Archives of Business Research – Vol.6, No.8
Publication Date: Aug. 25, 2018
DOI: 10.14738/abr.68.4843.
Algamal, Y., Khalil, N. M., Saleem, O., & Almughrabi, M. J. (2018). Removal of chromium (VI) from aqueous solution by natural clay. *Archives of Business Research,* 6*(8),* 357-364.

Removal of chromium (VI) from aqueous solution by natural clay

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ABSTRACT

The adsorption of chromium (VI) from aqueous solution was carried out using natural clay from western area in Saudi Arabia. The adsorbents used are characterized by X-ray diffraction (XRD) and other physico-chemical techniques. The various parameters affecting the adsorption process were investigated involving effect of initial concentration of Cr (VI) ion, temperature factor, dosage of adsorbent, pH of the solution, contact time and rotational per minute (RPM). Optimum conditions for adsorption process were; 50 mg/L^{-1} initial concentration of Cr(VI), adsorbent dose =1g, temperature ~ 25^{o}C, 3 hours contact time and pH=2, the obtained results were used to calculate the adsorption efficiency. Removal of chromium ion was found as highly depends on pH and initial Cr (VI) concentration of the solution. Langmuir isotherm was applied to get a maximum adsorption capacity of 18.68 mg/g. Although experimental data confirm with Langmuir isotherm model. The results of this study confirm that the material can be considered as effective adsorbents for the removal of chromium (VI).

Keywords: Natural clay; Adsorption; Chromium (VI); Isotherm; XRD.

INTRODUCTION

Recently the major problem for the researchers that related to our environment is the pollution whatever its kind, the disposal of the metal ions which becoming a harmful and causing a sever problems. Some of these metal ions are essential to our living but an increase in their quantities make trouble and affecting the resources. Among these ions is the chromium ion, which exists naturally as in natural mineral (rocks, soil) and in living system (animals and plants). Chromium (III) plays important role in biological activity using sugar, protein, and fat required by our body whereas Cr (VI) is a toxic one usually used as a mixture with copper and arsenic in manufacturing the pesticides commonly known as CCA (Chromated copper arsenate) [1]. Chromium (VI) causing a cancer to human by eating or breathing [2]. It can be deposited in soil and easily compounded with other particles resulting in different oxidizing states [3]. Authors reported another source of chromium (VI) that comes from water industries

(plastic containers and water pipes), tanning industries as well as electroplating process [3, 4]. Several methods like adsorption, ion exchange, membrane filtration and reverse osmosis were applied to remove Cr(VI) from industrial wastewater [4-6]. Adsorption process is commonly used to remove Cr(VI) from polluted water using different materials as adsorbent like charcoal, activated charcoal and activated aluminum [7], bentonite [4], wool [8], …. etc [9-11]. This study will focus on the adsorption of chromium (VI) from aqueous solution using natural clay collected from Khullais area in Kingdom of Saudi Arabia.

EXPERIMENTAL SECTION

Reagents:

Analar grades of $K_2Cr_2O_7$, HCl, NaOH were used. From these reagents, Stock solutions were prepared using double distilled water throughout the experiments. (500 mg/L using 1.414 g in 1000 ml of DD),1M of Hydrochloric acid and 1M of sodium hydroxide to adjust the pH values). The natural clay used was collected from Khullais area 90 km north Jeddah city, KSA. The chemical composition of the clay was checked using XRD technique.

Equipment:

XRF of the raw clay samples was testing using Philips X-ray fluorescence (XRF) machine while XRD was testing using D8 Advance Bruker Germany, Shaker Model GFL 3017 was used for shaking, pH meter (HANNA instruments) for measuring the pH values and UV-visible spectrophotometer (DR 5000, Hach, USA) also used. Atomic Absorption Spectrometry (AAS) (AA- 6200 Shimadzu) used to determine the total chromium concentration in the solution without botheration of its oxidation state of the metal [12]. The chromium hexavalent can be determined spectrophotometrically (Shimadzu (UV-1601), according to diphenyl carbazide-based method [13].

Methods:

The following adsorption processes were conducted, different concentration of Cr (VI) ions, varying the pH values, different RPM, different contact time, different amount of adsorbent and different range of temperature to study the equilibrium state. A 250 ml of Cr (VI) solution was transferred into a 500 ml conical flask and addition with the HCl/NaOH solution to adjust the desired pH value. To this solution, 1g of natural clay was added then shaken at 200 RPM for three hours. Flask well sealed and kept aside to decrease atmospheric loss. Then the solution was analyzed for chromium (VI) ions concentration after 24 hours. The Cr (VI) ions adsorbed on the surface of the adsorbent 'Q' was calculated using "Equation 1" as given below:

$$Q = \frac{(C0-C)V}{W} \qquad (1)$$

Where, 'C_0' represents initial concentration of Cr (VI) (mg/L) and 'C' the concentration of Cr (VI) at different interval time 't', 'V' represents the total volume taken in the conical flask and 'W' represents the amount of the adsorbent used. At equilibrium state 'C' becomes 'Ce' and 'Q' becomes 'Qe'.

A 100 ml of the stock solution of Cr (VI) ions (50 mg L^{-1}) was placed in 250 mL flask. Enough amount of 1M HCl solution is added to adjust the pH value at ~2, 1 g of the adsorbent (natural clay) was added to the solution, and then shaken at 200 RPM for a period of 3 hours at constant temperature 25.0 ± 0.2 °C. At different interval times, samples were collected and analyzed during the adsorption process to attain the equilibrium state. The percentage removal of chromium (VI) ions was calculated using "Equation 2". A duplicate run was done for checking

the adsorption of chromium ions on the surface of the conical flask in the absence of natural clay. This experiment showed no notable adsorption by the conical flask surface.

$$Cr(VI)removal\ \% = \frac{100(C0-C)}{C0} \quad (2)$$

Evaluation of various parameters on the adsorption process was conducted involving; different chromium (VI) solutions (20, 30, 40, 50, 100, 150, and 200 mg L^{-1}), different temperatures from 25°C to 40°C, pH range of 2.0 to 10.0, RPM from 30 to 200 RPM, contact time in the range of 30 minutes to three hours, amount of adsorbent ranging from 0.5 to 3.5 g.

Langmuir adsorption isotherm "Equation 3", can be applied to account for the equilibrium relationships between adsorbent and adsorbate [14].

$$\frac{Ce}{Qe} = \frac{1}{kQmax} + \frac{Ce}{Qmax} \quad (3)$$

Where 'C*e*'; the Cr(VI) concentration (in mgL^{-1}) at equilibrium state, 'Q*e*'; mass (in mg/g) of the adsorbed Cr(VI) ions at equilibrium state '*k*'; is the Langmuir constant (Lmg^{-1}), and 'Q_{max}'; the maximum value of adsorbed Cr(VI) ions (in mg /g). Thus, these constants relate the maximum adsorption capacity and the energy of adsorption.

RESULTS AND DISCUSSION

Characteristics of the adsorbents (Natural clay):

Chemical analysis of the raw clay sample is given in "Table 1". The table indicates that the used raw clay composed mainly of SiO_2, Al_2O_3 and Fe_2O_3 with considerable contents of Na2O and CaO. The loss of ignition was 12.03%, which corresponds to the evaporation of physical and chemical combined water together with the decomposed organic matter.

Table 1. Chemical composition of the natural clay

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	LOI
Weight %	58.10	13.11	9.60	5.11	2.05	12.03

"Figure 1" shows the mineral constituents of natural clay. The figure indicates that the clay sample contains quartz, nontronite in addition to some kaolinite and cronstedtite minerals.

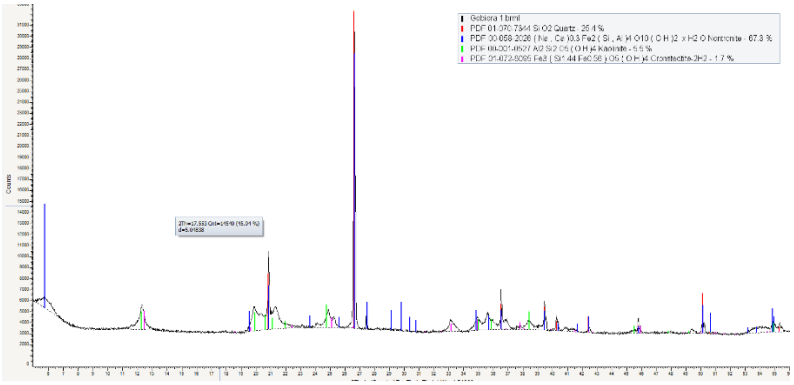

Figure 1. X-ray diffraction patterns of the natural clay

Effect of pH of the solution

"Figure 2", illustrates the effect of pH of the solution ranging from 2 to 10 on the removal of

total Cr(VI) ions from the solution (keeping other parameters constant i.e., initial concentration of Cr(VI), temperature 25^{o}C, RPM =180, time is 3 hours and using 1 g of clay. The maximum adsorption (75%) on natural clay was obtained at pH =2.0. It is a notable from the figure different removal percentage corresponds to different pH values (pH ranging from 2 to 4 the removal percentage ranging from (75 to 60%), pH ranging from 4 to 8 the removal is in the range of (60-50%) and pH = 8 to 10 the removal is (50 to 40%). This can be explained based on the possibility of formation of Cr(VI) anions in form of $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$, this can be explained in terms of chromium ions will have different states at different pH values [15] resulting in different charge density and easily can be bonded with the positively charged natural clay surface [14,16]. In addition, the lower efficiency (50%) of the adsorbent at high pH values, the anions undergo transformation into diverse oxidation states. The reduction of chromium (VI) to chromium (III) was studied spectrophotometrically using the natural clay at different pH values, with 50 mg/ L initial concentration of Cr(VI) solution [13].

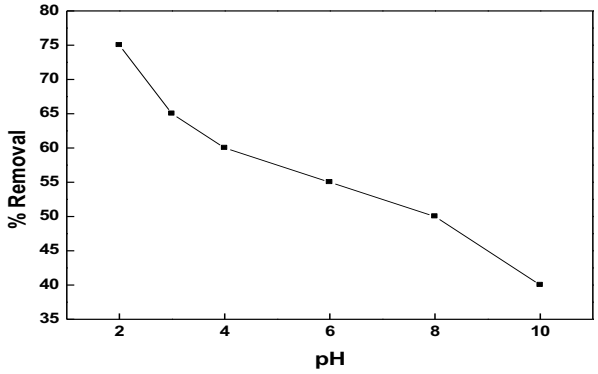

Figure 2. Effect of pH on Cr(VI) removal.

Effect of Cr(VI) concentration:

The efficiency percentage of Cr(VI) removal carried out at different concentrations of Cr(VI) ions varying from 50 to 200 mg/ L, keeping remaining factors constant (1 gm of natural clay, pH = 2, RPM =180 and contact time of 3 hours) is shown in "Figure 3". The removal efficiency is increased with increasing the initial concentration of Cr(VI) up to 150 mgL^{-1}. For concentration higher than 150 mg L^{-1}, the retention curves of total chromium and Cr(VI) start to advance further, suggesting chromium can have different oxidation state in these conditions. Assuming that the reduction of Cr(VI) to Cr(III) takes place on the natural clay and then releasing of the reduced form of chromium (III) leading to a curve retention. Same trend was reported with different adsorbents [17–23].

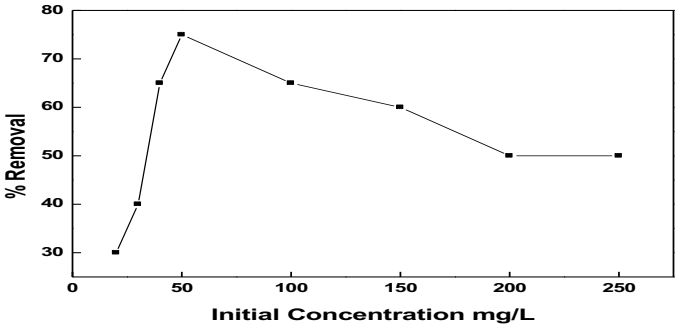

Figure 3. Effect of initial concentration on Cr(VI) removal.

Effect of adsorbent dosage:

The percentage removal of chromium ions with different amount of adsorbents ranging from 0.5 to 3.5 g of natural clay keeping remaining factors constant (50 mgL^{-1} of Cr(VI), pH = 2, RPM =180 and contact time of 3 hours) is shown in "Figure 4". The figure shows an increase of percentage removal of Cr (VI) when amount of adsorbent increased. From the figure, three stages in the curve could be recognized, the first increase ranging from 0.5 to 1 g, the second increase in the curve correspond to 1.0 - 3.0 g and the third stage in the curve for the amount 3.0 to 4.0g of adsorbent. This behavior is correlated with the chemical and mineralogical composition of the used clay i.e., the presence of SiO_2, Al_2O_3, Fe_2O_3, Na_2O and CaO in the form of quartz, nontronite, kaolinite and cronstedtite minerals which are known with the high adsorption capability [24,25]. As a result, the large amount of adsorbent (natural clay) enhances the uptake capacity of the adsorbent, and hence the metal ions can be easily occupying the active sites of the natural clay.

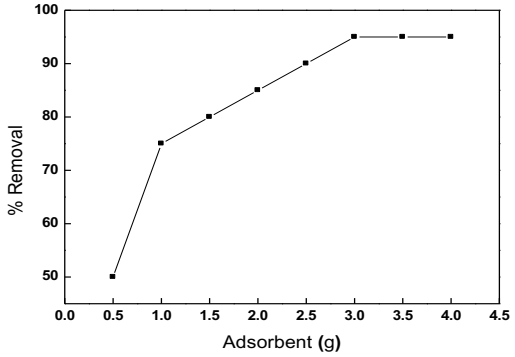

Figure 4. Effect of adsorbent dosage on Cr(VI) removal.

Effect of contact time:

The contact time plays an importance role in the adsorption process, keeping other parameters constants. "Figure 5", shows the percentage removal of Cr (VI) and the effect of contact time, the efficiency of removal of Cr(VI) increases with increasing the contact time, approximately 70-80 % of maximum removal of Cr (VI) is attained within 210 minutes and the maximum adsorption is attained in 180 minutes. This can be explained based on the presence of the positively charged surface of the adsorbent for anionic Cr (VI) species present in the solution. The retention in the curve may be explained in sense of the electrostatic hindrance caused by already adsorbed negatively charged Cr (VI) ions in the solution [26].

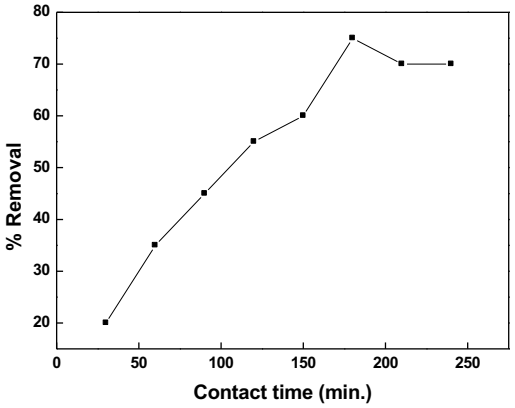

Figure 5. Effect of contact time on Cr (VI) removal.

Effect of temperature:

Temperature play also an important role on the process of adsorption. A range of 25°C to 40°C temperature were studied keeping other parameters like initial concentration, pH, RPM and adsorbent are constant. The obtained results show a decrease in percentage of adsorption with rise in temperature. This can be explained in terms of the desorption caused by the thermal energy. Thus, higher temperature results in higher mobility of the adsorbate causing desorption [27].

Effect of RPM:

The effect of RPM on the adsorption process was studied at different range 10 to 200 RPM keeping remaining parameters constant. "Figure 6", reveals an increase in the percentage of Cr (VI) removal with increase in RPM up to 180, so it has been taken as the optimum rotational per minute for this study.

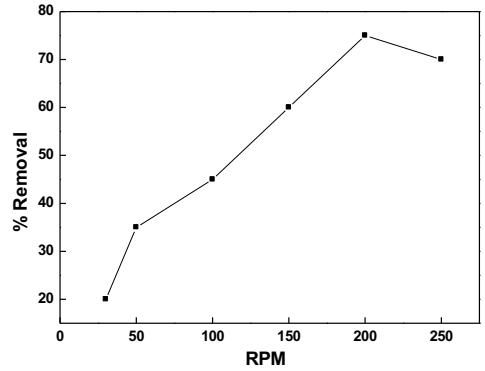

Figure 6. Effect of RPM on Cr (VI) removal.

Adsorption isotherm:

To determine the adsorption capacity, the Langmuir isotherm was applied, the isotherm also helping in modeling the equilibrium data equation (3). The experiment carried out at pH = 2. The points are fitted straightly "Figure 7", from a plot Ce/Qe versus Ce the values of 'Qmax' and 'k' are calculated (Langmuir constants) and their values are found to be 18.68 and 0.1265 respectively. The high value of correlation coefficient (R^2= 0.9857) indicates a good agreement with the parameters and confirms the monolayer adsorption of Cr(VI) onto the adsorbent surface. The importance of this isotherm supporting the feasibility of the natural clay as an efficient adsorbent in removing the chromium (VI) from aqueous solution.

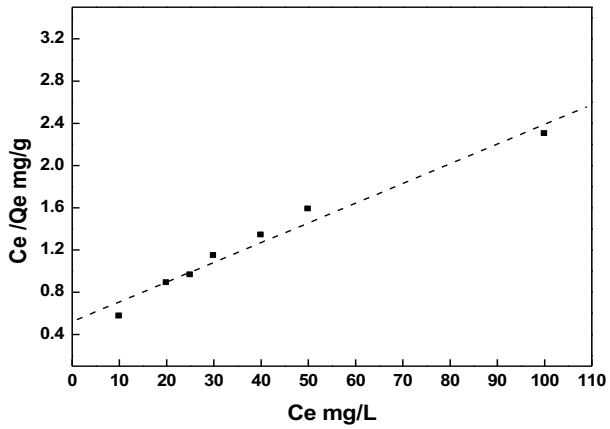

Figure 7. Langmuir isotherm for adsorption of Cr(VI) at 25°C.

CONCLUSIONS

From this study we can conclude that the natural clay collected from Khullais area in Kingdom of Saudi Arabia which is widely available, low cost and an effective adsorbent for Cr(VI) removal from aqueous solution at ambient pH since this material showed a relatively large capability of adsorption of chromium(VI) from aqueous solution. The following results were obtained:

- As pH increases % removal of Cr(VI) decreases and the maximum % removal of Cr(VI) at pH = 2
- As the contact time of adsorption increases the % removal also increases, and the optimum time is 180 min.
- As the amount of adsorbent increases, the % removal of Cr (VI) is also increases.
- As the temperature increases the % removal gets decreases.
- As the RPM increases the percentage removal gets increases and observed that the maximum % removal at 200 RPM.

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