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Selectivity and Reversibility of Perchlorate Adsorption by Exchange Resin and Activated Carbon

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1. Introduction

Perchlorate (ClO_4^-) has been widely used as a rocket propellant and in munitions in the United States as well as abroad. The improper disposal of perchlorate containing materials has resulted in a significant new threat to groundwater and drinking water supplies (Damian and Pontius, 1999; Urbansky, 1998, 1999). Because perchlorate ions are highly soluble and kinetically inert in dilute aqueous solutions, they can not be effectively removed from water. Ion-exchange technology is well known and has been widely used historically for water treatment (Gurol and Kim, 2000; Urbansky, 1998). However, the effectiveness of an ion exchange process depends on the selectivity of the ion-exchange resin and the concentrations of the contaminant ion itself as well as, other competing ions such as nitrate (NO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) in solution. The greatest challenge associated with using conventional ion-exchange technology is its regeneration (Gu et al., 2001). Regeneration depends on the reversibility between perchlorate as adsorbate and the exchange resin as adsorbent for adsorption and desorption. This study focused on a series of adsorption and desorption experiments to determine the selectivity and reversibility of perchlorate adsorption by activated carbon and exchange resin.

2. Materials and Methods

All chemicals used in the experiments were analytical grade and all stock solutions were prepared with deionized (DI) water from a Milli-Q water system. The perchlorate stock solutions were prepared by dissolving $Na_2ClO_4 \cdot H_2O$ (Fisher, USA) in DI water. For the kinetic experiments, 1.0 g of activated carbon and 0.5 g of exchange resin were added into a 50 mL centrifuge tube that was filled with a 25 mL solution of a desired concentration of perchlorate. The centrifuge tubes were capped and shaken at a speed of 130 rpm. Samples were taken from the tubes at different mixing times. In the adsorption and desorption tests, 0.5 g of exchange resin was added into a 50 mL centrifuge tube that was filled with a 25 mL solution containing 0.5% NaCl and the desired perchlorate concentration. After adsorption for 24 hours, the supernatant was carefully withdrawn using a pipet and then replaced with 25 mL of 0.5% NaCl solution. The tubes were shaken for 24 hours for desorption. All samples for perchlorate were analyzed by IC and IC-MS (Dionex, U.S.A.).

3. Results and discussion

Kinetic experiments were conducted to determine the rate of perchlorate

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adsorption by activated carbon and exchange resin. The results are presented in Fig.1 (a) and (b). The initial perchlorate concentration was 1000 and 10 mg/L for activated carbon and exchange resin systems, respectively. Perchlorate removal by activated carbon and exchange resin reached equilibrium after 180 min and 30 min of reaction time, respectively. Based on the results of adsorption kinetics, mixing times of 3 hours were used in the adsorption experiments for perchlorate by activated carbon and exchange resin.

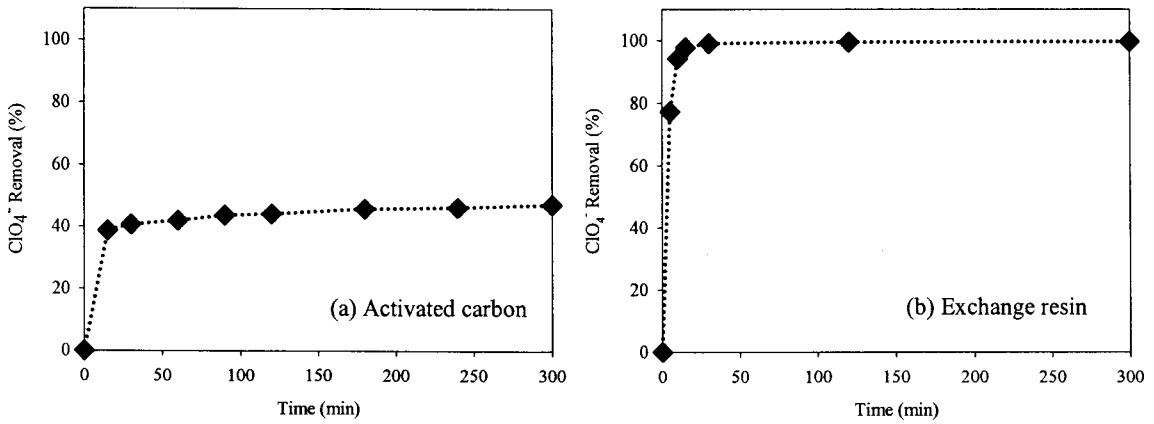

Fig. 1. Kinetics of perchlorate adsorption by (a) activated carbon and (b) SR-7 resin. Activated Carbon: Initial perchlorate = 1000 mg/L Activated carbon content = 1.0 g; Solution = 25 mL DI water. SR-7: Initial perchlorate = 10 mg/L; SR-7 content = 0.5 g; Solution = 25 mL DI water containing 0.5 % NaCl.

The adsorption isotherms and selectivity of perchlorate were determined a wide range of initial perchlorate concentration from 50 to 1000 mg/L for activated carbon and from 500 to 2500 mg/L for exchange resin at a pH 7.0 ± 0.2 (Fig. 2a). The selectivity coefficient, K_d (in mL/mg), was calculated as the ratio of the amount of perchlorate adsorbed per gram of exchange resin divided by the concentration of perchlorate in the equilibrium solution. The K_d values varied from 30 to 800 mL/g for activated carbon and from 130 to 12000 mL/g for exchange resin, respectively (Fig. 2b). The results indicated that the exchange resin has the very high selectivity for perchlorate.

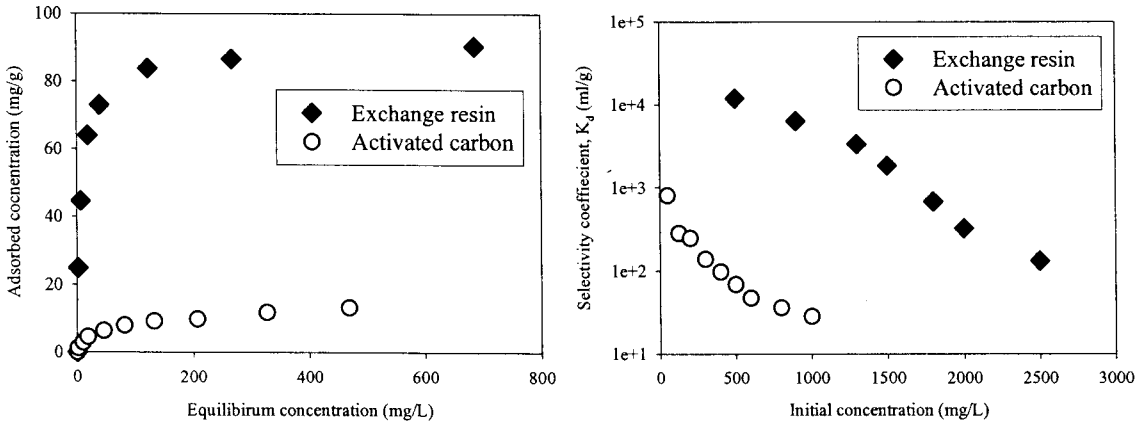

Fig.2. (a) The isotherm and (b) selectivity coefficient for adsorption of perchlorate by activated carbon and exchange resin. Activated carbon: Activated carbon content = 1.0 g; Solution = 25 mL containing 0.2% NaCl. pH = 7.0 ± 0.2. SR-7: SR-7 content = 0.5 g; Solution = 25 mL containing 0.2% NaCl. pH = 7.0 ± 0.2.

The reversibility of perchlorate adsorption was assessed by comparing the adsorption and desorption isotherms in a wide range of initial perchlorate concentration from 3 to 900 mg/L containing 0.5% NaCl for saturated exchange resin. The adsorption and desorption isotherms are shown in Fig. 3. The desorption isotherm is very similar to the adsorption isotherm, which indicates that the perchlorate adsorption by the resin was reversible. This result implies that the perchlorate saturated exchange resin can be regenerated if enough solution is used for regeneration.

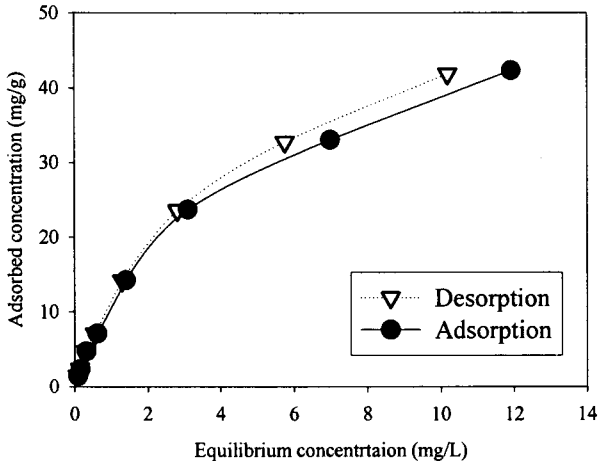

Fig.3. The adsorption and desorption isotherm of perchlorate by SR-7. SR-7 content = 0.5 g; Solution = 25 mL DI water containing 0.5 % NaCl, adsorption time-24 hours. Desorption of perchlorate by DI water containing 0.5 % NaCl, desorption time-24 hours.

4. Conclusions

The selectivity and reversibility of perchlorate adsorption by activated carbon and exchange resin were investigated from a series of adsorption and desorption experiments. Perchlorate adsorption reached equilibrium in 180 and 30 min by activated carbon and exchange resin, respectively. The selectivity coefficient for adsorption of perchlorate, K_d (in mL/g), was from 30 to 800 mL/g in activated carbon and from 130 to 12000 mL/g in exchange resin, respectively. Desorption experiments were conducted to determine the reversibility of perchlorate on exchange resin. The desorption isotherm was very close to adsorption isotherm, which indicates that perchlorate adsorption is a nearly reversible reaction. This implies that the saturated resin by perchlorate can be regenerated if enough solution is used.

Acknowledgement

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