Studies of Scandium (III) Ion Adsorption/Desorption from Acidic Sulfate Solutions Using Chelating Ion Exchangers

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Abstract

One of the potential sources of raw materials to produce Rare Earth Elements (REEs) and scandium is the technogenic waste of the alumina industry – red mud and dust from electrostatic precipitators of the bauxite sinter processing, in which REEs are concentrated during alkaline leaching. The developing of the new REEs recovery approach with the selective leaching by acid at pH > 3 in the presence of $MgSO_4$ leads to the formation of the solution with the low concentration of Fe and Ti and high amount of valuable elements that should be further processed to obtain REEs concentrate. The study contains research on the sorption recovery of Sc (III) ions from acidic sulfate solutions on selective chelating ion exchange resin Puromet MTS9580. The static sorption data was analyzed using the Langmuir, Freundlich, and Temkin isotherm models. The best fitting for the scandium (III) ions sorption was obtained using the Langmuir (the highest value of the correlation coefficient $R^2 = 0{,}9834$) and Freundlich isotherm models. The dynamic experiments results were better fitted to Thomas model with the equilibrium capacity more than 7 mg Sc per gram of resin.

Keywords: Sorption, Scandium, Isotherm, Sulfate solutions, Puromet MTS9580.

1. Introduction

One of knowing potential sources of raw materials to produce rare earth elements (REEs) and scandium is the technogenic waste of the alumina industry – red mud (RM) and dust from electrostatic precipitators (EPD) of the bauxite sinter processing, in which REEs are concentrated during alkaline leaching of aluminum-containing raw materials. Along with environmental pollution, they contain a relatively large amount of scandium and other rare earth elements. According to available estimates, 70–80 % of the world's scandium reserves are found in bauxites [1].

It can be summarized that despite such complex composition of aluminum-containing waste, its treatment can overcome the unfavorable environmental impacts of mining and be REEs sustainable source at the same time.

The hydrometallurgical technology of treatment of the listed wastes with the Sc and REE production involves the stages of leaching into the aqueous phase in the first stage and selective separation from the leaching solution in the second. The low extraction degree of rare metals at high costs forces the search for more efficient methods characterized by better selectivity.
In our previous studies [2] of the processes of hydrometallurgical treatment of aluminum raw materials, it was found that it is necessary to carry out leaching at pH < 2 in order to extract more than 50 % of REEs. Additional thermochemical or mechanical activation is required to intensify

the leaching process at a higher pH value. EPD particles previously washed from soda and aluminates using water (EPDW) have already thermal and alkaline activated and are sufficiently crushed. In addition, as a result of dust leaching with water, almost all REEs are concentrated in the solid residue because their content approximately doubles according to the analysis. The results of electron probe microanalysis (EPMA) showed that the scandium in the red mud obtained after EPD water leaching is mainly associated with iron minerals. However, scandium exhibits a direct dependence on magnesium extraction, but Sc particles are not associated with it according to EPMA. Therefore, we can conclude that magnesium acts as a leaching agent and helps to dissolve the adsorbed-on iron minerals REE.

We have proposed a novel method for rare earth elements extraction from RM with the addition of $MgSO_4$ at the stage of selective acid leaching at pH > 3, which can obtain a solution with a low content of Fe and Ti with a simultaneous high content of valuable elements [2]. The resulting solution is further processed into the required REE concentrate.

This study extends our previous work and estimates Sc recovery by chelating resin Puromet MTS9580 from sulfuric acid solutions since sorption extraction is the most promising among the methods for extracting Sc from complex productive leaching solutions.

2. Materials and Methods

2.1 Materials

The chelating ion exchange resin Puromet MTS9580 which has selectivity to rare earth elements was used in this study. A model solution was prepared with a scandium concentration of 1–20 mg L^{-1} at a pH = 3.5 to static adsorption experiments. The simulated solution for dynamic experiments containing 24 g L^{-1} $MgSO_4$ and 10 mg L^{-1} Sc was prepared by dissolving Sc_2O_3 in diluted sulfur acid. Specifically, a certain amount of $MgSO_4$ was added and stirred continuously until all had been dissolved by using a laboratory magnetic mixer (Daihan). The required pH values were adjusted by adding concentrated sulfuric acid. All chemicals used were of analytical grade.

2.2 Experimental Methods

The static adsorption was carried out by mixing 50 mL feed solution and 0,1 mL of resin in a conical flask at ambient temperature 25 °C and pH = 3,5 for 8 hours. Mixing took place on a rotary laboratory shaker PE-6410 (Ekros Group of companies). The dynamic adsorption was carried out by using a 5 ml ion exchange column. The dynamic ion exchange experimental unit is shown in Figure 1. The resin volume in the column was 2 mL. The peristaltic pump supplied the initial solution to the bottom of the ion exchange column at different speeds as 2.5, 5, and 7.5 mL per minute. Samples of ion-exchanged liquid that outflowed from the top of the column had been taken periodically for analysis. The saturated resins were washed with distilled water and then statically desorbed with 200 g L^{-1} Na_2CO_3 solution. The equilibrium ion concentrations of Sc (mg L^{-1}) and impurities in the solution samples were measured by using an inductive coupled plasma optical emission spectrometer (ICP-OES, Variant) via Varian AA-240FS spectrometer (Agilent Technologies, San Jose, CA, USA).

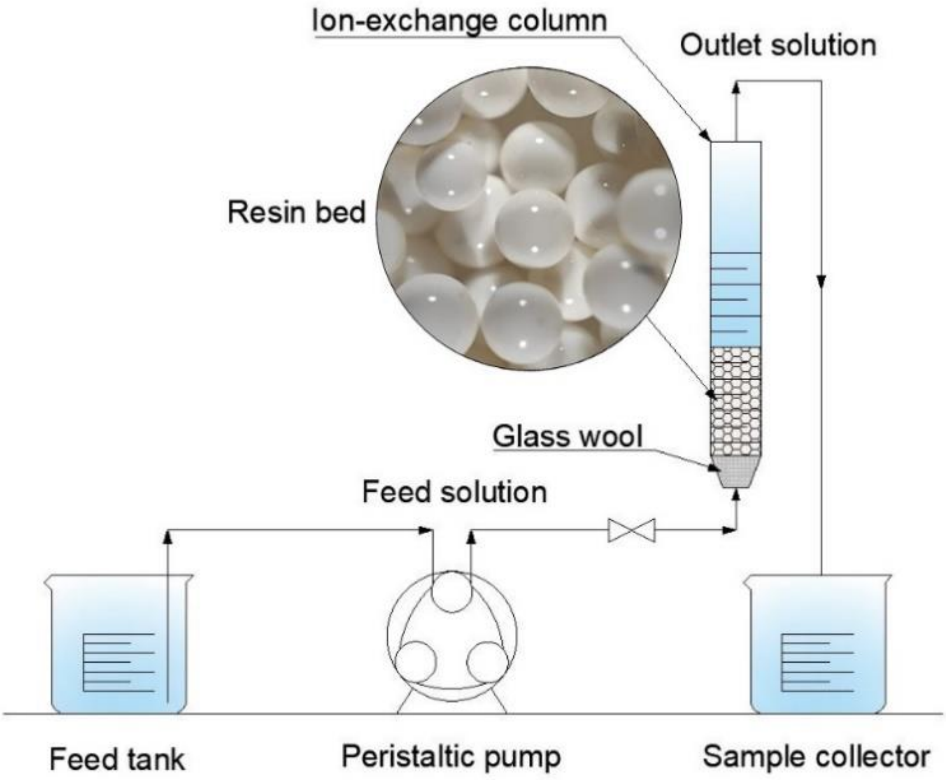


Figure 1. The dynamic ion exchange experimental unit.

2.3 Calculating Equation

For a quantitative description of the sorption equilibrium, equations of two-parameter models of Langmuir (Equation 1), Freundlich (Equation 2), and Temkin (Equation 3) were used, which are shown below.

$$Q = \frac{Q_\infty K_L c_p}{(1+K_L c_p)} \tag{1}$$

$$Q = K_F c_p^{\frac{1}{Q_\infty}} \tag{2}$$

$$Q = \frac{RT}{K_T} \ln Q_\infty c_p \tag{3}$$

where:

Q	The amount of adsorbed lanthanide, mmol g^{-1}
Q_∞	The limiting amount of adsorbed metal, mmol g^{-1}
K_L, K_F, K_T	Langmuir, Freundlich, Temkin isotherm constants
C_p	Equilibrium concentration of metal in solution, mmol L^{-1}
R	Universal gas constant
T	Temperature, K.

Breakthrough model parameters for MTS9580 such as correlation (R^2) and coefficients adsorption amount (mg/g) were calculated according to the model Equations 4–6: Modified dose response model (MDR, Equation 4), calculation of Q0 from MDR constant b (Equation 5), Thomas model (Equation 6).

$$\frac{C_t}{C_0} = 1 - \frac{1}{1+\left(\frac{F_t}{b}\right)^a} \tag{4}$$

$$Q_0 = \frac{bC_0}{m} \tag{5}$$

$$\frac{C_t}{C_0} = \frac{1}{1+e^{\left(\frac{K_t Q_0 m}{F} - K_t C_0 t\right)}} \tag{6}$$

where:

C, C_0	Concentration in moment t, and initial concentration, mg mL^{-1}
F_t	Cumulative flow-through, mL
a, b	MDR constants
Q_0	Maximum column loading metal capacity, mg g^{-1}
m	Mass of used resin, g
K_t	Thomas constant, L min^{-1} mg^{-1}
q_0	Equilibrium adsorbent capacity, mg g^{-1}
Q_0	Volumetric flow rate, mL min^{-1}.

3. Results and Discussion

3.1 Static Sc Extraction Experiments and Sorption Mechanism

Scandium sorption was carried out on model solutions with a concentration of 1-20 mg L^{-1} for 8 hours at a pH of 3.5 at a temperature of 25 °C. Based on the results, a sorption isotherm was obtained (Figure 2), which qualitatively indicates a high affinity of the ion exchange resin for this type of absorbed ions.

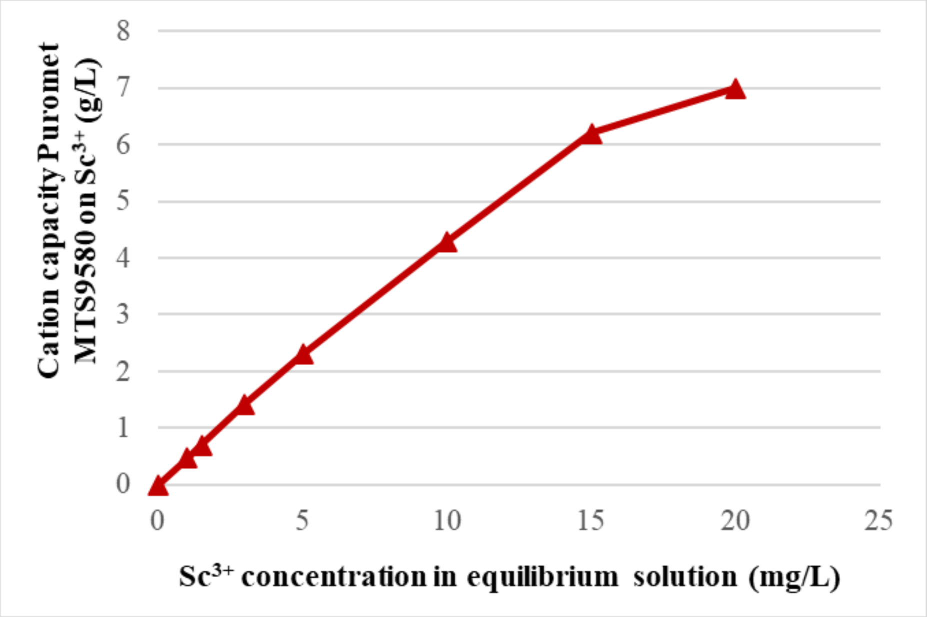
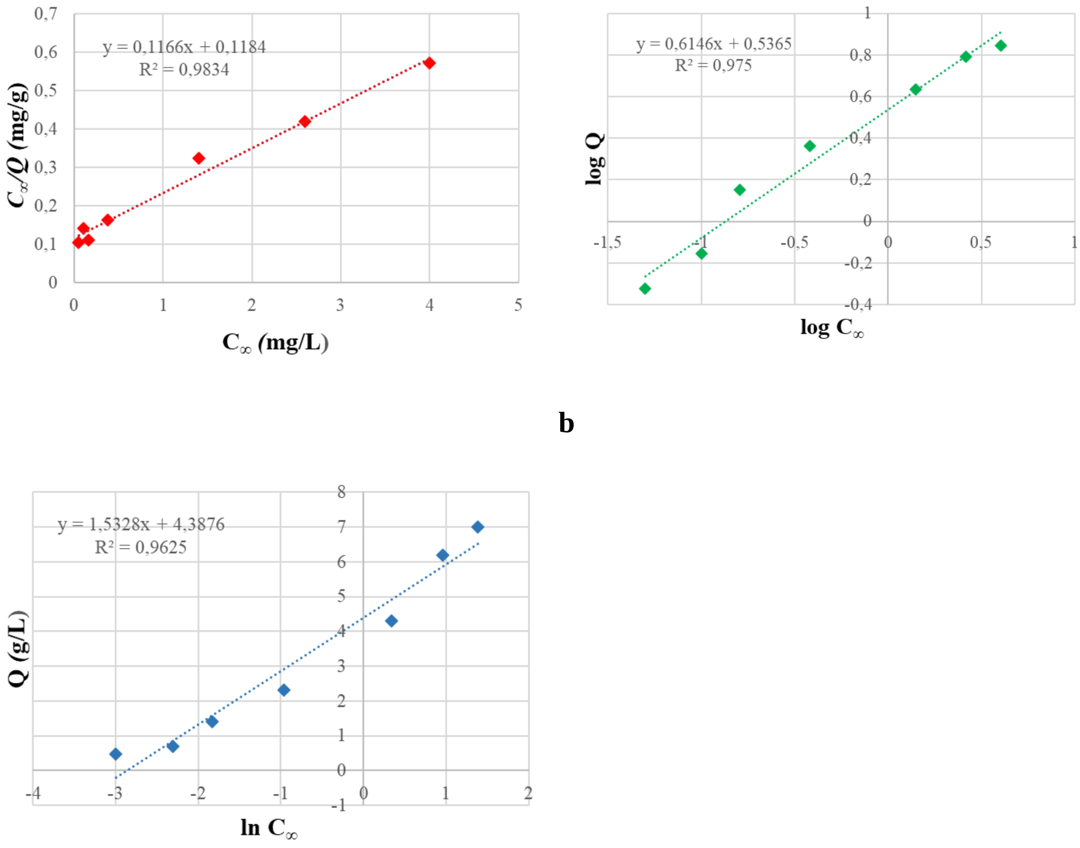


Figure 2. Scandium adsorption isotherm on Puromet MTS9580 from a model sulfuric acid solution at pH 3.5.

The static sorption data was analyzed using the Langmuir, Freundlich, and Temkin isotherm models. According to the equations of thermodynamic models (Equations 1–3), the linear forms of the scandium sorption isotherm on the Puromet MTS9580 ion exchange resin in the H^+-form at a temperature of 25 °C and pH = 3.5 were constructed, which are shown in Figure 3. From the coefficient values a and b of the equation of the straight line y = ax + b, the main thermodynamic parameters of the sorption equilibrium can be calculated. For each model, the equations (Figure 3) and the values of the multiple correlation coefficients R^2 (Table 1) were obtained.



a

b

c

Figure 3. Adsorption isotherms according to the equation: a - Langmuir, b - Freundlich, c – Temkin.

Table 1. Adsorption isotherm parameters for MTS9580.

Model	**Parameter**	**Value**
Langmuir	R^2	0.983
	Q_∞, g L^{-1}	8.576
	K_L, L mg^{-1}	0.985
Freundlich	R^2	0.975
	K_F, L/mg^{-1}	3.440
Temkin	R^2	0.963
	K_T, L mg^{-1}	1615

Scandium sorption data for Puromet MTS9580 are satisfactorily ($R^2 > 0.9$) described by straight lines and can be used to describe the sorption process and calculate thermodynamic parameters. To describe the sorption of Sc by the ion-exchange resin, the Langmuir model was successfully applied for scandium adsorption with correlation coefficients R2 = 0,983. The capacity constant according to the Langmuir equation KL = 0,985, while the maximum calculated capacity Q∞ = 8,576 g L^{-1}.

3.2 Column Adsorption and Breakthrough Modelling

Ion breakthrough was analysed using following breakthrough models commonly applied to ion exchange data based on the mass of resin: the modified dose–response (MDR) and Thomas model. Model fitting was performed for Sc breakthrough in OriginPro software using non-linear regression analysis.

The MDR model is given in Equation (4) [3], and commonly applied to ion exchange breakthrough data. From evaluating the MDR model, the maximum column loading capacity for each metal (Q0) can also be derived using Equation (5).

The Thomas model (Equation (6)) is based on the assumption that the process follows the Langmuir adsorption/desorption kinetics without axial dispersion [4, 5], and the uptake is governed pore-diffusion kinetics (mass transfer) at the resin–solution interface [6]. The main advantage of this model is its ease of use in predicting of breakthrough curves under various operating conditions.

Adsorption measurements are shown in Figure 4, where C/Co means the ratio of concentrations of Sc-ions in the collected effluent over the feed solution. The model constants (Kt, a, b) and base parameters are shown in Table 2.

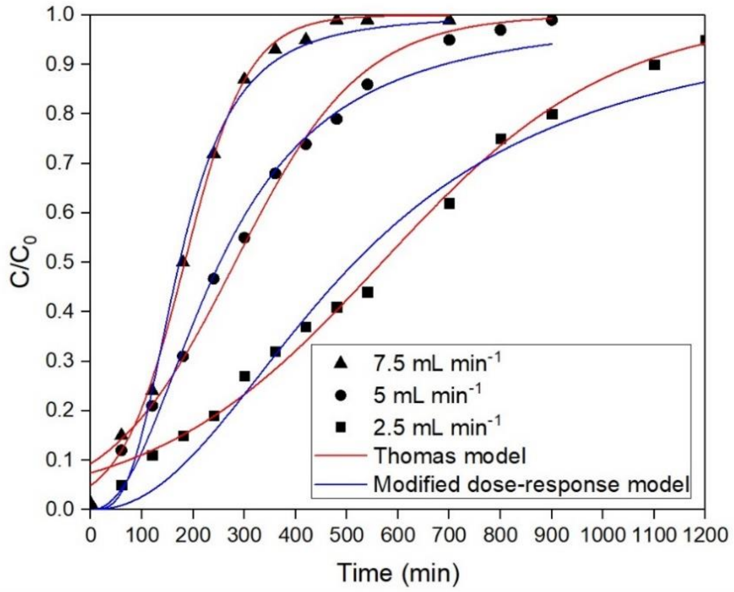


Figure 4. Breakthrough curves of Sc on MTS9580 at flow rate 2.5-7.5 mL/min (pH 2.6).

Table 2. Breakthrough model parameters for MTS9580 at different flow rates

Thomas model	**2.5 ml/min**	**5 ml/min**	**7.5 ml/min**
K_t (dm^3 min^{-1} mg^{-1})	0.00142	6.834*10-4	3.65*10-4
Q_e (mg g^{-1})	7.013	6.776	6.383
R^2	0.99	0.989	0.996
Modified dose-response model	**2.5 ml/min**	**5 ml/min**	**7.5 ml/min**
a	2.197	2.184	3.115
q_0 (mg g^{-1})	10.214	4.845	3.213
R^2	0.973	0.987	0.988

The results in Figure 4 and Table 2 suggest that the Thomas model is best-fitting breakthrough model with correlation coefficients higher than 0.99 for 2.5 rate flow. At the same rate the maximum adsorption capacity of Sc calculated according to Thomas was 7.013 mg g^{-1}, when according to MDR this value is too high (10.214).

3.3 Column Desorption

Desorption efficiency is also a key property when evaluates the adsorbtion process. The adsorbed Sc can be effectively desorbed by Na_2CO_3 solution, a kind of relatively very economic desorbent. Scandium desorption was carried out at room temperature for the resin with the highest calculated capacity (at a sorption rate of 2.5). The results shown in Figure 5 indicates that almost all Sc can be desorbed in 1,5 h (98 %). In 30 minutes, the degree of desorption was 80.06 %. The concentration of Sc in the desorption solution was 562 mg L^{-1} after 1.5 h of desorption, while Mg concentration was lower than 190 mg L^{-1}. This indicates a very high selectivity of the resin because concentration of Mg in the initial solution was 1000x higher.

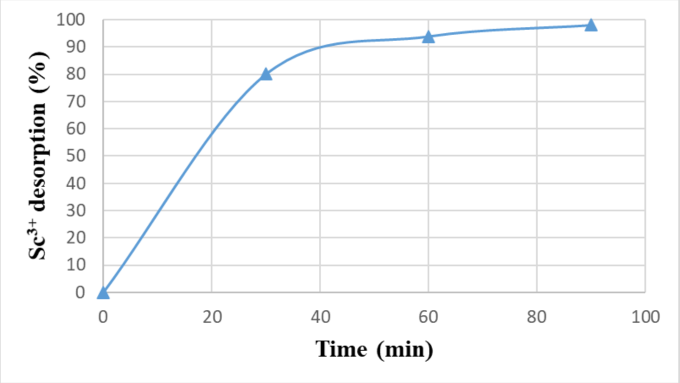


Figure 5. Sc desorption at different time.

4. Conclusions

Based on the results obtained from the current work, the predominant mechanism of sorption from model solutions for the simulated leach solution was studied. Sorption isotherms for a Sc monosolution under static conditions are satisfactorily described by the Freundlich and Langmuir equations, which indicates the formation of a monomolecular Sc layer on the surface of the MTS9580 resin, and all active centers have the same energy and enthalpy. The high values of the correlation coefficients R^2 for the equations of the breakthrough models indicate the applicability of the Thomas model for describing the Sc ions sorption from model Mg-containing solutions using Puromet MTS9580.

According to the Langmuir the maximum calculated capacity is 8,576 g L^{-1} when theoretical maximum capacity by Thomas model is 7,013 mg g^{-1}. The concentration of Sc in the desorption solution was 562 mg L^{-1} after 1.5 h of desorption, while Mg concentration was lower than 190 mg L^{-1}. However, the leaching solution obtained after the bauxite residue processing will contain other elements, especially Fe and Ti, that can affect resin capacity. Therefore, our future studies will be focused on the adsorption/desorption of REEs from the real leaching solutions.

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5. References

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