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Selective sorption of Sb(III) oxoanion by composite sorbents based on cerium and zirconium hydrous oxides

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ABSTRACT

Composite sorbents based on hydrous oxides of cerium and zirconium were used for selective removal of Sb(III) oxoanion. The effects of pH, concentration of Sb and accompanying anions in the feed solution and kinetic of the sorption were studied. Both $CeO_2.nH_2O$/XAD-7 and ZrO-PAN sorbents showed similar sorption capacity at all pH value which was studied. Sorbent $CeO_2.nH_2O$/XAD-7 showed higher removal efficiency than ZrO-PAN. In both cases, increased concentration of sulfates and chlorides in the feed solution caused a decrease of Sb(III) removal.

Keywords: sorption; antimony, hydrous oxides

INTRODUCTION

Antimony[1,2] occurs in natural waters in a variety of forms including particulate and soluble forms of both Sb(III) and Sb(V) and also in the form of organic antimony compounds. Toxicity of inorganic antimony is much greater than that of organic antimony species. Sb(III) is more toxic than the oxidized form Sb(V). The equilibrium of antimony forms in water solution is following:

$$Sb^{V}(OH)_6^- + 3\,H^+ + 2e^- = Sb^{III}(OH)_3 + 3\,H_2O \qquad \log K = 29{,}8$$

For selective separation of Sb from water solution several different methods exists, including sorption by chelating synthetic resin[3-6] or membranes[7,8] different types of biosorbents, i.e. baker's yeast cells[9], sorbent of chitosan base[10], rice husks[11], and sorption on inorganic sorbents as hydrous oxides or chlorides of Fe and Al[12], hydrous oxides of Ce and Zr[13].

In this work, composite sorbents with hydrous oxides of cerium ($CeO_2.nH_2O$/XAD-7) and zirconium (ZrO-PAN) were used for selective removal of Sb(III) oxoanion.

EXPERIMENTAL

Sorbent $CeO_2.nH_2O$/XAD-7 is a composite of non-ionogenic resin Amberlite XAD-7 and cerium oxide (made in laboratory of Department of industrial research in Tokyo, Japan[6]). Sorbent ZrO-PAN is a composite of zirconium oxide in polyacrylonitrile matrix (made in Department of Nuclear Chemistry, CTU Prague, Czech Republic[14-16]). Both sorbents have amphoteric character. For the sorption of Sb(III) oxoanion, sorbents were conditioned with acid or hydroxide solution.

Abbreviations Ce/N and Zr/N will be used hereafter for the sorbents conditioned by hydroxide solution while Ce/P and Zr/P will denote sorbents conditioned with acid.

Experiments were carried out by batch technique in two different modes of sorption shown in Table I.

Table I *Sorption conditions*

Mode		A	B
Solution volume	[mL]	20	1000
Sb concentration	[mg/L]	1-5	5
Cl^-, SO_4^{2-} concentration	[mg/L]	100-1000	100
Solution pH		3.5 - 6 - 9	
Sorbents volume	[mL]	-	0.5
$CeO_2.nH_2O$/XAD-7	[g]	0.080	-
ZrO-PAN	[g]	0.162	-
Contact time	[h]	24	0-24

Logarithms of distribution coefficients *log D* and concentrations of antimony in sorbent phase *q* were calculated according to equations (1) and (2), respectively:

$$\log D = \log \frac{q}{c_e} \quad (1)$$

$$q = \frac{(c_i - c_e)V}{m_s} \quad (2)$$

Where:

c_i concentration of ion A in the feed solution [mg/L]
c_e concentration of ion A in the exit solution [mg/L]
V volume of the feed solution [L]
m_s mass of the sorbent [g]

RESULTS AND DISCUSSION

During the ***type B*** batch experiments sorption of Sb(III) was successful on bots forms of sorbent $CeO_2.nH_2O$/XAD-7 (Fig.1). The effect of pH was the following: maximum of Sb(III) oxoanions from feed solution about 98% (log D ~ 3.3) were removed in all case. Sorption of oxoanion Sb(III) by sorbent ZrO-PAN was very similar in all cases (about 60%), log D were about 2.5. Lower sorption capacities of the sorbent ZrO-PAN were caused by rather high content of inert polyacrylonitrile.

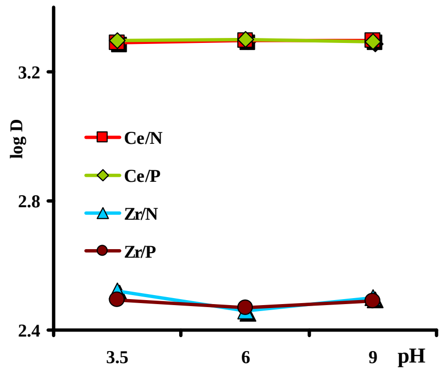

Figure 1 *Effect of pH on the distribution coefficient; c(Sb) = 5 mg/L, c(Cl^-, SO_4^{2-}) = 100 mg/L*

When the concentration of sulfates (as competitive oxoanion) and chlorides (as anion which is commonly preset in water) in the feed solution increased from 100 mg/L up to 1000 mg/L (pH = 6; c(Sb(III)) = 3 mg/L) (***type A***), the sorption capacities of the studied sorbens were very good, removal about 98% of Sb from feed solution. The values of distribution coefficients are listed in Table II. When the concentration of accompanying anions was 100 mg/L, the log D values were similar for both forms of the sorbents, in the case of sulfates and chlorides concentration of 1000 mg/L. ZrO-PAN performed better than the other sorbent. Similar results were obtained in the case of Sb(V) removal[13].

Table II *Effect of concentration of Cl^- and SO_4^{2-} on distribution coefficient of Sb(III) sorption*

	log D		
	c(Cl^-/SO_4^{2-}) [mg/L]		
	100/100 P-form	100/100 N-form	1000/1000 N-form
$CeO_2.nH_2O$/XAD-7	4.97	3.92	4.21
ZrO-PAN	4.97	3.85	4.56

When the concentration of antimony(III) in the feed solution increased from 1 mg/L up to 5 mg/L (***type A***), at pH = 6 the sorbent $CeO_2.nH_2O$/XAD-7 removed about 98% Sb(III) from feed solution, the sorbent ZrO-PAN removed about 99% in all the cases (Fig. 2). The values of distribution coefficients are listed in Table III.

Table III *Effect of concentration of Sb(III)in the feed solution on distribution coefficient of Sb(III) sorption*

	log D		
	$c_{Sb(III)}$ [mg/L]		
	1	**3**	**5**
Ce/N	4.11	3,92	4,87
Ce/P	4.98	-	4,96
Zr/N	5,09	3,85	4,33
Zr/P	4.97	-	4,96

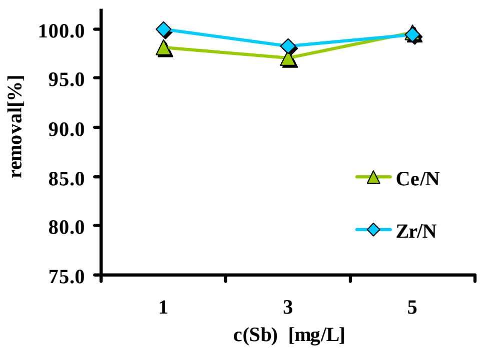

Figure 2 *Effect of concentration of Sb(III) in the feed solution on the distribution coefficient; pH = 6, c(Cl^-, SO_4^{2-}) = 100 mg/L*

Sorption kinetic study – all experiments were carried out by batch experiment ***type B***.

Removal of Sb(III) (Fig.3) (pH = 6) increases more rapidly in the case of sorbent Ce/N (37% after 60 minutes) 93% after 8 hours for both form of $CeO_2.nH_2O$/XAD-7 and after 24 hours both forms removed **99%** of Sb(III).

In the case of sorbent ZrO-PAN the sorption was slow and at all the time sorbent Zr/N was similar to Zr/P. Maximum removal of Sb(III) oxoanion was **59%**. In the case of sorption Sb(V)[13] the maximum removal was 70% and 35%, respectively. But it is necessarily to say, that the feed solution obtained 25 mg/L Sb(V) while in the case Sb(III) only 5 mg/L.

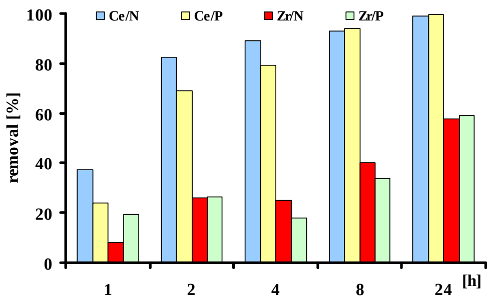

Figure 3 *Study of sorption kinetics; c(Sb) = 5 mg/L, $c(Cl^-, SO_4^{2-})$ = 100 mg/L, pH = 6*

CONCLUSIONS

Both forms of composite sorbents $CeO_2.nH_2O$/XAD-7 and ZrO-PAN selectively removed oxoanion of Sb(III). Sorption capacity was similar at all pH value which was studied. In the case of $CeO_2.nH_2O$/XAD-7, the increased concentration of sulfates and chlorides in the feed solution caused the decrease of Sb(III) removal, but not substantial. When the concentration of antimony(III) in the feed solution increased from 1 mg/L to 5 mg/L at pH 6, both sorbents removed about 98% Sb from feed solution in all the cases. Removal of Sb(III) increased more rapidly in the case of boths forms of $CeO_2.nH_2O$/XAD-7 and after 24 hours both forms removed **90%** of Sb(III). In the case of the sorbent ZrO-PAN, the sorption was slow and the maximum removal of Sb(III) oxoanion was **59%**.

Composite form of both sorbents, having a high breakthrough capacities, enables their utilization in packed column for selective removal of Sb(III) oxoanion from water solution, in the case of dynamic column experiments take into account problematic desorption.

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