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Removal of Cr (VI) from aqueous solution by newspapers

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ABSTRACT

The potential to remove Cr (VI) ions from aqueous solution using newspapers was investigated in the present study. The effects of relevant parameters such as solution pH, adsorbent concentration, and reaction temperature on Cr (VI) adsorption were examined. The adsorption of Cr (VI) ions onto newspapers was found to be highly pH-dependent and the highest uptake occurred at pH 1.0. The sorption equilibrium data were correlated to the Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevich equations. Five different non-linear error functions were examined and the result indicated that the Freundlich and Redlich-Peterson equations better fitted the equilibrium data than Langmuir isotherm. The maximum sorption capacity was found to be 55.06 mg/g at pH 1.0, adsorbent concentration 4 g/L and reaction temperature of 30 °C. Different thermodynamic parameters viz., changes in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were also evaluated and the results show that the sorption process was spontaneous and endothermic in nature. The kinetic experimental data were well fitted by the pseudo-second order, external film diffusion and diffusion models allowing the corresponding parameters to be evaluated. The sorption capacity increased with the decrease of adsorbent concentration.

1. Introduction

Cr (VI) is a toxic metal and on the list of priority pollutants due to its mutagenic and carcinogenic properties defined by the US EPA (Environmental Protection Agency). Cr (VI) is mainly from electroplating, leather tanning, textile dyeing and metal finishing industries. The US EPA requires Cr (VI) in drinking water and inland surface waters is 0.05 and 0.1 mg/L, respectively [1].

Conventional treatment technologies utilized in electroplating and metal finishing plants suffer from disadvantages such as high disposal and chemical costs and incomplete reduction of Cr (VI). Therefore, cost effective treatment technologies are needed to meet these requirements. Recently, a variety of low cost materials have been studied for their ability to remove Cr (VI) from aqueous solution and promising results are shown. Among these low cost adsorbents are dead microorganisms, clay minerals, agricultural wastes, industrial wastes and various other low cost materials [1–17].

Newspapers are complex materials and consist principally of cellulose which includes polar functional groups such as alcohols and ethers. These functional groups can be protonated at lower pH and therefore bind Cr (VI) by way of electrostatic interactions. In this study, newspapers were used for biosorption of Cr (VI) from aqueous solutions. Important factors affecting the biosorption such as solution pH, adsorbent concentration, and reaction temperature were investigated.

2. Materials and methods

The newspapers were cut into pieces (2 mm × 2 mm) and used as biosorbents for the following experiments. The stock solution was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) (AR grade) in de-ionized water. The stock solution was finally diluted to obtain standard solutions. Solutions of 0.1 mol/L NaOH and/or HCl were used for pH adjustment.

Batch adsorption experiments were carried out by shaking 0.2 g of sorbent with 50 mL aqueous solution of the desired concentration in a temperature-controlled water-batch shaker. Continuous mixing was provided during the experiments with a constant agitation speed of 200 rpm. Kinetic studies were carried out at constant pH 1.0 with initial concentration (100 mg/L) and adsorbent dose of 4 g/L at 30 °C. After shaking, the solution samples were withdrawn at suitable time intervals. For the isotherm studies, 0.2 g of newspapers was put into 50 mL solutions of various concentrations of Cr (VI). The flasks were shaken to reach equilibrium. A known volume of the solution was removed and centrifuged for Cr (VI) analysis. Effect of pH on the adsorption of Cr (VI) was studied by varying the pH from 1.0 to 7.0. The effect of temperature on adsorption equilibrium was studied by varying temperatures from 30 to 50 °C. Effect of sorbent concentration on uptake of Cr (VI) was investigated by varying the range of concentration from 1.0 to 6.0 g/L.

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The resulting solution was centrifuged and the supernatant liquid analyzed. The concentrations of Cr (VI) were determined using diphenylcarbazide method [1]. Diphenylcarbazide forms a red–violet complex selectively with Cr (VI), and the intensity of this complex was read at 542 nm using a UV–visible spectrophotometer.

The amount of Cr (VI) sorbed (q) in the sorption system was calculated using the mass balance:

$$q = \frac{V(C_\mathrm{i} - C_\mathrm{e})}{m} \tag{1}$$

The Cr (VI) percent removal (%) was calculated using the following equation:

$$Removal\,(\%) = \frac{C_\mathrm{i} - C_\mathrm{e}}{C_\mathrm{i}} \times 100 \tag{2}$$

where V is the solution volume (L), m is the mass of sorbent (g), and C_i and C_e (mg/L) are the initial and equilibrium metal concentrations, respectively.

3. Results and discussion

3.1. Effect of pH on adsorption

Fig. 1 shows the effect of solution pH on Cr (VI) removal. The results indicate that the adsorption removal decreased from 36.5 to 0.34% with increasing the pH from 1.0 to 7.0, suggesting that the removal was highly pH-dependent. The pH dependence of metal adsorption is largely related to the surface functional groups in the biosorbents and metal solution chemistry [18]. As mentioned above, newspapers consist mainly of the cellulose, which contains polar functional groups, alcohols and ethers. These polar functional groups were protonated at lower pH and therefore the surface of the adsorbent positively charged. On the other hand, the Cr (VI) in the solution exists mainly in three oxidation states, i.e. $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, the stability of these forms being dependent on the pH of the system:

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \leftrightarrow 2CrO_4^{2-} + 2H^+ \tag{3}$$

The dominant form of Cr (VI) is $HCrO_4^-$ over the range of $1.0 < \mathrm{pH} < 3.0$ while CrO_4^{2-} is dominant in the range of pH>6.0 [1]. Fig. 1 clearly indicates that it was $HCrO_4^-$ which was adsorbed preferentially onto the newspapers. In presence of H^+, the hydroxyl groups of cellulose (R–OH) were protonated:

$$R\text{–}OH + H^+ \leftrightarrow ROH_2^+ \tag{4}$$

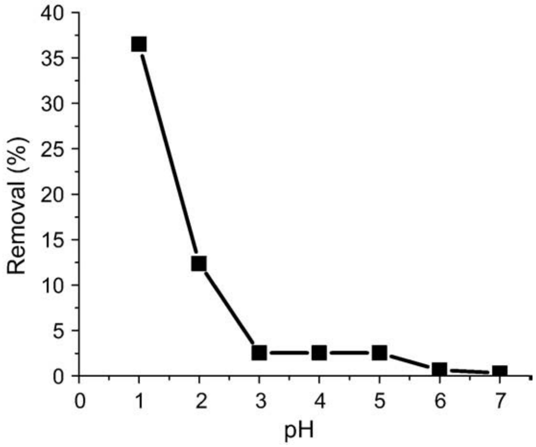

Fig. 1. Effect of pH on Cr (VI) removal (initial concentration 100 mg/L; adsorbent concentration 4 g/L; contact time 2 h; temperature 30 °C).

The adsorption process then proceeded due to the electrostatic attraction between these two counter ions:

$$R\text{–}OH + H^+ + HCrO_4^- \rightarrow R\text{–}OH_2^+\text{–}OCrO_3H^- \tag{5}$$

3.2. Kinetics and mass transfer analysis

Kinetic curve relating to the adsorption of Cr (VI) by newspapers are presented in Fig. 2. Inspection of the curve in Fig. 2 indicates that the amount of Cr (VI) adsorbed increased with agitation time and eventually reached the equilibrium in around 12 h. In all subsequent experiments, the adsorbents were left shaking for 12 h to ensure complete equilibrium. To further elucidate the adsorption mechanism and potential rate-controlling steps in the sorption process, the kinetic experimental data were tested using the pseudo-second-order, external film diffusion equation, and intraparticle diffusion models [19]:

3.2.1. The pseudo-second order kinetic model

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_{e,2}} \tag{6}$$

where q_t is the amount of Cr (VI) adsorbed (mg/g) at time t (min), $q_{\mathrm{e},2}$ the amount adsorbed (mg/g) at equilibrium and k_2 the adsorption rate constant [g/(mg min)].

3.2.2. External mass transfer equation

$$ln\left(\frac{C_t}{C_i} - \frac{1}{1 + m_1K}\right) = ln\left(\frac{m_1K}{1 + m_1K}\right) - \left(\frac{1 + m_1K}{m_1K}\right) \times \beta \times S \times t \tag{7}$$

where C_i is the initial adsorbate concentration (mg/L), C_t (mg/L) the adsorbate concentration after time t (min), m_1 the mass of the adsorbent per unit volume (g/L), K (L/g) the Langmuir constant obtained by multiplying q_L and b_L related to the capacity and energy of the adsorption, respectively, β (cm^2/min) the mass transfer coefficient, S (m^2/m^3) the outer specific surface of the adsorbate per unit volume. If the external film diffusion is only rate-controlling step, the plot of $\ln[(C_\mathrm{t}/C_0) - 1/(1 + \mathrm{m_1K})]$ versus time t should be a straight line.

3.2.3. The intraparticle diffusion equation

$$q_t = k_d t^{0.5} \tag{8}$$

where k_d [mg/(g min$^{0.5}$)] is the diffusion rate constant.

The plot of t/q_t vs. t is shown in Fig. 3(a) and examination of the plot shows that the pseudo-second-order equation accurately

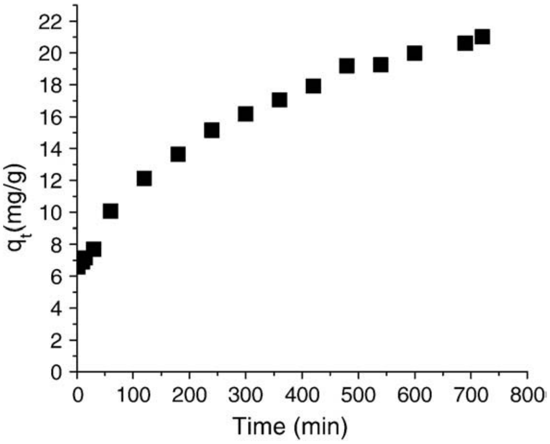

Fig. 2. Adsorption kinetics of Cr (VI) onto newspapers (initial concentration 100 mg/L; adsorbent concentration 4 g/L; solution pH 1.0; temperature 30 °C).