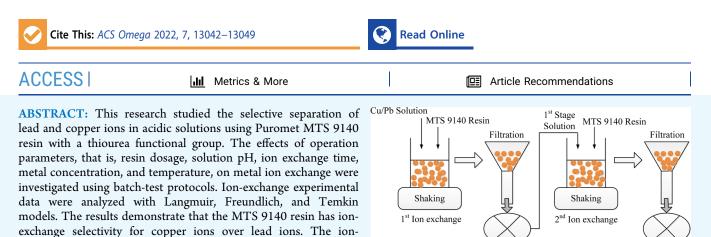


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Analysis

Separation of Lead and Copper Ions in Acidic Media Using an Ion-Exchange Resin with a Thiourea Functional Group

Salem Elfeghe, Qiuyue Sheng, and Yahui Zhang*



under 19% with MTS 9140 resin dosage of 0.070 g/mL in the pH range of 2.5 to 4.5. The kinetic studies showed that the ion exchange process could be better described by the pseudo-second-order model for lead and copper ions. The temperature dependence indicates the endothermic nature of the ion-exchange process. The resin also showed potential application as an effective adsorbent for removing heavy metal ions in water or wastewater treatment.

1. INTRODUCTION

Heavy metal ions are hazardous environmental pollutants, which can be toxic even at very low concentrations, hence posing great challenges to researchers addressing environmental degradation. Lead and copper ions are two of these environmental pollutants and are commonly present in industrial effluents from processes such as electroplating, chemical, petrochemical, and metallurgical operations.¹ Many different technologies are being used for treating wastewaters, such as precipitation, sedimentation, membrane filtration, electrochemical techniques, and ion exchange.^{2,3} Among these methods, ion exchange is considered to be the best process choice in many applications because it has high selectivity and can treat a large wastewater volume.⁴

exchange recovery of Cu exceeded 95%, while Pb coloading was

Numerous studies have been conducted on the removal and separation of toxic metals using different resins possessing various functional groups.^{5–7} A resin with a sulfonic functional group, for example, has been studied by Demirbas et al.⁸ They studied the ion-exchange mechanism of metal ions on Amberlite IR-120-sulfonated resin and investigated the influence of resin dosage, pH, and temperature. In addition, Pehlivan et al.⁹ reported the ion-exchange properties of Dowex 50 W resin toward Cu, Zn, Ni, Cd, and Pb, and the equilibrium ion-exchange capacity of resin for metal ions was explored using Freundlich and Langmuir isotherms. The resins with carboxylic functional groups were examined by Silva and Brunner.¹⁰ They found that the efficiency of the IRC-50 resin was lower than that of the IRC-86 resin for the ion exchange of Cd, Cu, and Pb, and the sorption of metal ions depended

strongly on the feed concentration. The Dow M-4195 resin with a quaternary ammonium function group has been studied by Diniz et al.¹¹ The production of pure manganese chloride solution with the Dow M-4195 resin from an acidic manganese chloride leach solution contaminated by Cu, Ni, Co, Pb, and Fe was demonstrated. Also, a resin with a tertiary amine functional group was tested by Jachuła et al.¹²

Analysis

The separation of Cu(II) and Pb(II) in the water system is a common practice in hydrometallurgy.^{13,14} However, currently, there is no theoretical standard for the choice of resins for a selective Cu(II) and Pb(II) separation in water solutions. It is well known that thiourea has strong complexing power to gold ions.^{15,16} As reported by Purolite Co., commercial polymeric exchanger Puromet MTS 9140 with a thiourea functional group was efficient for Au recovery. As copper and gold are both group IB metals in the periodic table, it may also have an ion-exchange preference for copper ions. Therefore, Puromet MTS 9140 and some commercial resins with various functional groups from different suppliers have been explored for such purposes. It was found that Puromet MTS 9140 with a thiourea group had a strong ion exchange preference for

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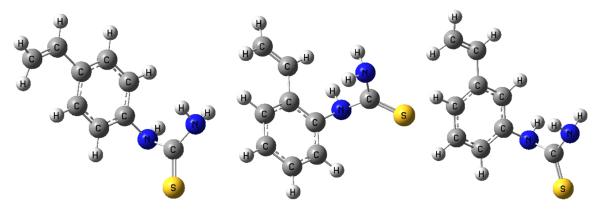


Figure 1. Three major structure units in the MTS 9140 resin: *p*-thiourea-styrene, *o*-thiourea-styrene, and *m*-thiourea-styrene (from left to right) (Blue: N, Yellow: S, Dark gray: C, Gray: H).

Table 1. 1-Physic	al and C	Chemical I	Properties o	f the	MTS	9140 Resin
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characteristics	physical form	shipping weight	particle size	specific Gravity
values	spherical beads	690–730 g/L	300–1200 µm	1.12
characteristics	matrix	functional group	total exchange capacity	temperature Limit
values	polystyrene DVB macroporous	thiourea	1 eq/L	100 °C

Cu(II) over Pb(II). Resins with a thiourea functional group are rarely reported to be used in the separation and recovery of Cu(II) and Pb(II). In this work, a systematic study on the selective separation of copper from lead in a water system using Puromet MTS 9140 resin has been conducted. Batch experiments were performed at different conditions of solution pH, resin dosage, metal concentration, and ion-exchange time in order to investigate the resin ion-exchange performance.

2. MATERIALS AND METHODS

2.1. Materials and Instruments. The macroporous polystyrenic chelating resin MTS 9140 with a thiourea group used in the experiments was supplied by Purolite USA. It contains three major structure units: p-thiourea-styrene, othiourea-styrene, and *m*-thiourea-styrene. Their molecular structures, built with GaussView 6.1.1 software, are illustrated in Figure 1. Its physical and chemical properties, as reported by the suppliers, are shown in Table 1. Other commercial resins were also provided by their producers. Before using for the ionexchange test, the resin was washed several times with deionized water to remove impurities, dried at room temperature for 10 d to constant mass, and stored safely in the lab for further experiments. Cupric chloride, CuCl₂·2H₂O, was purchased from A&C American Chemicals Ltd (Québec, Canada), and lead nitrate, $Pb(NO_3)_2$, was obtained from ACP Chemicals Inc. (Québec, Canada). A wavelength dispersive Xray fluorescence (WDXRF) spectrometer (model Supermini 200) was used for the metal concentration analysis, an orbital shaker (model Promax 2020) was employed for ion exchange tests with 20 mL of solutions in 125 mL flasks, and an Orion Star A211 pH meter was used for the solution pH measurement.

2.2. Experimental Procedures. To find the most selective resin for the separation of Cu(II) and Pb(II) in the water system, a number of commercial resins with different functional groups from various suppliers have been tested at the dosage range of 0.005-0.025 g/mL in a 20 mL solution containing 1800 mg/L Pb(II) and 1200 mg/L Cu(II) with pH 4.5 in a one-stage 2 h ion exchange.

Due to the low density of Puromet MTS 9140 resin, the resin cannot be totally submerged in the 20 mL water solution when the resin amount is over 1 g. Therefore, systematic ion-exchange batch tests with Puromet MTS 9140 resin were performed in two stages by shaking 125 mL flasks on an electrical shaker for a period of 2 h in each stage, as shown in Figure 2. Unless otherwise specified, the experiments were

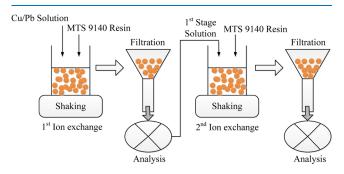


Figure 2. Flow sheet of the metal ion-exchange process using the MTS 9140 resin.

conducted at 20 ± 1 °C, with a shaking speed of 150 rpm, using 0.6 g dry resin in the1st ion-exchange stage and 0.8 g dry resin for the 2nd ion-exchange stage added in a 20 mL solution containing 1800 mg/L Pb(II) and 1200 mg/L Cu(II) with pH 4.5. After each ion-exchange stage, the resin was filtered out, and the metal concentration in the remaining solution was measured by X-ray fluorescence (XRF). For single metal ionexchange tests, separate 1800 mg/L Pb(II) solution and 1200 mg/L Cu(II) solution with pH 4.5 were used following a similar procedure, as mentioned above. The average value of duplicate experiments was taken. The reproducibility deviation of the measurements was within 10.0%.

The metal recovery was calculated through the difference between the initial metal concentration in the solution and the final concentration in the filtrate after ion exchange. The following formula was used to calculate metal removal efficiency (%).

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Removal (%) =
$$\frac{(C_i - C_f)}{C_i} \times 100$$

where C_i and C_f are the initial and final concentrations of the studied metal ions, respectively.

3. RESULTS AND DISCUSSION

3.1. Exploration of Resins for the Cu- and Pb-Selective Separation. In the ion-exchange process, the

Table 2. Resir	is Explored for the Ion Exchange of Lead and
Copper Ions ((Resin Dosage 0.025 g/mL)

function group	resin	Pb %	Cu %
sulfonic	Dowex G-26	99.9	96
	Amberlite IR-120 H	96	85
iminodiacetic	Purolite S930Plus	93	99
	Lewatit MonoPlusTP207	96	96
	Amberlite IRC784I	87	97
	Lewatit MonoPlus TP208	99.9	99.9
	Purolite S930EPlus	79	90
aminophosphonic	SIR 500	91	84
	Amberlite IRC747	99.9	99.9
	Purolite S940	79	58
	Purolite S950Plus	91	78
	Puromet MTS 9500	88	73
aminomethylphosphonic	Lewatit MonoPlus TP 260	97	96
phosphonic and sulfonic	Purolite MTS 9570	87	45
bis-picolylamine	Lewatit MDS TP220	98	93
carboxilic	Dowex Mac-3	31	4
	WAG RTI 26600	34	3
N-methylglucamine	Purolite S108	34	62
di-2-ethylhexylphosphate (D2EHPA)	Lewatit VP OC 1026	37	3
thiourea	Lewatit MonoPlusTP214	69	43
	PuroliteMTS 9140	3	43
trimethyl ammonium	Amberjet 4400 Cl	2	0
isothiouronium	Purolite MTS 9200	4	7
amidoxime	Puromet MTS 9100	43	25
thiol	Puromet MTS 9240	36	23
sulphonic and trimethylammonium	Amberlite IRN150	77	34

selection of proper exchange resins for the metal separation is one of the biggest challenges due to the availability of various commercial adsorbents. The efficiency of the ion-exchange system is controlled by resin selectivity.¹⁷ Various commercial resins with different functional groups from different suppliers have been tested at the dosage range of 0.005–0.025 g/mL in a 20 mL solution, which contains 1800 mg/L Pb(II) and 1200 mg/L Cu(II) with pH 4.5, in a one-stage ion exchange. The experimental results shown in Table 2 indicate that most of the studied resins have a high ion-exchange affinity for both the metals, for example, Lewatit MonoPlus TP208 and Amberlite IRC747 had a 99.9% removal rate for both Cu(II) and Pb(II) ions. They could be applied in the removal of both the metals from the water system, which is very important from the perspective of environmental remediation and protection. Of course, further studies are required. The possibility of Pb and Cu separation may be achieved by using Dowex Mac-3, WAG RTI 26600, Lewatit VP OC 1026, and Purolite MTS 9140

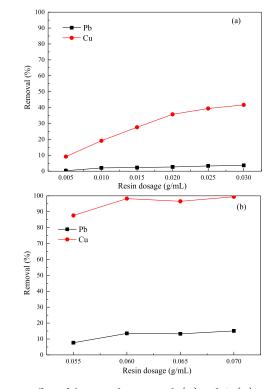


Figure 3. Effect of the resin dosage on Pb (II) and Cu(II) recoveries in binary metal solution in the 1st (a) and 2nd (b) ion-exchange stage.

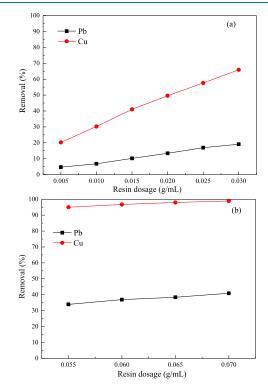


Figure 4. Effect of the resin dosage on Pb(II) and Cu(II) recoveries in the single metal solution in the 1st (a) and 2nd (b) ion-exchange stage.

resins, which have large differences in the ion-exchange preference between Cu(II) and Pb(II). Owing to the largest recovery difference for Cu(II) and Pb(II) ions, the MTS 9140 resin was chosen for copper and lead separation in this study

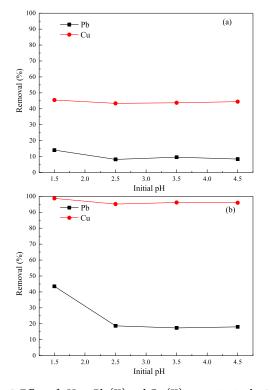


Figure 5. Effect of pH on Pb (II) and Cu (II) recoveries in the 1st (a) and 2nd (b) ion-exchange stage.

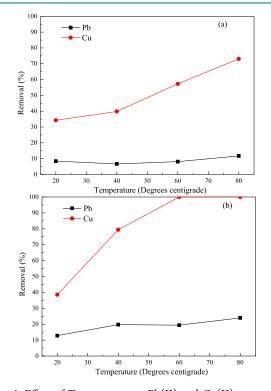


Figure 6. Effect of Temperature on Pb(II) and Cu(II) recoveries in the 1st (a) and 2nd (b) ion-exchange stage.

by improving its performance with two ion-exchange stages, as mentioned above. Systematic ion-exchange experiments were conducted for the separation of lead and copper ions from aN acidic water solution at different operating conditions of the pH, temperature, ion exchange time, agitation speed, and metal concentration.

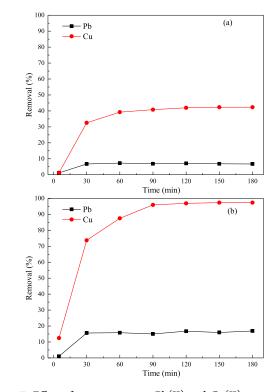


Figure 7. Effect of contact time on Pb(II) and Cu(II) recoveries in the 1st (a) and 2nd (b) ion-exchange stage.

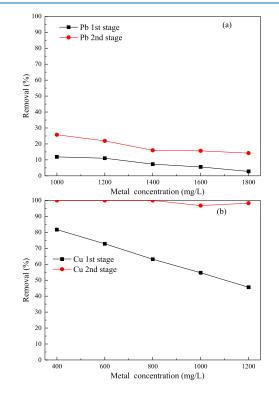


Figure 8. Effect of the initial metal concentration on adsorption of Pb(II) (a) and Cu(II) (b).

3.2. Effect of the Resin Dosage. The effect of the MTS 9140 resin dosage on ion-exchange recovery of Pb and Cu from the water solution was tested in the range of 0.005–0.070 g/mL resin while keeping the other parameters constant as described in Section 2.2.

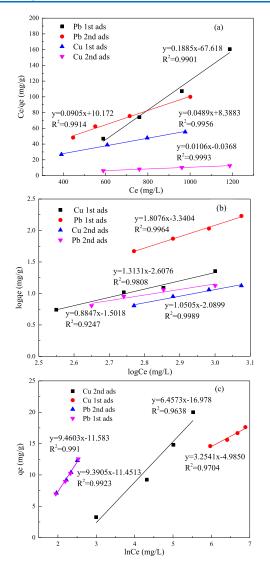


Figure 9. Langmuir isotherm (a), Freundlich isotherm (b), and Temkin isotherm (c) of Pb(II) and Cu(II) adsorption on the MTS 9140 resin.

Table 3. Isotherm Parameters for Pb(II) and Cu(II) Ion Exchange on the MTS 9140 Resin

	first ads. stage		second ads stage				
isotherm	Pb	Cu	Pb	Cu			
		Langmuir					
$Q^0 (mg/g)$	5.30	26.30	11.05	37.03			
b (L/g)	0.0027	0.0046	0.0084	0.0045			
R^2	0.9901	0.9956	0.9914	0.9993			
	Freundlich						
$K_{\rm F}$	0.00045	4.286	0.01379	2.59			
n	0.553	4.91	0.966	1.38			
R^2	0.9964	0.9808	0.9247	0.9989			
Temkin							
b_{T}	261.89	761.39	263.8	384.1			
В	9.4603	3.254	9.3907	6.547			
R^2	0.991	0.9704	0.9923	0.9638			

The ion-exchange results demonstrate that both metal recoveries increase with the resin dosage. The ion-exchange recovery was 3.64% for Pb and 41.68% for Cu at 0.03 g/mL

resin dosage (1^{st} ion-exchange stage, Figure 3a). Recovery increased to 15 and 99% for Pb and Cu, respectively, at 0.07 g/mL resin dosage after the 2nd stage ion exchange (Figure 3b).

To help understand the ion-exchange mechanism of Pb (II) and Cu(II) in the binary metal solution, the ion exchange of Pb (II) and Cu(II) with the MTS 9140 resin in a single 1800 mg/L Pb (II) solution and single 1200 mg/L Cu (II) solution was studied as shown in Figure 4a,b. It was found that the ionexchange recoveries for both Pb (II) and Cu(II) in the single metal solution were higher than those in the binary solution. Especially for Pb (II), its recovery can be over 40% at the resin dosage of 0.070 g/mL. This is because the MTS 9140 resin has a stronger ion-exchange preference for Cu(II) over Pb (II), and there are more adsorption sites for Pb(II) in the single metal solution.

3.3. Effect of pH. The effect of pH on the recovery of Pb(II) and Cu(II) ions was studied in the range of 1.5 to 4.5, and the results are shown in Figure 5a,b. The maximum recovery of Pb was at pH 1.5 in the 1st stage ion exchange, which agrees with the earlier results.¹⁸ Between pH 2.5 and 4.5, Pb recovery was constant in the range of 0.8%. Cu recovery was in the range of 43 to 45% and did not change much with pH. During the 2^{nd} stage, the recovery for Cu increased to 98% and was quite stable across the whole pH range. Precipitation of copper was observed at pH > 5. Therefore, the solution pH was kept at 4.5 in the subsequent tests.

3.4. Effect of Temperature. The influence of temperature on ion exchange of Cu(II) and Pb(II) ions on the MTS 9140 resin was studied at 20, 40, 60, and 80 °C. The recovery of Pb ions is not affected remarkably by temperature in both the first and second ion-exchange stages, while the ion-exchange recovery for Cu ions increased with a temperature rise. Cu recovery increased quickly to 73% at 80 °C in the first ion-exchange stage and reached 100% at 60 and 80 °C in the second ion-exchange stage, as shown in Figure 6a,b. This may be attributed to the endothermic character of this ion-exchange process as temperature increment favors an endothermic reaction thermodynamically.

3.5. Effect of Ion-Exchange Time. Ion-exchange time has an important effect on the recovery/removal of toxic metals using resins. The influence of contact time on Pb and Cu recoveries was tested up to 180 min, and the results are shown in Figure 7a,b. The metal recoveries increase with time. Ion exchange attains equilibrium in 30 min for lead and 90 min for copper. The metal removal percentage from water in the1st stage ion exchange was about 7% for Pb and 42% for Cu, while in the 2nd stage ion exchange, the cumulative recovery increased to 17 and 97% for Pb and Cu, respectively. Therefore, the MTS 9140 resin has a remarkable ion-exchange selectivity for Cu(II) over Pb(II).

3.6. Effect of the Initial Metal Ion Concentration. The effect of the initial metal ion concentration on Pb(II) and Cu(II) recoveries in the first and second ion-exchange stages is shown in Figure 8a,b. Lead recovery decreases slightly with the increase in the initial Pb concentration. However, Cu recovery at the 1st ion-exchange stage decreases remarkably at high initial Cu concentrations. The slight dependence of Pb recovery on initial Pb concentrations may refer to the higher affinity of the MTS 9140 resin to Cu ions over Pb ions, while the decrease of Cu recovery at a high concentration in the 1st ion-exchange stage is due to insufficient adsorption sites on resin at a high concentration of metal ions. This result has a similar trend to what was revealed by Zewail & Yousef.¹⁹

Table 4. Comparison of the Maximum Ion-Exchange C	Capacity of the MTS 9140 Resin with Some	e Other Adsorbents for Pb(II)
and Cu (II) Adsorption		

adsorbent	metal ions	reported sorption capacity(mg/g)	conditions	references
Na-Mt	Pb(II) and Cu(II)	53.8 and 9.53	pH = 6.5, na	23
Ca–Mt	Pb(II) and Cu(II)	34.2 and 6.61	pH = 6.5, na	23
Dowex 50W	Pb(II) and Cu(II)	45.5 and 20.2	pH = 6.7 and 5.0, 25 $^\circ C$	9
amidoxime-chelating resin (AO AN/MA)	Pb(II) and Cu(II)	12.4 and 127.7	pН 3.0, 25 °С	24
sugar beet pulp	Pb(II) and Cu(II)	36 and 20.9	pH = 5.5, 35 °C	25
activated carbon (ac) granular AC	Pb(II) and Cu(II)	8.28 and 5.59	pH = 5.0, 30 °C	26
dithiocarbamated-spororpollenin (DTC-S)	Pb(II) and Cu(II)	44.6 and 17.15	pH = 5.5, 20 °C	27
polystyrene microspheres	Pb(II) and Cu(II)	6.17 and 3.76	pH = 5.5, 20 °C	28
magnetic GO (simultaneous adsorption)	Pb(II) and Cu(II)	27.7 and 18.3	pH = 4.0, na	29
silica-supported dithiocarbamate	Pb(II) and Cu(II)	70.4 and 20.3	$pH = 6.0, 60 \ ^{\circ}C$	30
1,8-DAN/XAD-4	Pb(II) and Cu(II)	29.01 and 13.98	pH = 6–7, na	31
MTS 9140	Pb(II) and Cu(II)	11.05 and 37.07	$pH = 4.5, 20 \ ^{\circ}C$	this study

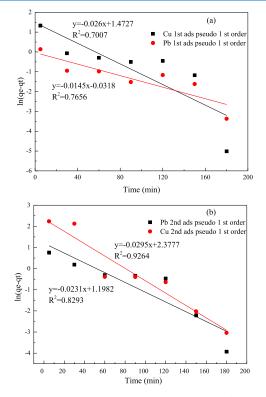


Figure 10. Pseudo-first order for adsorption of $\mbox{Pb}(\mbox{II})$ and $\mbox{Cu}(\mbox{II})$ onto the MTS 9140 resin for the 1st (a) and 2nd (b) ads stage.

3.7. Ion-Exchange Isotherms. The ion-exchange isotherms could be explained by Langmuir, 20 Freundlich²¹ and Temkin²² models. The linear forms of these isotherm models are represented with eqs 1-3, respectively.

Langmuir equation

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{-Q^0 b} + \frac{C_e}{Q^0} \tag{1}$$

where q_e is the equilibrium ion-exchange capacity of ions on the exchanger (mg/g); C_e , the equilibrium ion concentration in solution (mg/L); Q^0 , the maximum capacity of the adsorbent (mg/g); and b, the Langmuir ion-exchange constant (L/mg).

Freundlich equation

$$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{2}$$

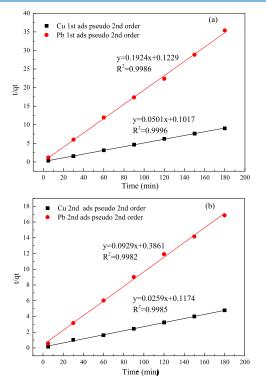


Figure 11. Pseudo-second order for adsorption of Pb(II) and Cu(II) onto the MTS 9140 resin for the 1st (a) and 2nd (b) ads stage.

Table 5. Kinetic Parameters for the Simultaneous Ion Exchange of Pb(II) and Cu(II) Ions Onto MTS 9140

	1st ads stage		2nd ad	ls stage	
equations	РЬ	Cu	Pb	Cu	
	Pseud	lo-First Order			
$q_{e'} \exp (mg/g)$	5.40	19.96	10.70	37.70	
$q_{e'}$ cal (mg/g)	0.9687	4.36	3.314	10.77	
$k_1 (m^{-1})$	-0.000081	-0.00014	-0.00013	-0.00016	
R^2	0.7660	0.7007	0.8290	0.9264	
Pseudo-Second Order					
$q_{e'}$ cal (mg/g)	5.19	19.96	10.76	38.60	
k_2 (g/mg min)	0.3012	0.0246	0.0223	0.00571	
R^2	0.9986	0.9996	0.9982	0.9985	

where the equilibrium capacity (q_e) and C_e are defined in the above model, K_F is the Freundlich constant (L/mg), and n is the heterogeneity factor.

Temkin equation

$$q_{e} = B \ln(K_{T}) + B \ln(C_{e}); B = \frac{RT}{b_{T}}$$
 (3)

where K_T (L/g) and B (J/mol) are the Temkin and the heat of sorption constants, respectively. R = universal gas constant (8.314 J/mol/K), and T = Temperature at 298 K.

All isotherm equations evaluated from the linear plots are presented in Figure 9a-c, and their calculated parameters are listed in Table 3.

Compared with the other two ion-exchange isotherms, the R^2 values for both metal ions in the Langmuir ion-exchange isotherm were all above 0.99 (very close to 1), as shown in Table 3, which means the Langmuir isotherm model fits the ion-exchange process best for both Cu (II) and Pb (II) ions. The values of the Freundlich ion-exchange isotherm constant, n, were 0.553/0.966 and 4.91/1.38 for Pb(II) and Cu(II), respectively. All the values were within 0–10, indicating that the sorption of lead and copper ions by the MTS 9140 macroporous resin was favorable. As shown in Table 4, the maximum ion-exchange capacity Q^0 values of MTS 9140 are higher than many adsorbents reported in the literature, especially for the removal of copper ions.

3.8. Ion-Exchange Kinetics of Cu(II) and Pb(II). A pseudo-first-order and a pseudo-second-order kinetic model were applied to study the mechanism of the two ion-exchange stages. The pseudo-first-order and the pseudo-second-order rates are expressed as eqs 4 and 5, respectively.³²

$$\ln(q_{e} - q_{t}) = \ln(q_{e}) - \frac{k_{1}t}{2.303}$$
(4)

$$\frac{t}{q_{\rm e}} = \frac{t}{q_{\rm e}} + \frac{1}{k_2 q_{\rm e}^2}$$
(5)

where q_t and q_e are the amounts of metal adsorbed at time t and equilibrium (mg/g), respectively, and k_1 is the first-order rate constant (min⁻¹). The slopes and intercepts of the plots of $\ln(q_e - q_t)$ versus contact time (t) were used to determine the first-order rate constant k_1 and equilibrium ion exchange capacity(q_e), as shown in Figure 10a,b for both the metals in the 1st and 2nd ion-exchange stages, respectively.

 k_2 is the second-order rate constant (mg/g min). The k_2 and q_e values were calculated from the slope and intercept of the linear plot of t/q_t versus t, as shown in Figure 11a,b for Pb and Cu in the 1st and 2nd ion-exchange stages, respectively. A comparison of the results with the correlation coefficients for the kinetic models is presented in Table 5. The correlation coefficients for the pseudo-second-order kinetic model for Pb and Cu in the two ion-exchange stages (1st stage 0.9986, 0.9996; 2nd stage 0.9982, 0.9985) were high and close to 1, and closer values of q_e exp and q_e cal show that the data fit well with the pseudo-second-order model, which suggests a chemical adsorption process.³

4. CONCLUSIONS

Puromet MTS 9140 resin with a thiourea group, which was rarely used in the separation of Cu(II) and Pb(II) in a water system, was found to have a strong ion-exchange preference for Cu(II) over Pb(II). In this work, a systematic study on the selective separation of copper from lead using Puromet MTS 9140 resin has been conducted. Experimental results revealed that metal recovery increased with time and attained an ionexchange equilibrium in 30 min for Pb(II) and 90 min for Cu(II) with initial concentrations of 1800 mg/L Pb and 1200 mg/L Cu. Metal recovery increased with a temperature rise, especially for Cu adsorption, which may be attributed to the endothermic nature of the ion-exchange process. A 97% recovery for copper and 17% recovery for lead was obtained at the resin dosage of 0.07 g/mL and pH 4.5 after a two-stage ion exchange, which demonstrated that the MTS 9140 resin had an excellent adsorption selectivity to Cu(II) over Pb(II). Langmuir, Freundlich, and Temkin isotherm models were constructed for analyzing the adsorption of Cu(II) and Pb(II) ions on the resin. The Langmuir isotherm was the best fit for both the metal ions. Adsorption kinetics analysis showed that the ion-exchange process complied with the pseudo-second-order kinetic model.

In this study, it was also found that Lewatit monoplus TP208 and Amberlite IRC747 resins had a high adsorption affinity for both Cu(II) and Pb(II) ions. They could be applied in the removal of both the metals from a water system for environmental remediation and protection. Further studies are required.

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Notes

The authors declare no competing financial interest.

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