded on a Phillips Xpert PRO diffractometer, (Holland) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$).

2.2. Adsorption Experiments

All used chemicals were of analytical grade. Cr (VI) stock solution was prepared by dissolving given potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in deionized water. Required concentrations of chromium were then prepared by diluting the stock.

The effect of some main factors including contact time (5 - 240 minutes), pH (2 - 10), the adsorbent dosage (0.5 - 4.5 g/50 mL), and initial concentration of Cr (VI) (2 - 10 mg/L) were investigated in a batch mood and isotherm and kinetic models were developed according to the experimental data. All experiments were conducted at room temperature. The pH of solutions was adjusted using 1 N NaOH or HNO_3 . To conduct each experiment, a desired concentration of Cr (IV) in fixed volume of 50 mL was exposed to a known amount of the adsorbent in a given pH and in pre-determined equilibrium time (except for isotherm studies in which the time varied from 5 to 240 minutes). At the end of the time, the solution was filtered through 0.45 μm membrane filter and residual Cr (IV) was analyzed at 540 nm by UV/V is spectrophotometer (model 1700, HACH) according to the standard methods of water and wastewater examination (11). For each experiment, a blank sample (i.e., without the adsorbent) was taken and the experiment result was subtracted from its result. The efficiency of removal was then achieved by the Equation 1:

$$R(\%) = \frac{C_0 - C_e}{C_0} \quad (1)$$

Where R was the removal efficiency (%), and C_0 and C_1 were the initial and equilibrium Cr (VI) concentrations (mg/L), respectively.

A standard plot of Cr (VI) concentration versus absorbance value (amount) of solution containing Cr (IV) ions (0.1 - 6 mg/L) was built. According to the Beer law, absorbance is directly proportional to concentration and

therefore the obtained plot should be a straight line. This graph was used to determine the concentrations of the unknown Cr (VI) ions (12).

2.3. Kinetic Studies

Investigation of kinetic models was conducted in FC dosage of 2.5 g/50 mL with initial concentration of chromium 2 - 10 mg/L and optimum pH of 2 at the following time intervals: 5, 30, 60, 90, 120, 150, 180, 210 and 240 minutes. Afterwards, pseudo-first order and pseudo-second-order models were included.

Various parameters including the structural properties of sorbent, nature and concentration of sorbate, and sorbent-sorbate interactions contributed in the kinetics of any sorption process (13). Two mass transfer equations; i.e., pseudo first-order and pseudo-second-order, were used to analyze kinetic data.

The pseudo first-order kinetic model is given as Equation 2:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where the q_e and q_t (mg g^{-1}), the amounts of Cr (VI), adsorbed at equilibrium and at any time (minute), respectively; and the constant k_1 (1/minute), the adsorption rate constant of pseudo-first-order reaction, were determined by the plot of $\log(q_e - q_t)$ against t .

And the pseudo-second-order kinetic model was given as Equation 3:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where, the q_e and q_t were defined above. And the constant K_2 (g/mg min) was the adsorption rate constant of pseudo-second-order adsorption.

2.4. Isotherm Studies

Isotherm studies were carried out at pH = 2, adsorbent dosage of 2.5 g/50 mL, Cr (VI) concentration of 2, 4, 6, 8 and 10 mg/L, and contact time of 90 minutes. The amount of Cr (VI) per unit mass of adsorbent q in (mg/g) was calculated using Equation 4:

$$q = \frac{(C_0 - C_e) V}{M} \quad (4)$$

where M was the mass of the FC used (g) and V the volume of the solution (L).

Three more known isotherm models namely Langmuir, Freundlich and Dubinin-Radushkevich fitted to the resulted data.

Langmuir adsorption isotherm was valid for monolayer adsorption on to a homogenous surface with a finite

number of identical sites also without interaction between adsorbed molecules. Based upon these opinions, the linearized form of Langmuir was expressed by Equation 5 (14):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}b} \quad (5)$$

where q_{max} was the maximum Cr(VI) adsorbed (mg/g), q_e the amount of Cr(VI) adsorbed per unit weight of FC at equilibrium time (mg/g) and b the Langmuir constant related to the affinity of binding sites (L/mg) computed by the plot of C_e/q_e against C_e .

A dimensionless separation factor (R_L) can be used to predict the affinity between the adsorbate and adsorbent. R_L was computed by the Equation 6:

$$R_L = \frac{1}{(1 + bC_0)} \quad (6)$$

The value of R_L demonstrated the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (1).

The Freundlich isotherm was an empirical equation used to describe the adsorption characteristics for the heterogeneous surface. The heterogeneity arose due to different functional groups on the surface and various adsorbent-adsorbate interactions (14, 15). The Linearizing equation Freundlich isotherm was expressed by the following Equation 7:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

where K_f and n were Freundlich constants showing the adsorption capacity (mg/g) and intensity, respectively, computed by the plot of $\log q_e$ versus $\log C_e$.

Dubinin-Radushkevich isotherm was generally applied to determine the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. This model often successfully fitted high solute activities and the intermediate range of concentrations data well. The linear form of this model was expressed by Equations 8 (15):

$$\ln q_e = \ln q_m - B\epsilon^2 \quad (8)$$

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9)$$

where ϵ was the Polanyi potential, R (J/m K) gas constant, T (K) absolute temperature and B (mg^2/kJ) a constant related to the adsorption energy.

The values of q_m and B were calculated from the intercept and slope of the plot $\ln q_e$ versus ϵ^2 . The mean energy of adsorption E (kJ/m) was calculated from the Equation 10.

$$E = \left[\frac{1}{\sqrt{2B_{DR}}} \right] \quad (10)$$

when $E < 8$ kJ/m or $8 \text{ kJ/m} \leq E \leq 16$ kJ/m, the removal mechanism occurred basically via physical interaction and or ion-exchange (3).

3. Results and Discussion

3.1. Characterization of Fire Clay

Fourier transformed infrared was performed to characterize the clay surface structure. Crystalline structure identifying was conducted using X-ray powder diffraction (XRD). According to FTIR spectra (Figure 1), the broad peaks around $3400\text{-}1$ and $3600\text{-}1$ attributed to O-H stretch indicating moisture in the structure, also the peak around 1630 indicating O-H groups of adsorbed water from outside environment. The peak of 1075 was related to Si bands. Remarkable changes were not shown in the spectra after chromium adsorption (the figure not shown).

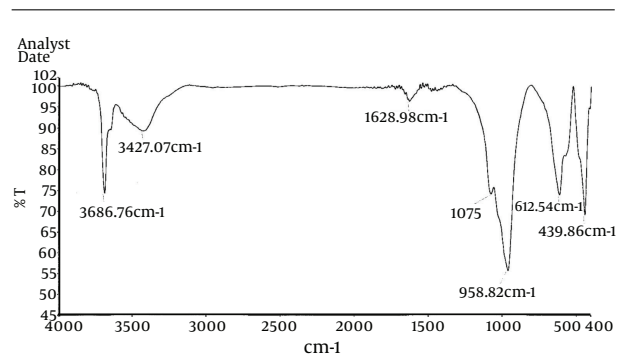


Figure 1. The Fourier Transformed Infrared Spectrum of Fire Clay

The XRD diffraction pattern (Figure 2) indicated the presence of crystalline phase in FC. The diffractogram pattern of FC resembled the pattern of JCPDS No. 87-2476 with a chemical name of magnesium silicate hydrate [$3 \text{ MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$].

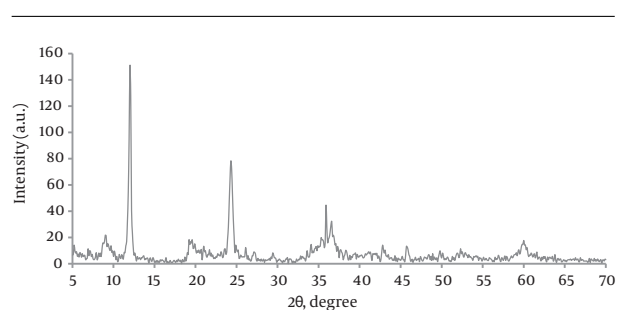


Figure 2. The Fire Clay Pattern of X-ray Powder Diffraction

3.2. Effect of Solution pH

Figure 3 shows the effect of solution pH on Cr (VI) removal by FC. The removal efficiency decreased from 45% to 9.71% as the pH increased from 2 to 10; however, the efficiency changes were not dramatic in range of 6 - 10. Solution pH had an important role in the adsorption process, since it can influence ionic species and adsorbent surface charge (16). In acidic environment, the main chromium species were HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and H_2CrO_4 , while in alkaline medium CrO_4^{2-} predominated. In an acidic condition, the adsorbent surface was protonated to a high extent. Thus the attraction between anionic species HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ with a positively charged adsorbent surface strongly increased. Increasing the pH of the solution decreased the extent of positive charge on adsorbent leading to weak bonding of negatively charged species on adsorbent surface. In an alkaline solution, other negative ions such as OH^- should compete with the major anion, CrO_4^{2-} ion, for the sorption sites on the adsorbent. Since higher chromium removal occurred at acidic pH and since the real chromium samples had acidic pH in nature, there was no need to lower the pH (7). This result was in agreement with the reports by Zhao et al. (17) and Chen et al. (14).

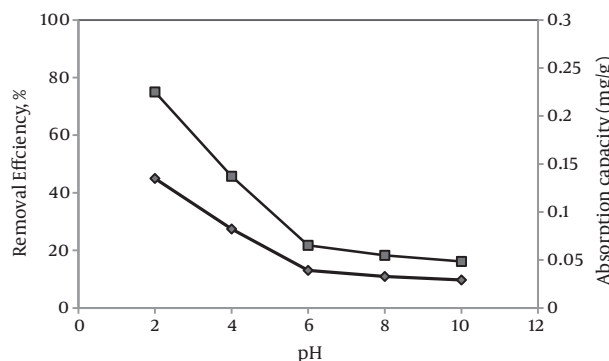


Figure 3. Effect of pH on Chromium Removal of Fire Clay (Initial Chromium Concentration = 5 mg/L, Adsorbent Dosage = 2 g/50 mL, Contact Time = 90 Minutes)

3.3. Effect of Adsorbent Dosage

Figure 4 shows the effect of adsorbent dose on removal of Cr (VI) at pH 2.0 and initial Cr (VI) concentration of 5 mg/L for 90 minutes. It can be observed that the adsorption of Cr (VI) depended on the amount of adsorbent added. Initially, at 0.5 g/50 mL of FC dose, 36.8% of Cr (VI) was removed and removal steadily increased up to 74% at 2.5 g/50 mL of adsorbent. Thereafter, the adsorption of Cr (VI) gradually (but not significantly) decreased, which indicated that 2.5 g/50 mL adsorbent was the optimum value to remove 5 mg/L of Cr (VI). Increase of Cr (VI) adsorption

on FC with increasing dosage, can be due to increase in active sites of adsorbent with increasing dosage (18). On the other hand, while increase of dosage led to improvement of removal efficiency but its adsorption capacity decreased (Figure 4), which was attributed to non-saturation of some active sites of the adsorbent. Therefore, the dosage of 2.5 g/50 mL of FC was considered as an optimum amount to adsorb Cr (VI). Similar results were found with the adsorption of Cr (VI) ions on natural Akadama clay and micro-vesicular volcanic. In these studies the maximum removal of Cr (VI) were exhibited at 40 and 100 g/L of the mentioned adsorbent, respectively (17, 19).

3.4. Effect of Contact Time and Kinetics

Two well-known pseudo-first-order and pseudo-second-order kinetic models were used in the experimental data to investigate the adsorption process. The kinetic sorption of Cr (VI) on FC was investigated as a function of contact time (5 - 240 minutes) at three different initial chromium concentrations (2, 5 and 10 mg/L). It was noticed that Cr (VI) removal increased with time. The adsorbent exhibited an initial rapid uptake of Cr (VI) followed by a slower removal rate that gradually reached an equilibrium condition. Nearly 29% removal of chromium was achieved within the first 90 minutes of contact time and therefore, the time was considered as an equilibrium time. Based on Figure 5 and Table 1, it is observed that the correlation coefficients (R^2) of pseudo-first-order model was 0.98, which was better than that of pseudo-second-order model, indicating that the pseudo-first-order equation fitted very well to the adsorption process. Nevertheless, a different phenomenon was observed in Cr (VI) adsorption by the modified wheat residue, micro-vesicular volcanic rocks and natural Akadama clay (14, 17, 19).

3.5. Isotherm Studies

The current study employed Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models to establish the relationship between the amount of adsorbed metal on to FC and its equilibrium concentration in aqueous systems. Therefore, Cr (IV) sorption by FC was investigated at three different initial chromium concentrations (2, 5 and 10 mg L⁻¹). It was observed that chromium uptake by FC decreased with increase in initial Cr (IV) concentration from 2 to 10 mg L⁻¹. Most of Cr (VI) interacted with the binding sites at low initial concentration, leading to the high percentage of Cr (VI) removal; while only part of Cr (VI) combined with the finite binding sites at high initial Cr (VI) concentration, resulting in relatively low percentage of chromium

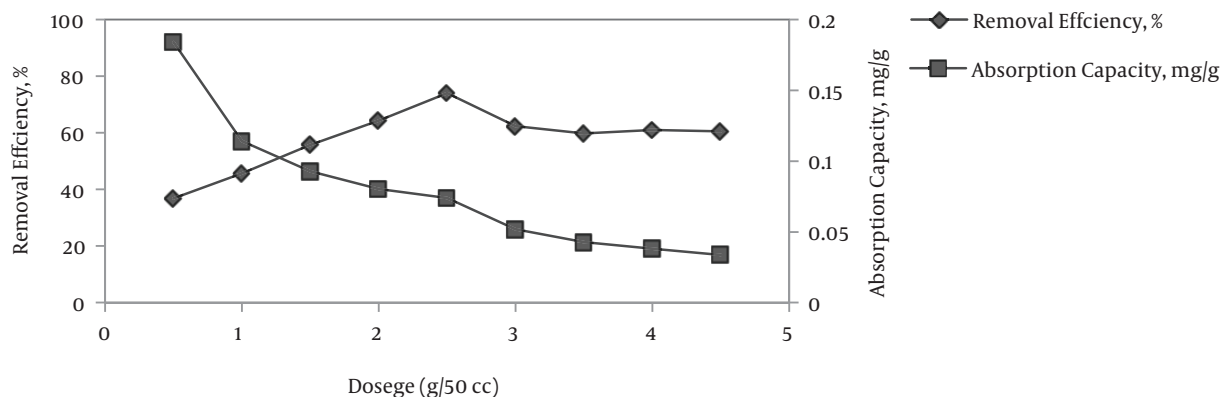


Figure 4. The plot of Percent Removal of Chromium as a Function of Adsorbent Dose (g/L) on Fire Clay (Cr (VI) Concentration = 5 mg/L, pH = 2 and Equilibrium Time 120 Minutes)

Table 1. Parameters of the Kinetic Models for Cr (VI) Sorption on Fire Clay

Adsorbate	Pseudo-First Order Model			Pseudo-Second Order Model		
	k_1	q_e , mg/g	R^2	k^2	q_e , mg/g	R^2
Cr (VI)	0.059	13.474	0.980	5.49	0.116	0.644

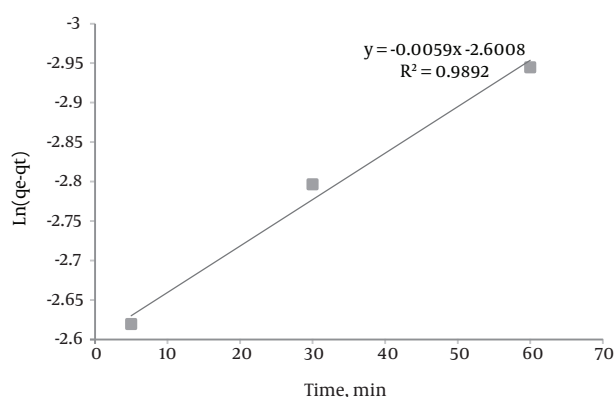


Figure 5. Pseudo-First Order Kinetic Model

removal by FC. Adsorption capacity increased to 90 minutes and then decreased. Therefore, this time was considered as equilibrium adsorption time. According to Table 2, the R^2 was very low, 0.64, indicating a poor fit of the monolayer Langmuir isotherm to the adsorption of Cr (IV) by FC.

The maximum monolayer coverage capacity (q_{max}) was 0.11 mg/g and b was 0.43 mg/L representing that the equilibrium sorption was favorable. If the value of n , in Freundlich isotherm, lies between 1 and 10, it indicates a favorable adsorption. The value of obtained n was 3.96, indicating a favorable adsorption process. Furthermore, the

value of the R^2 was 0.98. Thus the Freundlich isotherm gave a better fit to the data than Langmuir and Dubinin-Radushkevich isotherm models for Cr (IV) ions. Also as given in Table 2, $q_m = 14.29$ mg/g, $E = 2.1$ KJ/m indicated a physisorption process.

This observation agreed with the results obtained by Chen et al. (14), Albadarin et al. (2) and Zhao et al (17), but differed from many other studies. For example, when magnetic natural zeolite-polymer composite and Turkish montmorillonite clay were used for Cr (VI) adsorption, it was found that the Langmuir isotherm fitted better than Freundlich model (1, 3).

4. Conclusion

The results of the study showed that FC was not a potentially suitable option for Cr (VI) removal. A long equilibrium time and simultaneously low efficiency turned it to an unsatisfactory option for Cr (VI) adsorption. In addition, the optimum pH, removed in Cr (VI), was not in operational range of many treatment facilities that meant requiring for addition of much more acid than usual, which in turn resulted in other operational and handling problems. Therefore, it seems reasonable to search for more appropriate adsorbent for Cr (VI). Another option is the amendment of the adsorbent using various materials to promote its efficiency for Cr (VI). Anyway, more attempts should be done to improve this area.

Table 2. Langmuir, Freundlich and D-R Isotherm Parameters for Cr (VI) Sorption on Fire Clay

Adsorbate	Langmuir Isotherm			Freundlich Isotherm			D-R Isotherm		
	Qm, mg/g	B, mg/L	R ²	Kf, mg/L	n	R ²	qm, mg/g	E, kJ/m	R ²
Cr (VI)	0.11	0.43	0.64	44.70	3.96	0.98	14.29	2.12	0.55

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