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Batch study and kinetics of hexavalent chromium removal from aqueous solutions by anion exchange resin (Dowex 21 KCl)

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ABSTRACT

In this study, the removal of hexavalent chromium (Cr), a strong oxidant and also carcinogen and mutagen, from aqua solution was done using ion exchange process. The batch experiments were conducted to study the kinetics of Cr removal for the concentrations of 1–20 mg/L Cr solutions. The ion exchange resin dosage was 1 g dry weight of ion exchanger/L for Dowex 21 KCl. The removal efficiency observed for all the Cr concentrations and mixing time was over the 82% for Dowex 21 KCl. During the batch experiments, four different mixing time (15–90 min) and six different pH values (2–7) were evaluated to determine the optimum mixing time and pH value. The highest removal efficiency of hexavalent Cr was obtained using 30 rpm shaker speed at pH 6. The experimental data fitted well to the pseudo-first- and pseudo-second-order kinetic models and then the rate constants were evaluated. Finally, it was concluded that the hexavalent chromium ion exchange kinetics of dowex 21 KCl was well explained by first order kinetic model rather than second order kinetic model.

Keywords: Batch adsorption; Hexavalent chromium; Dowex 21 KCl; Anion exchanger; Kinetics study

1. Introduction

Chromium (Cr) is an environmentally significant element found in rocks, animals, plants, soils, volcanic dusts and gases and also used in various industrial processes such as tanning, stainless-steel production, electroplating, pigment fabrication and cements. [1–4]. The two main oxidation states of Cr, Cr(III) and Cr(VI), present in natural waters, significantly differ in biological, geochemical and toxicological properties [5,6].

Cr(III), over a narrow concentration range, is an essential trace nutrient for glucose metabolism humans. In contrast, the anionic compounds of Cr(VI) are reported to have a toxic effect on the biological systems [2].

Hexavalent chromium is a strong oxidizing agent and it is both toxic and carcinogenic for humans and animals [7,8]. Therefore, removal of hexavalent chromium in various samples is of great interest.

Hexavalent Chromium-containing wastewater is typically treated by chemical methods, which generally involves the reduction of Cr(VI) to Cr(III) by reductants and the subsequent adjustment of the solution pH to near-neutral conditions to precipitate the Cr(III) ions [9–12]. Apart from the precipitation method, lime coagulation, ion exchange, reverse osmosis and solvent extraction are some of other methods for hexavalent chromium removal [13,14]. This study looks into a batch ion exchange process, for the removal of hexavalent chromium using ion exchanger.

2. Experimental

All chemical analyses were performed according to standard methods [15]. A visible spectrophotometer

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(Hach Lange DR 2500 Model) was used for hexavalent chromium analysis. The pH values of the samples were adjusted using 1 N NaOH or 1 N H_2SO_4 of analytical grade.

2.1. Reagents and standards

All of the chemicals used were of analytical reagent grade, free from Cr traces. Ultra-pure water was used throughout the entire study.

2.1.1. Preparation of stock Cr solution

$K_2Cr_2O_7$, 2,828.9 mg (Sigma-Aldrich, AR) was dissolved in water and diluted to 1,000 mL; 1.00 mL = 1,000.0 μg Cr.

2.2. Ion exchange studies

During the batch study, the hexavalent chromium concentrations vary from 1 to 20 mg/L. The ion exchanger dosage equivalent to 1 g dry weight was added into each conical flask during all experimental study. The effect of pH on hexavalent chromium removal efficiency was studied by varying pH from 2 to 7 [12]; there is no experimental result more than pH 8 in this study due to Cr ions that tends to settle as chromium hydroxide, sample pH more than 7 [16]. The shaker speed was 30 rpm and time contact was about 30 min. To study the effect of speed on hexavalent chromium removal from solution by the Dowex 21 KCl, experiments were conducted by varying the stirrer speed from 30 to 150 rpm. The equilibrium kinetic studies were conducted for five different concentrations 1, 5, 10, 15, and 20 mg/L of Cr solutions adjusted to pH value 6.

3. Results and discussion

3.1. Effect of pH

Removal efficiency of Cr(VI) by Dowex 21 KCl at different pH at an initial concentration of 10 mg/L, mixing time 60 min and shaker speed 30 rpm are shown in Fig. 1.

Fig. 1 indicates that the optimum pH was observed with 95% Cr(VI) removal at pH 6. It is clear that pH determines the extent of the Cr(VI) removal [17–19].

Cr exists mostly in two oxidation states, Cr(VI) and Cr(III), and the stability of these forms is dependent on the pH of the system [20,21]. It is well known that the dominant form of Cr(VI) at pH 2.0 is $HCrO_4^-$. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms, CrO_4^{2-} and $Cr_2O_7^{2-}$. Maximum adsorption at pH 6 indicates that it is the CrO_4^- and $Cr_2O_7^{2-}$ form of Cr(VI) [20,21].

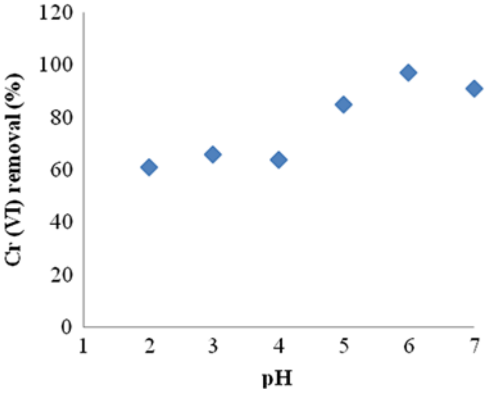

Fig. 1. Removal efficiency of Cr(VI) by Dowex 21 KCl at different pH at an initial concentration of 10 mg/L, mixing time 60 min and shaker speed 30 rpm.

3.2. Effect of speed

The speed of shaker plays an important role in the mass transfer of Cr from the solution to the ion exchange. The effect of speed on Cr removal efficiency was shown in Fig. 2.

Fig. 2 indicates that highest removal efficiency of hexavalent chromium was obtained using 30 rpm shaker speed. This may be due to the fact that at higher speed the influence of desorption was made.

3.3. Adsorption kinetics

Removal efficiency of Cr(VI) by Dowex 21 KCl at different mixing time and initial concentration at an pH 6 and shaker speed 30 rpm are shown in Fig. 3.

From the graph, it is clear that 82% Cr removal was achieved for the Cr concentrations 1, 5, 10, 15, and 20 mg/L for the all mixing times.

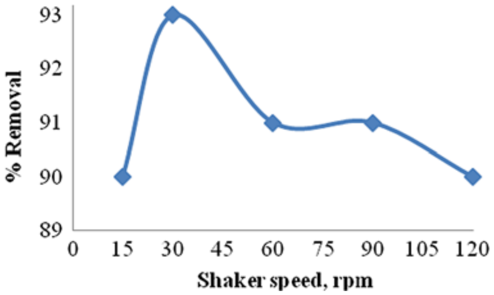

Fig. 2. Removal efficiency of Cr(VI) by Dowex 21 KCl at different shaker speed, at an initial concentration of 10 mg/L, mixing time 60 min.

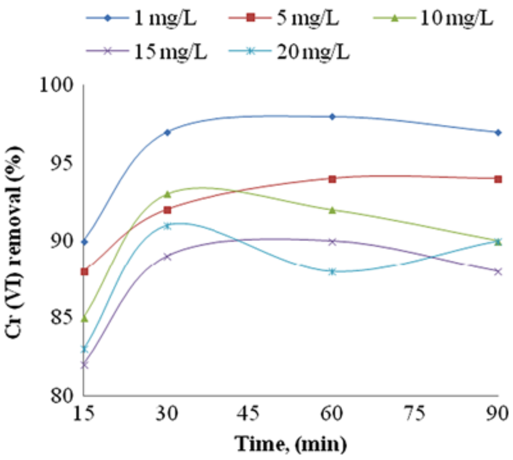

Fig. 3. The adsorption kinetics of Dowex 21 KCl.

In this study, the best removal efficiency was found as 91% for the highest initial Cr concentration (20 mg/L). According to that result, the maximum Cr removal was 18 mg/g Dowex 21 KCl. It was observed that the maximum Cr removal value was higher according to other papers [22–26].

The experimental ion exchange kinetic data were fitted with pseudo-first- and pseudo-second-order kinetic models.

3.3.1. *Pseudo-first-order kinetics*

The ion exchange kinetics explained by pseudo-first-order equation [17] is generally given as

$$\log(q_e - q) = \log q_e - (k_1/2.3063) \cdot t \tag{1}$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q is the amount of solute adsorbed at any time t per unit weight of adsorbent (mg/g), and k_1 is the rate constant of pseudo-first-order sorption (1/min).

The plots were drawn for Eq. (1) for the all concentrations (1–20 mg/L). Approximately linear plots were obtained for all the five concentrations which were shown in Fig. 4. The kinetic constant k_1 for the five different concentrations was obtained from the slopes of the plots and indicated in Table 1. The smallest correlation coefficient obtained from the first order kinetic is 0.7214. The largest one is 0.8993.

3.3.2. *Pseudo-second-order kinetics*

The sorption kinetics explained by pseudo-second-order equation [17] is given as

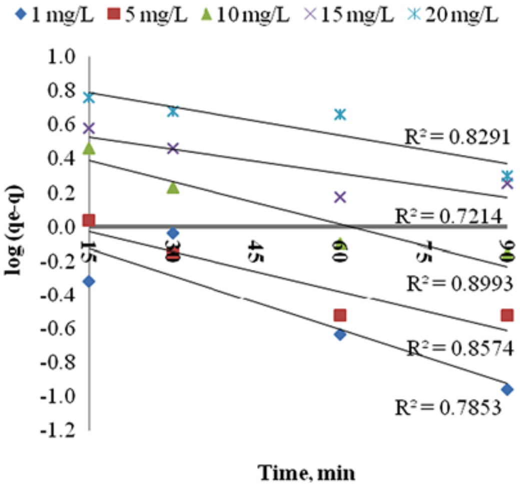

Fig. 4. Pseudo-first-order kinetics of Dowex 21 KCl for different initial concentrations at optimum pH 6.

Table 1
Pseudo-first-order adsorption rate constants for different initial concentrations

Initial concentration (mg/L)	k_1 (min^{-1})	R^2
1	0.0106	0.7853
5	0.0078	0.8574
10	0.0083	0.8993
15	0.0047	0.7214
20	0.0056	0.8291

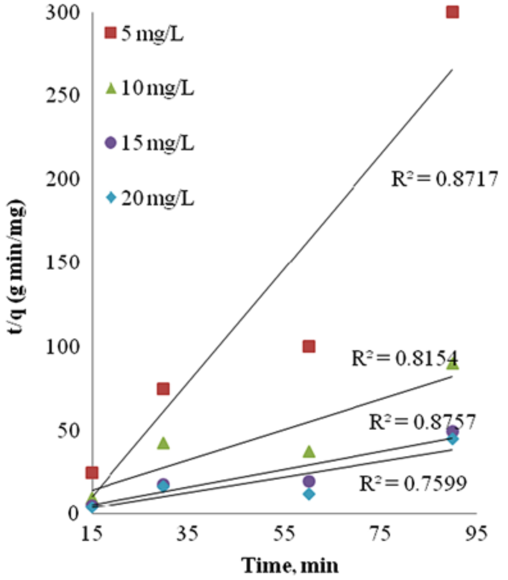

Fig. 5. Pseudo-second-order kinetics of Dowex 21 KCl for 5–20 mg/L initial concentrations at optimum pH 6.

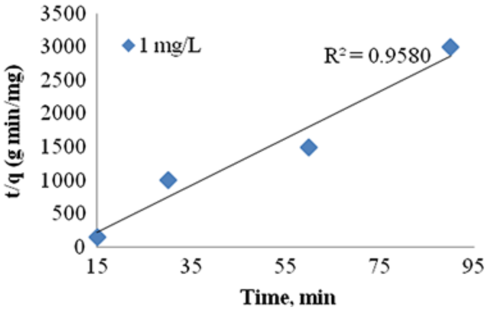

Fig. 6. Pseudo-second-order kinetics of Dowex 21 KCl for 1 mg/L initial concentrations at optimum pH 6.

Table 2
Pseudo-second-order adsorption rate constants for different initial concentrations

Initial concentration (mg/L)	k_2 (g/mg min)	R^2
1	35.1980	0.9580
5	3.3900	0.8717
10	0.9019	0.8154
15	0.5300	0.8757
20	0.4620	0.7599

$$dq/dt = k_2 (q_e - q)^2 \tag{2}$$

where k_2 is the rate constant in g/mg min. Integration of Eq. (2) for the boundary conditions $t = 0$ to $t > 0$ and $q = 0$ to $q > 0$ and then rearrangement yields the following linear form

$$1/q_t = 1/K_2 q_e^2 + t/q_e \tag{3}$$

The values of k_2 are determined from the intercept of second order Eq. (3) from graph shown in Figs. 5 and 6. The values of k_2 and R^2 are indicated in Table 2. The smallest and largest correlation coefficients obtained from the second-order kinetics are 0.7599 and 0.9580 which are still better than the correlation coefficients of the first-order kinetics.

4. Conclusion

The Dowex 21 KCl was reported as an effective ion exchange resin for the treatment of hexavalent chromium. It was capable of removing 82% of Cr from the aqueous solutions of concentrations 1, 5, 10, 15 and 20 mg/L for all mixing time. The adsorption kinetics was well explained by pseudo-first-order kinetics rather than the psedo-second-order kinetics.

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