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Selective Sorption of Sb(V) 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(V) oxoanion. The effects of pH, concentration of Sb and accompanying anions in the feed solution and kinetic of the sorption were studied. Both $\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$ and ZrO-PAN sorbents showed maximum sorption of Sb(V) oxoanions at pH of 3.5. Sorbent $\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$ 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(V) removal.

Keywords: sorption; antimony, hydrous oxides

INTRODUCTION

Antimony 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)^{1,2}. In the surface waters Sb(V) is the prevailing form. Therefore, the selective removal of pentavalent antimony from aqueous solutions is an important problem with wide applicability.

For selective separation of Sb from water solution several different methods exist³⁻¹⁰, including sorption by chelating synthetic resin, different types of biosorbents and sorption on inorganic sorbents (as hydrous oxides of Fe, Al, etc.).

In this work, composite sorbents with hydrous oxides of cerium ($\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$) and zirconium (ZrO-PAN) were used for selective removal of Sb oxoanions.

EXPERIMENTAL

Sorbent $\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$ is a composite of non-ionogenic resin Amberlite XAD-7 and cerium oxide (made in laboratory of

Department of industrial research in Tokyo, Japan⁶). Sorbent ZrO-PAN is a composite of zirconium oxide in polyacrylonitrile matrix (made in Department of Nuclear Chemistry, CTU Prague, Czech Republic¹¹⁻¹³). Both sorbents have amphoteric character. For the sorption of Sb(V) 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		<u>A</u>	<u>B</u>
Solution volume	[mL]	20	1000
Sb concentration	[mg/L]	1 - 25	25
Cl ⁻ , SO ₄ ²⁻ concentration	[mg/L]	100 - 1000	100
Solution pH		3.5 - 6 - 9	
Sorbents volume	[mL]	-	0.5
$\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$	[g]	0.080	-
ZrO-PAN	[g]	0.162	-
Contact time	[h]	24	0 - 24

Distribution coefficients D and concentrations of antimony in sorbent phase q were calculated according to equations (1) and (2), respectively.:

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

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

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

The effect of pH (Fig.1) on the sorption of Sb(V) during the *type B* batch experiments was the following: for both forms of sorbents $\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$ and ZrO-PAN, maximum sorption of Sb(V) oxoanion was achieved at **pH 3.5**, where logarithms of distribution coefficient ($\log D$) were 3.15 and 2.23, respectively. Lower sorption capacities of the sorbent ZrO-PAN were caused by its rather high content of inert polyacrylonitrile.

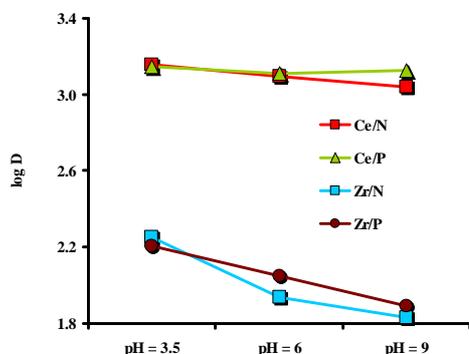


Figure 1 Effect of pH on the distribution coefficient; $c(\text{Sb}) = 25 \text{ mg/L}$, $c(\text{Cl}^-, \text{SO}_4^{2-}) = 100 \text{ mg/L}$

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 at pH = 3.5 and the concentration of Sb(V) was 25 mg/L (*type A*), the sorbent $\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$ removed about 88% and 66% of Sb from feed solution, respectively, while the sorbent ZrO-PAN removed about 95% in both cases. 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.

Table II Effect of concentration of Cl^- and SO_4^{2-}

	log D		
	c(Cl ⁻ , SO ₄ ²⁻) [mg/L]		
	100/100 P-form	100/100 N-form	1000/1000 N-form
CeO₂.nH₂O/XAD-7	4.98	3.28	2.70
ZrO-PAN	4.99	3.17	3.38

When the concentration of antimony(V) in the feed solution increased from 1 mg/L up to 25 mg/L (Fig.2) at pH = 3.5 and the concentration of accompanying anions was 100 mg/L (*type A*), the sorbent ZrO-PAN removed about 99% in both cases, while the sorbent $\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$ removed about 99% and respectively 88% Sb from feed solution.

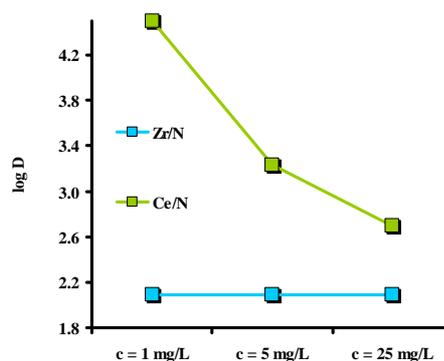


Figure 2 Effect of concentration of Sb in the feed solution on the distribution coefficient; pH = 3.5, $c(\text{Cl}^-, \text{SO}_4^{2-}) = 100 \text{ mg/L}$

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

Removal of Sb(V) (Fig.3) (pH = 3.5) increased more rapidly in the case of the sorbent Ce/P (26% after 60 minutes and 41% after 4 hours) for both forms of $\text{CeO}_2.n\text{H}_2\text{O}/\text{XAD-7}$; after 24 hours both forms removed 70% of Sb(V).

In the case of the sorbent ZrO-PAN, the sorption was slow, the sorbent Zr/N being better than Zr/P at any duration of sorption. Maximum removal of Sb(V) oxoanion was 35%.

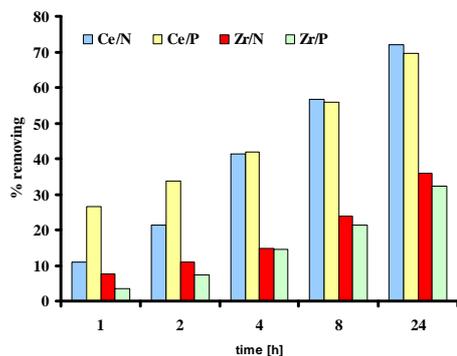


Figure 3 Study of sorption kinetics; $c(\text{Sb}) = 25$ mg/L, $c(\text{Cl}^-, \text{SO}_4^{2-}) = 100$ mg/L, $\text{pH} = 3.5$

CONCLUSIONS

Both forms of composite sorbents $\text{CeO}_2 \cdot n\text{H}_2\text{O}/\text{XAD-7}$ and ZrO-PAN selectively removed oxoanion of Sb(V) . Maximum sorption was achieved at at the pH 3.5. In the case of $\text{CeO}_2 \cdot n\text{H}_2\text{O}/\text{XAD-7}$, the increased concentration of sulfates and chlorides in the feed solution caused the decrease of Sb(V) removal. When the concentration of antimony(V) in the feed solution increased from 1 mg/L to 25 mg/L at pH 3.5, the sorbent ZrO-PAN removed about 99% in all the cases, while the sorbent $\text{CeO}_2 \cdot n\text{H}_2\text{O}/\text{XAD-7}$ removed about 99% and respectively 88% Sb from feed solution. Removal of Sb(V) increased more rapidly in the case of boths forms of $\text{CeO}_2 \cdot n\text{H}_2\text{O}/\text{XAD-7}$ and after 24 hours both forms removed **70%** of Sb(V) . In the case of the sorbent ZrO-PAN , the sorption was slow and the maximum removal of Sb(V) oxoanion was **35%**.

Composite form of both sorbents, having a high breakthrough capacities, enables their utilization in packed column for selective removal of Sb(V) oxoanion from water solution.

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