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Adsorption of chromium (VI) by strong alkaline anion exchange fiber in a fixed-bed column: Experiments and models fitting and evaluating

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Continuous fixed-bed column studies for Cr (VI) removal from aqueous solutions were carried out by using Strong Alkaline Anion Exchange Fiber (SAAEF) as an absorbent. The effects of initial concentration, pH value, bed depth, temperature and flow rate were examined. The results showed a forward breakthrough point and decreasing exhaustion time with initial concentration, pH value and flow rate increasing. The optimum bed depth could be calculated when the loading density is about 0.20 g cm^{-3}. The Thomas, Adams–Bohart, Yoon–Nelson and Clark models were applied to predict the adsorption under varying experimental conditions. The Thomas model was in good agreement with the experimental data in representing the whole breakthrough curve while the Adams–Bohart model was valid when $c_t/c_0 < 0.5$ and the Yoon–Nelson and Clark models were less satisfactory.

1. Introduction

Chromium (VI) is one of the priority heavy metal pollutants to the environment for its carcinogenic and mutagenic properties [1,2]. Many separation techniques have been applied to remove Cr (VI) from wastewater, e.g., co-precipitation, coagulation, membrane filtration, adsorption and ion-exchange [3]. Alternative adsorbents were investigated in search for an effective low-cost technology for the treatment of Cr (VI). Bioadsorbents, e.g., brewers draff, grape waste, peat moss, sawdust, fruit peel [4,5] and nature materials, such as akadama clay, sawdust, and parthenium hysterophorus weed [6–8] were used due to low-cost, local availability and minimal pre-treatment requirements but the efficiency for Cr (VI) removal is relatively low with equilibrium adsorption capacity smaller than 50 mg L^{-1}; Modified natural materials, e.g., modified lignocellulosic materials, activated alumina, organo-bentonite and chitosan [9–12], are common Cr (VI) adsorbents as well. Active carbon is a widely utilized absorbent in Cr (VI) adsorption for its large volume of micropores and mesopores, providing a high surface area and having high chemical and thermal stability [13–15]. Polymers, e.g., ion exchangers, are currently studied due to their high Cr (VI) removal capacity (higher than 150 mg g^{-1}), good adsorption kinetics and regeneration properties [16–20].

Strong Alkaline Anion Exchange Fiber (SAAEF) is a new kind of fabric absorption and separation material. Cr (VI) adsorption thermodynamics onto SAAEF showed a spontaneous, entropy-driven and endothermic process [21]. Furthermore, Cr (VI) adsorption onto SAAEF was a fast equilibrium process through kinetics study [22].

To develop an economically viable Cr (VI) removal system, continuous fixed-bed adsorption of Cr (VI) using SAAEF was introduced. The effects of initial Cr (VI) concentration, pH value, column height, temperatures and flow rate on the fixed-bed adsorption process were examined and common dynamic models, i.e., the Thomas, Adams–Bohart, Yoon–Nelson and Clark models, were fitted and evaluated using linear and nonlinear regression analysis.

2. Materials and methods

2.1. Materials and regents

Strong alkaline anion exchange fiber was synthesized by grafting copolymerization of styrene and divinylbenzene onto polypropylene fiber induced by ^{60}Co γ-ray co-irradiation followed by chloromethylation and amination [23]. SAAEF was pretreated by 50 vol% HCl for 24 h. Simulated aqueous solutions of Cr (VI) were prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in distilled water. The initial pH value of Cr (VI) solution was adjusted with sodium hydroxide (NaOH) and hydrochloric acid (36% HCl).

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All chemicals and reagents used were of analytical grade without further purification.

2.2. Equipments

A PHS-25 precision acidity meter purchased from Shanghai Precision & Scientific Instrument Co., Ltd.; A AR2140 electronic balance provided by Ohaus Co., Shanghai; A DHG-9055A electric blast oven obtained from Shanghai Yi Heng Scientific Instrument Co., Ltd.; A YZ1515x peristaltic pump provided by Longer Precision Pump Co., Ltd.; A BSZ-160F computer automatic collector purchased from Shanghai Jing Ke Industrial Co., Ltd.; A 501A super digital display constant temperature water-bath provided by Shanghai Sheng Xin Scientific Instrument Co., Ltd. were used.

2.3. Analyses method

Cr (VI) concentration was determined by Optima 7000DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP–OES). The standard sample was provided by PerkinElmer. Adsorption capacity of SAAEF was calculated by the following equation:

$$q = \frac{c_0V_0 - c_1V_1}{m} \tag{1}$$

where c_0 and c_1 are the Cr (VI) concentration of influents and effluents, respectively (g L^{-1}); m is the weight of SAAEF (g).

2.4. Fixed-bed adsorption experiments

Cr (VI) adsorption was conducted using the lab-scale setup. 0.50 g SAAEF was packed in a glass column (length and internal diameter are 12.0 and 1.0 cm, respectively) with heating jacket connected to a thermostatic bath. The influent was pumped from the container to the fixed-bed with a peristaltic pump at a specified flow rate. Prior to each run, the column was purged with HCl equivalent to the adsorption process. The effluent at preset times was analyzed.

3. Results and discussion

3.1. The optimization operating conditions for fixed-bed adsorption of Cr (VI)

3.1.1. The effect of pH value

The Cr (VI) adsorption capacity of SAAEF with different pH values are shown in Fig. 1. The results indicate that the Cr (VI) adsorption capacity increased from 198.6 mg g^{-1} at pH 0.5 to 201.1 mg g^{-1} at pH 2.0 but decreased to 146.5 mg g^{-1} at pH 6.0. This trend is also consistent with previous results for Cr (VI) adsorption in static experiments [21].

This may be due to the different adsorption mechanism between Cr (VI) ions and the activated sites on SAAEF under different pH values. The proposed reaction pathway between Cr (VI) ions and activated sites on SAAEF are as follows [24]:

$$2P-CH_2N^+(CH_3)_3CL^- + Cr_3O_{10}^{2-} \rightarrow [P-CH_2N^+(CH_3)_3]Cr_3O_{10} + 2CL^- \ (\text{pH } 1.0\text{–}2.0) \tag{2}$$

$$2P-CH_2N^+(CH_3)_3CL^- + Cr_2O_7^{2-} \rightarrow [P-CH_2N^+(CH_3)_3]Cr_2O_7 + 2CL^- \ (\text{pH } 2.0\text{–}6.0) \tag{3}$$

$$2P-CH_2N^+(CH_3)_3CL^- + CrO_4^{2-} \rightarrow [P-CH_2N^+(CH_3)_3]CrO_4 + 2CL^- \ (\text{pH} > 6.0) \tag{4}$$

Therefore, the Cr (VI)/Cl$^-$ stoichiometric retention ratio was decreasing with pH increasing in the regime of $\text{pH} > 1.0$. The decreasing activated sites required for the same Cr (VI) uptake improves the Cr (VI) adsorption capacity at lower pH. However, some amount of Cr (VI) converts to H_2CrO_4 when $\text{pH} < 1.0$, resulting in a slight decrease in the Cr (VI) at pH 0.5.

3.1.2. Effect of initial concentration

The effect of initial Cr (VI) concentration in the influent was investigated and the results are shown in Fig. 2. Within the test concentration regime from 1.05 g L^{-1} to 8.91 g L^{-1}, the optimum Cr (VI) adsorption was achieved at 4.45 g L^{-1} with maximum Cr (VI) adsorption capacity of 201.2 mg g^{-1}, which is 38.6% higher than at 1.05 g L^{-1}. However, a slight decrease to 178.3 mg g^{-1} is observed when the concentration was extremely high (8.91 g L^{-1}).

At the lower concentration (<5.0 g L^{-1}), the amount of Cr (VI) ions dominates the Cr (VI) adsorption onto SAAEF in the dynamic process. In general, with the concentration increasing, more available Cr (VI) surrounded the activated sites on SAAEF and the exchange efficiency improved. However, an over-concentrated solution provided a "crowded" diffusion path for Cr (VI) ions onto the activated sites. A substantial increase in the concentration with an increasing competition between Cr (VI) ions led to a decrease in Cr (VI) adsorption capacity.

3.1.3. Effect of loading density (D/R)

Fig. 3 shows the Cr (VI) adsorption capacity of SAAEF using various D/R values from 2.6 cm to 6.0 cm. The samples were

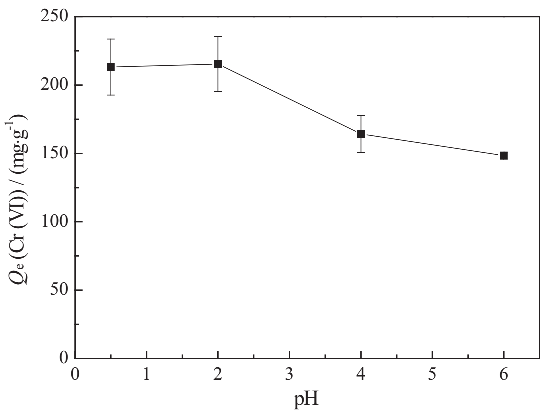

Fig. 1. Effect of pH on Cr (VI) fixed-bed adsorption onto SAAEF (Conc. = 3.94 g L^{-1}; T = 20 °C; flow rate = 0.43 mL min^{-1}; D/R = 3.2 cm).

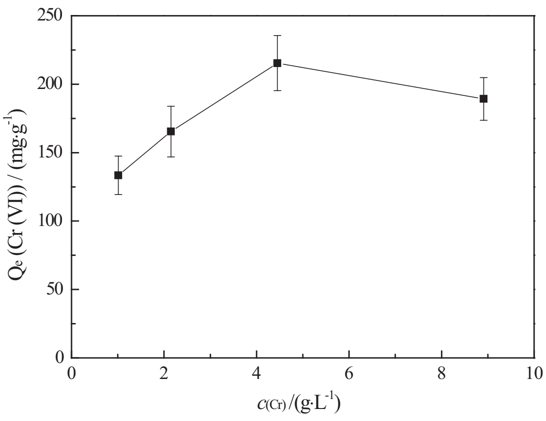

Fig. 2. Effect of concentration on Cr (VI) fixed-bed adsorption onto SAAEF (pH = 2.0; flow rate = 0.43 mL min^{-1}; D/R = 3.2 cm; T = 20 °C).