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KINETICS STUDY OF MOLYBDENUM SORPTION ON AMINO-FUNCTIONALIZED COPOLYMER

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ABSTRACT

Macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) [PGME-deta] functionalized with diethylene triamine was used for removal of Mo(VI) oxyanions from aqueous solutions. Kinetics of Mo(VI) sorption was investigated in batch experiments by varying initial Mo(VI) concentration. Sorption kinetics data was fitted to chemical-reaction and particle-diffusion models. It was shown that Mo(VI) sorption adhered to the pseudo-second-order kinetic model, with a definite influence of pore diffusion. The maximum Mo(VI) sorption capacity at pH 2.0 and 298K was 391 mg g⁻¹.

INTRODUCTION

Molybdenum (Mo) is a relatively rare chemical element that became of great importance in alloys production and as an inhibitor for steel corrosion due to its low toxicity [1]. In aqueous environment, Mo exists mainly in the form of molybdate and/or other Mo polyanions, depending on the solution pH. At low concentrations, Mo is essential for normal growth of animals and plants, but it can be also considered as a pollutant when its concentration exceeds 5 mg dm⁻³ in the environment (surface and ground water). The degree of toxicity of Mo and its compounds ranks between Zn(II) and Cr(III) compounds [2]. Therefore, the removal of those species from the environment is a matter of vital importance. Polymeric resins have been increasingly investigated as sorbents for the sorption of toxic pollutants because of their controllable pore structure, stable physical and chemical properties and their ability of regeneration and reuse. The presented work was directed at the removal of Mo(VI) oxyanions from aqueous solution using macroporous PGME-deta. Kinetic data were collected at four different initial concentrations and analyzed using four kinetic models including the evaluation of the kinetic parameters.

EXPERIMENTAL

Macroporous crosslinked copolymer of glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA) were prepared through suspension copolymerization (EGDMA content was 20 mass %) and functionalized with diethylene triamine, as described elsewhere [3]. The sorption kinetics of Mo(VI) oxyanions from aqueous solutions with different initial concentrations ($C_i = 0.01, 0.02, 0.05$ and 0.1M ; $\text{pH}=2.0$) was studied in batch experiments at room temperature ($T=298\text{K}$). For determination of Mo(VI) sorption rates, 0.50 g of copolymer PGMA-deta was contacted with 50 cm^3 of metal salt solution. In each experiment, 0.5 cm^3 were withdrawn from the system at predetermined time intervals, diluted to 50 cm^3 and Mo(VI) residual concentration was determined by ICP-OES (Thermo Scientific iCAP6000).

RESULTS AND DISCUSSIONS

The speciation of Mo(VI) oxyanions and the surface charge of sorbent are dependent on pH value and initial concentration [4]. In this study, the maximum experimental sorption capacity for PGME-deta was found to be 391 mg g^{-1} at 298K . Namely, at pH 2.0 a large number of PGME-deta amino groups are in their protonated cationic form and electrostatic interaction occurs between the sorbent and negatively charged oxyanions in solution leading to Mo(VI) uptake. For example, Elwakeel et al. reported Mo(VI) sorption capacity of $336\text{-}380\text{ mg g}^{-1}$ for chemically modified magnetic chitosan resins [2]. Magnetic resins grafted with tetraethylenepentamine displayed Mo(VI) sorption capacity of $407\text{-}593\text{ mg g}^{-1}$ [1].

Table 1. Kinetic models.

| Kinetic model | Equation | Ref. |
|---------------|---|------|
| PFO | $\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303}$ | [5] |
| PSO | $\frac{t}{Q} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$ | [5] |
| IPD | $Q_t = k_{id} t^{1/2} + c_{id}$ | [5] |
| Mckay | $\log(1 - F) = -\left(\frac{S}{2.303}\right)t$ | [6] |

Table 1. where: Q_t -amount of sorbed metal ions at time t , Q_e -amount of sorbed metal ions at equilibrium, k_1 -PFO rate constant, k_2 -PSO rate constant, k_{id} -IPD coefficient, C_{id} -intercept of IPD plot, S -rate parameter. Kinetic parameters calculated from these four kinetic models are presented in Table 2.

In order to investigate the controlling mechanism of Mo(VI) sorption by PGME-deta, the sorption data were treated with four kinetic models i.e. the pseudo-first-order (PFO), the pseudo-second-order (PSO), the intraparticle diffusion (IPD) and the Mckay's model. The applied equations are listed in

Table 2. Kinetic parameters for Mo(VI) using PGME-deta as sorbent (pH=2.0, T=298K)

| C_i , M | 0.01 | 0.02 | 0.05 | 0.1 |
|---|-------|--------|--------|--------|
| Q_e , mg g ⁻¹ | 91 | 155 | 210 | 391 |
| PFO | | | | |
| $k_1 \cdot 10^3$, min ⁻¹ | 2.76 | 2.53 | 2.76 | 4.14 |
| Q_e^{calc} , mg g ⁻¹ | 69 | 108 | 164 | 277 |
| R^2 | 0.906 | 0.953 | 0.980 | 0.906 |
| PSO | | | | |
| $k_2 \cdot 10^3$, g mg ⁻¹ min ⁻¹ | 0.105 | 0.0530 | 0.0358 | 0.0367 |
| Q_e^{calc} , mg g ⁻¹ | 97 | 161 | 222 | 400 |
| R^2 | 0.983 | 0.978 | 0.980 | 0.997 |
| IPD | | | | |
| k_{1id} , mg g ⁻¹ min ^{-0.5} | 3.05 | 5.33 | 6.84 | 20.5 |
| C_{1id} , mg g ⁻¹ | 13.7 | 17.4 | 21.5 | 22.8 |
| R^2 | 0.987 | 0.997 | 0.961 | 0.981 |
| k_{2id} , mg g ⁻¹ min ^{-0.5} | 1.47 | 2.72 | 3.80 | 3.96 |
| C_{2id} , mg g ⁻¹ | 35.1 | 51.2 | 66.6 | 239.3 |
| R^2 | 0.999 | 0.998 | 0.983 | 0.993 |
| McKay | | | | |
| $S \cdot 10^3$, min ⁻¹ | 3.71 | 3.59 | 3.27 | 7.05 |
| R^2 | 0.955 | 0.987 | 0.955 | 0.993 |

As shown in Table 2, the PSO equation fitted well the experimental data, indicating that the Mo(VI) oxyanions sorption onto PGME-deta is surface-reaction controlled.

Most sorption processes take place through multistep mechanism, especially when porous sorbents are used [7]. Due to the fact that PFO and PSO kinetic models cannot show influence of diffusion on the process, IPD and McKay's models were applied. IPD plots showed two different slopes of the linear plots in two different time intervals, with a non-zero values of C_{id} (Figure 1), suggesting that IPD was rate-controlling, but not exclusively. The sorption of Mo(VI) ions onto PGME-deta is controlled by IPD along with boundary layer diffusion [2].

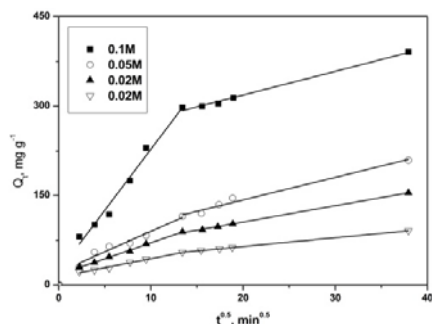


Figure 1. IPD plots for Mo(VI) by PGME-deta at 298K and pH 2.0

At different Mo(VI) concentration Mckay's plots were linear in the initial 180-min period with $R^2 \geq 0.955$ and passed quite near the origin, as an indication that IPD was a major rate determining mechanism particularly in the initial sorption period (Figure not shown).

CONCLUSIONS

The removal of Mo(VI) oxyanions from aqueous solutions was studied using macroporous amino-functionalized crosslinked copolymer, PGME-deta. Kinetics of Mo(VI) sorption was investigated in the initial metal concentration range 0.01-0.1M and analyzed using four kinetic models. Mo(VI) sorption by PGME-deta obeys the PSO kinetic model. The results show that the sorption reaction is controlled by IPD with some degree of boundary layer control. Mckay's model confirms that Mo(VI) sorption is pore diffusion controlled especially in initial period of the reaction.

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