

Removal of aqueous cyanide from alkaline solutions using a weak base anion exchanger in comparison with a strong base anion exchanger

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The gel weak base anion exchanger Purolite A847 has been proofed and compared with the macroporous strong base anion exchanger Purolite A500PS as a suitable adsorbent for the simultaneous removal of free cyanide and Ag-CN complex from an alkaline aqueous mixture under batch and fixed bed conditions. The determined capacities of Purolite A847 are apparently lower than those of Purolite A500PS and depend on the concentration of free cyanide in a solution: at higher concentrations of free cyanide the total capacity of an anion exchanger is lower. The experimental adsorption data obtained in batch were interpreted in terms of the pseudo-second-order reaction rate (q_e , initial sorption rate h , rate constant k_2) and intraparticle diffusion kinetic models. The values of q_e , h and k_2 for free cyanide on Purolite A847 were lower than those of the Ag-CN complex. Sorption of free cyanide and the Ag-CN complex from the alkaline mixture on Purolite A847 corresponds to the general selectivity order for weak base anion exchangers. Column dynamic behaviour peculiarities were studied with the selected breakthrough concentration in an effluent of 0.1 mg/L of silver or free cyanide. The experimental data were analyzed using the Yoon and Nelson empirical model parameters (rate constant K , time required for 50% breakthrough τ , removal capacity Q). The increase in free cyanide influent concentration parameters $\tau_{Ag(I)}$ and $Q_{Ag(I)}$ for Ag-CN complex sorption on Purolite A847 decreases markedly when $K_{Ag(I)}$ increases, while on Purolite A500PS $\tau_{Ag(I)}$ and $Q_{Ag(I)}$ increase with slight changes in $K_{Ag(I)}$. The regeneration of both the anion exchangers Purolite A847 and Purolite A500PS using 5% NaOH is sufficiently effective, with a higher recovered amount of free cyanide and a lower amount of the Ag-CN complex from Purolite A500PS.

Keywords: sorption, anion exchanger, free cyanide, silver cyanide complex

INTRODUCTION

Cyanides are used in a number of metallurgical and chemical processes, including silver plating in the flatware and hollowware trade, the electronics and aerospace industries and find their way into wastewater streams in the form of free cyanide, simple salts or complexes. They are highly toxic both for environmental and human health and, consequently, should be removed from wastewaters prior to discharge [1]. The silver plating bath contains silver in the form of potassium silver cyanides and free potassium cyanide. Because of the high cost of the metal salts used in silver plating, recovery technologies are widely practiced. Moreover, the effluent pre-

treatment regulations and treatment and disposal costs are significant financial factors for reusing rinsewater as well as recovering metals and metal salts from spent process baths and rinsewater. The European Union (EU) specifies 0.05 mg/L total CN safe for both acute and long-term exposure in drinking water [2]. Unfortunately, in effluents from electroplating plants, plating batch and plating rinse the amount of cyanides can reach as high as 100 g/L when compared to the level 0.05 mg/L and can suppress the Best Available Technology (BAT) [3]. The European Union legislation has created a strict legislative framework to ensure the safe use of cyanide and to ensure that dangers to human health and the environment are controlled, where the Integrated Pollution Prevention Directive 96/61/EC is the most representative document of the European Commission (EC) [4].

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The member states are required to take that into account when the BAT is being developed.

Cyanide can be treated and removed by one of several processes such as alkaline breakpoint chlorination, INCO process (by SO_2/air), copper-catalyzed hydrogen peroxide, Caro's acid, natural attenuation, cyanide recovery, ozonation, electrolytic oxidation, ion exchange, acidification, AVR process, lime-sulfur, reverse osmosis, activated carbon adsorption, thermal hydrolysis and biological treatment [5–8]. Most of these methods are commercially available, but to a greater or lesser extent associated with certain disadvantages such as time consumption or need for significant chemicals input which cannot be reused [9–11]. Hence many investigations have been carried out for the improvement of the existing methods and search for new methods for the removal of cyanide from industrial wastewater.

The ion exchange method is known as one of the most efficient methods in terms of time and cost reduction for metal and cyanide recovery, with the possibility of resin regeneration, this allows the care and recycling of water-based process solutions, recycling of rinse water and treatment of wastewater prior to discharge into the environment to high levels of purity – to comply with the regulations for discharge [12–13].

Various strong base anion exchange resins for the removal of free cyanide or free cyanide and complex cyanides were tested and reported that the anion exchange resins Amberlite IRA958, Amberlite IRA900, Amberlite 400 and Amberlite IRA402 are capable of removing free cyanide and heavy metal Fe, Zn, Cu complexed cyanides [14–15]. Simultaneous removal of free cyanide and complexes of Cu-CN, Zn-CN, Cd-CN using the anion exchanger Dowex 1 \times 8–50 in semi-fluidized and fluidized beds was studied [16]. It was demonstrated that free cyanide had selectivity about 3.3 times lower than that of the cyano-metal complexes. The strong base anion exchanger Purolite A500 reduced the concentration of cyanides in the form of Ag-CN, Cu-CN to 2.5 mg/L from 45 to 65 mg/L [17]. The Dowex 21K XLT strong base resin was used for the selective adsorption of gold-cyanide complex only, in the presence of lead-cyanide complexes. The removal efficiency maximum value for the gold-cyanide complex was about 93% for 10 g/L of the resin concentration, while adsorption for lead-cyanide complexes did not almost proceed at pH 13. The adsorption capacity of Dowex 21K XLT resin for gold- and lead-cyanide complexes was about 32 and 0.8 mg/g-dry mass, respectively [18]. The removal of only free cyanides using the strong basic anion exchanger Purolite A-250 was studied under static conditions using the fixed bed column [11]. It was found that the maximum adsorption capacity was equal to 44 mg CN^-/g . The research authors suppose that this resin will find applications around the globe under various weather and wastewater conditions. It should be noted that metal cyanide complexes are strongly retained by strong base anion resins and are difficult to remove with conventional strong base regeneration [19].

Unfortunately, the behaviour of free cyanide and the Ag-CN complex in the adsorption on weak base anion exchangers has not been adequately studied, notwithstanding the fact that they have a great advantage over the strong base because can be regenerated by simply shifting the pH to values higher than pK_a [19]. The presence of functional strong base groups, quarternary amine, within the weak base anion exchanger changes the selectivity for the gold and silver cyanide complex in the pH range 10 to 11. The examination of several weak base anion exchangers has shown that a good selectivity for the gold and silver cyanide complex could be achieved by the presence of 16% strong base functional groups, whereas by the presence of 36 and 77% within two other resins did not change the selectivity for the gold and silver cyanide complex. Hypercrosslinked anion exchange resins Macronet MN100 and 300, containing weak base (tertiary) and strong base (quaternary amino) functional groups, were evaluated for Au-CN and Ag-CN complex recovery from alkaline cyanide solutions [20]. The authors concluded that the extraction of gold and silver cyanides from cyanide solutions proceeds via two different modes based on the basicity of the functional groups. The influence of the following factors such as a balanced degree of hydrophobicity of the polymer matrix and a high surface area of the weak base hypercrosslinked anion exchanger was pointed out.

As mentioned above, the use of a strong base anion exchanger, usually in metallurgical processes, is determined by the precious metal extraction as a cyanide complex from a mixture with free cyanide. Meanwhile, if the main goal is to eliminate harmful free cyanides, especially from electroplating waste waters, perhaps a weak base anion exchanger can be used.

This paper deals mainly with the performance of the weak base anion exchanger Purolite A847 in the simultaneous recovery of the silver cyanide complex (Ag-CN) and free cyanide ions from alkaline cyanide solutions in comparison with the performance of the strong base anion exchanger Purolite A500PS. Batch experiments were run to measure the sorption equilibrium, kinetics and diffusion parameters. Additionally comparative sorption/desorption experiments in the columns of the weak base Purolite A847 and strong base Purolite A500 are presented.

MATERIALS AND METHODS

Anion exchangers and chemicals

Two types of anion exchangers obtained from Purolite International Ltd. were used: gel, polyacrylic-divinylbenzene, weakly basic Purolite A847 (functional groups $-\text{HN}^+(\text{CH}_3)_2$, total capacity 1.6 mol/L) and macroporous, styrene-divinylbenzene, strongly basic, type I Purolite A500PS (functional groups $-\text{N}^+(\text{CH}_3)_3$), total capacity 0.8 mol/L). The pH stability limits for both anion exchangers are 0–14 pH, whereas pH operating limits are 5 to 10 for Purolite A500PS, and pH 0 to 9 for Purolite A847. Purolite A847 is recommended

for the demineralization of water high in the organic matter, whereas Purolite A500PS as an organics scavenger from industrial and domestic water supplies. They were obtained in the Cl form. Conversion into the OH form was carried out by treating the resins with 5 bed volumes (BV) of 4% NaOH at a flow rate of 4 mL/min ($BV = \text{volume of treated solution}/\text{volume of resins}$). After rinsing with distilled water for excess alkalinity elution, the resin samples were sieved in the range of 0.315–1 mm.

The chemical characteristics of the anion exchangers, including strong base and total capacity, were determined later [21, 22].

Batch experiments

Sorption capacities at equilibrium were determined by the batch method with a shaking speed of 100 rev/min⁻¹ and the change in the model solution concentrations before and after the contact with an anion exchanger in an Erlenmeyer flask at 20.0 ± 0.1 °C until the adsorption equilibrium was reached. Approximately 0.2 g of the dry anion exchanger was added to 25 ml of the solution in which the initial $[\text{Ag}(\text{CN})_2^-]/[\text{CN}^-]$ molar ratios were 1:2, 1:3 and 1:8. The model solutions were prepared by dissolving $\text{KAg}(\text{CN})_2$ and NaCN in distilled water and adjusted to pH 10.5. The equilibration time, determined after adsorption studies at various time intervals, was 1 h. After equilibrium had been reached, the suspension was centrifuged in a closed tube for 5 minutes at 4500 rpm, and then it was filtered through the Wathman 41 filter paper.

Kinetic curves were recorded when the samples of sorbent 0.2 g were equilibrated with 25 ml of the mixture with the initial concentrations CN^- 101 mg/L and Ag(I) 161 mg/L, the $(\text{Ag}(\text{CN})_2^-/\text{CN}^-)$ molar ratio (1:2.6) and pH 10.5 at 20 °C during the predetermined time. Then the solutions were withdrawn and the residual concentrations of free cyanide and Ag(I) were measured.

The data obtained from sorption experiments were used to calculate the sorption capacity $q_{e, \text{exp}}$ (mg/g) at the equilibrium time and q_t (mg/g) at the phase contact time t :

$$q_{e(t)} = \frac{(C_0 - C)V}{m} \quad (1)$$

Here C_0 and C are the concentrations (mg/L) in the solution before and after sorption, respectively, V is the volume of the solution (L) and m is the mass of the dry anion exchanger (g). q_e values were obtained by contacting anion exchangers with the model solutions for 72 hours.

Fixed-bed experiments

The column studies were conducted simulating the conditions used in the electroplating wastewater treatment by ion exchange resins [23]. The measurements of sorption/desorption curves were performed in a 1 cm diameter column, filled with 5 mL of a swollen anion exchanger. Two model solutions were prepared by dissolving $\text{KAg}(\text{CN})_2$ and NaCN in distilled

water and adjusted to pH 10.5. The concentration of free cyanide in both solutions was 208 mg/L, whereas the concentration of Ag(I) was 310 mg/L in the first solution and 82.5 mg/L in the second one. The first solution concentration corresponded to the concentration in the silver plating waste water equal to the 100 times diluted silver plating electrolyte (1:8). The model solutions were passed through the anion exchanger bed at the volume velocity of 1 mL/cm² min. The desorption was applied with an anion exchanger completely saturated by $[\text{Ag}(\text{CN})_2]^-$ and CN^- using eluent 5% NaOH and keeping the volume velocity of 0.5 mL/cm² min. The effluent or eluent was collected in the fractions and the concentrations of Ag(I) and free cyanide were determined. The column capacity at breakthrough (E_b , mg/L), column capacity at 50% breakthrough (Q , mg/L) and column utilization efficiency (λ , %) were computed from breakthrough curves according to the equations:

$$E_b = \frac{VC_0}{V_s} = BV_b C_0, \quad (2)$$

$$Q = \frac{C_0 U \tau}{V_s}, \quad (3)$$

$$\lambda = \frac{E_b}{Q} 100\%, \quad (4)$$

where V is the volume of the filtrate until breakthrough (mL), C_0 is the concentration of the initial solution (mg/L), V_s is the resin volume (mL), BV_b is the bed volume, U is the linear flow rate (mL/min). Q is the capacity of the column at 50% breakthrough (mg/L) that is completed at $t = \tau$ and the column will be exhausted at $t = 2\tau$.

The concentration of Ag(I) was determined using ICP optical emission spectrometry (Optima 7000DV, Perkin Elmer); the concentration of free cyanide was determined using the titrant 0.01 M AgNO_3 with a potassium iodide indicator.

RESULTS AND DISCUSSION

Effect of contact time and initial solution concentration

To evaluate the time of CN^- and Ag-CN sorption equilibrium, their concentrations in the solution after equilibration with the anion exchanger vs the contact time were measured (Fig. 1a). Figure 1a suggests that after 1 h no or very little increase in the concentration took place. Therefore it was assumed that the sorption of CN^- or Ag-CN complex in a binary mixture achieved the equilibrium within 1 h.

The experimental Ag-CN complex and free cyanide adsorption capacities (q_e) of two resins from the model silver-cyanide solution measured under static conditions are shown in Table 1. The determined capacities of Purolite A500PS are

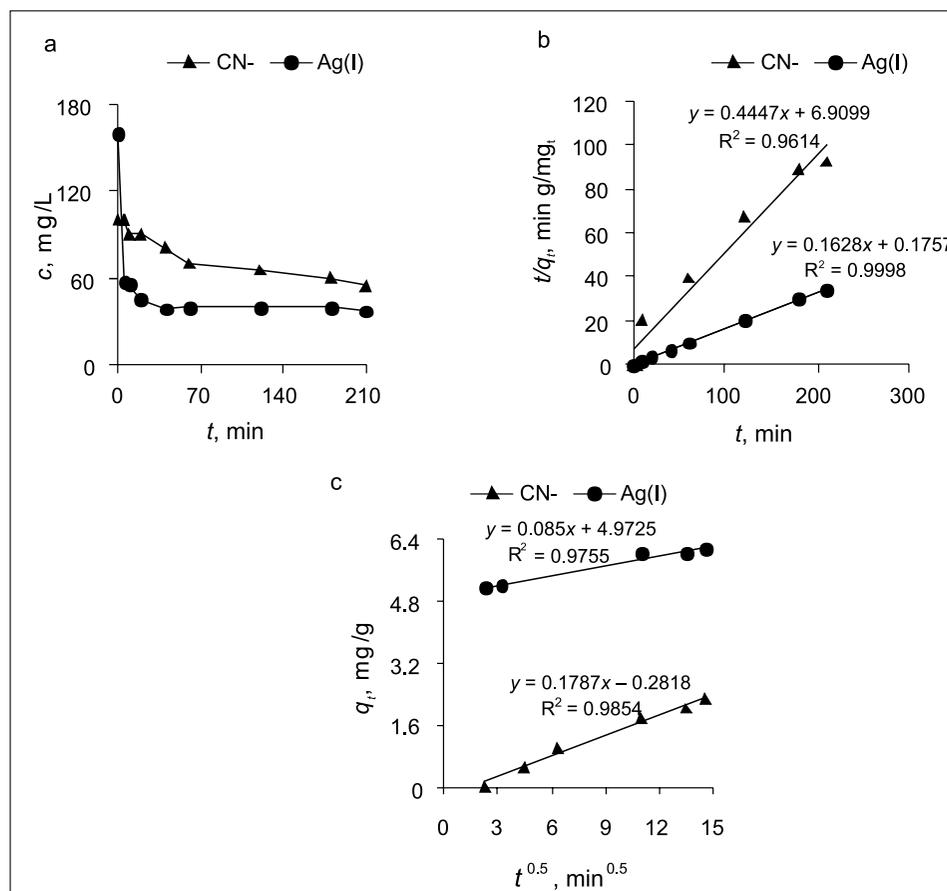


Fig. 1. Kinetic curves for the sorption of free cyanide and Ag-CN complex (Ag(I)) on Purolite A847: a) experimental, b) pseudo-second-order kinetic model, c) intraparticle diffusion model. Conditions: mass of the anion exchanger 0.2 g; the influent concentration molar ratio of $[\text{Ag}(\text{CN})_2^-]/[\text{CN}^-] = 1/3$

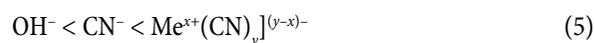
apparently higher than those of Purolite A847. The concentration of the Ag-CN complex sorbed on both the anion exchangers depends on the concentration of free cyanide in the solution: the higher the concentration of free cyanide the lower the total capacity of the anion exchanger. According to the study of the authors [24], the Ag-CN appears to be sorbed as a mixture of $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_3]^{2-}$ ions with a higher proportion of the former, while the Ag-CN is sorbed as the $[\text{Ag}(\text{CN})_2]^-$ ion when the aqueous concentration of free cyanide is zero. If the free cyanide concentration were increased, the formation of higher cyano complexes would occur. That would require two or three times as many exchanger places as compared to the $[\text{Ag}(\text{CN})_2]^-$ ion. Therefore, some results for the Ag-CN anion exchanger capacity could show a disagreement, depending on the silver cyanide salt used.

Table 1. Experimental sorption capacities at equilibrium

Molar ratio $[\text{Ag}(\text{CN})_2^-]/[\text{CN}^-]$	$q_{e, \text{exp}}$ mg/g			
	Purolite A847		Purolite A500PS	
	Ag(I)	CN ⁻	Ag(I)	CN
1:8	2.8	4	4	6
1:3	6.1	2.2		
1:2	6.4	2.7	14.6	4.8

Despite the fact that the total capacity of the strong base anion exchanger Purolite A500PS is two times lower (0.8 mol/L) than that of Purolite A847 (1.6 mol/L), silver cyanide and free cyanide uptake capacities q_e are lower for the latter.

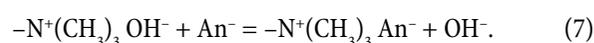
According to the established different selectivity orders [23] for the strong base anion exchanger



and the selectivity order for the weak base anion exchanger



the Purolite A500PS strong base anion exchanger in the OH⁻ form is more selective for the Ag-CN complex than the Purolite A847 weak base anion exchanger. Due to the fact that the determined pK_a values for Purolite A500P and Purolite A847 were 3.2 and 5.5, respectively, and that there was a portion of the 0.6% strong base capacity in Purolite A847, the main reaction for the adsorption of anions (An^-) CN⁻ and Ag-CN in an alkaline solution may be proposed as follows:



Similar results were obtained for the Ag-CN adsorption on weak base anion exchangers A7 with secondary amine functional groups and a 0.6% portion of strong base functional groups (manufacturer Diaprosim), MG1 with polyamine functional groups and a 3.9% portion of strong base functional groups (manufacturer Ionac) [19]. Loading capacities of the Au-CN complex at pH 10 onto A7 and MG1 were 2.0 and 0.9 g/L, respectively. Macronet anion exchangers with tertiary amino functional groups and a portion of strong base functional groups of 10–20% in MN 100 and of 5–15% in MN 300 (manufacturer Purolite) showed uptake capacities of 0.08 and 0.2 mmol/g, respectively [20].

Sorption kinetics

From a practical point of view, the kinetic modeling is important because it enables to identify the time profile of adsorption capacity of the adsorbent. Besides, the processes such as chemisorption, physical sorption, ion exchange, or complexation can affect sorption kinetics as profoundly as they affect the equilibrium [25]. Two models like the pseudo-second-order for the determination of the nature of sorption and the intraparticle diffusion model for the study of mass transfer effects have been applied.

The pseudo-second-order model, based on the assumption that the sorption follows second-order chemisorption, was selected because there is no need to know the equilibrium capacity from the experiments as it can be calculated from the model. The rate constant of sorption was determined using the pseudo-second-order equation [26, 27]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (8)$$

where k_2 (g/(mg min)) is the pseudo-second-order rate constant; q_t (mg/g) and q_e (mg/g) are the amounts of CN⁻ or Ag-CN at time t and at equilibrium, respectively; $\frac{1}{k_2 q_e^2} = h$ (mg/(g min)) can be regarded as the initial adsorption rate. k_2 , h and q_e can be calculated from the intercept and slope of the plot, respectively. The plot of t/q_t vs t shows a linear relationship with high correlation coefficients (R^2) in the range of 0.96–0.99 confirming a good agreement of the kinetic model with the experimental data (Fig. 1b, Table 2). In addition, the calculated q_e values also agree with the experimental sorption data for free cyanide as well as for the Ag-CN complex. This suggests that the sorption on Purolite A847 data are well represented by the pseudo-second-order kinetics and supports the assumption that the rate-limiting step of CN⁻ and Ag-CN complex uptake may be chemisorption.

The data tabulated in Table 2 suggest that the values of q_e and the rate constant k_2 for free cyanide on Purolite A847 were lower than those for the Ag-CN complex and correspond to the general selectivity order for weak base anion exchangers (Eq. 6). The pseudo-second-order kinetic analysis reveals that the value of the initial adsorption rate (h) for free cyanide adsorption was higher than that for Ag-CN complex adsorption. Due to a lower CN⁻ concentration in the solution as compared to that of Ag-CN the probability of collisions between CN⁻ ions is lower and hence the faster CN⁻ ions could be bonded to the active sites on the surface of the anion exchanger.

The sorption rate control consists of two steps: mass transfer in either the bead (intraparticle diffusion) or the liquid (film diffusion), whichever is slower. The pseudo-second-order kinetic model cannot identify the diffusion mechanism. To elucidate the diffusion mechanism, the kinetic results were analysed using the intraparticle diffusion model, which is expressed as [28, 29]

$$q_t = k_{id} t^{0.5} + A, \quad (9)$$

where q_t is the amount of sorbate on the surface of the sorbent at time t (mg/g), t is the time (min), k_{id} is the intraparticle diffusion rate constant (mg/g min^{0.5}), which can be evaluated from the slope of the linear plot of q_t versus $t^{0.5}$ as shown in Fig. 1c. The intercept of the plot (A (mg/g)) reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step is. According to this model, the plot of q_t versus the square root of time ($t^{0.5}$) should be linear if intraparticle diffusion is involved in adsorption, and if these lines pass through the origin, then intraparticle diffusion is the rate-controlling step. The calculated intraparticle diffusion coefficient k_{id} values are presented in Table 2. From Table 2 it can be seen that the value of diffusion rate k_{id} of free cyanides was higher than that of the Ag-CN complex, while the boundary layer effect was lower. However, the linear plots did not pass through an origin (Fig. 1c). This indicates that the intraparticle diffusion on Purolite A847 was not only a rate controlling step, particularly for Ag-CN complex sorption, but film diffusion can also take place.

Sorption studies in the fixed bed experiment

It is well documented that the anion exchange resins are prominent sorbents for the removal of cyanides in the fixed bed column because their mode of operation is simple, susceptible to reach high removal efficiency, and can be easily transferred

Table 2. Parameters of pseudo-second-order rate and intraparticle diffusion models for free cyanide and silver cyanide adsorption on Purolite A847

Sorbate	Parameters of pseudo-second-order rate kinetic model				Parameters of intraparticle diffusion model		
	k_2 , g/mg min	q_e , mg/g	h , min	R^2	k_{id} , mg/g min ^{0.5}	A , mg/g	R^2
CN ⁻	0.028	2.24	6.909	0.961	0.178	0.281	0.985
Ag(I)	0.150	6.14	0.175	0.999	0.085	4.972	0.975

from laboratory to industrial application [11, 12, 30]. The following parameters were used to compare the weak base Purolite A847 and strong base anion exchanger column dynamic behaviour under identical experimental conditions: (1) bed volumes of the solution treated at breakthrough of silver and free cyanide (BV_b); (2) column capacity at breakthrough (E_b), column capacity at 50% breakthrough (Q , mg/L) and column utilization efficiency (λ , %). The silver cyanide and free cyanide breakthrough concentrations were 0.1 mg/L. The obtained breakthrough profiles are presented in Figs. 2 and 3 while these breakthrough curve parameters are described in Table 2.

The obtained breakthrough profiles (Figs. 2 and 3) and breakthrough curve parameters (Table 3) were found to be highly dependent on the initial solution concentrations, es-

pecially for the Purolite A500PS column. Higher removal efficiencies for free cyanide and Ag-CN complex from the alkaline mixtures obtained for the strong base anion exchanger Purolite A500PS column as compared to those of the weak base anion exchanger Purolite A847 column could be explained in accordance with Eq. 7, where only strong base functional groups participate. Free cyanide removal efficiency (λ) by the Purolite A500PS column increased more than threefold with an increase in free cyanide concentration in the initial solution from 2 to 8 M, while the removal efficiency of the Ag-CN complex decreased 7.8 times. With an increase in the free cyanide concentration in the initial solution the removal efficiency of Ag-CN complex by the Purolite A847 column decreased somewhat 1.4 times, while that of free cyanide remained practically unchanged. The difference in Ag-CN complex

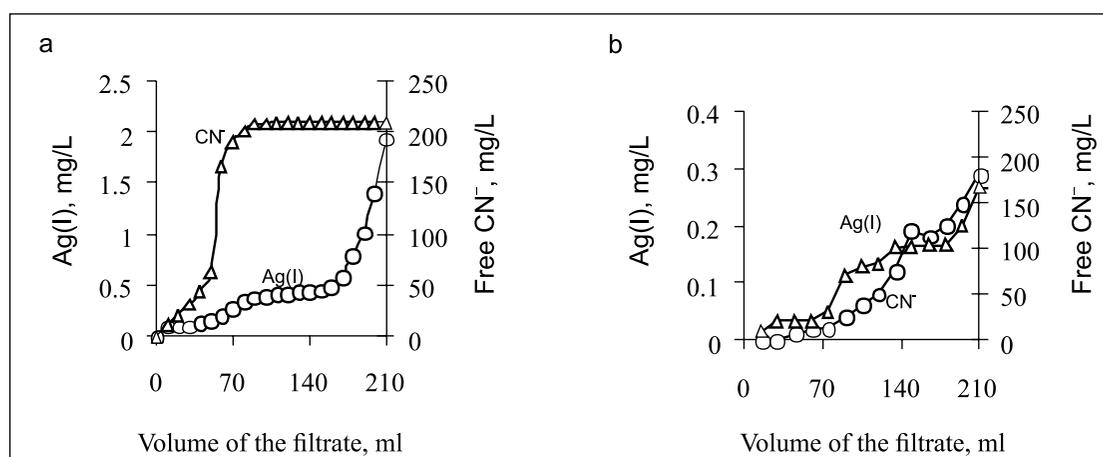


Fig. 2. Breakthrough curves for the sorption of Ag-CN complex (Ag(I)) and free CN^- by Purolite A847 (a) and by Purolite A500PS (b) at the influent concentration molar ratio of $[\text{Ag}(\text{CN})_2^-]/[\text{CN}^-] = 1/2$

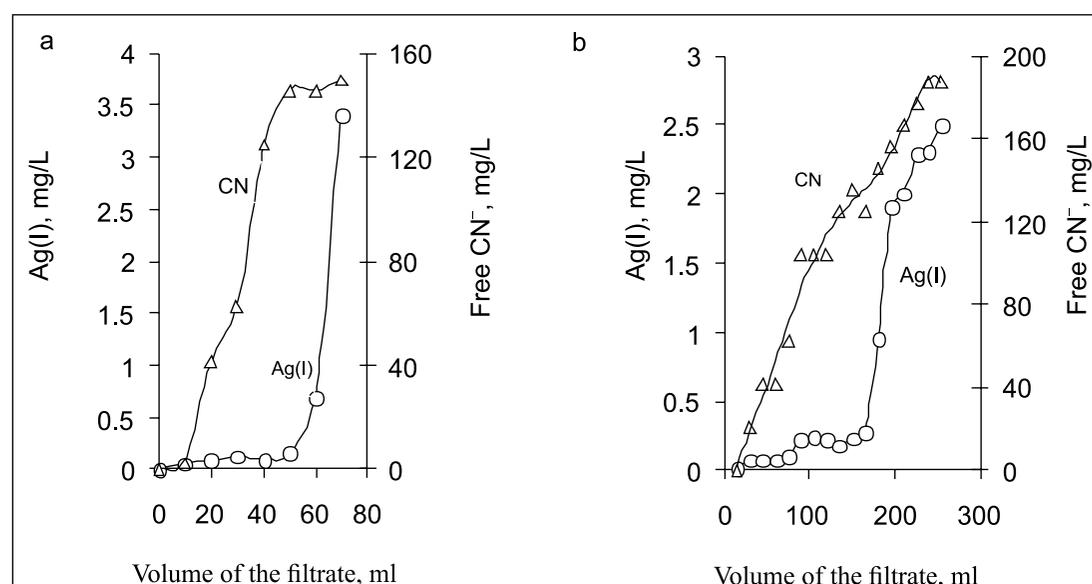


Fig. 3. Breakthrough curves for the sorption of Ag-CN complex (Ag(I)) and free CN^- by Purolite A847 and Purolite A 500PS from the solution at the influent concentration molar ratio of $[\text{Ag}(\text{CN})_2^-]/[\text{CN}^-] = 1/8$

sorption by the investigated anion exchangers corresponds to the established selectivity orders for the OH⁻ form of strong base anion exchangers (Eq. 5) and for the OH⁻ form of a weak base anion exchanger (Eq. 6): the Purolite A500PS strong base anion exchanger in the OH⁻ form is more selective for the Ag-CN complex than Purolite A847.

Table 3. Dependence of column parameters on the influent solution composition

Influent [Ag(CN) ₂] [CN ⁻]	Ag(I)			CN ⁻		
	BV ₀	E _v , mg/L	λ, %	BV ₀	E _v , mg/L	λ, %
Purolite A847						
1:8	20	165	1.9	0.1	0.208	3.6
1:2	60	495	2.7	10	208	3.8
Purolite A500PS						
1:8	140	770	1.6	70	970	13.5
1:2	80	1653	12.4	10	277	4.4

The empirical model by Yoon and Nelson has been used to study the column adsorption kinetics [31]. This model is simpler than other models, including the Adams–Bohart model or the Thomas model, and requires no data about the characteristics of the system such as the type of the adsorbent and the physical properties of the adsorption bed. Several authors have used the Yoon and Nelson model in the study of column adsorption kinetics [32–35]. The linearized form of the Yoon and Nelson model is as follows:

$$t = \tau + \frac{1}{K} \ln \left(\frac{C}{C_0 - C} \right). \quad (10)$$

Here τ is the time when $C/C_0 \approx 0.5$ (min); C_0 , C are the concentrations of the initial solution and effluent (mg/L); K is the Yoon and Nelson rate constant (1/min).

The regression coefficient R^2 selected as an indicator of fitting of experimental points with the mathematical equation of the model from the linear dependence of the plot (Table 4) was relatively high for both anion exchangers at the investigated solution concentrations. The slope of the plot $\ln[C/(C_0 - C)]$ versus time t was used for the determination of K , while the intercept to τ (Table 5).

Table 4. Yoon–Nelson model equation linear relationships

Influent [Ag(CN) ₂] [CN ⁻]	Mathematical equation for Ag(I)/CN ⁻ : $y = t$; $x = \ln[c/c_0 - c]$	
	Ag(I)	CN ⁻
Purolite A847		
1:8	$y = 13.47x - 134.54$; $R^2 = 0.9394$	$y = 79.28x + 1.37$; $R^2 = 0.9417$
1:2	$y = 7403x + 428.97$; $R^2 = 0.8596$	$y = 67.40x + 131.2$; $R^2 = 0.8669$
Purolite A500PS		
1:8	$y = 48.49x + 467.87$; $R^2 = 0.9345$	$y = 54.08x + 125.35$; $R^2 = 0.9559$
1:2	$y = 41.03x + 409.22$; $R^2 = 0.9610$	$y = 47.18x + 149.93$; $R^2 = 0.9452$

Table 5. Yoon–Nelson model parameters (K , τ) and the removal capacity (Q) calculated for Purolite A847 and Purolite A500PS

Influent [Ag(CN) ₂] [CN ⁻]	$K_{Ag(I)}$ min ⁻¹	$\tau_{Ag(I)}$ min	$Q_{Ag(I)}$ g/L	K_{CN} min ⁻¹	τ_{CN} min	Q_{CN} g/L
Purolite A847						
1:8	0.074	134.5	4.140	0.013	1.37	0.03
1:2	0.014	428.9	8.920	0.015	131.2	2.730
Purolite A500PS						
1:8	0.021	467.9	14.410	0.017	125.4	2.610
1:2	0.024	409.2	3.380	0.021	149.9	3.120

The competition between free cyanide and Ag-CN complex anions for the strong base functional groups determines the Yoon–Nelson model parameters (Table 5). The results show that the rate constant (K_{CN}), time required for 50% breakthrough (τ_{CN}) for both anion exchangers decreased with an increase in the free cyanide influent concentration. Also, the removal capacity (Q_{CN}) decreased with an increase in the free cyanide influent concentration. At the same time, an increase in the free cyanide influent concentration leads to a marked decrease in $\tau_{Ag(I)}$ and $Q_{Ag(I)}$ values for the weak base Purolite A847 and $K_{Ag(I)}$ increase, however, $\tau_{Ag(I)}$ and $Q_{Ag(I)}$ for the strong base Purolite A500PS increase, whereas $K_{Ag(I)}$ changes slightly.

Comparison of Purolite A847 and Purolite A500PS adsorption abilities and desorption efficiencies allows to decide about a more effective use of the ion exchange method. Desorption was characterized by the desorbed concentration of silver (I) and free cyanide in the eluate (Fig. 4). The initial slopes of the curves reflect different regeneration levels of the two anion exchangers, attained with the first portions of 5% NaOH and faster stripping of the Ag-CN complex and free cyanide from the Purolite A847 as compared to that from Purolite A500PS. This corresponds to the location of the Ag-CN complex, CN⁻ and OH⁻ in the selectivity order for the OH⁻ forms of the strong base anion exchanger (Eq. 5) and the weak base anion exchanger (Eq. 6). Consequently, the selectivity order for the weak base Purolite A847 indicates the possibility of desorption of free cyanide and Ag-CN complex using the common alkalis (Fig. 4a). The strong

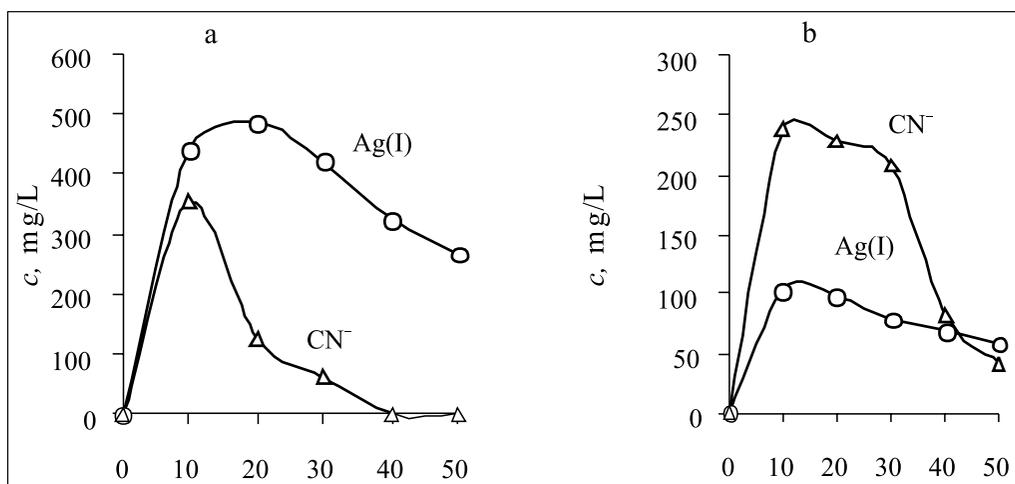


Fig. 4. The elution of Ag-CN complex (Ag(I)) and CN⁻ from Purolite A847 (a) and Purolite A500PS (b)

base anion exchanger Purolite A500PS is more selective for the Ag-CN complex than the weak base anion exchanger Purolite A847, therefore the Ag-CN complex is bonded by the strong base anion exchanger Purolite A500PS so firmly that it cannot be eluted using the common alkalis (Fig. 4b). A higher recovery efficiency of the Ag-CN complex obtained with 2BV of the eluent is demonstrated by Purolite A847 when compared to Purolite A500PS, while Purolite A500PS is more effective for the free cyanide recovery (Fig. 4). The recovered concentrations of Ag-CN complex and free cyanide c_R (g/L) from the 1 L solution were calculated according to the equation

$$c_R = \frac{c_e 1000}{V_a}, \quad (12)$$

where c_e is the total concentration of silver or free cyanide in 20 ml of the eluate (mg/L), V_a is the volume (L) of the anion exchanger.

The recovered amount of Ag(I) for Purolite A847 is higher when compared to that for Purolite A500PS: 46.1 and 20.1 g/L, respectively, while the recovered amount of free cyanide is higher for Purolite A500PS when compared to that for Purolite A847: 46.6 and 23.9 g/L, respectively.

CONCLUSIONS

Both the weak base anion exchanger Purolite A847 and the strong base Purolite A500PS may be employed for the simultaneous removal of free cyanide and the Ag-CN complex from an alkaline aqueous mixture. The concentration of free cyanide and the Ag-CN complex sorbed on both the anion exchangers Purolite A847 and Purolite A500PS depends on the concentration of free cyanide in the solution: the higher the concentration of free cyanide the lower the total capacity of anion exchanger.

The kinetics of simultaneous sorption of free cyanide and the Ag-CN complex on Purolite A847 is well represented

by the pseudo-second-order kinetics that confirms the assumption that the uptake may occur through chemisorption. The calculated intraparticle diffusion rate constants of free cyanides on Purolite A847 was higher than that of the Ag-CN complex, while the boundary layer effect was lower. The sorption of Ag-CN complex was controlled by intraparticle and film diffusion.

The competition between free cyanide and the Ag-CN complex for the strong base functional groups in the fixed bed column determines the Yoon-Nelson model parameters. The increase in free cyanide influent concentration leads to a marked decrease in the model parameters for the Ag-CN complex sorption on Purolite A847 ($\tau_{Ag(I)}$ and $Q_{Ag(I)}$) but increase in the rate constant $K_{Ag(I)}$, while on Purolite A500PS $\tau_{Ag(I)}$ and $Q_{Ag(I)}$ increased with a slight change in the rate constant $K_{Ag(I)}$.

The eluation of free cyanide using 5% NaOH from Purolite A847 is lower than that from Purolite A500PS, 23.9 and 46.6 g/L, respectively, whereas the eluation of Ag-CN complex from Purolite A847 is higher, 46.1 and 20.1 g/L, respectively.

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CIANIDŲ ŠALINIMAS IŠ ŠARMINIŲ TIRPALŲ SILPNAI BAZINIŲ ANIJONITU, PALYGINTI SU STIPRIAISI BAZINIŲ ANIJONITU

Santrauka

Statinėmis ir dinaminėmis sąlygomis tirtas laisvųjų cianidų ir sidabro cianido komplekso vienalaikis šalinimas iš šarminių tirpalų naudojant gelinį silpnai bazinį anijonitą Purolite A847 ir makroporinį stipriai bazinį anijonitą Purolite A500PS. Nustatyta, kad Purolite A847 sorbcinė geba yra mažesnė už Purolite A500PS ir mažėja didinant laisvųjų cianidų koncentraciją tirpale. Statinėmis sąlygomis gauti sorbcijos kinetikos duomenys įvertinti naudojant pseudoantrojo laipsnio reakcijos (pusiausviroji sorbcinė geba q_e , pradinis sorbcijos greitis h , greičio konstanta k_2) ir vidinės difuzijos modelio (greičio konstanta k_{id}) kriterijus. Laisvųjų cianidų sorbcijos anijonitu Purolite A847 q_e ir k_2 vertės yra mažesnės už Ag-CN komplekso vertes. Laisvųjų cianidų ir Ag-CN komplekso sorbcija iš šarminio mišinio anijonitu Purolite A847 atitinka bendrąją silpnai bazinių anijonitų atrankos eilę. Dinaminėmis sąlygomis atlikti tyrimai atsižvelgiant į 0,1 mg/L laisvųjų cianidų ir sidabro proveržio koncentraciją. Eksperimentiniai duomenys analizuoti taikant Yoon ir Nelson empirinį modelį (greičio konstanta K , 50 % proveržio trukmė τ , sorbcinė geba Q). Didinant pradinę laisvųjų cianidų koncentraciją tirpale, Ag-CN komplekso sorbcijos Purolite A847 anijonitu $\tau_{Ag(l)}$ ir Q_{Ag} vertės gerokai sumažėja, bet $K_{Ag(l)}$ padidėja, o anijonitu Purolite A500PS, priešingai, $\tau_{Ag(l)}$ ir $Q_{Ag(l)}$ vertės padidėja, $K_{Ag(l)}$ šiek tiek pakinta. Anijonitai Purolite A847 ir Purolite A500PS efektyviai regeneruojami 5 % NaOH. Purolite A500PS regenerate laisvųjų cianidų koncentracija didesnė, o Ag-CN komplekso koncentracija mažesnė, palyginti su Purolite A847 regenerato koncentracija.