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Experiments on the Removal of Chromium (VI) from its Aqueous Solution in Batch Reactors

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Abstract: The adsorption of chromium (VI) onto activated carbon experimented in a batch reactor under two different conditions, namely, initial metal ion concentration and adsorbent dosages. For the five different initial metal ion concentrations such as 500, 600, 800, 900, 1000 mg/L, the steady-state values of chromium removal efficiency were 64, 92, 83, 71 and 66 %, respectively, using 5 grams of activated carbon under shaking at the end of 8th hour. The equilibrium of the process was found to fit into the two well-known adsorption models, Freundlich and Langmuir. It was also observed that the experimental kinetic data followed the first order rate expression.

Keywords: chromium (VI); adsorption; Freundlich and Langmuir isotherms

1. Introduction

Heavy metal pollution of the environment has been augmented since 1900 and poses chief environmental and human health problems worldwide. Sources of anthropogenic metal pollution comprise smelting of ores, mining, electroplating, painting, dyeing, tanning and the application of fertilizers and municipal sludge on land (1). Hexavalent chromium is formed owing to the oxidation of Cr (III) compounds which permeates down into the soil during the rainy season and contaminates the underground water. The hexavalent chromium is of specific concern due to its great toxicity. It is known to be cancer-causing and mutagenic to living organisms. Thus it is necessary to remove or recover chromium before disposal of industrial waste. Chromium, one of the extensively used heavy metals, in trace amounts is an essential element in the diet of some animals and probably of a human being also. Much has been reported by scientists on the treatment of chromium-bearing effluents (2-13). Traditionally, chromium removal is made by chemical precipitation. However, this method is not completely feasible to reduce chromium concentrations to levels as low as required by environmental legislation.

Adsorption is the selective collection and concentration onto solid surfaces of particular types of molecules contained in a liquid. This process plays an important role in industries. Activated carbon has been widely used as an adsorbent in food, beverage, pharmaceutical, chemical, textile and other industries (14). In municipal water supply and other water industries, it had become the standard adsorbent. Adsorption is an alternative method to treat the industrial effluents containing chromium

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because of its low cost and high metal binding capacity. The metal binding capacity of activated carbon for chromium is important in designing adsorption contacting systems. The aim of the present work is to determine the adsorption capacity of activated carbon for hexavalent chromium in aqueous solution.

2. Materials and Methods

2.1. Adsorbent

Commercially available, activated carbon, purchased from Sd. Fine Chemicals Limited, Mumbai was used as an adsorbent.

2.2. Preparation of Synthetic Effluent

In order to have uniform characteristics and to avoid interference with other elements, the synthetic effluent for the present study was prepared by dissolving the known amount of potassium chromate (K_2CrO_4) in distilled water. For 1000 mg/L hexavalent chromium concentration 3.7349 g AR grade K_2CrO_4 was dissolved in 1.0 litre of distilled water.

2.3. Experimental Procedure

Batch reactors were employed in carrying out the experiments. 100 ml of the synthetic effluent with the known quantity of activated carbon were added to the 250 ml batch reactors and agitated continuously in a rotary shaker and the temperature was maintained at 30ºC. The samples were removed at regular time intervals, filtered with Whatman filter paper No. 44 and the filtrate was analyzed for its residual chromium (VI) concentration. The experimentations were done out to find out the influence of operational parameters like initial concentrations and adsorbent dosages. The equilibrium study was carried out by varying the initial metal concentration and by keeping the temperature constant. The adsorption experimental data was analyzed for kinetic models.

2.4. Analysis of chromium (VI) ions

The concentration of chromium (VI) ions was analyzed by spectrophotometer at 540 nm using diphenyl carbazide as the complexing agent by following the standard procedure given by APHA (15).

3. Results and Discussion

3.1. Effect of Contact Time

In the adsorption system, contact time plays a vital role. The adsorption tests were carried out at various contact times, ranged from one to nine hours for the five different initial concentrations of 500, 600, 800, 900 and 1000 mg/L. At the end of the 8th hour, it attained equilibrium. For every one hour, 10 % of chromium metal was removed due to adsorption of chromium by 5 g of activated carbon (Figure 1). The result clearly indicates that the chromium removal efficiency increased with increase in time and similar results were made by Viswanadham et al. (16) in their work on removal of zinc and nickel ions using a biopolymer, chitin.

3.2. Effect of Initial Concentration

For the five different initial concentrations of synthetic chromium effluent such as 500, 600, 800, 900, 1000 mg/L, the steady-state values of chromium removal efficiency were 64, 92, 83, 71 and 66 %, respectively, using 5 grams of activated carbon under shaking at the end of 8th hour (Figure 2). The lowest equilibrium metal removal efficiency of 64 % was recorded with the initial concentration of 500 mg/L could be attributed to the lowest concentration. The maximum metal removal efficiency of 92 % was obtained at the end of the 8th hour with the initial concentration of 600 mg/L. Furthermore, when the initial concentration was increased, the percentage removal efficiency decreased. These findings corroborate with the investigation carried out by Das et al. (17) on hexavalent chromium removal.

3.3. Effect of Adsorbent Dosage

The experiment was repeated for the different dosage values of activated carbon such as 3, 4, 5, 6, and 7 grams for 600 mg/L and the corresponding values of equilibrium metal removal efficiency obtained were 64, 60, 92, 58, and 97.14 %, respectively, at the end of 8th hour (Figure 3). Increase in adsorption of metals with an increase in adsorbent dosages could be ascribed to the availability of more active adsorbing sites. Finding akin to this study was reported by Mullai et al. (18) in their work on hexavalent chromium using industrial waste biomass.

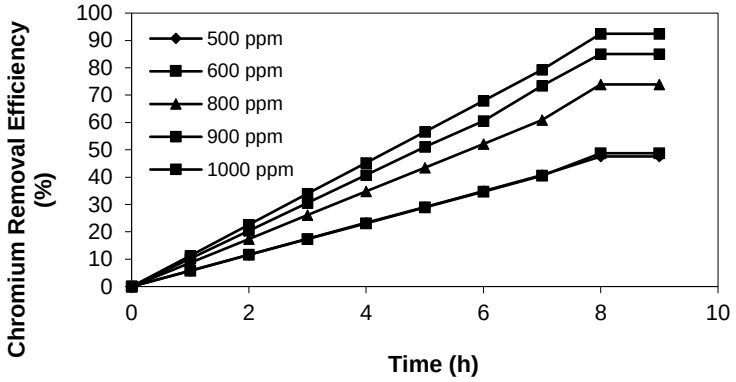

Figure 1. Effect of contact time on the chromium (VI) removal efficiency

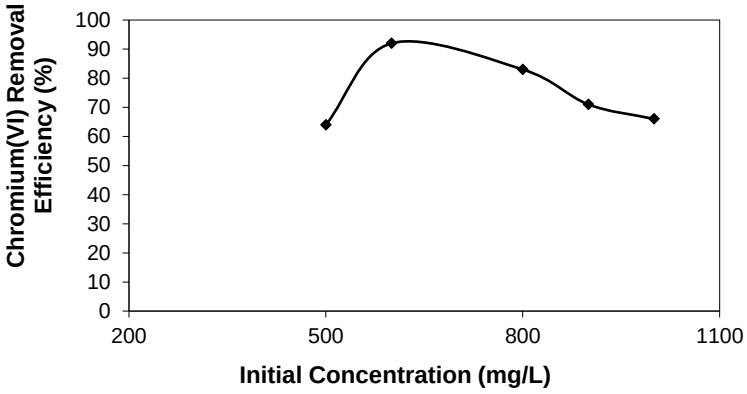

Figure 2. Effect of initial concentration on the chromium (VI) removal efficiency

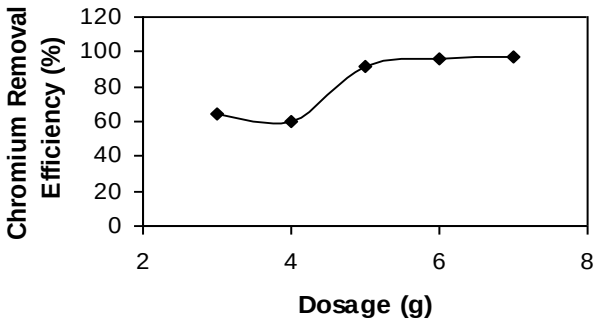

Figure 3. Effect of dosages on chromium (VI) removal efficiency

3.4. Equilibrium Study

Analysis of equilibrium data is important for design purpose in developing an equation describing the process. For equilibrium modeling of the adsorption systems, the equilibrium data obtained was fitted with the two well-known adsorption models, Langmuir and Freundlich models, using their linearized forms. The Langmuir isotherm model is expressed as,

$$q_e = \frac{Q^o b C_e}{1 + bC_e} \tag{1}$$

where, qeq (mg/g) and Ceq (mg/L) are the amount of metal ion per unit weight of adsorbent and unadsorbed metal ion in solution at equilibrium, respectively. Q° (mg/g) is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer on the surface and b (l /mg) is a constant related to the affinity of the binding sites.

The Freundlich isotherm is based on the heterogeneous surface is expressed as

$$q_e = K_F C_e^{1/n} \tag{2}$$

where K_F and n are the Freundlich constants. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. The experimental data were found to fit with the Langmuir and Freundlich isotherms (Figures. 4 and 5). The Langmuir and Freundlich adsorption constants were evaluated from the isotherms. The isotherm constants values of Q°, b, K_F and n were 133.33 (mg/g), 0.00015 (l/mg), 0.02 (l/g) and 1.002, respectively. Q° (mg/g) is important to identify the highest uptake capacity and the activated carbon possesses reasonable sorption efficiency in comparison with other adsorbents (16, 19). The value of b implies the strong bonding of Cr (VI) to activated carbon at these experimental conditions.

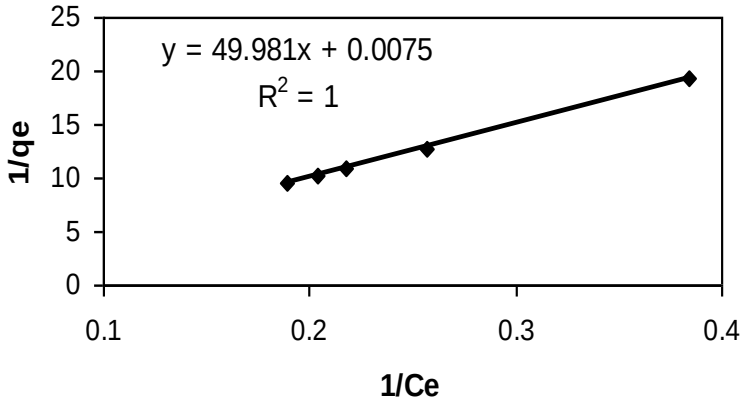

Figure 4. The Langmuir plot for the adsorption of chromium (VI) by activated carbon

Since R_L value lies between 0 and 1 the reported isotherm represents the favourable adsorption. According to Treybal (21), the values n >1 represent favourable Freundlich isotherm adsorption condition and the same was obtained in the present investigation. Furthermore, the higher correlation coefficients (R^2 = 1.000) showed that both the Freundlich and Langmuir models are very suitable in describing the adsorption equilibrium of the metal by activated carbon in the studied concentration range.

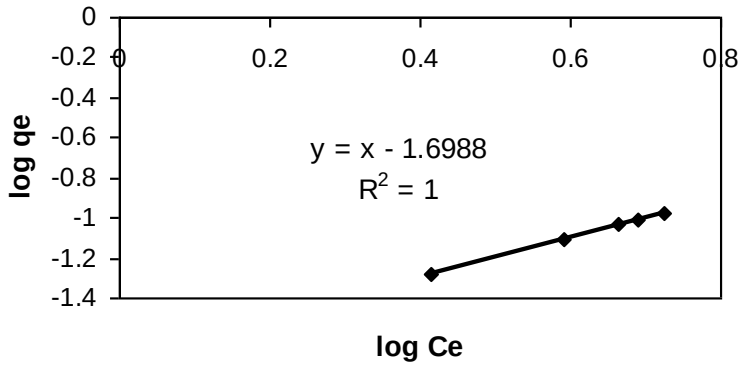

Figure 5. The Freundlich plot for the adsorption of chromium (VI) by activated carbon

The essential characteristics of Langmuir isotherm can be described by a separation factor (20) which is defined by

$$R_L = \frac{1}{1 + bC_i} \tag{3}$$

3.5. Kinetic Study

The rate constant for the adsorption of chromium was studied in the light of Lagergren's equation

$$\frac{dq}{dt} = K_{1,ad}(q_e - q) \tag{4}$$

where, q and qe are the amounts of metal ions on adsorbent (mg/g) at the time t and equilibrium, respectively. $K_{1,ad}$ is the first order rate constant (1/min). q is calculated as,

$$q = \frac{(C_o - C_f)V}{W} \tag{5}$$

where, C_o = Initial concentration of the metal in solution (mg/L); C_f = Final concentration of the metal in solution (mg/L); V = Volume of sample taken in the reactor (L); W = Mass of adsorbent (g).
The integrated form of Eq. (4) is

$$\log(q_e - q) = \log q_e - \frac{K_{1,ad}}{2.303}t \tag{6}$$

A straight line of log (q_e - q) versus t suggests the applicability of this model. In order to fit the Eq. (6) to data obtained experimentally, the equilibrium sorption capacity, q_e must be determined. From the slopes of plot of log (q_e - q) versus t obtained at the initial concentrations of chromium such as 500, 600, 800, 900 and 1000 mg/L, first-order rate constant ($K_{1,ad}$) values such as 0.0387, 0.0274, 0.2977 and 0.3180 h^{-1} were determined (Figure 6). The correlation coefficients for the first-order kinetic model obtained at the studied concentrations were high.

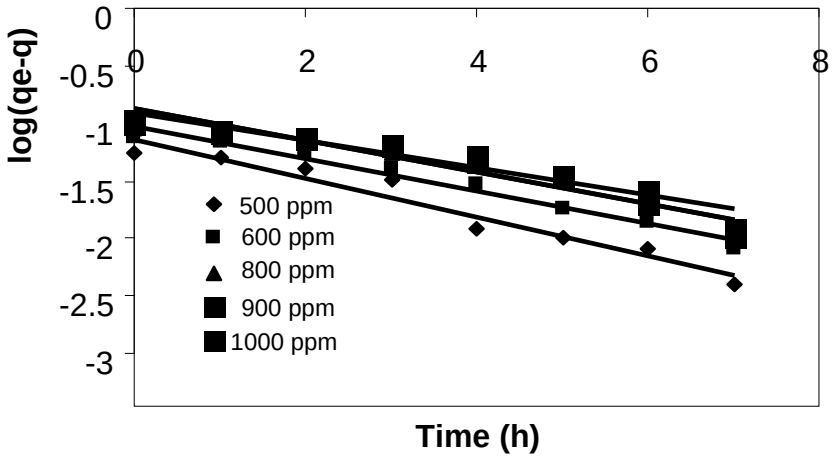

Figure 6. The first order kinetics

4. Conclusions

The results obtained in this study revealed the potential application of the activated carbon in the removal of metal ions from the aqueous solution. The equilibrium time was found to be 8 hours. The equilibrium of the process was fitted into the two well-known adsorption models, Freundlich and Langmuir. In the kinetic studies, using lagergrens equation, the first order rate equation fitted well to the studied concentration range.

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Conflicts of Interest: The authors declare no conflict of interest.

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