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Selective Recovery of Scandium (Sc) from Sulfate Solution of Bauxite Residue Leaching Using Puromet MTS9580 Ion-Exchange Sorption

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Abstract: Rare earth elements (REEs) and Sc are concentrated in aluminum production byproducts. The novel REEs recovery approach, which involves leaching with acid at a pH > 3 in the presence of $MgSO_4$, results in the formation of a pregnant leach solution (PLS) with a low concentration of iron (Fe) and titanium (Ti) and a large number of valuable elements. This work studies the application of chelating resin Puromet MTS9580 in the sorption recovery of Sc from sulfate solutions. To analyze the static Sc sorption data, Langmuir, Freundlich, and Temkin isotherm models were used. The Langmuir isotherm model was the best fitted to the experimental data, with a coefficient of determination (R^2) of 0.983. The dynamic adsorption experiment was conducted using a PLS and a simulated solution without contaminants. Adsorption of Sc from the simulated solution was better fitted to the Thomas model with a Sc capacity greater than 6.4 mg mL^{-1}. Because Ti had a gradual decrease in C/C_0, which the Thomas model was unable to simulate, the modified dose-response (MDR) model fitted better with PLS with a Sc capacity greater than 3.8 mg mL^{-1}. The $NaHCO_3$ solution (200 g L^{-1}) effectively desorbed Sc (>98%) from simulated and PLS solutions after 1.5 h of stirring in a batch mode. After 1.5 h of desorption, the concentration of Sc in the desorption solution was 461.5 mg L^{-1}, while the concentration of Mg and Ti was lower than 200 mg L^{-1} and 50 mg L^{-1}, respectively.

Keywords: chelating resin; Sc recovery; selective sorption; adsorption isotherm; sulfate solution; Puromet MTS9580; red mud

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1. Introduction

Rare earth elements (REEs) and Scandium (Sc) are found in many secondary resources, including the bauxite residue (BR) from the alumina industry. During bauxite alkaline leaching in the Bayer process and during sintering with sodium carbonate [1,2], REEs are concentrated in BR and in dust from electrostatic precipitators (ESPDs) [3]. Despite the toxicity, excessive alkalinity, and complex composition of aluminum production byproducts, treatment to recover REEs can overcome the negative impacts of these factors on the economy. Therefore, the concentration of REEs must be taken into account when extending the laboratory study of BR processing to a larger scale.

Sc, which is estimated to have 70–80% of world reserves in bauxites, is far more economically valuable than the rest present in BR REEs [4]. Environmental analyses of hydrometallurgical processes that induce higher flexibility, reduced energy consumption, and other aspects stimulate the development of technologies based upon them [5,6].

The Sc concentrate-obtaining process involves several different approaches, including the stage of leaching into the aqueous phase and the stage of selective recovery from the pregnant leach solution (PLS). The extraction of target elements is commonly accomplished by aqueous solutions of mineral acids such as HCl, H_2SO_4, or HNO_3, as it ensures maximum extraction into the leachate. The obtained PLS is traditionally characterized by a high salt background, high acidity ($pH < 2$), and a low concentration of Sc. In order to concentrate the element and separate it from lixiviants, the most established methods such as ion exchange or solvent extraction are applied [5–7].

In solvent extracting (SX) to concentrate Sc from red mud processing solutions, organophosphorus solvents such as di-(2-ethylhexyl)phosphoric acid (D2EHPA/DEHPA/HDEHP/P204) [8–11], tributyl phosphate (TBP) [9], bis(2,2,4 trimethylpentyl)phosphinic acid (Cyanex 272) [10], and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP/EHEHPA/PC-88A/Ionquest 801/P507) [11,12] are the most prevalent, defined by high selectivity to scandium. But even D2EHPA, the most-used Sc solvent [13] with a high extraction capacity, has a low capacity for Sc when it is mixed with Ti, Th, other REEs, and several other impurity elements [13]. Furthermore, the tendency of D2EHPA to emulsify leads to the loss of the extracted component [13]. On the contrary, substantial quantities of BR or acidic leach solutions that have been processed are accompanied by the irreversible consumption of the costly extraction reagents themselves [7].

Due to the easy separation between liquid and solid phases, adsorption through ion exchange (IX) has been considered an alternative technique that is simple to apply, inexpensive, and has low hazardous emissions (gaseous, organic) [14]. The recovery of metals from dilute solutions can be achieved using sorbent materials, which include novel promising substances such as solvent-impregnated resins (SIRs) and Levextrel resins, commonly referred to as TVEX [15].

Solvent-impregnated resins (SIRs) are prepared by loading or soaking the material in a solution of an organic solvent. The SIR matrix solvent will selectively recover metal ions from the leachate, and these ions will diffuse in the resin phase [16]. The alternative resin is Levextrel, which is produced by the polymerization of styrene and divinylbenzene macroporous copolymers in the presence of extractant, which is incorporated during the synthesis [17]. Based on some extractants used to recover scandium, the following impregnates and TVEX containing TBP (TVEX-TBP) [18], D2EHPA (VP OC 1026) [19], Cyanex 272 (TP 272) [20], and PC 88A (Amberlite XAD 7HP resin) [21] were obtained and tested for the concentration of Sc in hydrometallurgical processing of various mineral raw materials and concentrates.

SIRs combine both the beneficial and negative aspects of both the ion exchange and liquid–liquid extraction in a polymeric-material adsorbent. SIRs can recover ions from very diluted solutions but they have a low capacity and are prone to fouling because of their aqueous solubility [22]. TVEX, unlike SIRs, cannot be washed out by acid solutions and requires a strongly acidic medium (up to 8 M HCl or 6 M H_2SO_4) for selective recovery [7,18]. Searching for optimum conditions, it had not been reported that such a medium would be selective for the separation of Fe and Al from Sc at the stage of sorption and desorption.

Since the majority of feed sources containing REEs are acidic, strong acid cation resins (SACs) containing cations as counterions are the preferred choice for REEs and Sc recovery [23,24]. In order to obtain a mixed rare earth product at the adsorption of La, Sm, and Ho in the study [25], SAC demonstrated the following selectivity order in a widely applicable sulfuric acid media: $\mathrm{REE} \approx \mathrm{Th} > \mathrm{Fe} \approx \mathrm{Al}$. However, it is known that SACs have higher selectivity towards light REEs rather than heavy REEs and Sc [26–28]. The absence of selectivity towards heavier lanthanides can be overcome by the presence of chelating ligands on anion exchangers.

The chelating resins (CR) were designed to overcome the limited selectivity of conventional anion and cation exchange resins. The ion exchange occurs according to Equation (1):

$$R_2SO_4 + 2[Sc(SO_4)_2]^- \rightarrow 2R[Sc(SO_4)_2] + SO_4^{2-}, \quad (1)$$

where R is the functional group of the resin. Numerous researchers have examined their potential application in the recovery and purification of individual REEs, and CR application is prevalent [20,25,29]. CR can adsorb REEs both from strongly acidic solutions (0.5–1.0 M) and from diluted solutions (at pH > 3) [25]. Bao et al. [20] showed that Sc (III) adsorption capacity on chelating resins decreases with increasing sulfate concentration because of the formation of the anionic sulfate complex. As more ammonium sulfate is added, the distribution coefficient of average lanthanides (La, Lu, and Sm) decreases faster than that of Sc in the study [30]. Nonetheless, further study is required to assess the practical applicability of these types of resins in a real sulfate environment. Furthermore, new chelating resins must be developed and studied in order to recover Sc from a sulfate-based solution.

It can be summarized that the shorter lifespan of SIRs and TVEX imposes limitations on their industrial application in comparison to conventional and chelating ion-exchange resins. Despite the available data on the use of ion exchangers to recover REEs from BR leaching solutions, the search for new separation materials to improve selectivity towards Sc, minimize reagent consumption, and establish greener processes is still ongoing. Table 1 summarizes the performance of previous studies on the subject of Sc adsorption using different adsorption materials.

Table 1. Sc adsorption efficiency using different adsorption materials.

Reference	pH/Medium Concentration, g L^{-1}	Initial Sc Concentration	Resin/Delivery Form	Functional Group	Maximum Capacity q_0
[18]	2–8 M HCl	from 0.08 M to 0.33 M (15 g L^{-1})	TVEX	di-isooctyl methyl phosphonate (DIOMP); tributyl phosphate (TBP) and phosphine oxide with different alkyls	–
[19]	pH 1.6 obtained after leaching coal fly ash with 0.5 M H_2SO_4	50–1200 mg L^{-1}	VP OC 1026 (SIR, H^+)	di-(2-ethylhexyl)	8.0–24.0 mg g^{-1}
			TP 272 (SIR, H^+)	bis-(2,4,4-trimethylpentyl) phosphinic acid	
			TP 260 (CR, Na^+)	aminomethyl-phosphonic acid (AMPA)	–
[20]	pH 2.5	50 mg L^{-1}	TP 272 (SIR, H^+)	bis-(2,4,4-trimethylpentyl) phosphinic acid	11.3 mg g^{-1} pseudo-second order
			TP 260 (CR, Na^+)	aminomethyl-phosphonic acid (AMPA)	35.5 mg g^{-1} at pH 1.5 for 36 h (66.2 mg g^{-1} pseudo-second order)
			TP 209 (CR, Na^+)	iminodiacetate acid (IDA)	25.1 mg g^{-1} at pH 3 for 36 h (22.5 mg g^{-1} pseudo-second order)
[21]	pH 0.5–3.5	50 mg L^{-1}	XAD-7HP (SIR)	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) + neodecanoic acid (Versatic 10)	48.0 mg g^{-1}
[24]	pH 2–4 in synthetic solution NO_3^- 180 g L^{-1}	0.12 g L^{-1} in synthetic solution PLS with 100–200 mg L^{-1}	Purolite D5041 (NH^+, H^+)	phosphorus	16.4 g L^{-1} (H^+) 26–30 g L^{-1} (NH_4^+)
			Purolite C115 (NH^+, H^+)	carboxyl	23–27 g L^{-1} (NH_4^+)
[31]	–	130 mg L^{-1}	Lewatit TP 260 (CR, H^+)	bis(2-ethylhexyl)phosphoric acid (D2EHPA)	1460 mg L^{-1}
			Lewatit VP OC 1026 (SIR, Na^+)	aminomethyl-phosphonic acid (AMPA)	310 mg L^{-1}
[32]	H_2SO_4 solution 5 g L^{-1}	0.78 mg L^{-1}	Tulsion CH 93 (CR, Na^+)	aminomethyl phosphonic acid (AMPA)	40 mg g^{-1}
			Purolite D5041 (Cationite)	phosphate	33 mg g^{-1}

Table 1 shows that resins can adsorb up to 70 mg g^{-1} of Sc but real leaching solutions can rarely have as much scandium as in these studies (50–1200 mg L^{-1}). The decrease in the concentration of Sc in the PLS in [32] led to a significant decrease in the capacity of the resin. Hence, in this study, an attempt was made to recover scandium from PLS containing up to 12 mg L^{-1} of Sc, albeit with a minimal amount of impurities, in order to demonstrate the feasibility of obtaining a rich eluate suitable for producing scandium concentrate in a single stage. In our previous studies [33,34] on the processes of aluminum raw material hydrometallurgical treatment, it was suggested that REEs could be recovered from BR with the addition of $MgSO_4$ at the stage of selective acid leaching at pH > 3. Thus, it is possible to obtain a solution with a low content of Fe and Ti and a simultaneous high content of valuable elements. Since ion-exchange sorption is the most favorable method for recovering Sc from complex PLS, this study extends our previous work and estimates Sc recovery from sulfuric acid solutions. We used the chelating resin Puromet MTS9580 for the study because it previously demonstrated [35] a high capacity for Sc adsorption and selectivity.

2. Materials and Methods

2.1. Materials and Reagents

In this study, the chelating ion-exchange resin Puromet MTS9580 from the company Purolite® (Purolite Co., Ltd., Beijing, China) was used for REEs' recovery from sulfuric acid leaching solutions. The resin has phosphonates as functional groups [28], which are phosphonic acid derivatives in a polystyrene–divinylbenzene (St–DVB) matrix. Therefore, it has a selectivity to scandium and HREE against trivial impurities, such as Al (III) and Fe (III). The resin samples were converted from the chloride form using treatment with 100 g L^{-1} H_2SO_4 and deionized water until the pH of the eluate was neutral.

A simulated solution with a scandium concentration of 1–20 mg L^{-1} at a pH of 3.5 was prepared by dissolving Sc_2O_3 (with a purity of 99%) in dilute (1 M) sulfuric acid. To evaluate the effect, specifically, of the presence of magnesium cations on the Sc adsorption under dynamic conditions, a certain amount of $MgSO_4$ (analytical grade) was added to the solution and continuously stirred until complete dissolution using a laboratory magnetic stirrer (Daihan Scientific Co., Ltd., Seoul, Republic of Korea). The simulated solution contained 24 g L^{-1} of $MgSO_4$ and 10 mg L^{-1} Sc to approximate the data from real leaching solutions.

The required pH values were adjusted by adding 1 M H_2SO_4. The pH measurements were conducted using a portable pH meter HI 83141 (Hanna Instruments, Inc., Smithfield, RI, USA), which was equipped with a combined pH electrode HI 1230B. Before measurements, the pH meter was calibrated using standard solutions (Hanna Instruments, Inc., Smithfield, RI, USA).

The study of the adsorption of Sc in the column was conducted by utilizing a PLS that was obtained following sulfuric acid leaching of ESPDW (a solid phase or BR obtained after pre-leaching of ESPD with water) in the presence of magnesium cations [33]. The conditions of ESPD water leaching to maximize the concentration of REEs in ESPDW were previously investigated in [36]. A new portion of ESPDW was leached using a sulfuric acid solution obtained in the previous cycle or a new solution for a first cycle at the optimal parameters (T = 80 °C, C_{MgSO4} = 36 g L^{-1}, liquid to solid ratio (L/S) = 10, and pH = 3.5) for 1 h, yielding a three-cycle solution enriched with REEs. Table 2 shows the chemical composition of PLS. All the other reagents used were of analytical quality.

2.2. Experimental Methods

A weighed amount of resin was placed into a laboratory flask or column. Batch and column adsorption experiments were conducted on simulated solution and PLS at a room temperature of 22 ± 2 °C.

The batch adsorption was conducted by mixing 50 mL of simulated solution containing scandium in the concentrations of 1–20 mg L^{-1} at a pH = 3.5 with 0.1 mL of chelating resin in a conical flask for 8 h. In batch experiments, a rotary laboratory shaker PE-6410 (ECROS, Saint-Petersburg, Russia) was used to mix at a speed of 60 rpm.

Table 2. The chemical composition of pregnant leaching solution (PLS) obtained via leaching of bauxite residue with a sulfuric acid solution at T = 80 °C, C_{MgSO4} = 36 g L^{-1}, liquid to solid ratio (L/S) = 10, and pH = 3.5 for 1 h.

Element	**Al**	**Ca**	**Mg**	**Ti**	**Fe**	**Sc**	**Y**	**La**	**Ce**	**Nd**	**Sm**	**Th**
Content, mg L^{-1}	274.1	621.1	7270.0	1.6	50.7	12.3	14.9	7.7	16.8	11.0	3.8	0.6
RSD, %	0.30	0.72	1.62	0.61	1.24	1.23	1.17	2.23	1.15	2.36	1.35	0.61

RSD–relative standard deviation.

The column adsorption was performed using a 3 mL plastic ion-exchange column. The ion-exchange experimental unit is shown in Figure 1. The resin volume in the column was 2 mL. The transmission rate of 2.5 to 7.5 mL min^{-1} during the adsorption was established using a peristaltic pump LOIP LS-301 (Laboratory Equipment and Instruments Ltd., Saint-Petersburg, Russia), which supplied the initial solution to the bottom of the ion-exchange column. Samples of ion-exchanged liquid that came out of the top of the column were taken periodically for analysis. A new portion of fresh resin was taken for each established speed.

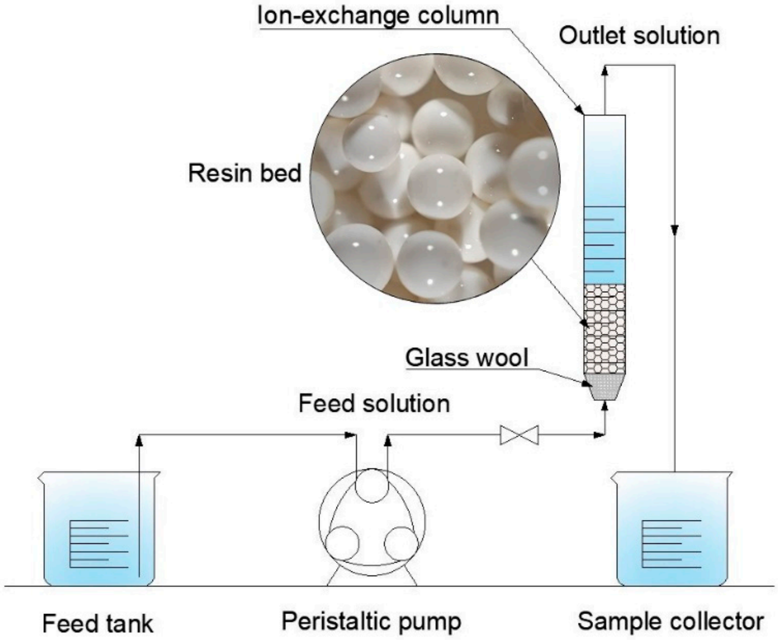

Figure 1. The column ion-exchange experimental unit.

The resin used for desorption was saturated using the model solution and the PLS solution after ESPDW leaching at a sorption rate of 7.5 mL min^{-1}. The resins that were saturated were thoroughly rinsed with distilled water and then desorbed within a timeframe of 30 min to 2 h in a batch mode by mixing 50 mL of solution containing 200 g L^{-1} $NaHCO_3$ with 0.1 mL of pregnant resin. To ensure reproducibility of the results, the batch experiments were conducted twice, while the column experiments were conducted with constant sampling.

2.3. Analysis

The equilibrium ion concentrations of Sc (mg L^{-1}) and impurities in the resulting solution samples diluted with 5% HNO_3 were measured using an inductive coupled plasma optical emission spectroscopy (ICP-OES) using Vista Pro spectrometer (Varian Optical Spectroscopy Instr., Mulgrave, Australia) and atomic absorption spectroscopy (AES) using Varian AA-240FS spectrometer (Agilent Technologies, San Jose, CA, USA).

For quality assurance, samples were analyzed twice with a relative standard deviation not exceeding 3%.

2.4. Calculating Methods

2.4.1. Adsorption Efficiency Calculations

The sorption capacity of the resin at equilibrium was calculated using Equation (2), where Q is the amount of metal ions adsorbed onto the resin (mg g^{-1}); C_0 and C_t are the initial and equilibrium metal concentrations (mg mL^{-1}); V is the volume of the solution (L); and V_r is the volume of the resin (mL).

$$Q = (C_0 \times C_t) \times V / \times V_r, \tag{2}$$

The desorption degree (D in %) was calculated using Equation (3):

$$D = \frac{m_{desorbed}}{m_{resin}} \times 100, \tag{3}$$

where $m_{desorbed}$ is the mass of the element desorbed from the resin; m_{resin} is the mass of the sorbed element.

The distribution coefficient (K_d) and the separation factor ($\beta_{A/B}$) were calculated using Equations (4) and (5):

$$K_d = Q_d / C_e, \tag{4}$$

$$\beta_{A/B} = K_{d\ A} / K_{d\ B}, \tag{5}$$

where K_d is the ratio of the sorbed amount of metal in dynamic column divided by its equilibrium concentration in the solution (mL g^{-1}); Q_d is the dynamic adsorption capacity (mg mL^{-1}); β is the ratio of the distribution coefficient of two metals A and B ($K_{d\ A} \geq K_{d\ B}$).

2.4.2. Adsorption Isotherm Studies

To quantify the sorption process of Sc (III) in batch experiments, the equations of two-parameter models of Langmuir (Equation (6)), Freundlich (Equation (7)), and Temkin (Equation (8)) were used.

$$Q = \frac{Q_m K_L C_e}{(1 + K_L C_e)}, \tag{6}$$

$$Q = K_F C_e^{\frac{1}{n}}, \tag{7}$$

$$Q = \frac{RT}{K_T} \ln A_T C_e, \tag{8}$$

where Q is the amount of adsorbed metal at adsorption equilibrium (mg mL^{-1}); Q_m is the maximum amount of adsorbed metal (mg mL^{-1}); C_e is the equilibrium concentrations of the element in solution (mg mL^{-1}); K_L is the Langmuir isotherm constant; K_F and n are two constants of Freundlich model; K_T and A_T are two constants of Temkin model; R is universal gas constant (8.314 J $mol^{-1} \cdot K^{-1}$); T is temperature (K).

2.4.3. Adsorption Column Studies

The dynamic adsorption system from PLS for MTS9580 resin was analyzed using the MDR and Thomas models in accordance with Equations (9) and (11): MDR model (Equation (9)), calculation of q_0 using the constant b of MDR model (Equation (10)), Thomas model (Equation (11)).

$$\frac{C_t}{C_0} = 1 - \frac{1}{1 + \left(\frac{V_t}{b}\right)^a}, \tag{9}$$

$$q_0 = \frac{bC_0}{V_r}, \tag{10}$$

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{\left(\frac{K_t Q_0 V_r}{F} - K_t C_0 t\right)}}, \tag{11}$$

where C_t and C_0 are the concentrations in moment t and initial concentration (mg mL^{-1}); V_t is the outlet solution volume in moment t; a and b are MDR model constants; q_0 and Q_0 are maximum column loading metal capacity (mg mL^{-1}); V_r is volume of used resin (mL); K_t is Thomas constant (L min^{-1} mg^{-1}); q_0 is equilibrium adsorption capacity (mg g^{-1}); F is the volumetric flow rate of the column (mL min^{-1}). Model fitting was performed for Sc adsorption isotherms and breakthrough curves in OriginPro software (version 9.9.0.225, OriginLab Corporation, Northampton, MA, USA) using non-linear regression analysis.

3. Results and Discussion

For the recovery of Sc and rare earth elements from sulfate solutions, chelating resins are observed as the best choice [23]. The sorption capacity and selectivity of chelating ion exchangers are primarily influenced by the nature and relative position of the functional groups. Chelating ligands, especially those containing phosphorus, are of particular interest. In acidic systems, chelating resins with phosphonic functional groups adsorb rare earth elements, U and Fe, and make it possible to separate Sc micro quantities from other REEs [37]. Marhol et al. [38] have discovered that phosphinic ion exchangers exhibit a strong affinity for scandium (III), which is consistent with the affinity series: Sc (III) > Fe (III) > In (III) > Ga (III) > Al (III) > La (III).

The ion-exchange resin was chosen based on its functional groups, affinity, and selectivity with respect to scandium. Even though the REEs' (III) ion exchange with anion chelating complexes is still a poorly studied area, as indicated by the literature data, the REEs' distribution efficiency from sulfate-based solutions on resin is as follows: chelating resin > strong anion resin > strong cation resin. The stability of the sulfate complexes is not apparent to be dependent on the REE (III) ion radius, with the exception of Sc, which exhibits a significantly higher distribution coefficient than the other elements [19,39]. It is possible to separate scandium from other elements because many elements, as well as rare earth elements, have slight or no adsorption on anion-exchange resins from sulfate or sulfuric acid medium.

According to thermodynamics, Sc forms stable positive- and negative-charged complexes in sulfate media. The main forms of Sc's existence in solution are complexes of the anionic type $[Sc(SO_4)_2]^-$, $[Sc(SO_4)_3]^{3-}$ (pH range 1.6–6.0) [26,40]. As the concentration of sulfate ions in an aqueous solution increases, Sc anionic forms become dominant, thus decreasing Sc adsorption capacity on weak cation exchangers (WACs) with chelating amino methyl phosphonic acid groups [20]. For trivalent REEs, only the $[LnSO_4]^+$ and the $[Ln(SO)_4]^{2-}$ complexes where the cation type is recognized as dominant were identified [41,42]. Thus, Sc behavior in sulfate media combined with selective desorption is crucial for designing a new effective approach.

3.1. Batch Sc Adsorption Experiments and Study of Sorption Mechanism

The batch adsorption experiments were carried out on simulated solutions with concentrations of 1–20 mg L^{-1} Sc. Based on the obtained results, a sorption isotherm was constructed (Figure 2). The obtained results indicate a high affinity of the chelating ion-exchange resin for this particular type of adsorbed ion. Following the thermodynamic models' equations, the static sorption data were analyzed using the Langmuir, Freundlich, and Temkin isotherm models (Figure 2). For each model, the primary thermodynamic parameters of the sorption equilibrium and the values of the multiple correlation coefficients R^2 (Table 3) were obtained.

The Langmuir model was successfully applied to describe the Sc adsorption with the ion-exchange resin with $R^2 = 0.983$. According to the Langmuir equation, the capacity constant $K_L = 0.985$, while the maximum calculated capacity $Q_m = 8.576$ mg mL^{-1}. The Langmuir isotherm is generally suited for describing the chemisorption process on chelating ion-exchange resins, wherein ionic or covalent chemical bonds are formed between the adsorbent and the adsorbate.

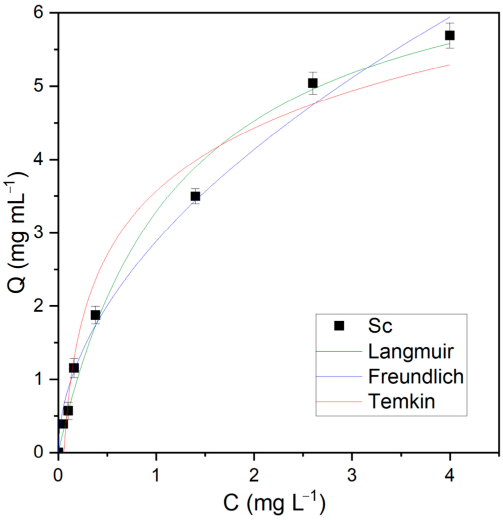

Figure 2. Langmuir, Freundlich, and Temkin adsorption isotherms obtained for Sc adsorption on MTS9580 from simulated sulfuric acid solutions at pH 3.5.

Table 3. The isotherm parameters for Sc adsorption on MTS9580 from simulated solutions at pH 3.5.

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

3.2. Column Adsorption and Breakthrough Modeling

3.2.1. Adsorption Study from Simulated Solution

The ion breakthrough of the simulated solution was analyzed using the following breakthrough models, which are commonly applied to ion-exchange data based on the mass of the resin: the MDR model and the Thomas model.

Equations (9) and (10) [43] are used to apply the MDR model to ion-exchange breakthrough data. Using Equation (10), the maximum column loading capacity for each metal (Q_0) can be estimated by assessing MDR model data. Furthermore, the MDR model generally reduces the error resulting from the Thomas model, especially when the breakthrough curve is shorter or longer.

The Thomas model (Equation (11)) assumes that the process follows the Langmuir adsorption/desorption kinetics without axial dispersion [44], and that the uptake is adjusted by pore-diffusion kinetics [45]. The main advantage of this model is its ability to predict breakthrough curves under different operating conditions.

The adsorption experimental data at different flow rates of 2.5, 5, and 7.5 mL per minute are shown in Figure 3, where C/C_0 is the ratio of Sc-ion concentrations in the collected effluent over the feed solution. The base parameters and model constants (Kt, a, b) are shown in Table 4.

The results in Figure 3 and Table 3 suggest that the breakthrough data fits well with the Thomas model, with correlation coefficients higher than 0.99 for the 2.5 mL min^{-1} flow rate. The maximum adsorption capacity of Sc calculated according to the Thomas model was 7.013 mg mL^{-1}, which is close to the measured (based on the final solution) value of 6.7 mg mL^{-1}. According to the MDR model, this value was too high (10.214 mg mL^{-1}). As the dynamic capacity of the resin for Sc decreased slightly (to 6.3 mg mL^{-1}) upon increasing the flow rate to 7.5 mL min^{-1}, this flow rate was selected for experiments utilizing PLS.

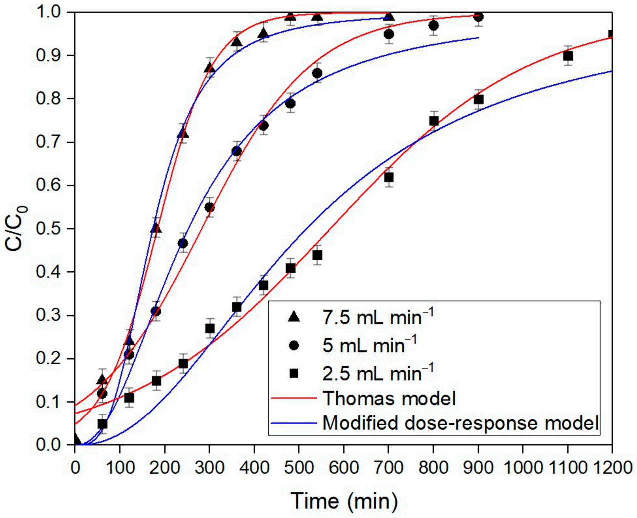

Figure 3. Column adsorption of Sc from a simulated solution on MTS9580 at flow rate of 2.5–7.5 mL min^{-1}.

Table 4. Thomas and MDR model parameters for Sc adsorption on MTS958 from a simulated solution at different flow rates.

Thomas Model	**2.5 mL min^{-1}**	**5 mL min^{-1}**	**7.5 mL min^{-1}**
K_t (L min^{-1} mg^{-1})	0.00142	6.834×10^{-4}	3.65×10^{-4}
Q_0 (mg mL^{-1})	7.013	6.776	6.383
R^2	0.99	0.989	0.996
Modified dose-response model	2.5 mL min^{-1}	5 mL min^{-1}	7.5 mL min^{-1}
a	2.197	2.184	3.115
q_0 (mg mL^{-1})	10.214	4.845	3.213
R^2	0.973	0.987	0.988

3.2.2. Adsorption Study from PLS

The metal adsorption from a PLS containing 12.3 mg L^{-1} of Sc, 50.7 mg L^{-1} of Fe, and 1.6 mg L^{-1} of Ti at a flow rate of 7.5 mL per minute was evaluated. Figure 4 shows the obtained breakthrough curves.

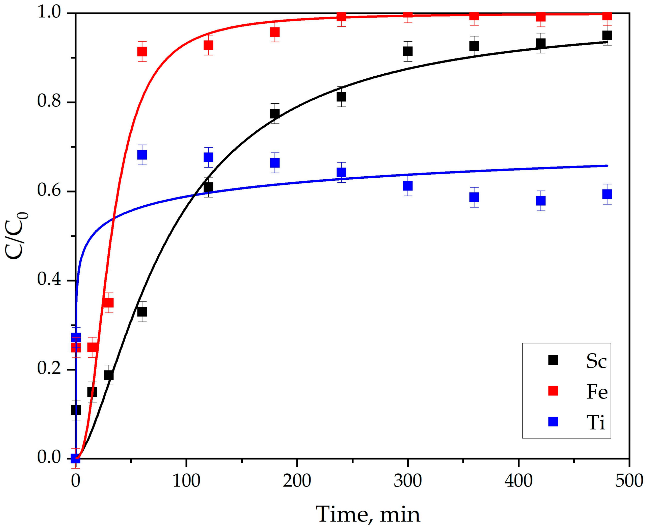

Figure 4. MDR model column adsorption on MTS9580 at PLS flow rate of 7.5 mL min^{-1}.

Compared to a simulated solution, the MDR model had a better-fitting result with PLS since a gradual decrease in C/C_0 was observed for Ti, which could not be fitted using the Thomas model. The model constants and the dynamic resin capacity calculation results for the MDR model are shown in Table 5.

Table 5. MDR model parameters of column adsorption on MTS9580 from PLS.

MDR Model	Sc	Fe	Ti
a	0.679	1.532	0.187
q_0 (mg mL^{-1})	3.888	0.343	0.082
R^2	0.984	0.997	0.905

The adsorption of Fe (III) was observed at the initial moment but after 100–200 min there was no further adsorption. In addition to the adsorption of Sc on the resin, significant adsorption of Ti was observed, which is believed to be attributable to the similarity of Ti properties to REEs [40]. However, due to the selective nature of leaching, the concentration of Ti in solution does not exceed 1.6 mg L^{-1}, resulting in a very low capacity for Ti. It should be noted that the dynamic exchange capacity of MTS9580 for Sc, as determined in this study, was more than 18 times greater (3.77 mg mL^{-1} vs. 0.20 mg mL^{-1}) than that obtained in [35], which may be attributed to the higher concentration of Sc in PLS obtained after BR leaching. On the contrary, the dynamic exchange capacity of MTS9580 for Fe, as determined in this study, was 3.65 times lower (0.343 mg mL^{-1} vs. 1.254 mg mL^{-1}) compared to that obtained in [35] due to the lower concentration of Fe in the PLS (50 mg L^{-1} vs. 180 mg L^{-1}). Additionally, the high content of Al and Mg in the PLS contributed to their adsorption. The resin's capacities for Al and Mg were 1.5 and 4.2 mg mL^{-1}, respectively.

Based on the column experiments, the dynamic exchange capacity (Q_d), the distribution coefficient (K_d), and the separation factor ($\beta_{Sc/Ti,Fe}$) were calculated (Table 6).

Table 6. Results for Sc, Ti, and Fe column adsorption on MTS9580 from PLS.

Element	Sc	Ti	Fe
$\beta_{Sc/E}$	-	0.25	6.90
K_d (mL g^{-1})	0.40	1.61	0.06
Q_d, mg mL^{-1}	3.77	1.14	2.81

The high affinity of the Puromet MTS9580 ion-exchange resin for Sc is confirmed by the Q_d and K_d values for Sc (III), as well as the high $\beta_{Sc/E}$ value for Fe (III), despite the fact that the Fe concentration in the solution was four times greater than the Sc concentration.

3.3. Desorption Studies

It is also important to evaluate the desorption efficiency of the adsorption process. It is known that adsorbed Sc can be effectively desorbed from the resin with sodium bicarbonate solution, a kind of relatively economical desorbent. For saturated Puromet MTS9580 resin, the scandium desorption was carried out at room temperature for 30, 60, 90, and 120 min. The results are presented in Figure 5.

The results in Figure 5a show that 98% of Sc, from saturated, using a simulated solution resin, can be desorbed within 1.5 h. The degree of desorption reached 80% after 30 min. After 1.5 h of desorption, the final eluate contained up to 562 mg L^{-1} of Sc, while the Mg concentration was below 190 mg L^{-1}. This indicates that the resin is very selective towards Sc or rare earth elements since the concentration of Mg in the initial sulfate solution was 1000 times higher.

Figure 5b indicates that scandium desorption above 90%, from saturated, using PLS resin, can be achieved within 30 min and that almost complete Sc desorption occurs within 2 h. The degree of Ti desorption was less than 40%, and the concentration of Fe in the eluate was below 20 mg L^{-1}. The desorption data of resin saturated using PLS showed that the concentrations of Mg and Ti were lower than 200 mg L^{-1} and 50 mg L^{-1}, respectively (Table 7).

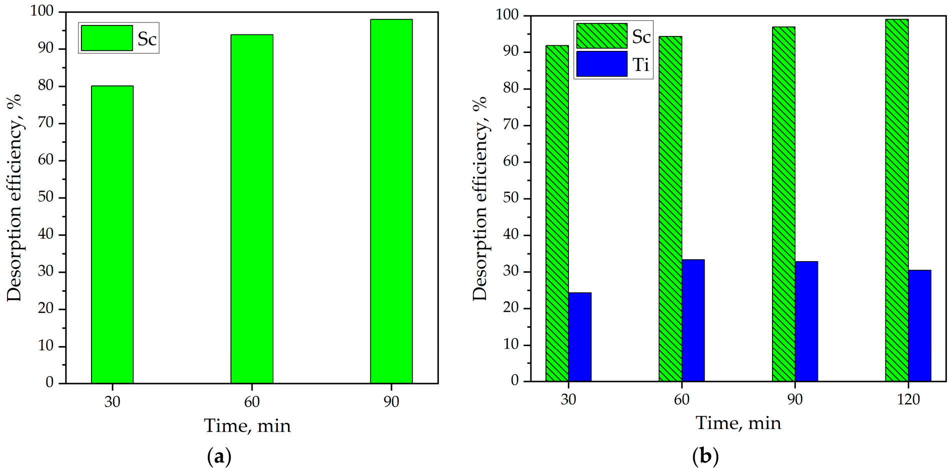

Figure 5. Desorption efficiency with $NaHCO_3$ solution (200 g L^{-1}) from MTS9580, saturated using a model solution (**a**); PLS (**b**).

Table 7. The chemical composition of eluate after desorption of MTS9580, saturated using PLS.

Element	Al	Ca	Mg	Ti	Fe	Sc	Y	La	Ce	Nd	Sm	Th
mg L^{-1}	61.6	500.6	195.9	48.8	16.1	461.5	9.4	4.3	6.2	5.0	1.9	1.2
RSD, %	1.03	0.99	1.89	0.96	1.83	1.79	3.35	3.75	3.80	3.20	3.14	3.13

After Sc desorption and washing with deionized water, the resin was regenerated with a sulfuric acid solution with a concentration of 200 g L^{-1}, and the degree of the remaining elements' desorption exceeded 95%, i.e., almost complete resin regeneration was achieved. The regeneration sulfate solution can be used to leach new portions of BR (Figure 6).

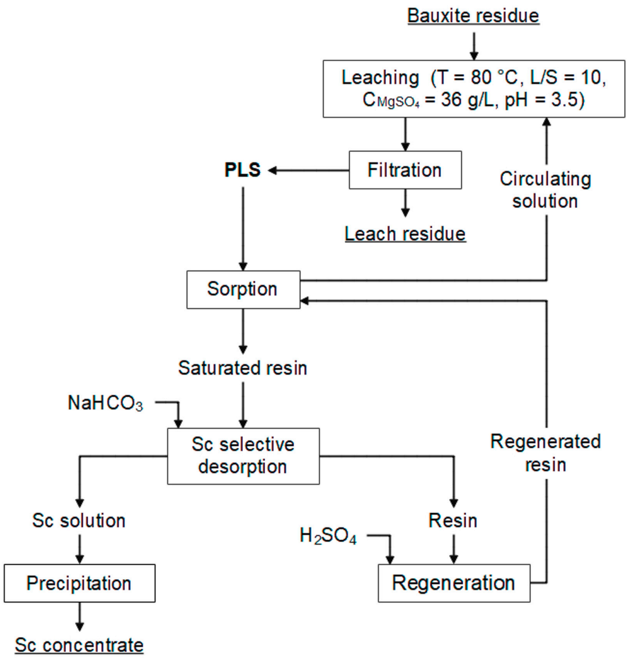

Figure 6. The principal flowsheet of Sc concentrate obtained from PLS using Puromet MTS9580 ion-exchange sorption.

Future research will focus on obtaining the Sc concentrate and other REE concentrates from the circulating solution and testing the resin's stability.

4. Conclusions

Based on the findings obtained from the present research, the predominant mechanism of sorption from simulated and pregnant leach solutions was examined on the chelating ion-exchange resin Puromet MTS9580. It is proposed to recover Sc first since it is more expensive than the rest of the BR elements.

1. For the adsorption of Sc on resin, Langmuir equations adequately describe the sorption isotherms under batch conditions. This indicates the chemisorption process on the chelating resin;
2. The high values of R^2 for the equations of the breakthrough models indicate that the Thomas model is applicable to describing the Sc adsorption from simulated Mg-containing solutions. According to the Langmuir model, the maximum calculated capacity for the batch process was 8.576 mg mL^{-1}, while the maximum capacity for column sorption obtained using the Thomas model was 7.013 mg mL^{-1};
3. The results of the column adsorption study using PLS showed that significant sorption of Ti in addition to Sc was observed. This is apparently due to the properties of Ti being close to the properties of REEs;
4. Sc can be efficiently desorbed (>98%) with $NaHCO_3$ solution (200 g L^{-1}) from both simulated and real solutions within a duration of 1.5 h. After 1.5 h of desorption, the concentration of Sc in the desorption solution was 461.5 mg L^{-1}, while the concentration of Mg and Ti was lower than 200 mg L^{-1} and 50 mg L^{-1}, respectively. This indicates that the resin is very selective towards Sc or rare earth elements.

The high affinity and selectivity of Puromet MTS9580 make it a promising sorbent for the recovery of scandium from PLS of selective leaching of BR. Obtaining Sc and other REE concentrates from desorption solutions will be discussed in future studies.

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