

Article

A High-Efficiency Approach for the Synthesis of N235-Impregnated Resins and the Application in Enhanced Adsorption and Separation of Vanadium(V)

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Abstract: Trialkylamine (N235)-tributyl phosphate (TBP) impregnated resins (N-TIRs) were prepared, so as to evaluate the effects of the addition of TBP on the preparation and adsorption performance of N235-impregnated resins (NIRs). The results show that TBP can obviously increase the impregnation ratio and shorten the impregnation equilibrium time of the N-TIRs when compared to that of the NIRs (57.73% versus 36.95% and 5 min versus 240 min). It is confirmed that TBP can interact with N235 during the impregnation process, which shorten the adsorption equilibrium time and increases the adsorption capacity of the N-TIRs for V(V) when compared to that of the NIRs (6 h versus 10 h and 50.95 mg·g⁻¹ versus 46.73 mg·g⁻¹). The kinetics fitting results demonstrate that the adsorption of V(V) onto N-TIRs and NIRs all conform to pseudo-second order kinetic model and chemical reaction is the rate-limiting step of the whole adsorption process. In the meanwhile, the reaction constant (K_s) implies that the chemical reaction rate of V(V) with the impregnated extractants in N-TIRs is faster than that in NIRs. The N-TIRs present higher stability and selectivity than NIRs. This study manifests that the addition of a secondary reagent may be a potential and novel technique on the preparation of SIRs and the enhancement of adsorption and separation for ions.

Keywords: solvent-impregnated resins; trialkylamine; tributyl phosphate; vanadium; separation; kinetics

1. Introduction

Solvent-impregnated resins (SIRs) that were prepared by incorporating extractants onto polymeric matrix have been widely applied in the fields of separation and purification for metals [1–3] and organics [4,5] from aqueous solutions, due to their high selectivity, operational simplicity, and environmental friendliness [6,7], which can be traced back to the pioneering work that was conducted by Warshawsky [8], Grinstead [9], and Kroebel and Meyer [10] in the early 1970s. Thus, the preparation and application of the SIRs in analytical and environmental chemistry, hydrometallurgy, and radiochemistry fields are still intensive research topics [11]. However, there are some problems that are embedded in SIRs, such as time-consuming of the impregnation process for the extractants impregnating onto the macroporous matrix, long time of the adsorption equilibrium and low



adsorption capacity of the SIRs for metal ions, which may impede the industrial application of SIRs. For instance, Liang et al. [6] investigated the adsorption and separation of V(IV) from the vanadium leaching solution containing Fe(III) and Al(III) with D2EHPA-impregnated resins (DIRs). It was found that the impregnation equilibrium time exceeds 24 h and the adsorption capacity of the DIRs for vanadium (IV) is about 16.0 mg·g⁻¹ after a 18 h long reaction. Navarro et al. [12] prepared the SIRs containing Cyanex 921 and used it to adsorb Cd. The results showed that the impregnation process is time-consuming (about 24 h) and the SIRs just have an adsorption capacity of 13 mg·g⁻¹ for Cd after 18 h adsorption.

Tributyl phosphate (TBP), as a common extractant and modifier, is widely applied in the solvent extraction of metals. Some researchers have proved that the addition of TBP to D2EHPA can improve the phase separation and extraction efficiency [13–15]. For example, Ma et al. [13] studied the separation of V(IV) and Fe(III) from the acid leach solution of stone coal by D2EHPA/TBP, and found that V(IV) and Fe(III) can be effectively separated while using the combination of D2EHPA and TBP. In addition, fewer stages could be used to achieve the required zinc recovery and its effective separation from solutions containing other metal ions by using TBP as a modifier [16]. Based on the fact that a positive synergic effect on the extraction of targeted metals can be achieved by introducing a secondary reagent, such as TBP, Zheng et al. [17] introduced TBP into the DIRs and investigated the adsorption performance of the D2EHPA-TBP impregnated resins (D-TIRs) for V(IV). The results revealed that the D-TIRs have higher adsorption capacity for V(IV) at shorter adsorption equilibrium time and have better separation capability of V(IV) from Fe(II) and Al(III) when compared with DIRs.

In our previous work, we have prepared trialkylamine N235-impregnated resins (NIRs) and used it for the adsorption of vanadium on account of their high affinity to V(V) in a low pH environment [18]. As is known to us, there are few published papers in open literature on the addition of TBP into NIRs and the adsorption characteristics of such prepared SIRs for V(V). In this study, the objective of introducing TBP into NIRs is to improve the performance of the extractant and resolve the aforementioned problems concerning to SIRs. The effects of molar ratio of N235 to TBP, extractants concentration and impregnation time on the impregnation ratio and adsorption performance of the N235-TBP impregnated resins (N-TIRs) for V(V) were studied. The adsorption isotherms and kinetics of V(V) were investigated, so as to analyze the improvement mechanism for V(V) adsorption onto N-TIRs. In addition, the selectivity and stability of the N-TIRs were also investigated in the adsorption process. The study may propose a new sight on the preparation of SIRs by introducing a secondary reagent and promote the development and application of SIRs in the fields of separation and recovery of metals from aqueous solution.

2. Materials and Methods

2.1. Materials

Trialkylamine (N235, R₃N, R = C₈–C₁₀), as supplied by Qinshi Technology Co., Ltd., Zhengzhou, China, was used as the primary extractant. Tributyl phosphate (TBP) was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The petroleum ether with a boiling point range of 60–90 °C (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used to dilute the mixture of N235 and TBP for preparing SIRs. The pure V(V) solution was prepared by dissolving V₂O₅ in the diluted H₂SO₄ solutions (pH = 0.8) to keep the concentration of V(V) at about 1350 mg·L⁻¹. The simulated vanadium-bearing solutions containing 1350 mg·L⁻¹ vanadium, 9450 mg·L⁻¹ aluminum, 2025 mg·L⁻¹ iron, 405 mg·L⁻¹ phosphorus, and 135 mg·L⁻¹ silicon, which refers to the actual acid leaching solution [19], were prepared by two steps. Firstly, the pH of the pure V(V) solution was adjusted to about 1.6 while using concentrated sodium hydroxide. Secondly, some amounts of Al₂(SO₄)₃·18H₂O, Fe₂(SO₄)₃·9H₂O, Na₃PO₄·12H₂O and Na₂SiO₃·9H₂O (purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were added into the pure V(V) solution, subsequently, the mixtures were filtrated after that the solutions were clear. Then, the pH of the filtrate was adjusted to 1.8 by using concentrated sulfuric acid. All of these chemical reagents are of analytical grade.

Macroporous resin Amberlite[®] XAD-16HP provided by Shanghai Anland Co., Ltd. (Shanghai, China), was used as a support resin for preparing SIRs. The physical characteristics of XAD-16HP resins are shown in Table 1. The resins were screened to keep the size range of 0.425–0.850 mm and were pretreated, as follows, for the preparation of SIRs [20]. Firstly, the resins were soaked in ethanol for 4 h to remove the remaining monomers and other types of impurities, followed by washing with deionized water until the effluent was clear, and then filtered and dried at 60°C in a vacuum oven for 12 h.

Fable 1. Physical c	characteristics of	XAD-16HP resin.
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Parameters	Value		
Pore volume	$1.82 \text{ mL} \cdot \text{g}^{-1}$		
Specific surface area	$\geq 800 \text{ m}^2 \cdot \text{g}^{-1}$		
Average pore diameter	15 nm		
Particle size	0.425–0.850 mm		
Matrix	Phenyl ethylene-divinyl benzene		

2.2. Preparation of SIRs

N235 was firstly mixed with TBP according to different molar ratios and the mixtures were diluted by petroleum ether, then the diluted N235-TBP were mixed with the pretreated resins at the liquid to solid ratio of 25:1 mL·g⁻¹. Subsequently, the mixtures were shaken at 25 °C in a constant temperature bath oscillator (SHA-2, Jintan Yitong Electronic Co., Ltd., Jintan, China) for a different amount of time. After the impregnation, the resins were separated using a Buchner funnel and then washed with deionized water until the effluent was clear. Finally, the obtained N-TIRs were heated at 60 °C in a vacuum oven for 12 h to remove the remaining diluent prior to use. The impregnation ratio of the N-TIRs, η (%), i.e. the ratio of the loaded extractants onto the SIRs, was calculated according to Equation (1):

$$\eta = \frac{m_2 - m_1}{m_2} \times 100\% \tag{1}$$

where m_1 is the weight of the pretreated resins (g), m_2 is the weight of the dry N-TIRs (g).

2.3. Static Adsorption Experiments

All of the static adsorption experiments were conducted, unless specified, by using the pure V(V) solution. First, the N-TIRs were added to the V(V)-bearing solution (as the liquid to solid ratio of 20:1 mL·g⁻¹, pH = 1.8) in a conical flask, then the mixture was shaken (120 rpm) in a bath oscillator at 25 °C for different contacting time. Finally, the resins were filtered and the adsorption capacity of the SIRs for V(V) (Q_M), the distribution coefficient (D), and separation factor (β), were calculated according to Equations (2)–(4), respectively:

$$Q_{\rm M} = \frac{(C_0 - C_{\rm e})V}{m_2}$$
(2)

$$D = \frac{Q_{\rm e}}{C_{\rm e}} \tag{3}$$

$$\beta_{\rm A/B} = \frac{D_{\rm A}}{D_{\rm B}} \tag{4}$$

where *V* is the volume of V(V) solution (L), C_0 and C_e are initial and equilibrium concentrations of V(V) in the solutions (mg·L⁻¹), respectively, and m_2 is the weight of the dry N-TIRs (g). Q_e is the equilibrium adsorption capacity of the N-TIRs for metal ions (mg·g⁻¹). D_A and D_B are the distribution

coefficient of V(V) and impurity ion between N-TIRs and the aqueous solution, respectively. $\beta_{A/B}$ represents the separation factor of ion A over B.

2.4. Cyclic Adsorption Experiments

The N-TIRs were separated from the V(V)-bearing solutions after adsorption equilibrium, and they were then added to 40 mL Na₂CO₃ solutions with a mass concentration of 18 wt %. After shaking for 12 h at room temperature, the N-TIRs were filtered and washed with dilute sulfuric acid (pH = 1.8) until the pH value of the eluent was about 1.8 and were re-used for the next static adsorption for V(V), the process of which was the same as that depicted in Section 2.3.

2.5. Analytical and Testing Methods

The concentration of V(V) in the solution was determined by ferrous ammonium sulfate titration while using 2-(phenylamino)-benzoic acid as indicator [21]. The concentration of other metal ions in the aqueous solutions was determined by Inductively Coupled Plasma Atomic Emission Spectrometer (Optima4300DV, PerkinElmer, Waltham, MA, USA). The change of characteristic absorption peaks of different SIRs was obtained by Fourier transform infrared spectroscopy (VERTEX 70, Bruker, Germany). The N-TIRs and NIRs after adsorption of V(V) were carefully split by blade from the core and the cross section of resins were inspected and scanned by scanning electron microscopy (SEM, JSM-IT300, JEOL Co., Tokyo, Japan), equipped with an energy dispersive spectrometer (EDS, Oxford, UK) to observe the vanadium distribution in the pores of the SIRs.

3. Results and Discussion

3.1. Effects of Impregnation Conditions on the N-TIRs

3.1.1. Effects of the Used Mixtures

The effects of the molar ratio of N235 to TBP on the impregnation ratio of N-TIRs and the adsorption capacity for V(V) are shown in Figure 1.



Figure 1. Effects of the molar ratio of N235 to tributyl phosphate (TBP) on the preparation of N235-TBP impregnated resins (N-TIRs) and adsorption capacity for V(V) (Extractants concentration = $1.0 \text{ mol} \cdot \text{L}^{-1}$) ($C_0(V) = 1200 \text{ mg} \cdot \text{L}^{-1}$, 14 h adsorption time, 25 °C).

Figure 1 shows that the impregnation ratio of the N-TIRs significantly decline with the decrease of the molar ratio of N235 to TBP, which may be attributed to the different affinity of N235 and TBP for the support resins. As is known to us, the weak polar N235 have relatively higher affinity for the non-polar matrix of the resins matrix (Phenyl ethylene-divinyl benzene) in comparison to polar TBP [17]. As the molar ratio of N235 to TBP decreases, the content of N235 decreases and thus the impregnation ratio of the N-TIRs decline with the decreasing molar ratio. The adsorption capacity of the N-TIRs for V(V) firstly increases and then decreases with the decrease of the molar ratio. As shown in Figure 1, the decrease of the impregnation ratio is not obvious when the molar ratio of N235 to TBP declines from 10:0 to 9:1, but the adsorption capacity increases somewhat, which may be ascribed to that the addition of TBP improves the extractability of N235 for V(V). However, the amount of effective N235 declines when the molar ratio of N235 to TBP decreases from 9:1 to 0:10, thus the adsorption capacity of the N-TIRs for V(V) declines. As a result, the optimal molar ratio of N235 to TBP was selected as 9:1 for the following adsorption experiments.

3.1.2. Effects of Extractants Concentration

Figure 2 shows the change of the impregnation ratio and adsorption capacity for V(V), along with the extractants concentration.



Figure 2. Effects of extractants concentration on the impregnation ratio of N-TIRs and adsorption capacity for V(V) (N235: TBP = 9:1).

The results show that the impregnation ratio (η) increase approximately linearly with the increase of the extractants concentration, while the adsorption capacity of the N-TIRs for V(V) firstly increases sharply and then tends to reach saturation with the increasing extractants concentration. According to our previous work [7], the extractant is preferentially adsorbed in the micropores as wall-spreading to form a monolayer, resulting in the relatively lower impregnation ratio at low extractants concentration. Whereas, XAD-16HP resin that was used in this study is mainly composed of mesopores and macropores, with the increasing content of the extractants, the extractants more likely accumulate in these pores as pore-filling to form multilayer, which lead to the higher impregnation ratio at high extractants concentration. It is interesting to observe that the adsorption capacity of the N-TIRs for V(V) just increase slowly though the impregnation ratio of the N-TIRs obviously increase as the extractants increase from 1.0 to 2.0 mol·L⁻¹. As more extractants accumulate in the mesopores and macropores as multilayer, the impregnation ratio of the N-TIRs is close to the peak (59.9%), which results in that the effective N235 reacting with V(V) does not increase remarkably in spite of the augment of the loaded extractant [20]. No significance difference is observed in the adsorption capacity when the extractants concentration is higher than 1.6 mol·L⁻¹ (Figure 2). Therefore, the optimal extractants concentration is selected as 1.6 mol·L^{-1} in the impregnation process.

3.1.3. Effects of Impregnation Time

The impregnation ratio and the adsorption capacity of the N-TIRs at different impregnation times, ranging from 5 min to 360 min, are shown in Figure 3.



Figure 3. Effects of impregnation time on the impregnation ratio of N-TIRs and adsorption capacity for V(V) (N235: TBP = 9:1, Extractants concentration = $1.6 \text{ mol} \cdot \text{L}^{-1}$).

It is observed from Figure 3 that the impregnation ratio just increases slightly (from 57.73% to 59.12%) with the impregnation time increasing from 5 min to 360 min. The results indicate that the impregnation process of the N-TIRs accomplish faster (about 5 min) than that of the NIRs (about 240 min) [19], attributing to the addition of TBP [22]. The "interface modifier", TBP, can improve the phase separation rate, i.e., accelerate the molecular motion rate between the aqueous and organic phases [14,23], thus the addition of TBP can obviously shorten the impregnation equilibrium time of the N-TIRs. As is presented in Figure 3, the adsorption capacity of N-TIRs for V(V) firstly slowly declines and then keeps constant with the increasing impregnation ratio. Based on the discussion in Section 3.1.2, the impregnation ratio of the N-TIRs approach to the peak value (59.9%), resulting in that the extractant effectively reacting with V(V) just slightly decrease, thus the adsorption capacity of N-TIRs for V(V) firstly slowly declines and then keeps constant.

3.2. Characterizations of N-TIRs and NIRs

3.2.1. FTIR Analyses

Figure 4 presents the FTIR spectra of the N-TIRs and NIRs. A literature shows that the characteristic vibration bands of P=O, 1281 cm⁻¹, would appear in the SIRs containing TBP [17]. It is obviously found that the characteristic adsorption peak of N235 (C–N bonds, 1099 cm⁻¹) shifts to the lower wavenumber (1096 cm⁻¹) and the intensity of the C–N bonds decreases (Figure 4a),

and the P=O stretching bands also shifts to lower wavenumber 1263 cm⁻¹ (Figure 4b), which may be attributed to that N235 is involved with TBP [23]. Therefore, it may be concluded that an interaction between TBP and N235 has occurred during the impregnation process, rendering the improvement of the impregnation rate and the impregnation ratio of the extractants onto the resins.



Figure 4. FTIR spectra of N235-impregnated resins (NIRs) (a) and N-TIRs (b).

3.2.2. SEM-EDS Analyses

Figure 5 presents the distribution of V(V) on the cross section of NIRs and N-TIRs after the adsorption of V(V). It can be obviously seen from the cross section of NIRs (Figure 5(a2)) and N-TIRs (Figure 5(b2)) that V(V) distribute deeper into the pores of the N-TIRs than in NIRs, implying that the more extractants reacting with V(V) can enter deeper into the pores of the resins during the impregnation process by adding TBP, which is consistent with the fact that the impregnation ratio of N-TIRs is higher than that of NIRs. In the meanwhile, the distribution of V(V) on the cross section also verifies that more V(V) are loaded onto the N-TIRs than onto NIRs.



Figure 5. Cont.



Figure 5. Scanning electron microscopy-energy dispersive spectrometer (SEM-EDS) plane scan analyses of the cross section of NIRs (**a1**): the morphologies; (**a2**): the distribution of V(V) and N-TIRs (**b1**): the morphologies; (**b2**): the distribution of V(V) after adsorption of V(V).

3.3. Adsorption of V(V) onto the N-TIRs and NIRs

3.3.1. Effects of Initial V(V) Concentration

The adsorption of V(V) by N-TIRs and NIRs were conducted at different initial V(V) concentration, ranging from 100 mg·L⁻¹ to 1350 mg·L⁻¹.

As is found in Figure 6, the adsorption capacity of N-TIRs and NIRs for V(V) both approximately logarithmically grow with the increase of the initial V(V) concentration. The equilibrium adsorption capacity of the N-TIRs is evidently higher than that of the NIRs when the initial V(V) concentration exceeds 500 mg·L⁻¹. The higher impregnation ratio of the N-TIRs leads to higher adsorption capacity for V(V) onto such SIRs than that onto NIRs.



Figure 6. Effects of initial V(V) concentration on the adsorption capacity of the N-TIRs and NIRs for V(V).

3.3.2. Adsorption Isotherm

In general, the Langmuir and Freundlich isotherm models are widely used to depict the adsorption of metal ions onto SIRs [11,24,25]. Langmuir model is commonly used to describe the uptake of metal ions that occurs on a homogeneous surface by monolayer adsorption without any interaction between the adsorbed ions, and the Freundlich model assumes that the adsorption of metal ions occurs on a heterogeneous surface by monolayer adsorption. The isotherm models are listed as Equations (5) and (6), respectively.

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{1}{Q_0 K_{\rm L}} + \frac{C_{\rm e}}{Q_0} \tag{5}$$

$$\log Q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{6}$$

where Q_e is the amount of adsorbed metal ions per unit mass of SIRs at equilibrium (mg·g⁻¹), C_e is the concentration of metal ions at equilibrium in raffinate (mg·L⁻¹), Q_0 is the adsorbent capacity (possible maximum amount of metal ions adsorbed per unit mass of SIRs, mg·g⁻¹), K_L is Langmuir isothermal adsorption equilibrium constant (L·mg⁻¹), and K_F and n are the Freundlich constants for adsorption capacity and adsorption intensity, respectively.

The fitting results of Langmuir and Freundlich isotherm model for N-TIRs and NIRs are shown in Figure 7, and the parameters of Langmuir and Freundlich isotherm models are listed in Table 2.



Figure 7. Langmuir (a) and Freundlich (b) isotherm for V(V) adsorption onto N-TIRs and NIRs.

Table 2. Parameters of the Langmuir and Freundlich isotherm models for V(V) adsorption.

CID	Langmuir			Freundlich		
SIRs -	Q ₀	K _L	R^2	n	K _F	R^2
N-TIRs	92.59	0.0124	0.7558	1.37	1.9253	0.9944
NIRs	107.53	0.0029	0.7810	1.23	0.5459	0.9923

Figure 7 manifests that the Freundlich isotherm models fits better for V(V) adsorption onto N-TIRs and NIRs when compared with Langmuir isotherm models due to that the goodness of fit (R^2) with Freundlich isotherm for N-TIRs (0.994) and NIRs (0.9923) are closer to 1 than that of the Langmuir isotherm models for the two SIRs. As can be seen from Table 2, the fitting parameters (n and K_F) for N-TIRs are both higher than that for NIRs, implying that V(V) is more easily absorbed on the N-TIRs and the adsorption capacity of V(V) is higher than that of NIRs, which is consistent with the experiment data.

3.3.3. Effects of Adsorption Time

The effects of contacting time on the adsorption capacity of the N-TIRs and NIRs for V(V) are shown in Figure 8.



Figure 8. Effects of contacting time on the adsorption capacity of the N-TIRs and NIRs for V(V).

Figure 8 reveals that the adsorption capacity of the N-TIRs and NIRs for V(V) both firstly rapidly increase and then tend to balance with the increasing contacting time. The adsorption capacity of the N-TIRs for V(V) equilibrates at about 6 h as $50.95 \text{ mg} \cdot \text{g}^{-1}$, but that of the NIRs continuously increases after 6 h, and finally reaches equilibrium at about 10 h as $46.53 \text{ mg} \cdot \text{g}^{-1}$. It is evident that the adsorption capacity of the N-TIRs for V(V) is always higher than that of the NIRs over the whole contacting time (Figure 8), attributing to the higher impregnation ratio of the N-TIRs in comparison to that of the NIRs, which is also demonstrated in the section "SEM analyses".

3.3.4. Adsorption Kinetics

As is mentioned above, the adsorption equilibrium time of N-TIRs is shortened to 6 h in comparison to that of NIRs (Ca. 10 h), implying that the addition of TBP can accelerate the adsorption rate of V(V) to some extent. The two commonly used kinetic models, pseudo-first order kinetic and pseudo-second order kinetic models [11,24], are used to depict the adsorption process of V(V) to verify the promotion mechanism for V(V) adsorption, which are listed as Equations (7) and (8), respectively.

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{7}$$

$$\frac{t}{Q_{\rm t}} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_{\rm e}} \tag{8}$$

where Q_t is the adsorption capacity (mg·g⁻¹) for V(V) onto the SIRs at any moment, *t* is the adsorption time (h), and K_1 (h⁻¹) and K_2 (mol·L⁻¹·h⁻¹) are the adsorption rate constant of pseudo-first order kinetic model and pseudo-second kinetic model, respectively.

The fitting results of pseudo-first order kinetic and pseudo-second order kinetic models for the adsorption of V(V) onto different SIRs using the two kinetic models are shown in Figure 9, and the fitting parameters are listed in Table 3.



Figure 9. Fitting of the pseudo-first order kinetic (**a**) and pseudo-second order kinetic model (**b**) for V(V) adsorption onto N-TIRs and NIRs.

SIRs -	Pseudo-First Order			Pseudo-Second Order		
	Q_{e}	K_1	R^2	Qe	<i>K</i> ₂	<i>R</i> ²
N-TIRs NIRs	7.16 5.66	$0.4769 \\ 0.1886$	0.8251 0.8936	55.25 52.63	0.0349 0.0118	0.9998 0.9957

Table 3. Fitting parameters of the kinetic models for V(V) adsorption onto the SIRs.

The fitting results manifest that the pseudo-second order kinetic model fits better for the adsorption process of V(V), which indicates that the rate-limiting step of V(V) adsorption may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between the impregnated extractants and V(V) [26]. The adsorption rate constant K_2 of N-TIRs (0.0349) is larger than that of NIRs (0.0118), implying that N-TIRs can reach adsorption equilibrium faster than NIRs, which is identical to the experimental data.

In order to fully confirm the rate limiting step of V(V) adsorption, the shrinking core model (also called adsorption diffusion models) [11] was used to fit the adsorption processes of V(V). The relationship between reaction time and the degree of fractional conversion ($F = Q_t/Q_e$) are given as Equations (9)–(11) [27]:

(a) When the fluid film diffusion controls:

$$F = \frac{3C_{\rm AO}K_{\rm mA}}{\alpha r_0 C_{\rm SO}}t\tag{9}$$

(b) when the intraparticle diffusion controls:

$$3 - 3(1 - F)^{\frac{2}{3}} - 2F = \frac{6D_{\rm r}C_{\rm AO}}{\alpha r_0^2 C_{\rm SO}}t$$
(10)

(c) when the chemical reaction controls:

$$1 - (1 - F)^{\frac{1}{3}} = \frac{K_{\rm S}C_{\rm AO}}{r_0}t\tag{11}$$

where *a* is the stoichiometric coefficient, C_{SO} is the concentration of solid reactant at the bead's unreacted core (mol·L⁻¹), C_{AO} is the initial concentration of V(V) in bulk solution (mol·L⁻¹), K_{mA} is the mass transfer coefficient of V(V) through the liquid film (m·s⁻¹), K_s is the reaction constant based on surface(m·s⁻¹), and r_0 is the radius of SIRs (m).

Figure 10 shows the fitting results for the adsorption of V(V) by the shrinking core model, and the fitting parameters are listed in Table 4. It is evident that the chemical reaction kinetic model fits the adsorption of V(V) better than other models, verifying that the chemical reaction is the rate-limiting step of V(V) adsorption. In the meantime, the reaction constant K_s of N-TIRs (2.06×10^{-3}) is larger than that of the NIRs (1.36×10^{-3}), indicating that the chemical reaction rate of V(V) with the extractants in the pores of the N-TIRs is faster than that in the pores of the NIRs, which may be ascribed to the fact that the interaction of N235 and TBP improves the extractability of the extractants.



Figure 10. Fitting for the adsorption of V(V) by Shrinking core mode (**a**) fluid film diffusion, (**b**) intraparticle diffusion, and (**c**) chemical reaction.

Table 4. Parameters of the shrinking core model for V(V) adsorption onto the solvent-impregnated resins (SIRs).

CID		V			
SIKs	Fluid Film Diffusion	Intraparticle Diffusion	Chemical Reaction	кs	
N-TIRs	0.7316	0.9586	0.9896	$2.06 imes 10^{-3}$	
NIRs	0.8708	0.9931	0.9905	$1.36 imes10^{-3}$	

3.4. Separation of V(V) from Complex Solution

The separation factor (β) for V(V) over impurities onto N-TIRs and NIRs are depicted in Figure 11. It is found that the separation factors for V(V) over impurities onto N-TIRs are all obviously higher than that of NIRs, indicating that the selectivity of the N-TIRS is superior to that of NIRs, which is attributed to that the addition of TBP can obviously improve the extractability of N235 that is loaded onto the N-TIRs for V(V). In conclusion, the selectivity of NIRs is improved by adding TBP.



Figure 11. The separation factor for V(V) over impurities onto N-TIRs and NIRs.

3.5. Stability of the SIRs

The cyclic adsorption-desorption experiments of the N-TIRs and NIRs were carried out so as to investigate the stability of the SIRs during cyclic use. Figure 12 reveals that the adsorption capacity of N-TIRs and NIRs for V(V) both decline with the increasing of the cyclic times. Nevertheless, the decrement in the adsorption capacity of NIRs is more obvious than that of N-TIRs. As is depicted in Figure 12, the adsorption capacity of N-TIRs for V(V) is 91.50% of the initial value after the ninth cyclic adsorption in comparison to that 77.83% for the NIRs. As mentioned above, the extractants going deeper into the pores of the N-TIRs is difficult to lose from the pores of N-TIRs when compared to that impregnated in the shallower pores of NIRs [20]. Thus, the stability of N-TIRs is stronger than that of NIRs.



Figure 12. Stability of the N-TIRs and NIRs during cyclic use.

4. Conclusions

N-TIRs were prepared so as to investigate the effects of the addition of TBP on the preparation process of NIRs and the adsorption performance of such prepared SIRs for V(V). The significant characteristics of the N-TIRs are obtained, as follows:

- (1) The addition of TBP can accelerate the impregnation rate and improve the impregnation ratio of N235 onto the macroporous resins. The impregnation equilibrium time of N-TIRs can be significantly shortened to 5 min in comparison to that of NIRs (240 min) and the impregnation ratio of N-TIRs (57.73%) is higher than that of the NIRs (36.95%).
- (2) FTIR analyses demonstrate that N235 can interact with TBP during the impregnation process, resulting in the improvement of the extractability of N235, which enhances the adsorption capacity and the separation capability of the N-TIRs for V(V) when compared with that of the NIRs (50.95 mg·g⁻¹ versus 46.73 mg·g⁻¹). It is confirmed by SEM-EDS analyses that more extractants can enter deeper into the pores of the resins with the addition of TBP, thus the stability of the N-TIRs is higher than that of the NIRs during the cyclic use.
- (3) The kinetics results show that the pseudo-second order model fits better for the adsorption process of V(V) onto the N-TIRs and NIRs, and the chemical reaction is the rate-limiting step of the adsorption process of V(V). The reaction constant (K_s) implies that the reaction rate of V(V) with extractants impregnated onto N-TIRs is faster than that onto NIRs, which results in the shorter adsorption equilibrium time of the NTIRs (6 h) when compared to NIRs (10 h).

In sum, the addition of TBP can impose many positive effects on the preparation of NIRs and adsorption performance for V(V), such as accelerating the impregnation rate and improving the impregnation ratio of the extractants onto the NIRs, obviously shortening the adsorption equilibrium time of the NIRs and enhancing the adsorption capacity and stability of the NIRs. This study may propose a new sight on the preparation of SIRs by adding a secondary reagent to improve the performance of SIRs.

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