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Removal and Recovery of Mo(IV) from Aqueous Solutions by D201 Resin: Adsorption and Column Studies

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The adsorption and desorption properties of D201 resin for Mo(IV) have been investigated in CH_3COOH-CH_3COOAc medium. A series of experiments were conducted in a batch system to assess the effect of the system variables, *i.e.*, initial pH, contact time and temperature. The optimal pH for the adsorption was 5.5 and the maximum adsorption capacity was 501.4 mg/g at 298 K. The apparent adsorption rate constant were $k_{288\ K} = 2.69 \times 10^{-5}\ s^{-1}$; $k_{298\ K} = 2.85 \times 10^{-5}\ s^{-1}$; $k_{308\ K} = 4.37 \times 10^{-5}\ s^{-1}$; $k_{313\ K} = 4.61 \times 10^{-5}\ s^{-1}$, respectively. The adsorption isotherms data fitted well to Langmuir model. Finally, Mo(IV) could be eluted by using 1.25 mol/L NaOH solution and the resin can be regenerated and reused without apparent decrease of adsorption capacity.

Keywords: D201 resin, Mo(IV), Adsorption, Kinetics, Langmuir model.

INTRODUCTION

Industrial wastewater is usually an integral part of chemical/petrochemical by-products, which are suspended or dissolved in the process water. Amongst the most common pollutants contained in such industrial wastewater are heavy metals (molybdenum, cadmium, mercury, *etc.*)[1,2]. These heavy metals are associated with spent catalysts used in the reaction unit of a process plant.

Molybdenum is an essential trace element for both animals and plants and its deficiency is significant in many regions of the world. In contrast, molybdenum is toxic at high concentrations and continued intake of molybdenum by humans leads to weakness, headache, irritability, lack of appetite, *etc*[3]. Therefore, removal of molybdenum from wastewaters and ground waters is of significant importance from an environmental point of view.

Adsorption is one of the more effective and economic techniques for removal of molybdate ion. Various adsorbents used for the removal of molybdate from aqueous solution are nano-ball allophane[4], ferrihydrite[5], pyrite[6] and chitosan beads[7], but with low adsorption capacity. D201 resin is a polymeric material containing a functional group ($-N^+(CH_3)_3$). It can exchange with anion and nitrogen atom can coordinate with metal ion. Therefore, D201 resin is widely used in the removal of metal ions from aqueous solutions. In this work, the sorption properties of D201 resin for Mo(IV) were investigated. Some basic sorption parameters were determined. Elution was achieved using sodium hydroxide.

EXPERIMENTAL

Shimadzu UV-2550 UV-VIS spectrophotometer; DSHZ-300A and the THZ-C-1 temperature constant shaking machine; Mettler toledo delta 320 pH meter; Molresearch analysis-type ultra-pure water machine were used in this study.

Macroporous type D201 resin was provided by the Chemical Plant of Nankai University (Tianjin, China). The aqueous stock solution containing 2 mg/mL Mo(IV) was prepared by dissolving 1.8403 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (with a purity of 99.99 %) into 0.5 L purified water. Buffer solutions ranging from pH 4.5 to 6.5 were prepared from 0.4 mol/L sodium acetate and 0.4 mol/L acetic acid. All other chemicals were of analytical grade.

Adsorption equilibrium experiment: 15 mg treated resin was weighed and added into a conical flask and then a desired volume of buffer solution at pH 5.5 was added. After 24 h, a required amount of standard Mo(IV) solution was added. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until adsorption equilibrium was reached. The procedure of kinetic tests was identical to that of the equilibrium tests.

Column experiment: Continuous packed bed studies were performed in a fixed bed mini glass column (Φ3 mm × 30 cm) with 150 mg resin. D201 resin in the column was presoaked for 24 h before starting the experiment. The Mo(IV) solution of 0.20 mg/mL and flow rate of 0.15 mL/min was passed continuously through the stationary bed of sorbent in up-flow mode to avoid channeling of the effluent. The experiment was continued until a constant Mo(IV) ions concentration was obtained. The column studies were performed at the optimum pH 5.5 and at 25 ºC to be representative of environmentally relevant conditions.

Elution test: 15 mg resin was added into a mixed solution of pH 5.5 buffer solution and the desired amount of standard Mo(IV). After the equilibrium was set up, the concentration of Mo(IV) in the aqueous phase was determined and the sorption capacity of the resin for Mo(IV) was obtained. The resin separated from the residual aqueous phase was washed three times with pH 5.5 buffer solution. The resin which had adsorbed Mo(IV) was shaken with the eluant. After reaching equilibrium, the concentration of Mo(IV) in the aqueous phase was determined and then the percentage of elution was obtained.

Analysis of Mo(IV) ions: The concentration of Mo(IV)-ion in the aqueous phase was determined by the colour reagent of NH_4SCN at 470 nm. The adsorption capacity (Q, mg/g) and distribution coefficient (D, mL/g) were calculated as follows:

$$Q = \frac{C_o - C_e}{W} V \quad (1)$$

$$D = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \quad (2)$$

where C_o is initial concentration in solution (mg/mL), C_e is equilibrium concentration in solution (mg/mL), V is solution volume of solution (mL), W is resin dry weight (g).

RESULTS AND DISCUSSION

Influence of pH on the distribution coefficient (D): In this work, the pH values of 30 mL of each of the model solutions, containing 10 mg of Mo(IV) metal ions, were adjusted to a range of pH 4.5-6.5 using CH_3COOH-CH_3COONa buffer solutions at 25 ºC to reach equilibrium absorption. The influence of pH on the adsorption behaviour of D201 resin for Mo(IV) is shown in Fig. 1. The results show that the distribution coefficient (D) is the highest at pH = 5.5 and decreases by either raising or lowering pH. Hence, all the following experiments were carried out at pH 5.5.

Adsorption isotherms: The Langmuir and Freundlich isotherms are studied by varying the initial concentrations (7 mg/30 mL, 8 mg/30 mL 9 mg/30 mL, 10 mg/30 mL, 11 mg/30 mL) of the Mo(VI) ion solutions at 288, 298 and 308 K. The adsorption data were analyzed to see whether the isotherm obeyed the Langmuir[8] and Freundlich[9] isotherm models. The linear forms of the Langmuir and Freundlich isotherms are represented by the following equations:

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

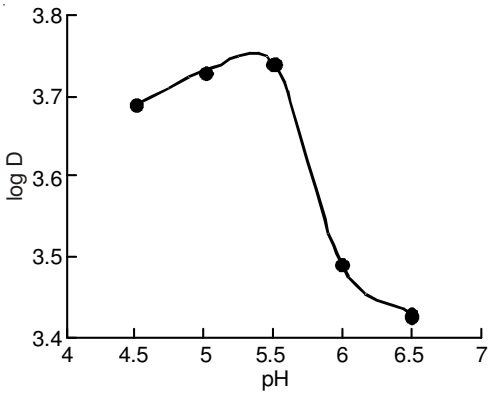

Fig. 1. Effect of pH on distribution coefficient of Mo(VI), resin 15 mg; $[Mo(VI)]_0$ =10 mg/30 mL; T = 298 K; 100 rpm

Freundlich isotherm:

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F \quad (4)$$

where Q_m is the maximal adsorption capacity (mg/g), Q_e is the amount of Mo(IV) adsorbent at equilibrium (mg/g) and K_L is the Langmuir constant which reacts quantitatively the affinity between the D201 resin and Mo(IV) ions. K_F is Freundlich constant and n (dimensionless) is the heterogeneity factor.

According to the results, higher R^2 values ($R^2_{288\,K} = 0.9951$, $R^2_{298\,K} = 0.9953$, $R^2_{308\,K} = 0.9945$) were obtained from Langmuir model for Mo(IV) than from the Freundlich model ($R^2_{288\,K}$ = 0.9480, $R^2_{298\,K}$ = 0.9192, $R^2_{308\,K}$ = 0.9575), suggesting the applicability of Langmuir model to this system. This indicates that the adsorption of Mo(IV) by D201 is mono layer type and agrees with the observation that the metal ion adsorption from an aqueous solution usually forms a layer on the adsorbent surface. The numerical values of n at equilibrium lies between 3.8 and 6.4, indicating that Mo(IV) ions is favorably adsorbed by D201 resin at all the studied temperatures[10].

Determination of sorption rate constant at different temperature: The experiment was carried out with 15 mg resin, 10 mg/30 mL of Mo(IV) metal ions at 288, 298, 308 and 313 K with samples taken out at intervals to determine the remaining concentration. According to the Brykina *et al.*[11] method, the sorption rate constant *k* can be calculated from -ln (1 – F) = kt, (where $F = Q_t/Q_e$, Q_t and Q_e are respectively the sorption amounts at time t and at equilibrium). The slope of the straight line plot of - ln (1-F) *vs.* t, yields the sorption rate constant k at the various temperatures ($k_{288\,K} = 2.69 \times 10^{-5}\ s^{-1}$; $k_{298\,K} = 2.85 \times 10^{-5}\ s^{-1}$; $k_{308\,K} = 4.37 \times 10^{-5}\ s^{-1}$; $k_{313\,K} = 4.61 \times 10^{-5}\ s^{-1}$). According to Boyd's liquid film spreading equation, it can be deduced from the linear relationship between -ln (1-F) and t, that liquid film spreading is the predominant step of the sorption process[12-14].

Dynamic adsorption curve: The dynamic experiments were carried out in glass columns wet-packed. Sample solution flowed through the glass column at constant flow rate and the Mo(IV) contents in the effluent liquid were monitored by ultraviolet-visible spectroscopy analysis. A solution having a known concentration of 0.20 mg/mL of Mo(IV) was continuously fed into the column. When the concentration of Mo(IV) emerging from the bottom of the column was equal to that entering the top of the resin bed, the experiment was terminated,

TABLE-1
ELUTION TEST OF Mo(IV) FROM LOADED D201 RESIN

Composition of NaOH (mol/L)	0.25	0.50	1.00	1.25	1.50	1.75	2.00	2.25
Elution (%)	79.7	79.6	84.0	99.8	98.6	87.5	84.3	83.1

then a plot of C_e/C_o *versus* the volume of effluent gave a typical breakthrough curve in Fig. 2. The dynamic saturated adsorption capacity is 476.3 mg/g. It is less than the maximum uptake capacity (501.4 mg/g) because the contact time of the ion concentration with resins was transitory in the dynamic adsorption process[15].

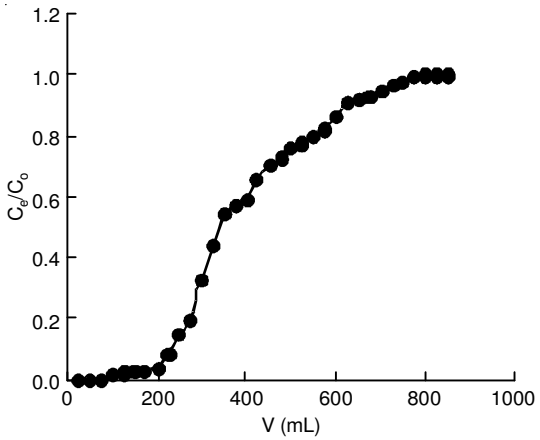

Fig. 2. Dynamic adsorption curve. (resin 150 mg, pH = 5.5, C_0 = 0.20 mg/mL, flow rate = 0.15 mL/min)

Elution and regeneration of resin: Whether an adsorbent is economically attractive in removal of metal ions from aqueous solution depends not only on the adsorptive capacity, but also on how well the adsorbent can be regenerated and used again. In this work, when NaOH was used as an eluant, the percentage of elution varies with 0.25 to 2.25 mol/L NaOH and reaches 99.8 % in 1.25 mol/L NaOH were listed in Table-1. In order to show the reusability of the adsorbent, adsorption-desorption cycle of metal ion was repeated five times by using the same beads. The adsorption capacities for the D201 resin did not noticeably change during the repeated adsorption-desorption operations. These results show that the D201 resin has good regeneration ability.

Conclusion

In this study, batch adsorption experiments for the removal of Mo(IV) from aqueous solutions had been carried out using D201 resin. The molybdate ion can be optimally adsorbed on D201 resin in the CH_3COOH-CH_3COONa buffer system at pH 5.5. The saturated adsorption capacity on the resin was 501.4 mg/g at 298 K. Under the experimental conditions, the adsorption rate constant is $k_{298\ K} = 2.85 \times 10^{-5}\ s^{-1}$. The equilibrium adsorption is well described by the Langmuir isotherm model. The Mo(IV) adsorbed on D201 resin can be eluted by using 1.25 mol/L NaOH solution as an eluant indicating that the resin can be regenerated and reused.

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