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Adsorption Kinetics of Cobalt (Co^{2+}) from Organic Media by Cation Exchange Resin

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Abstract In this work, the adsorption kinetics of Co (II) ions in RESINEX™ K8 cation exchange resin in three different aqueous-organic acidic media were investigated. The reaction had an endothermic form since the adsorption capacity increases with temperature. We observed that positive ΔG values lead to a thermodynamically non-spontaneous adsorption of CO(II) complexes. The enthalpy (ΔH) and entropy (ΔS) changes due to the adsorption process were also calculated. The extracted R^2 values for the three organic acids were close to unity, indicating that the Langmuir isotherm model provides a better fit for the Co(II) adsorption compared to Freundlich, Temkin and D-R isotherm models. Finally, kinetic studies were carried out.

Keywords Adsorption, Resin, Cobalt, Langmuir isotherm model, Kinetic study.

Introduction

Removal of ions by ion-exchange methods has become of significant scientific and industrial concern in the recent years due to its high efficiency and low cost [1—3]. The ion exchange material may be defined as a medium facilitating exchange of ions with an aqueous solution. Ion exchange using clays has been studied by mineralogists. In these materials consisting of laminae superposed on each other, cations are located in the interlayer space to compensate for the negative charge arising from the substitution of structural ions by ions of lower charge. This ion exchange phenomenon explains soil solidification of polder systems in The Netherlands.

Synthetic analogues of the clay cation exchange emerged in the form of ion exchange resins (IER) in the 1950s. These materials consist of polymer chains that are cross-linked by specific agents. The exchange groups that are partially or completely ionized in wa-

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Table 1. Adsorption isotherm parameters for 7.7 mmol/L of Co(II) on RESINEX™ K8 at 298, 308 and 318 K in aqueous-organic acids solutions.

Langmuir parameters				Freundlich parameters		
Qo	b	R_L	R^2	n	K_f	R^2
(mg/g)	(L/mg)				(mg/g)	
Acetic acid						
35.71	0.19	0.011	0.9980	9.69	60.30	0.72449
Tartaric acid						
38.36	0.36	6.1×10^{-3}	0.9987	13.65	54.35	0.97740
Citric acid						
39.60	1.8	1.2×10^{-3}	1.000	10.00	59.20	0.99990

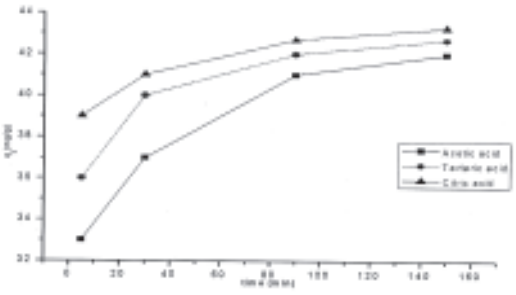

Fig. 1. Effect of contact time on the adsorption uptake of Co(II) in the presence of organic acids at 25°C.

ter can be both acidic or alkaline, as well as weak or strong. The IER used currently for the fluid treatment of the various circuits in nuclear power plants consist of a polystyrene skeleton in which the polymer chains are cross-linked by the Divinylbenzene (DVB). The benzene rings are functionalized with sulfonic acids in the case of cation exchange resins, or with quaternary ammonium compounds in the case of anion exchange resins. It should be noted that only the cation exchange resins have functional groups on the DVB, as the steric hindrance of quaternary ammonium compounds is too large. The cation exchange resins (also called cationic resins) therefore carry negative charges in their structure, which are corrected by Na^+ or H^+ ions. Similarly, in the anion exchange resins (or anionic resins) positive charges in their structure are corrected by Cl^- or OH^- ions.

Recently, many investigations have been carried out aiming to obtain an efficient IER material with enhanced parameters that highly influence the resin performance, such as water retention, DVB ratio, exchange capacity, particle size and density [4—7]. In this context, Yin et al. [8] synthesized a novel composite adsorbent silica gel (SG-PS-azo-SSA). Their findings indicated that better adsorption capacity was achieved for Cu(II), Ag(I) and Au(III). On the other hand, for removing divalent metal ions from wastewaters, Kolodynska [9] used strongly basic anion exchangers in the presence of a new generation chelating agent. Recently, Hamed et al. [10] studied ion exchange of Co(II) on Dowex-HCR S/S cation exchanger resin. According to the reported findings, Co(II) ion adsorption reached equilibrium within 40 minutes. Thus, the authors concluded that Co(II) ion removal from aqueous solution can be increased by increasing the resin dosage, initial metal concentration and temperature. Li et al. [11] conducted the characterization of Cr(III) adsorption on IRN77 cation-exchange resin, revealing that the IRN77 resin had fast kinetics and high exchange capacity towards the Cr(III) ions in aqueous solutions. In addition, kinetics studies showed that the temperature had a positive effect on the diffusion processes. Moreover, the results indicated that the Cr(III) adsorption mechanism was endothermic and that the ion exchange was entropy-driven.

In the current study, the adsorption processes of Co(II) ions in RESINEX™ K8 as a cation exchange resin was investigated in three different aqueous-organic acidic media (aqueous-acetic, tartaric and citric acid solutions). Then, the parameters influencing the adsorption process, such as contact time, initial organic acid concentration and temperature, were investigated. Finally, kinetic studies were carried out on 7.7 mmol/L divalent metal ion concentration at different temperatures (25, 35 and 45 °C) in aqueous-organic acids solutions and 0.05M of used organic acid.

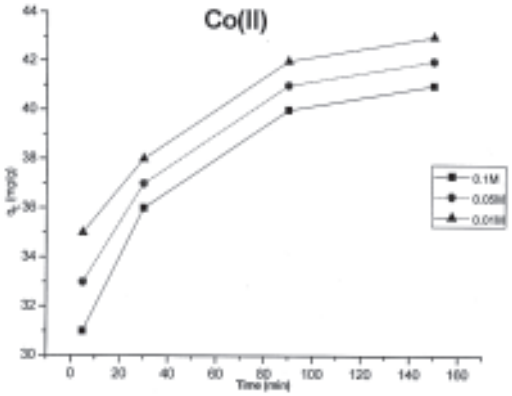

Fig. 2. Effect of the Co(II) adsorption by RESINEX™ K8 at different acetic acid concentrations at 25 °C.

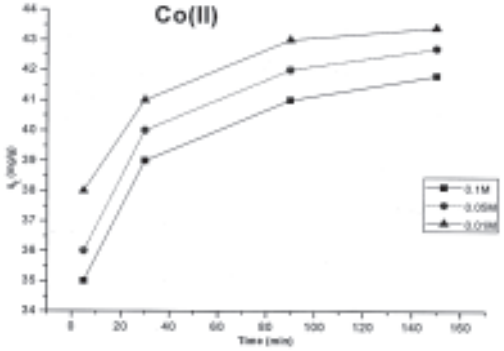

Fig. 3. Effect of the Co(II) adsorption by RESINEX™ K8 at different tartaric acid concentrations at 25 °C.

Materials and Methods

All the materials and chemicals (Aldrich, USA) were of analytical grade and were used as received. Stock solutions of Co(II), Mn(II) and Ni(II) were prepared by dissolving their respective chlorides (AR Grade) in distilled water. The stock solution was diluted with distilled water to obtain the desired concentrations. Strong cation exchange of RESINEX™ K8 in hydrogen form used in this work was purchased from Jacobi Swedish Company (Sweden).

A 1M hydrochloric acid (HCl) solution was used to convert the resin to the hydrogen form. The resin was then washed by deionized water. The resin generation procedure followed the manufacturer's recommendations. After generation, the resin-H was dried and was kept at room temperature.

The adsorption capacity in mg/g of the adsorbent (q_e) and the metal ion adsorption percentage (Ad%) were estimated via the following equations:

$$q_e = (C_o - C_e)\ V/1000 \times W \quad (1)$$

$$Ads\% = (C_o - C_e) \times 100/C_o \quad (2)$$

where C_o and C_e are the initial and final metal ion concentrations, respectively, V is the aqueous phase volume (ml) and W is the weight of the adsorbent used (g). Data were extracted at 24 h from the equilibrium time [12].

Results and Discussion

Study of contact time effect on Co(II) adsorption

The time taken at constant Co(II) concentration (7.7 mmol/L) at 25 °C and organic acid concentration of 0.05M for the uptake of the Co(II) ions in aqueous-acetic, tartaric and citric acid solutions depends on the nature of Co(II)-organic acid complex solutions (Fig. 1). Fig. 1 shows the obtained adsorption kinetic curves for $[Co(OA)]^{n+}$ complexes. The equilibrium of the phase contact time is obtained in 5 to 150 minutes. After this time period (150 min), no significant changes in adsorption were observed. Therefore, this higher resin adsorption rate at the beginning of the reaction can be explained by the fact that a greater number of ion exchanging sites with functional groups is available at the surface area and gradually becomes exhausted. Hence, the adsiorption rate of the cation exchange resin depends on the ion transport rate. These findings are in accordance with those reported by Ugurlu [13].

Table 2. Adsorption isotherm parameters for 7.7 mmol/L of Co(II) on RESINEX™ K8 for 298 K, 308 K and 318 K in aqueous-organic acid solutions.

Temkin parameters			D – R parameters			
A_T	B_T	R^2	β	Xm	E	R^2
L/g	J/mol			(mg/g)	kJ/mol	
			Acetic acid			
3.34×10^{-6}	4.62	0.98587	2.13×10^{-5}	37.80	153.8	0.73527
			Tartaric acid			
3.90×10^{-7}	3.70	0.98111	8.30×10^{-6}	39.80	245.8	0.74058
			Citric acid			
2.10×10^{-8}	2.95	0.98116	4×10^{-6}	40.60	318.4	0.92914

In general, the ion exchange rate of Co(II) follows in the order Citric > tartaric > acetic acid solution. Hence ion size strongly affects the adsorption process [14]. Among the three aqueous-organic acid complex solutions examined in this study, the order of the Co(II) percentage uptake is as follows: Aqueous-acetic acid (92.6%) < aqueous-tartaric acid (94.1%) < aqueous-citric acid (95.4%).

Study of the effect of organic acid concentrations on Co(II) adsorption

The data presented in Figs 2—4 pertains to the RESINEX™ K8 $[Co(OA)]^{n+}$ complexes, indicating that the rate at which complexes are bound by the resin decreased when the concentration of the three organic acids (acetic, tartaric and citric) increased, while lower q_e (uptake) values were obtained. However, the percentage uptake for Co(II) at different aqueous-acetic acid concentrations is 94.8%, 92.6% and 90.4%, compared to 95.6%, 94.1% and 92.1% for aqueous-tartaric acid and 97.6%, 95.4% and 93% for aqueous-citric acid, respectively.

At higher concentrations mass transport and diffusion of these Co(II) complexes are inhibited. This outcome is may be due to steric hindrance, as well as the crowding effect of $[Co(OA)]^{n+}$ complexes in the adsorption solution. For the studied Co(II) complexes, the adsorption decreases as the concentration increases.

Study of the Co(II) adsorption processes

The data presented in Table 1 were obtained by applying the Freundlich isotherm model, indication that the adsorption values are below those obtained experimentally ($q_{e,\,exp}$). The R^2 values in the case of Freundlich isotherm ranged from 0.724 to 0.977 for Co(II)-acetate and Co(II)-tartrate, indicating that Freundlich model is not suitable for cobalt Co(II) in these adsorption media. On the other hand, the R^2 values for Co(II)-citrate medium were equal to unity, indicating that the Freundlich model is suitable for cobalt Co(II) in this adsorption medium.

The high K_L values in Table 1 were obtained for the RESINEX™ K8 strong acid cation exchange resin. In general, the following order is observed: Co(II)-acetate < Co(II)-tartrate < Co(II)-citrate complexes. These results are aligned with those presented earlier. The R^2 values obtained from the Langmuir isotherm model were 0.998 and 0.999 for Co(II)-acetate and Co(II)-tartrate, respectively, indicating that this model is suitable for cobalt Co(II) in these adsorption media. The degree of cation exchange resin suitability for the adsorption of the studied metal complexes

Table 3. Kinetic parameters for 7.7 mmol/L of Co(II) on RESINEX™ K8 at different temperatures (298, 308 and 318 K) in aqueous organic acid solutions.

	PFO model			PSO model				Intraparticle diffusion model		
	$q_{e,1,cal}$	K_1	R^2	$q_{e,2,cal}$	K_2	h	R^2	K_{int}	C	R^2
	(mg/g)	(min^{-1})		(mg/g)	(g/mg min)	(mg/g min)		($mg/g\ min^{-0.5}$)	(mg/g)	
					Acetic acid					
Temp. K										
298	10.46	0.026	0.99775	42.6	7.8×10^{-3}	13.60	0.99926	0.918	31.49	0.94957
308	11.25	0.024	0.99809	41.1	6.5×10^{-3}	10.98	0.99907	1.03	28.48	0.94003
318	12.40	0.021	0.97969	39.8	5.4×10^{-3}	8.60	0.99845	1.18	25.32	0.94229
					Tartaric acid					
298.	6.86	0.026	0.96754	43.12	0.013	24.2	0.99985	0.65	35.37	0.8656
308	9.76	0.033	0.99873	42.10	0.011	19.5	0.99975	0.84	32.16	0.8599
318	13.21	0.039	0.99835	41.20	8.2×10^{-3}	13.9	0.9997	1.04	28.91	0.8602
					Citric acid					
298	4.69	0.0230	0.99866	43.6	0.018	34.2	0.99989	0.43	38.3	0.95218
308	4.50	0.0245	0.99854	42.5	0.017	30.7	0.99993	0.41	37.4	0.93771
318	4.67	0.0248	0.99975	41.6	0.014	24.2	0.99995	0.42	36.4	0.94166

was also evaluated using the values of the adsorption factor constant (R_L).

The R_L values of the studied $[Co(OA)]^{n+}$ complexes on the RESINEX™ K8 cation exchange resin are shown in Table 1. As can be seen, R_L for Co(II) adsorption is in the 0–1 range, implying that the Co(II) adsorption in the different adsorption media onto RESINEX™ K8 was favorable. Moreover, the much lower R_L values suggest better Co(II) adsorption.

The Temkin and Pyzhev isotherm for Co(II) is shown in Table 2, where B_T is the adsorption heat. We can observe lower B_T values (<8.0) for Co(II), indicating existence of weak cohesive forces between the cation exchange resin and Co (II) ions. The process, as indicated bt B_T values, can be expressed as physical adsorption [13].

In order to investigate the adsorption mechanism, the Dubinin Radushkevich (D-R) isotherm model was adopted by assuming a heterogeneous surface. The calculated values of used adsorption isotherm parameters–Dubinin-Radushkevich (D-R) isotherm constants, monolayer capacity (X_m) and adsorption energy (β)–for Co(II) complexes are shown in Table 2.

The calculated R^2 values for the three organic acids indicate that, in comparison with Freundlich. Temkin and D-R isotherm models, the Langmuir isotherm model for the Co(II) adsorption provides the best fit to the data. In addition, the obtained values of *n* indicate the availability of Co(II) adsorption onto resin from aqueous solution. These values suggest that RESINEX™ K8 is better adsorbent for the removal of Co(II) from aqueous-organic acid solutions. From the data shown in Table 1 and 2, we can infer that the Co(II) adsorption process of onto RESINEX™ K8 is of physiochemical adsorption type [15].

Study of the Co(II) adsorption kinetics modeling

Kinetic studies were carried out on divalent metal ion concentration of 7.7 mmol/L at different temperature (25, 35 and 45 °C) in aqueous-organic acid solutions and 0.05 M of used organic acid. Using kinetic models, the experimental results show that the k_2 values of were greater than the k_1 values of the $[Co(OA)]^{n+}$ adsotption on the RESINEX™ K8 at low temperature (25 °C).

The correlation coefficient values (R^2) for the adsorp-

tion cobalt complexes in Co(II)-acetate, Co(II)-tartrate and Co(II)-citrate solutions were equal to 0.998, 0.968 and 0.999, respectively, for the pseudo first-order (PFO) kinetic model. Their respective values increased to 0.999, 1.0 and 1.0 when the pseudo second-order (PSO) kinetic model was used. The data obtained from the second-order equation are in a better agreement with the experimental values than those yielded by the first-order model (Table 3). Consequently, the PSO and the first-order equations were selected as the most adequate to model the Co(II) complex adsorption rates with organic acids. Hence, the PSO is more suitable than the PFO kinetic model for describing the adsorption of divalent metal ions onto RESINEX™ K8.

Table 3 presents the extracted values of k_{id}. These values confirm the contribution of the surface adsorption in the rate controlling step. In addition, this contribution is also confirmed by the large value of the intercept of the plots, which reflects the boundary layer effect.

For all low molecular weight organic acids solutions, the plots of q_t as a function of $t^{0.5}$ are represented by a linear function that does not pass through the origin of the coordinate system, indicating that the Co(II) adsorption processes in Co(II)-acetate, Co(II)-tartrate and Co(II)-citrate solutions is not controlled solely by intra-particle diffusion.

Study of the effect of temperatures and thermo-dynamics of Co(II) adsorption (AH, ΔS, and ΔG)

These studies were carried out at the divalent metal ion concentration of 7.7 mmol/L at different temperature (25, 35 and 45 °C) in aqueous-organic acid solutions and 0.05M of used organic acid. The thermodynamic parameters for $[Co(OA)]^{n+}$ complex adsorption on RESINEX™ K8 strong acid cation exchange resin was calculated and the findings are presented in Table 4. We can observe that the Co(II) uptake decreases with the increase in temperature, indicating exothermic reaction. However, the percentage uptake for Co(II) at different temperatures of aqueous-acetic acid was 92.6%, 88.8% and 86.2%, while it was 94.1%, 91.5% and 89% in aqueous-tartaric acid and in the case of aqueous-citric acid, it was 95.4%, 92.8% and 90.6%, respectively.

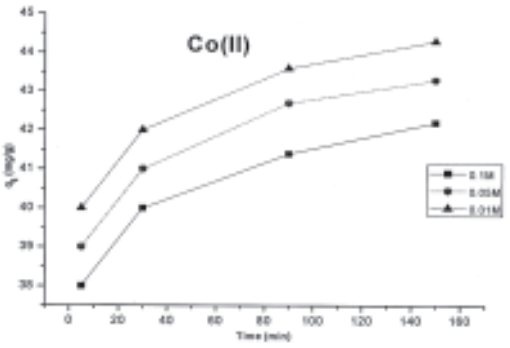

Fig. 4. Effect of the Co(II) adsorption by RESINEX™ K8 at different citric acid concentrations at 25 °C.

The positive ΔG values demonstrate that the adsorption of Co(II) complexes on the RESINEX™ K8 resin is thermodynamically nonspontaneous. In addition, as the reaction temperature increases, ΔG also increases, indicating that the adsorption process is critical at high temperatures. As shown in Table 4, the changes in enthalpy (ΔH) and entropy (ΔS) were estimated using the Van't Hoff equation.

The enthalpy changes (ΔH) for RESINEX™ K8 as a strong acid cation exchange resin were -19.01, -19.01 and -20.60 kJ/mol. These values indicate that physico-chemical adsorption predominates. Negative values lead to an exothermic adsorption process type. The negative values of the entropy change (ΔS) show no affinity for $[Co(OA)]^{n+}$ complexes with RESINEX™ K8 as a strong acid cation exchange resin with a increase in temperature [16, 17].

Study of the activation energy (Ea) of Co(II) adsorption

Activation energy value (Ea, kJ/mol) was obtained and the findings are presented in Table 4. Generally, the activation energy is lower than 8.0 kJ/mol, since

Table 4. Thermodynamic parameters for 7.7 mmol/L of Co(II) on RESINEX™ K8 at 298 K, 308 K and 318 K in aqueous-organic acid solutions.

	ΔG (KJ/mol)	ΔS (J/mol k)	ΔH (LJ/mol)	A	Ea (kJ/mol)
			Acetic acid		
Temp. K					
298	-0.53	-62.87	-19.01	5.3×10^{-5}	-5.30
308	0.60	–	–	–	–
318	1.27	–	–	–	–
			Tartaric acid		
298	-1.15	-62.9	-19.01	8.3×10^{-5}	-5.34
308	-0.17	–	–	–	–
318	0.56	–	–	–	–
			Citric acid		
298	-1.81	-63.9	-20.60	1.3×10^{-3}	-2.79
308	-0.63	–	–	–	–
318	0.26	–	–	–	–

the forces involved in physical adsorption are low. Activated and non-activated forms generally characterize the adsorption process [18]. By using the Arrhenius equation, which provides the reaction rate temperature dependence, activated chemical adsorption is characterized by activation energy (Ea), which renged from 8.4 kJ/mol to 83.7 kJ/mol. On the other hand, non-activated adsorption is characterized by null activation energy. Hence, the results presented in this work suggest a non-activated form. The negative activation energy value suggests that the increase in solution temperature hinders Co(II) adsorption onto the cation exchange resin in all adsorption systems studied.

Conclusion

The investigation of the adsorption kinetics of Co(II) ions in RESINEX™ K8 as a cation exchange resin in three different aqueous-organic acidic media showed that the adsorption capacity increases with temperature. We determined the enthalpy (ΔH) and entropy (ΔS) changes for the cobalt adsorption process. The extracted values of R^2 for the three organic acids were close to unity, indicating that the Langmuir isotherm model for the Co(II) adsorption provides a better fit to the experimental data relative to Freundlich, Temkin and D-R isotherm models. Our findings might be applicable for other heavy metals. However, further investigation are recomended to evaluate the adsorption of cobalt on different materials.

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