Removal of Cr (III) from aqueous waste using Spent Activated Clay

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Abstract: This work has been carried out to investigate the sorption behavior of spent activated clay with respect to Cr(III), in order to consider its application for nuclear waste water treatment. The sorption experiments were performed under batch process with metal ion concentration, adsorbent dosage, pH, time and temperature as variable. In order to clarify the adsorption kinetics of Cr³⁺ ions on treated-SAC, Lagergren’s pseudo-first-order and pseudo-second-order kinetics models were applied to the experimental data. The thermodynamic parameters: the enthalpy change, entropy change and Gibbs free energy change for sorption process were studied. The adsorption of Cr³⁺ on treated-SAC occurs spontaneously and its endothermic in nature. The positive value of ΔS° suggests an increased randomness at solid/solution interface during the adsorption Cr³⁺ ions onto treated-SAC. This study presents the suitability of SAC for the removal of radioactive chromium waste from liquid radioactive waste. This paper also gives a detail description of SAC preparation and characterization.

Keywords: Activated clay; Adsorption; Heavy metals; Radioactive wastes

1. Introduction

One of the heavy metals that has been a major focus in water and wastewater treatment is chromium. Trivalent chromium and hexavalent chromium are the two common existing oxidation states of chromium found in the environment [1]. Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern [2]. Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, pigments, iron and steel industries and inorganic chemicals production [3]. Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard [4]. There are various methods to remove Cr(III) including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis [5]. These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost [6]. For this purpose in recent years, investigations have been carried out for the effective removal of various heavy metals from solution using low-cost adsorbents which are economically viable. A number of researchers have recently investigated the use of solid industrial and agro-based wastes as adsorbents for heavy metals [7-11].

Spent Activated clay (SAC) so-called spent bleaching earth, contains about 20–30% oil by weight and constitutes a major loss of oil for the oil processing industries. Also the use and disposal of the spent activated clay are becoming a potential problem of concern in the producing countries because of the rapid growth of the industry and the concomitant rapid increase in the generation of the waste materials [12,13]. Currently, oil-laden spent activated clays are mainly disposed of in landfills or in waste dumping ground as the spent clays are considered nontoxic. This method of disposal causes environmental concern because of their pyrolytic nature and also the possibility of the leaching of the oil into the surrounding water resources. While efforts to reduce the loss of oil and to minimize clay dosage in the refining process continue, the possibility of recycling the clay has been studied and reviewed [14-16].

In the present work, adsorptive removal of Cr(III) from aqueous solution was studied by using treated-SAC. The operation parameters that affect the adsorption process such as: agitation time, pH, initial Cr(III) concentration, adsorbent dosage, and temperature were investigated. The kinetics and thermodynamics of adsorption process were also evaluated in the light of current known models. Results of this study will be useful for future scale up and can also serve as base-line data for using this waste as a low-cost adsorbent for treatment Cr(III)-rich effluents.
2. Experimental procedures

2.1. Preparation of adsorbent

Spent activated clay (SAC) was obtained from Alexandria Company for oils and soap in Alexandria governorate in the northern of Egypt. The commercial virgin activated clay was provided by the edible oil company. This material is montmorillonite activated by sulphuric acid. After the clay was used to remove the color from edible oil, the color of AC would change from white to brownish. It contains 20-30% of oil by weight. To recover more activated sites for adsorption, SAC was treated with methanol as follows: (1) Mix a weighted amount of 20 g of SAC (W1) with 450 mL of methanol. (2) Shake the mixture by using a magnetic stirrer at 300 rpm for 1 hr at room temperature 25 °C. (3) Separate the solution via a 0.45 mm filter paper to collect the treated-SAC. (4) Record the final pH of the solution at the end of shaking. (5) The percentage of edible oil extracted was determined as below. Amount of oil extracted % = [(W1 - W2)/(W1)] x100

2.2. Clay mineral characterization

The specific surface area of the AC, SAC, and treated-SAC were measured using the standard volumetric method by nitrogen adsorption at 77 K (Nova 2000 series, high speed gas sorption, Quantachrome Corporation, USA) controlled by NOVA for Windows® Version 1.12. The pH value of SAC was determined instrumentally (Ultrameter™, Myron L Company, USA) from immersing it in distilled water. X-Ray diffraction (XRD) patterns for AC, SAC, treated-SAC, and Cr(III) adsorbed on treated-SAC were recorded by using PHILIPS X-ray unit (PW 1830), with diffractometer (PW 3710/31), scintillation counter (PW 2563/00), Ni filter at 40 kV and 30 mA. Samples were irradiated and analyzed between 2 and 60° (2θ).

2.3. Batch adsorption experiments

All chemicals used were of AR grade (WinLab, UK). Chromium solution was prepared by dissolving 0.637 g of Cr₂(SO₄)₃.15H₂O in double distilled water and used as a stock solution containing 100 mg/L of Cr³⁺ solution. Cr(III) in the solution before and after adsorption was measuring using Inductively Coupling Plasma (ICP) (Ultima 2 Jobin Yvon, France). The initial metal ion concentration ranged from 20-100 ppm. All experiments were carried out at room temperature 25 ± 1 °C, pH 3.5, adsorbent dosage of the treated-SAC 1 g, and contact time 10 days except as stated otherwise. Standard base of 0.1 M NaOH and acid of 0.1 M HCl were used for pH adjustment. For the effect of pH on adsorption, the pH of solution was maintained at 3, 3.5, 4, 7, 8, and 10. For the effect of temperature on adsorption, experiments were conducted under different temperature at 20, 25, 40, and 60 °C. For the effect of contact time, the solution was maintained without separation for contact time for 0.5 hr, 1 hr, 3 hrs, 1 day, 3 days, 7 days, 10 days, 14 days, and 21 days. For the effect of adsorbent dosage, the experiments were carried out by adding different amount of the treated-SAC into the solution 0.5, 1, 2, 4, and 6 g. The general experimental procedures were described as follows: (1) prepare a series of 125 mL polyethylene bottles containing 30 mL of Cr(III) concentration (100 mg/L). (2) Add a given amount of the treated-SAC (1 g) into the solution. (3) Adjust the solution pH to 3.5 by either 0.1 M NaOH or 0.1 M HCl. (4) Shake the mixture on a magnetic stirrer at 300 rpm for 15 min at room temperature 25 ± 1 °C. (5) Record the final pH of the solution at the end of shaking. (6) Leave the solution without separation for contact time 10 days. (7) Filter the adsorbent through a 0.45 mm filter paper to collect the supernatant. (8) Analyze the residual Cr(III) concentration in each of the supernatants using ICP. (9) All data were triplicated and the average values were taken in the data analysis. (10) The adsorption percentage (D) and adsorption capacity or amount adsorbed per unit mass of treated-SAC (q) are given by:

\[ D = \left( \frac{C_0 - C_f}{C_0} \right) \times 100 \%
\]
\[ q = \frac{(C_0 - C_f)V}{W}
\]

Where, D is the adsorption percentage (%), q is the adsorption capacity (mg/g), Co and Cf are the initial and final concentration of heavy metal left in solution (mg/L), V is the volume of the aqueous solution (L), and W is the mass of the treated-SAC (g).

3. Results and Discussion

3.1. Properties of SAC

The physical and chemical properties of AC have been supplied to Alexandria Company for Oils and Soap from the exporting company of the virgin product. The pH value of SAC is 3.5 indicating that it considered as an acidic adsorbent [13]. Such low pH value could be attributed to the activation procedure of clay with acid in manufacturing process. The AC has a surface area of 9.83 m²/g, whereas the surface area of SAC and treated-SAC were found to be 2.85 m²/g and 5.91 m²/g, respectively. It appears that the washing process has cleared the pore of the SAC particle from residual oil, thereby cleaning its pore size and surface area that allowed more sorption processes.

3.2. Effect of contact time
As seen in Fig. 1, which represents the percentage removal of Cr\(^{3+}\) ions from aqueous solution versus contact time, a rapid adsorption appeared within 30 min contact time 20.28%, followed by a progressive and much slower uptake within 60 min 29.22%. Approximately, it reaches equilibrium after about 180 min 59.05%. Further increasing the time after equilibrium shows that the rate of adsorption remains almost constant.

3.3. Effect of pH

The influence of pH on the adsorption percentage of Cr\(^{3+}\) ions was studied and the results are also presented in Fig. 2. As expected, the maximum removal of Cr\(^{3+}\) ions on treated-SAC increased from 47.09% to 62.58% with an increase in pH of the solution from 3 to 4. Thereafter, the adsorption increased significantly with the increase of pH value reaching a maximum value 81% at pH 7. The maximum value of Cr\(^{3+}\) ions removed at pH 10 was determined as about 99.88%.

3.4. Effect of initial metal ion concentration

Fig. 3 also shows the effect of varying concentration of Cr\(^{3+}\) ions from 20 to 100 mg/L. The percent adsorption of Cr\(^{3+}\) ions increased from 23.9% to 59.8% with increasing the initial concentration of Cr\(^{3+}\) ions in aqueous solution.

3.5. Effect of adsorbent dosage

The effect of mass of the adsorbent on the uptake of Cr\(^{3+}\) ions is also depicted in Fig. 4. There is a substantial increase in percentage adsorption from 37.39% to 59.8% when the dosage of the adsorbent increased from 0.5 to 1 gm. With increasing adsorbent up to 6 gm, the adsorption percentage deemed almost constant.

This trend is obvious because as adsorbent dose increases the number of adsorbent particles also increase that makes the greater availability of exchangeable sites for adsorption [17]. Nevertheless, amount of metal ions adsorbed per unit mass decreased with an increase in adsorbent dosage, this
result may be due to the metal ions can easily access to the adsorption sites when the amount of treated-SAC is small. With increasing treated-SAC content, metal ions find it difficult to approach the adsorption sites due to overcrowding of treated-SAC mineral particles. In addition higher adsorbent amount creates particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length. Both of which contribute to decrease the amount adsorbed per unit mass [18,19].

3.6. Effect of temperature

The effect of temperature on the adsorption percentage of Cr\textsuperscript{3+} ions was investigated under thermal conditions in the temperature range of 20–60 °C. The temperature dependence of the Cr\textsuperscript{3+} adsorption isotherm is also presented in Fig. 5. The percentage removal of Cr\textsuperscript{3+} ions from aqueous solution increased from 44.43% to 72.37% as the temperature increased.

3.7. Adsorption kinetics

In order to clarify the adsorption kinetics of Cr\textsuperscript{3+} ions on treated-SAC, Lagergren’s pseudo-first-order and pseudo-second-order kinetics models were applied to the experimental data.

The linearized form of the pseudo-first-order rate equation by Lagergren is given as:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \] (1)

Where \( q_e \) and \( q_t \) (mg/g) are the amounts of metal ions adsorbed at equilibrium (mg/g) and t (min), respectively, and \( k_1 \) is the rate constants of the equations (min\(^{-1}\)). The rate constants \( k_1 \) can be determined experimentally by plotting of \( \ln(q_e - q_t) \) versus t. The plots of \( \ln(q_e - q_t) \) versus t for Lagergren first-order model and the \( R^2 \) value for this model do not fit a pseudo-first-order kinetic model. Experimental data were also applied to the pseudo-second-order kinetic model which is given in the following form [20]:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left( \frac{1}{q_e} \right) t \] (2)

Where \( k_2 \) (min/g/mg) is the rate constant of the second-order equation, \( q_t \) (mg/g) the amount of adsorption at time t (min), and \( q_e \) is the amount of adsorption at equilibrium (mg/g).

Fig. 6 presents the plot of \( t/q_t \) versus t for the adsorption of Cr\textsuperscript{3+} ions on treated-SAC at room temperature. The result obtained revealed that adsorption of Cr\textsuperscript{3+} ions onto treated-SAC obeyed well the pseudo–second–order kinetic model. The correlation coefficient value \( R^2 \) for the pseudo–second–order model was found to be 0.09891. The value of rate constant \( k_1 \) and \( k_2 \) were calculated from slope and intercept of the plot, respectively, and data are given in Table 1. The well fitted linear regression suggested that the pseudo–second–order kinetic model gives a more realistic description of Cr(III) adsorption kinetic. In the view of these results, the rate controlling step could be described as chemisorption or chemical sorption mechanism between adsorbate and adsorbent. Similar results were reported for the adsorption of the same metal ion on different adsorbent and different metal ions on the same adsorbent [21,22].

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\hline
\( q_e \) (mg/g) & 5.4739 & 3.676639 & \\
(\text{min}^{-1}) & 0.027 & 0.004505 & \\
\hline
\end{tabular}
\caption{Parameters for adsorption of Cr\textsuperscript{3+} ions onto treated-SAC.}
\end{table}
3.8. Thermodynamic study

The thermodynamic parameters for the present system including Gibbs free energy of adsorption $\Delta G^\circ$, changes in enthalpy of adsorption $\Delta H^\circ$, and changes in entropy of adsorption $\Delta S^\circ$ were calculated using van't Hoff equation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$  \hspace{1cm} (3)

$$\Delta G^\circ = -RT \ln k_d$$  \hspace{1cm} (4)

$$\ln k_d = (\Delta S^\circ/R) - (\Delta H^\circ/RT)$$  \hspace{1cm} (5)

Where, $R$ is the ideal gas constant (J/mol.K), and $T$ is temperature (K). The data obtained from the adsorption experiments of Cr(III) at 20, 25, 40, and 60 °C were also used for the calculation of thermodynamic properties. Fig. 7 shows linear plot of ln $k_d$ versus 1000/T at the range of temperature investigated. The values of $\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept, respectively. The values of $\Delta G^\circ$ were estimated by using equation 4. The calculated thermodynamic parameters are presented in Table 2. The Negative values of $\Delta G^\circ$ show that, under standard conditions, the adsorption of Cr$^{3+}$ on treated-SAC occurs spontaneously. The higher negative value of $\Delta G^\circ$ was found for the system with higher temperature. The change in enthalpy $\Delta H^\circ$ value is positive, indicating that the adsorption of Cr$^{3+}$ is endothermic in nature. Cr$^{3+}$ ions uptake increased with increase in temperature. The adsorption of Cr$^{3+}$ also requires a diffusion process, which is an endothermic process; i.e. increase in temperature favours adsorbate transport within the particles of the adsorbent. The positive value of $\Delta S^\circ$ suggests an increased randomness at solid/solution interface during the adsorption Cr$^{3+}$ ions onto treated-SAC. Based on above results, the adsorption of Cr(III) is a spontaneous process at high temperature and endothermic in nature. This behaviour of Cr$^{3+}$ ions has also been investigated in other studies [23,24].

Table 2: Thermodynamic Parameters for the adsorption of Cr$^{3+}$ by treated-SAC.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol.K)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>-7.74649</td>
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<td>298</td>
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<tr>
<td>333</td>
<td>-12.0709</td>
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</tbody>
</table>

Fig. 7- Van't Hoff plot of Cr$^{3+}$ adsorption by treated-SAC.

3.9. XRD analysis

The XRD patterns of AC and SAC, and treated-SAC are shown in Fig. 8. It reveals that AC, SAC, and treated-SAC are composed mainly of montmorillonite, quartz and cristobalite at $2\theta = 26.55^\circ$ and $21.8^\circ$. Clearly, the observable crystalline structures of XRD patterns are very similar [25-27]. We can deduce that the edible oil bleaching process and the treatment of the SAC with methanol did not affect the main structure of the AC. Adsorption of Cr$^{3+}$ ions are presented in Fig. 1d. A slight shifting in basal spacing as well as obvious change in diffraction intensity is notice. This result implies that metal ions were sorbed on treated-SAC introducing some changes into the crystal structure of treated-SAC [28].

4. Conclusions

From this study we concluded that:

1- A rapid adsorption appeared within 30 min contact time and the adsorption percent was 20.28%, followed by a progressive and much slower uptake within 60 min and reached to equilibrium after about 180 min to become 59.05%.

2- The adsorption increased significantly with the increase of pH value reaching a maximum value (81%) at pH 7. The maximum value of Cr$^{3+}$ ions removed at pH 10 was 99.88%.

3- The percent adsorption of Cr$^{3+}$ ions increased from 23.9% to 59.8% with increasing the initial concentration of Cr$^{3+}$ ions in aqueous solution from 20-100 ppm.

4- There is a substantial increase in percentage adsorption from 37.39% to 59.8% when the dosage of the adsorbent increased from 0.5 to 1
gm. With increasing adsorbent up to 6 gm, the adsorption percentage deemed almost constant.

5- The percentage removal of Cr\(^{3+}\) ions from aqueous solution increased from 44.43% to 72.37% as the temperature increased from 20 to 60 °C.

6- The adsorption of Cr\(^{3+}\) on treated-SAC occurs spontaneously. The higher negative value of \(\Delta G^\circ\) was found for the system with higher temperature.

7- The change in enthalpy \(\Delta H^\circ\) value is positive, indicating that the adsorption of Cr\(^{3+}\) is endothermic in nature.

8- The positive value of \(\Delta S^\circ\) suggests an increased randomness at solid/solution interface during the adsorption Cr\(^{3+}\) ions onto treated-SAC.

Fig. 8- XRD patterns of a) AC, b) SAC, c) Treated-SAC, and d) Cr(III) adsorbed on treated-SAC.

References


2. Torresdey J. L. G., Tiemann K. J., and Armendariz V., Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of Avena monida (Oat) biomass, J. Hazard. Mater. 80 (1-3) (2000) 175–188.


