Removal of Cr (VI) from aqueous solution using activated charcoal

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Abstract: - The use of activated charcoal as treatment material for the removal of Cr (VI) from aqueous solution was investigated. Maximum adsorption of Cr (VI) was achieved under acidic pH (pH=4) after a contact time of approximately 120 minutes. The activated charcoal was treated in order to vary the pH from acid to base so that its influence on the removal of the metal ions could be investigated. In order to study possible structural changes of the treatment material (activated charcoal), scanning electron microscopy (SEM) and UV-VIS molecular adsorption spectrometer, before and after adsorption of Cr (VI) was investigated in detail to validate the adsorption of the heavy metal. Detailed investigation included the effects of initial concentration, adsorbent dose, contact time, pH of solution for the adsorption process and the evaluation of optimum conditions required for a high yield of Cr (VI) removal. The Langmuir adsorption isotherm model was applied to analyse the adsorption data. The results show that activated charcoal was found effective for the removal of Cr (VI) from aqueous solutions. The purpose of the study was to determine the capabilities for Cr (VI) removal of the activated charcoal and the influence that pH values have over the treatment efficiency in order to obtain the best conditions necessary for water treatment.

Key-Words: - activated charcoal, Cr (VI), adsorption, SEM, UV-VIS, water treatment

1 Introduction

Heavy metals are an important environmental problem cause by their toxic effects and the fact that they cannot be degraded [1]. The metal ion pollution is caused by heavy metals such as: Cd, Pb, Cr, Cu and Ni. One of the common toxic pollutants is chromium, which cause severe environmental and public health problems like cancer, epigastric pain, nausea, vomiting, severe diarrhea and haemorrhage [2]. Chromium is used in different industries including: electroplating, nuclear power plant, water cooling and chromate preparation [3]. Chromium exists in 3 forms such as Cr(0), Cr(III), and Cr(VI). Comparing these species, hexavalent form is more toxic than the trivalent form [4]. Cr (VI) exists in many forms such as: chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$ and hydrogen chromate $HCrO_4^-$. In acid solutions when pH is low than 1 the predominant form is H_2CrO_4, when pH is between 2-6 the predominant forms are $HCrO_4^-$ and $Cr_2O_7^{2-}$, while in the basic solution the predominant form is CrO_4^{2-}[5].

The commonly methods of removing chromium are as follows: ion exchange [6], sedimentation [7], electrochemical processes [8, 9], coagulation/flocculation [10], filtration and membrane processes [11, 12], chemical precipitation, adsorption [13] and solvent extraction [14, 15]. The most used method to remove heavy metals is the adsorption due to their advantages of high efficiency and low cost [5]. Due to properties such as large surface area, microporous structure, and high adsorption capacity, activated charcoal has been used as an adsorbent to remove heavy metals from aqueous solution [16].

The objective of the paper is to evaluate the effectiveness of adsorption for removing Cr(VI) ions from aqueous solution using an efficient material as activated charcoal powder. Many studies are focused on adsorption of heavy metals onto bulk or granular materials [17]. The parameters that affect the adsorption process are: solution pH, initial concentration, dose of activated charcoal and time.

2 Materials and methods

All materials use in these experiments were analytical grade and purchased from Merck Company. The stock solution of Cr (VI) had a concentration of 1000 mg/l. This solution was diluted as required to obtain standard solutions containing 10, 15, 25, 35 and 50 mg/L of Cr (VI). The tests were developed under acid and basic pH conditions by adding 0.5 N H_2SO_4 and 0.5 N NaOH

solutions. The pH values were measured using pH meter Consort C381. The concentrations before and after adsorption were determined using UV-VIS Molecular Absorption Spectrometer (Model Cintra 202) with wavelength 110-900 nm.

Activated charcoal was obtained from Sigma-Aldrich. The activated charcoal was in the form of untreated powder with surface area of 100-400 mesh. In order to establish the pH of activated charcoal, 4g of carbon was weighed into a 250 ml beaker, 100 ml of distilled water was added, then covered with a watch glass and boiled on the hot-plate for 5 minutes. The supernatant liquid was pour off as soon as possible and cooled to 60ºC. The decanted portion was cooled at 24ºC room temperature and the pH was measured to one decimal point. Characterization of the activated charcoal morphology was investigated in detail using scanning electron microscopy (SEM QUANTA 450 FEG).

For adsorption experiments, 100 ml of Cr(VI) solution (10-50 mg/L) was added to 0.1 respectively 0.5 g of activated charcoal. The experiment was conducted under acidic and basic conditions. The contact time was between 15 and 120 minutes. After 15 minutes the solution was filtered through 0.45 µm membrane filter and analysed for Cr(VI). The Cr(VI) was analysed by using 2 ml 1.5-diphenylcarbazide and 2 ml phosphoric acid in order to form a coloured organo-metallic complex which was detected by a spectrophotometer at a wavelength of 540 nm.

The percentage removal of Cr(VI) was calculated by using the following equation:

$$\% \text{ efficiency} = \frac{C_0 - C_e}{C_0} \, 100 \qquad (1)$$

where C_0 are the initial chromium concentration in mg/L and C_e (mg/L) chromium concentration at time t.

The amount of Cr(VI) on activated charcoal adsorbed equilibrium, (mg/g), was calculated using the following equation:

$$q_m = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

Where: q_m (mg/g) is the amount of chromium adsorbed per unit weight of adsorbent, C_e (mg/L) is chromium concentration at any time and C_0 is the initial chromium concentration in mg/L. V is the volume of the solution (L) and W is the adsorbent weight (g).

Langmuir isotherm

Langmuir isotherm was used to obtain the maximum adsorption capacity. The isotherm Eq. 3 is given by:

$$\frac{C_e}{q_e} = \frac{1}{bC_m} + \frac{1}{Q_m C_e} \qquad (3)$$

where, b is adsorption equilibrium constant (mg/L), Q_m is the quantity of adsorbate and q_e is the amount adsorbed on unit mass of the adsorbent (mg/L) when the equilibrium concentration is C_e (mg/L).

The slope and the intercept of this line then give the values of constants Q_m and b. A further analysis of the Langmuir equation can be made on the basis of the separation factor R_L, given by equation:

$$R_L = \frac{1}{1 + bC_e} \qquad (4)$$

For a favourable adsorption the value of R_L lies between 0 and 1; $R_L > 1$ represents an unfavourable adsorption, $R_L = 1$ represents the linear adsorption and $R_L = 0$ represents that the adsorption operation is irreversible.

3 Results and discussion

3.1 Effect of pH

The effect of pH on the adsorption of chromium by activated charcoal was studied as function of time for two values of pH of 4 and 8. Figure 1 presented only the concentration of 25 mg/L because the result are the same in all the cases respectively the efficiency % is slightly different at acid and basic pH. Figure 1 shows that during the 120 minutes, the Cr(VI) removal efficiency is quite high under acidic conditions (pH=4) of about 98%, in comparison with an efficiency removal of 83% under basic conditions (pH=8).
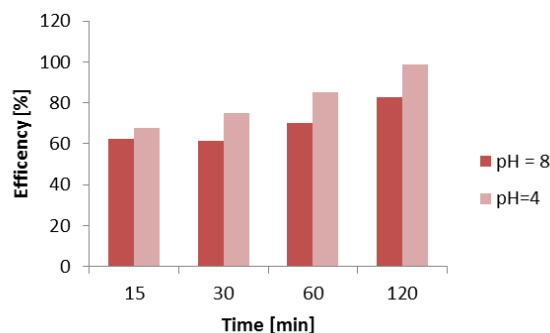

Fig.1: Effect of pH on Cr (VI) removal

3.2 Effect of adsorbent amount

Study on the effect of activated charcoal amount for Cr(VI) removal was investigated as a function of the adsorbent capacity and efficiency of Cr(VI). The influence of activated charcoal amount at optimum pH 4 for two values of adsorbent dose of 0.1 and 0.5 g/L onto the Cr(VI) adsorption is shown in fig. 2 for a constant initial concentration of 10 mg/L. In the case of using a dose of 0.1g activated charcoal, and calculating after 120 minutes the removal efficiency was increased from 34.2 % to 59.3% while in case of using of 0.5 g activated charcoal and calculating after 120 minutes the removal efficiency was increased from 90.3% to 100%. The increase in Cr (VI) removal with increasing in activated charcoal amount is due to the increase in surface area and adsorption sites available for adsorption. For the rest of the study, the best amount of activated charcoal was chosen to be 0.5 g/L.
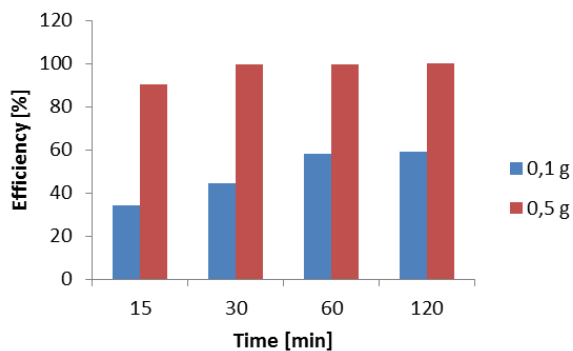

Fig. 2 - Effect of amount of activated charcoal on the adsorption of Cr(VI) at initial concentration of 10 mg/L and initial pH 4;

3.3 Effect of contact time

The effect of contact time of Cr(VI) adsorption on activated charcoal was investigated to study the efficiency of Cr(VI). Fig. 3 shows the efficiency of Cr(VI) for different values of initial Cr(VI) concentration ranging from 10 to 50 mg/L at pH 4. It is evident from this figure that the adsorption of Cr(VI) increased with contact time increase from 15 min to 120 min. It can be observed that the lowest concentration of 10 mg/L shows the highest removal efficiency in comparison with the other concentrations (from 15 to 50 mg/L). Also, it can be observed that after 120 minutes is the most efficient contact time, the removal efficiency increasing from 30.4% to 100% with decreasing of concentrations from 50 to 10 mg/L.
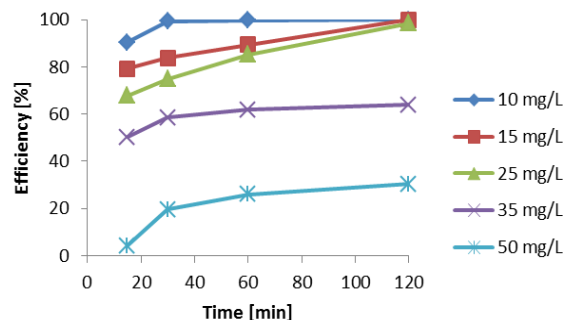

Fig 3 - Effect of contact time (min) on Cr(VI) removal by activated charcoal (adsorbent dose 0.5 g/L, pH 4, concentration 10-50 mg/L)

3.4 Effect of initial concentration

The initial concentration of Cr(VI) significantly influences adsorption of Cr(VI). The effect of initial Cr(VI) concentration was studied by varying it from 10-50 mg/L, at optimum pH=4 and 0.5 g/L amount of activated charcoal, obtained results are presented in Fig. 4.

The results show that with increasing of Cr(VI) concentration from 10 to 50 mg/L, the percentage removal decreases from 100% to 33.3%. The decrease of efficiency can be explained by the fact that above a certain concentration, the absorbent has a limited number of active sites.
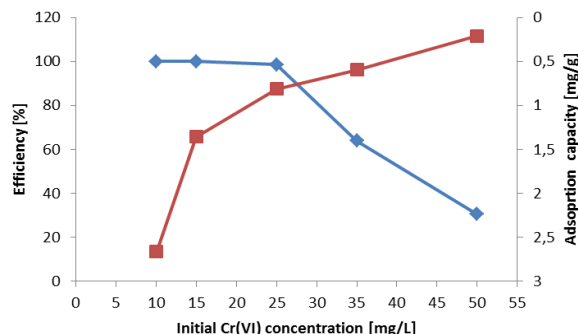

Fig. 4 - Effect of initial Cr(VI) concentration and adsorption capacity of Cr(VI) using activated charcoal and initial pH 4

3.4 Langmuir Isotherm

Langmuir equation is represented by the variation of C_e/q_e versus C_e. The Langmuir constant q_m (maximum adsorption) is 2.6 mg/g in the initial pH=4. The Langmuir constant, b (adsorption energy) is 0.196 mg/L and the regression correlation coefficient (R^2=0.9906), which confirms the adsorption of Cr(VI) onto the activated charcoal surface. The dimensionless parameter, R_L=0.096 (0 < R_L < 1) is found in the range of 0.69-0.99 which

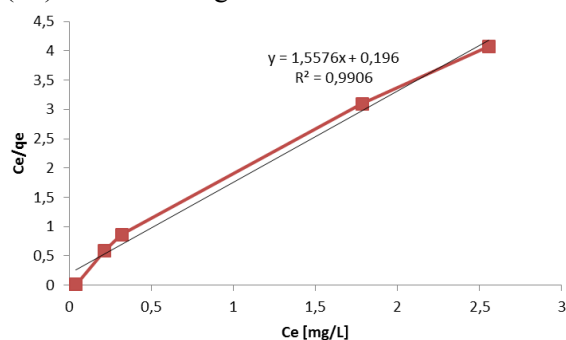confirms the favorable adsorption process for Cr(VI) removal using activated charcoal.

y = 1,5576x + 0,196
R² = 0,9906

Fig. 5 - Langmuir adsorption isotherm

3.5 Scanning electron microscopy

SEM was carried out in order to observe the changes in surface morphology of adsorbents after adsorption. To confirm the presence of Cr(VI) onto activated charcoal surface a SEM imagine is presented in Fig. 6, were we can observe lighter areas that confirm the presence of Cr(VI) on of the activated charcoal surface
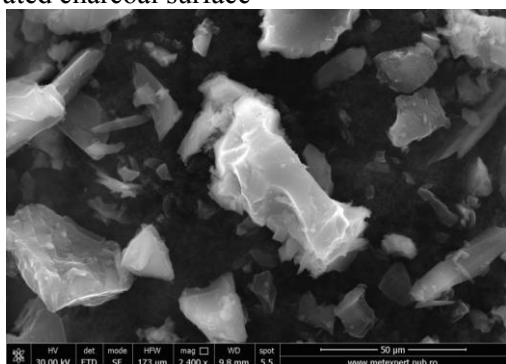

Fig. 6 - SEM micrograph of sample after adsorption of Cr(VI)

4 Conclusions

In the present paper, the results suggest that the adsorption is influenced by the various parameters such as pH, contact time, adsorbent amount, and initial Cr(VI) concentration. At pH 4, the effectiveness of adsorption of activated charcoal was found to be the highest compared to pH 8. It was found that, using activated charcoal as an adsorbent, the maximum capacity obtained for Cr(VI) adsorption is 2.6 mg/L in comparison with the literature indicate a value of 0.82 mg/g in case of using agricultural waste biomass. The maximum efficiency of chromium removal was 100% after 120 minutes.

It was concluded that activated charcoal is a good adsorbent and has an efficient adsorption of chromium from aqueous solutions.

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