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CHELATING COPOLYMERS: METAL SORPTION KINETICS AND REUSABILITY

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Abstract

Macroporous crosslinked poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate), PGME, was synthesized by suspension copolymerization and functionalized with diethylene triamine, PGME-deta. Kinetics for Au(III), Ag(I) and Cu(II) sorption, as well as the possibility of repeated recovery of Cu(II) ions was investigated.

Introduction

The most important properties of chelating copolymers are high capacity and selectivity, fast kinetics and possibility of the repeated application. In this study, macroporous PGME synthesized by suspension copolymerization and functionalized with diethylene triamine (PGME-deta) was used for metal ions sorption. Kinetic data for Au(III), Ag(I) and Cu(II) were analysed with the pseudo-first and pseudo-second order kinetic models. The potential reusability of PGME-deta for Cu(II) sorption was tested in several sorption/desorption cycles.

Experimental

Macroporous PGME (surface area 50 m^2g^{-1}, pore diameter 53 nm, particle size 150-500 μm) was prepared by suspension copolymerization [1]. PGME-deta was obtained by heating the mixture of 3.6 g of PGME, 15.7 g of diethylene triamine and 100 ml of toluene at 80 ^{0}C for 6 h. Modified sample (surface area 70 m^2g^{-1}, pore diameter 42 nm, particle size 150-500 μm) was filtered, washed with ethanol and dried. For determination of Au(III), Ag(I) and Cu(II) sorption rate, 0.5 g of copolymer was contacted with 50 cm^3 of metal salt solution (0.05 M). The experimental data were treated with pseudo-first and pseudo-second-order equations [2]. For regeneration experiments, PGME-deta (0.1 g) was contacted with 10 cm^3 of 0.05 M $CuCl_2$ (sorption time 120 min). The loaded samples were stripped with 0.1 and 1 M H_2SO_4 (20 cm^3, desorption time 30 min), filtered, dried and treated with metal salt solution. For neutralization, samples were treated with 0.1 or 1 M NaOH, before next sorption cycle. The Ag(I) and Au(III) concentration was determined by Inductively Coupled Plasma (ICP-OES, Perkin Elmer, Model ICP\6500), while the concentration of Cu(II) was determined by atomic absorption spectrometry (AAS, SpektrAA Varian Instruments).

Results and Discussion

For practical use, the rapid sorption of metal ions by amino-functionalized PGME is beneficial, providing a short solution-sorbent contact time in the actual process. The sorption of Cu(II), Ag(I) and Au(III) for PGME-deta was rapid (Fig. 1), with $t_{1/2}$ values (time required to reach 50% of the total sorption capacity) of 1, 2 and 5 minutes, respectively. The correlation coefficients, R^2, as well as theoretical and q_{eq} values calculated for two kinetic models (Table 1) suggest that Au(III), Ag(I) and Cu(II) sorption on PGME-deta proceeds according to pseudo-second order kinetics and depends both on metal concentration and the properties of chelating copolymer.
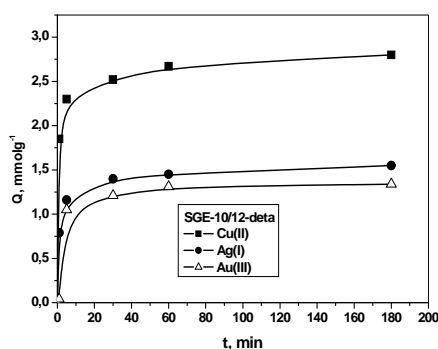

Fig. 1. Sorption of Cu(II), Ag(I) and Au(III) ions vs. time, on PGME-deta [metal ions initial concentration 0.05 M, pH=4 for Cu(II); pH=5.5 for Ag(I) and pH=0.3 for Au(III)].

Table 1. Kinetic data for Au(III), Ag(I) and Cu(II) sorption on PGME-deta.

Sample	$q_{e,exp}$, mmolg^{-1}	Pseudo-first order kinetics			Pseudo-second order kinetics		
		k_1, min^{-1}	q_{eq}, mmolg^{-1}	R^2	k_2, gmmol^{-1}min^{-1}	q_{eq}, mmolg^{-1}	R^2
SGE-10/12-deta, 0.05 M Me solution							
Au(III)	1.30	0.0296	0.32	0.961	0.252	1.32	0.999
Ag(I)	1.45	0.0494	0.64	0.792	3.33	1.45	0.999
Cu(II)	2.80	0.0451	1.12	0.781	0.681	2.80	0.999

The stripping of Cu(II) with H_2SO_4 leads to an initial capacity loss of 50 % in first sorption/desorption cycle (Fig. 2a) and decrease of capacity in the following cycles. After additional treatment with NaOH, amino groups become active again and capacity of poly(GMA-*co*-EGDMA)-deta for Cu(II) ions increases (Fig. 2a).

a)　　　　　　　　　　　　　　b)
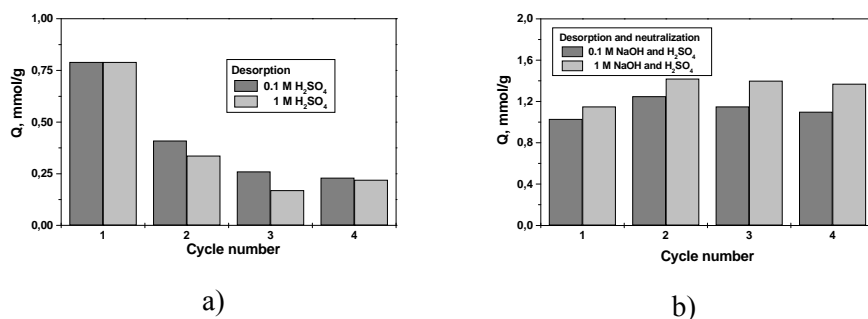
Fig. 2. Sorption/desorption and repeated use of PGME-deta with H_2SO_4
a) without and b) with neutralization [34].

Conclusion

The sorption of Cu(II), Ag(I) and Au(III) by PGME-deta is rapid and proceeds according to pseudo-second order kinetics. Additional treatment with NaOH after stripping of Cu(II) with acid enhances the regeneration and reusability of PGME-deta.

Acknowledgement

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