# BIOSORPTION OF SCANDIUM AND YTTRIUM FROM SOLUTIONS

G.I. Karavaiko, A.S. Kareva, Z.A. Avakian, V.I. Zakharova, and A.A. Korenevsky*
Institute of Microbiology, Russian Academy of Sciences
Prospect 60-Letya Oktyabrya, 7/2, 117811 Moscow, Russia

## SUMMARY

The usage of biosorbents allows separation of scandium and yttrium from each other and from Fe, Al, Ti, Si, and Ca in hydrometallurgical processing of ores and wastes. It was shown that sorption of scandium and yttrium increased with the increase in pH of solution. Initial rate of scandium sorption depended on the biomass type; however 85-98% of scandium was sorbed within 10-30 min with most biomass types tested. The presence of aluminum, iron (III), and titanium in the solution inhibited sorption of scandium and particularly yttrium. After four cycles of sorption, 98.8% of scandium and 87% of yttrium was extracted from red mud leach solution by the biomass of *Saccharomyces cerevisiae* and *Aspergillus terreus*, respectively. Selectivity of the process of scandium and yttrium recovery could be achieved during sorption and also desorption, when solubilization of sorbed associated elements was inhibited by high pH values.

## INTRODUCTION

Microorganisms exhibit high efficiency of the sorption of some elements (U, Ag, Au, Mo, Cr, etc.) (Avakian, 1988; Volesky, 1994; Korenevsky and Karavaiko, 1993). The ability of microorganisms to sorb rare earth elements so far remains virtually unstudied. Scandium and yttrium are typical scattered lithophilic elements. They are present in bauxites, tungsten, uranium, tin ores, etc. (Korshunov *et al.*, 1987). The content of rare earth elements in red mud, which is a by-product of bauxite treatment, increases 2-5 times as compared with the initial bauxite. Acid leaching of red mud produces solutions containing Sc, Y, and also associated elements (Fe, Al, Ti in high concentrations and some other elements). Extraction and ion exchange techniques are normally used for yttrium and scandium recovery from solutions. However, extraction techniques are inefficient for solutions with scandium concentrations below 20 mg/l, while ion exchange resins do not allow complete and selective recovery of Sc and Y from complex solutions (Korshunov *et al.*, 1987). The aim of this study was to investigate the ability of microorganisms to sorb scandium and yttrium from model and industrial solutions and the influence of some metals usually present in red mud leach solutions on the process.

## MATERIALS AND METHODS

Fungal and yeast biomass was used in the experiments. Fungi were grown on Czapek medium, and yeasts were grown on Reader medium. Cultures were incubated at 30°C on a shaker at 220 rpm. Fungal biomass was separated from the culture liquid by filtration (pore size, 0.4 μm) and washed three times with distilled water acidified with 5 M $HNO_3$ to pH=2. The biomass of yeasts was separated from the culture liquid by centrifugation at 4500 g and washed three times with acidified distilled water. Biomass of fungi (0.2 g/l, dry wt) and yeasts (0.5 g/l, dry wt) used for sorption was put into 250-ml flasks with 20-ml aliquots of yttrium or scandium solutions and mixed on a shaker (220 rpm) at 20-25°C for 1 h. Desorption was carried out with 20 ml of 10% w/v $Na_2CO_3$, other conditions being the same as for sorption.

Red mud was leached with hot 30% nitric acid at a solid phase/liquid phase ratio of 1:3.

Scandium and yttrium concentrations in solutions were determined by the plasma emission spectral method; iron, aluminum, and Ti concentrations were dertermined by the atomic absorption method.

X-ray microanalysis was carried out on a JEM-100CXII electron microscope equipped with an EM-ASID4D scanning unit and a Link 860 X-ray analyzer with an E5423 detector.

## RESULTS AND DISCUSSION

The investigations showed that the biosorption of scandium and yttrium is pH-dependent. The biomass sorption capacity was low at pH below 0.5, changed insignificantly between pH 0.5-2.0, and rapidly increased with an increase of pH above 3.0. (Fig. 1). This increase in sorption may be mainly attributed to the scandium and yttrium hydrolysis. The sorption capacity of the biomass depended on the concentration of Sc and Y in the solution and, at pH 4.5, reached 35-40 mg Sc or Y/g dry wt for fungi and 12-15 mg Sc or Y/g dry wt for yeasts at saturation.

Because of the low sorption at pH below 0.5, red mud leach solution was diluted with distilled water before sorption to decrease the acidity. Increasing pH of red mud leach solution above 1.0 caused precipitation of ferric and titanium hydroxides and losses of scandium and yttrium due to co-precipitation. Taking into consideration that scandium sorption changed insignificantly between pH 0.5-1.0 and to avoid excessive dilution, the pH value was adjusted to 0.6. This pH value was chosen for all experiments described below.

A temperature increase from 5 to 50°C produced a 10-15% decrease in Sc and Y sorption by microbial biomass.

The study of scandium sorption dynamics showed that the initial sorption rate depended on the biomass type; however, 85-98% of scandium was sorbed within 10-30 min with most biomass types tested. (Fig. 2).

The presence of a plateau in the scandium sorption isotherms (Fig. 3) suggests that the process of scandium biosorption can be described by the Langmuir equation (Adamson, 1976):

$$X = \frac{X_{max} \cdot K \cdot C_{eq}}{1 + K \cdot C_{eq}},$$

where X is the biomass sorption capacity, $X_{max}$ is the maximum biomass sorption capacity, $C_{eq}$ is the equilibrium concentration of the metal in solution, and K is the adsorption equilibrium constant.
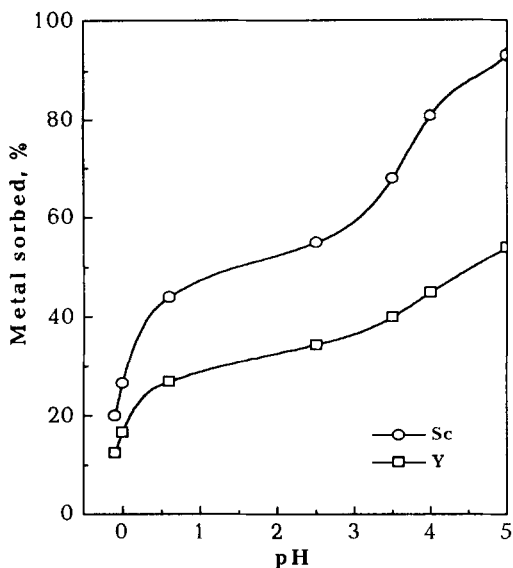
**Fig. 1.** Effect of pH on scandium sorption by the biomass of *S. cerevisiae* at an initial concentration of 25 mg Sc/l.

Data fit by the Langmuir equation produced values for $X_{max}$ and K presented in Table 1. These data show that the highest maximum scandium sorption capacities and highest adsorption equilibrium constants (and hence the highest affinity) were observed with the biomass of *Rhizopus arrhizus* and *Aspergillus terreus.*

All tested microbial biomass types sorbed virtually all scandium and yttrium from solutions containing only scandium or yttrium. Scandium completely inhibited sorption of yttrium, but yttrium did not affect the sorption of scandium (Table 2).

It is evident from Table 2 and Fig. 4 that iron and aluminum inhibit sorption of scandium and yttrium and produce a significant inhibitory effect when present together.

**Table 1.** Langmuir parameters of scandium biosorption pH=0.6.

| Microorganisms | Maximum sorption capacity ($X_{max}$) | Adsorption equilibrium constant (K) | $r^2$ (P=0.95) |
|---|---|---|---|
| *Saccharomyces cerevisiae* | 6.01 ± 0.10 | 0.35 ± 0.01 | 0.99 |
| *Candida valida* | 4.49 ± 0.09 | 0.18 ± 0.01 | 0.99 |
| *Aspergillus niger* | 2.29 ± 0.19 | 0.31 ± 0.01 | 0.99 |
| *Aspergillus terreus* | 6.88 ± 0.04 | 0.62 ± 0.03 | 0.99 |
| *Rhizopus arrhizus* | 16.45 ± 0.50 | 0.59 ± 0.05 | 0.99 |

Note: Data were obtained by the least squares method using STATISTICA software (StatSoft Inc.).

**Table 2.** Effect of associated elements on the biosorption of scandium (pH=0.6).

| Microorganisms | Extraction of Sc, %[a] | | | | |
|---|---|---|---|---|---|
| | Sc | Sc+Y | Sc+Al | Sc+Fe | Sc+Al+Fe |
| *Aspergillus niger* | 98.0 | 98.0 | 68.4 | 56.0 | 33.0 |
| *Aspergillus terreus* | 99.8 | 99.8 | 77.9 | 58.8 | 36.0 |
| *Candida valida* | 99.7 | 99.7 | 82.7 | 73.5 | 58.7 |
| *Saccharomyces cerevisiae* | 99.5 | 99.5 | 94.0 | 91.0 | 72.3 |

Note: The metal concentrations were the following: Sc, 12 mg/l; Fe, 12.9 g/l; Al, 10.6 g/l; Y, 30.9 mg/l.
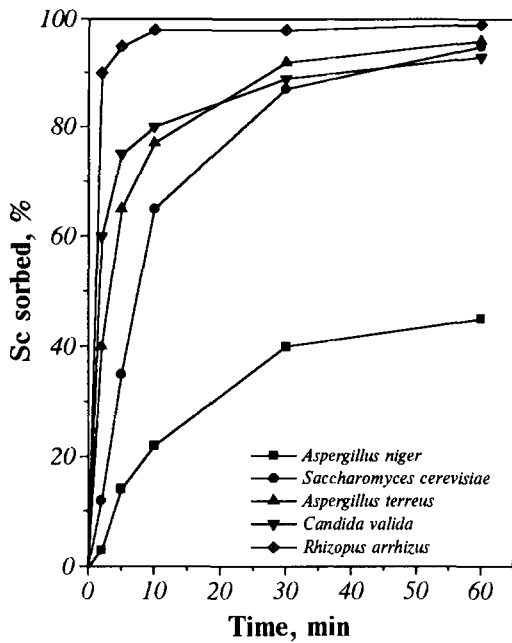[a] The values are means of three replicates.

**Fig. 2.** Dynamics of scandium biosorption at pH=0.6 and an initial concentration of scandium of 10 mg/l.
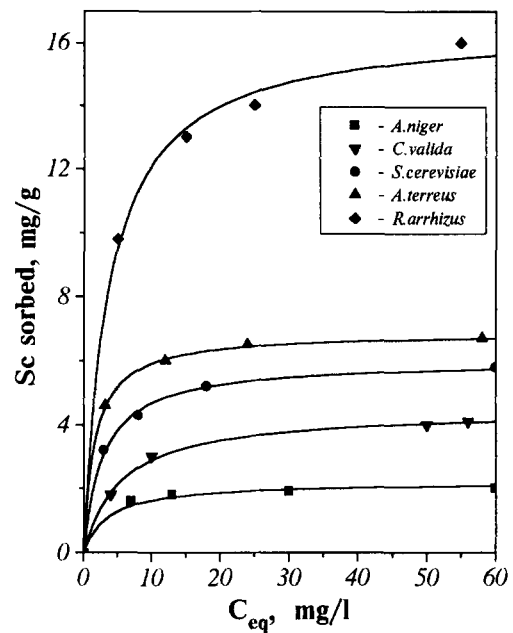
**Fig. 3.** Isotherms of scandium biosorption at pH=0.6.

Titanium inhibited sorption of scandium and yttrium to a greater extent than Fe or Al did. An increase in Ti concentration in the solution from 0.5 to 5.0 g/l increased the inhibition of scandium sorption from 15 to 50%. The sorption of Y was suppressed by 56% at a Ti concentration of 0.25 g/l.

The inhibition of scandium sorption by Al, Fe, and Ti was the least with the biomass *S. cerevisiae* (Table 2). Therefore, this biomass was selected for scandium sorption from red mud leach solution. After four cycles of sorption/desorption, 98.8% of scandium was extracted (Table 3), while yttrium almost entirely remained in the solution. Yttrium could be recovered selectively from the solution after the sorption of scandium.

Comparison of data in Table 2 and Figure 4 shows that the yttrium sorption was inhibited by Al, Fe, and Ti stronger than the sorption of scandium. Only the biomass of *A. terreus* showed satisfactory sortion of yttrium from red mud leach solution. After four cycles of sorption, 87% of the yttrium was extracted with the biomass of *A. terreus*.

It was found that 10% w/v $Na_2CO_3$ was the optimum concentration for scandium and yttrium desorption. In this case, 99.5% efficiency of desorption was achieved. Sorbed Al, Fe, and Ca were not desorbed. Titanium concentration in the desorbate was slightly higher than in the initial solution (Table 3).
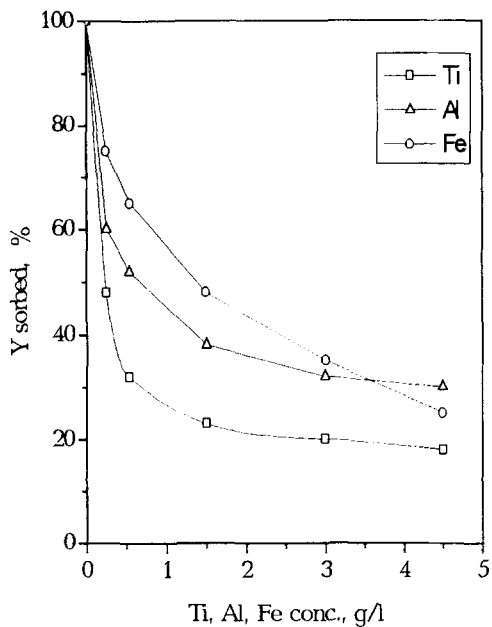
**Fig. 4.** Effect of titanium, aluminum, and ferric ions on sorption of yttrium by the biomass of *S. cerevisiae* at pH=0.6 and an yttrium concentration of 24 mg/l.

During scandium sorption from red mud leach solutions and subsequent desorption, the sorption capacity of biomass considerably decreased. After four sorption/desorption cycles, the biomass sorption capacity was only 45% of the initial value.

Sorption of scandium and associated elements by the biomass of *S. cerevisiae* was studied by X-ray microanalysis. The peaks of S, P, K, and Ca were present in the spectrum of intact biomass. The spectrum of the biomass after sorption had a pronounced scandium peak (Fig. 5). After a number of sorption/desorption cycles, the Al content sharply increased in the biomass. The content of Fe, Ti, and Ca increased to a lesser extent, S concentration changed slightly, K could not be detected in the biomass, and P content decreased drastically. Obviously, the observed reduction of the biomass sorption capacity resulted from irreversible sorption of aluminum, ferric, calcium, and titanium ions and biomass degradation.

**Table 3.** Recovery of scandium from red mud leach solutions with the biomass of *S. cerevisiae*.

| | Content, g/l | | | | | | |
|---|---|---|---|---|---|---|---|
| | Sc, mg/l | Y, mg/l | Al | Fe | Ti | Si | Ca |
| Initial solution | 1.69 | 7.96 | 2.01 | 1.68 | 0.35 | 0.02 | 2.14 |
| Sorbate[a] | 0.02 | 7.92 | 1.96 | 1.65 | 0.31 | 0.0 | 2.07 |
| Desorbate[b] | 30.15 | 0.30 | 0.0 | 0.05 | 0.49 | 0.01 | 0.01 |

([a]) After four subsequent sorption/desorption cycles.
([b]) For desorption, one and the same solution was used four times.
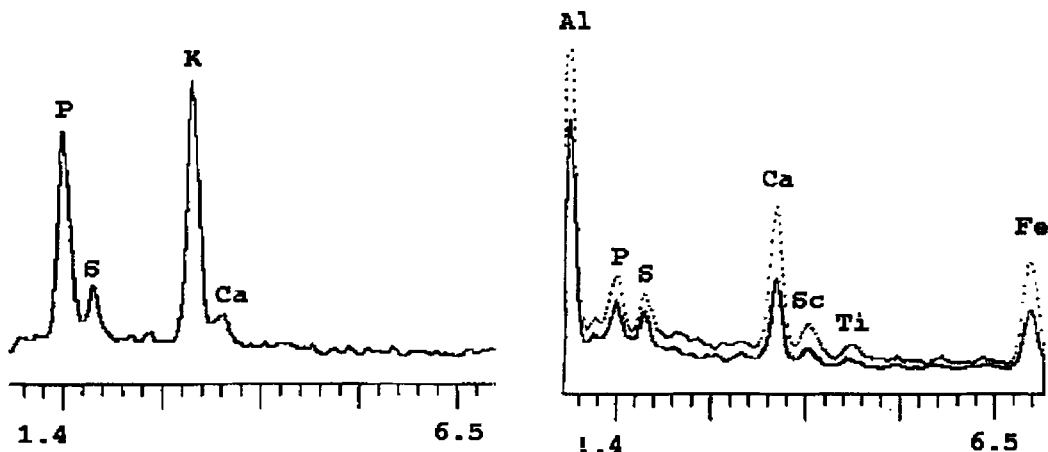
**Fig. 5** X-ray spectra of the biomass of *S. cerevisiae* before (left) and after (right) nine scandium sorption/desorption cycles (two replicate experiments).

## CONCLUSIONS

Microorganisms effectively sorb scandium and yttrium from solutions at low scandium and high associated element concentrations. Selectivity of the process of scandium and yttrium recovery can be achieved during sorption and also desorption, when solubilization of associated elements is inhibited by high pH values.

## ACKNOWLEDGMENTS

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