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이온 교환 수지에 대한 금속 이온의 흡착 거동 및 메카니즘 연구

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Adsorption Behaviors and Mechanism of Single/Multi-Metals by Ion Exchange Resins

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Abstract: Adsorption of Fe(Ш), Co(II), Cu(II), Zn(II) and K(I) by strong acid resins, Dowex 50WX2 200-400 (H) and Amberlite IRP-69, was studied to investigate the adsorption behaviors and mechanism in single-metal and multi-metal systems. The results showed that 99.9% Fe(III) can be removed by Dowex 50WX2 200-400 (H) in 100 min ([Fe(Ш)] < 40 mg/L, resin amount = 50 mg, pH = 3.0, 60 ℃). Mechanism studies revealed that Langmuir model and pseudo-second-order kinetic equation illustrate better fit for the adsorption of Fe(Ш). Furthermore, the investigations on multi-metal adsorption indicated that resins display a similar adsorption ratio for the same-valence metal ions (Co(II) = Cu(II) = Zn(II)), and a more selective adsorption for high-valence metal ions than low-valence metal ions (Fe(III) > Co(II) > K(I)). The above results can be used for the treatment of wastewater and the recovery of metals from the spent catalysts.

Keywords: adsorption, ion exchange, metal, kinetic, separation.

Introduction

In recent decades, metals have played an increasingly important role in chemical production and human life, especially transition metals, which have been widely used in catalysts,[1] electroplating, batteries, etc.. However, the heavy metals[2] (Fe, Co, Cu) in industry wastewater are harmful to ecological environment, and discharging them directly pollutes the water and soil, further endangers biological life and human health. In addition, discarding the rare metals and precious metals (Pt, Pd, Rh) in spent catalysts leads to the waste of resources.[3] Therefore, separation and recovery of transition metals from these wastes is particularly significant for environmental protection and secondary use concern. At present, various techniques have been employed to separate metals from solution such as precipitation, solvent extraction, membrane filtration, and ion exchange.[4] In the early research, precipitation was widely applied in separation of metals from aqueous solution. Meanwhile, it has been found to be in efficient.[5] Solvent extraction is another common method used in metals recovery, which can improve the adsorption selectivity and efficiency. However, the use of organic solvents has caused secondary pollution to the environment.[6] Membrane separation was also discovered as a viable way to separate metals.[4] The implementation of this method can reduce the use of organic solvents, but the filter membrane is easily clogged. With the development of advanced technology in separation areas, ion exchange was presented with high metal selectivity and efficiency.[7] It is generally employed in water treatment, metal separation, and catalysis.[8,9] These resins used today are typically made of small beads of highly crosslinked polymers that contain functional groups which facilitate the ion

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exchange.[10,11] Consequently, metals can be separated from the solution by ion exchange when their concentration is low. Moreover, ion exchange is environment friendly, and the resins can be reused for many times after the adsorption-desorption process.

Nowadays, many studies on ion exchanges have been devoted to the separation of metals. Molybdenum can be separated from chloride leach liquors in Nguyen's survey which verified the possibility of Mo separation among Co and Al with AG1-x8 resin.[12] Aboul-Magd found that Dowex HRWX2-Na exhibits great adsorption for Fe(III), Cu(II), and Zn(II) in the presence of acid or organic solute.[13] Also, Duclos proposed to recover Pt from fuel cell catalysts by combining extraction, ion exchange, and precipitation, resulting in 76% Pt being recovered as solid $(NH_4)_2PtCl_6$.[14] Moreover, Sun published a literature about the recovery of Pt from chloride leaching solution in which 99.6% Pt was obtained after the elution step.[15] In the above work, ion exchange has been shown to be an efficient method for separating metals, and the choice of resin is especially crucial.

Many factors affect the adsorption capacity of resins, the most significant is the functional group of which the resin contains.[16,17] A variety of resins were examined for the removal of metals from various solutions. It was reported to have removed Cu(II) from aqueous solution by using Dowex HCR S/S and Dowex Marathon C, strong acid cation resins with functional group $-SO_3H$, which resulted in a more than 98% Cu(II) removal efficiency under optimum conditions.[18] The adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) was surveyed using Amberlite IR-120 synthetic resin, whose functional group is also $-SO_3H$.[19] These bivalent metals could be removed completely from aqueous solution but the marked selectivity of an individual ion by this resin was not shown. Diphonix, a chelating resin, was used for Fe(III) removal from cobalt sulfate solution. Fe(III) was able to be separated efficiently from the Fe(III)-Co(II) acid solution when the acidity was controlled at pH = 1.[20] A number of papers reported metal recovery from solutions by different types of resins. As shown in Table 1.

Pertinent data was obtained from Table 1, and it revealed that strong acid cation resins with $-SO_3H$ group have a superior affinity for metal cations, which provides a basis for the choice of resins in our research. Amberlite IR-120 resin also showed similar adsorption capacity with metals of the same valence but is not studied further. Also, most of the methods previously mentioned require several adsorption and multiple cycle steps. Therefore, the easily operable and efficient resins are needed to

Table 1. Evaluation of Adsorption Capacity for Metals by Different Resins

Name	Type	Functional group	Adsorption ratio	Optimum conditions	Application
Purolite C160[18]	Strong acid cation (Na+)	$-HSO_3$	Cu(II) 97%	Cu(II)200 ppm, pH=3, 25 ℃, resin:0.06 mg/25 mL, 120 min	Recovery of metal from catalysts
Dowex HCR-W2[18]	Strong acid cation (Na+)	$-HSO_3$	Cu(II) 83%	Cu(II)200 ppm, pH=3, 25 ℃, resin:0.08 mg/25 mL,120 min	Recovery of metal
Dowex HCR S/S[19]	Strong acid cation (Na+)	$-HSO_3$	Cu(II) 98%	Cu(II)80 mg/L, pH=4.5, 25 ℃, resin:0.2 g/100 mL, 180 min	Treatment wastewater
Dowex Marathon C[19]	Strong acid cation (Na+)	$-HSO_3$	Cu(II) 98%	Cu(II)80 mg/L, pH=4.5, 25 ℃, resin:0.2 g/100 mL, 180 min	Treatment of wastewater
Amberlite IR-120[2]	Strong acid cation (H+)	$-HSO_3$	Ni(II) 99% Pb(II) 99% Cd(II) 99%	Ni(II),Pb(II) 0.001 mol/L, 20 ℃, pH=4,90 min, resin:0.1 g	Separation of metal
Amberjet4200[15]	Weak base anion	$-NH_2$	Pt(IV) 81%	Pt(IV) 2 g/L, 25 ℃, resin: 20 mg/L	Separation of metal
Diphonix[20]	Chelating resin	$-PO(OH)_2$	Fe(III) 100%	Fe(III), Co(II) 20 mg/L, 25 ℃, resin: 50 mg,100 mL,24 h,	Separation of metal
Dowex Marathon C[10]	Strong acid cation (H+)	$-HSO_3$	Fe(III) 97%	Fe(III)50 mg/L, pH=4, 25 ℃, resin: 3.5g/L,rate:10L/h	Recovery of metal from catalysts
Z-Fe resin[8]	Chelating resin	=C=N-OH-	Fe(III) 89% Cu(II) 33%	Cu(II)40 g/L, Fe(III) 36 g/L, 20 ℃, pH=1.4, 25 mL, 60 min, resin1.2 g/L	Separation of metal
LSC-500[8]	Chelating resin	$-OH$ $-PO(OH)_2$	Fe(III) 76% Cu(II) 75%	Cu(II)40 g/L, Fe(III)36 g/L 20 ℃, pH=1.4, 25 mL, 60 min, resin1.2 g/L	Separation of metal

investigate the separation of these metals.

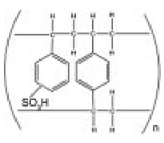
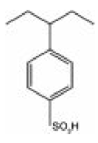
Two strong acid cation resins, Dowex 50WX2 200-400 (H) and Amberlite IRP-69, were typically chosen as for this report. These two resins are easily obtained for laboratory and industry use and are selected because of their low price. This research aims to test an efficient resin to separate Fe(III) from aqueous solution in sing-metal system and study the adsorption behaviors and rules of the resins for Co(II), Cu(II) and Zn(II) ions in multi-metal system. The research investigated the effect of contact time, pH, temperature, metal concentration, and resin dosage for effective metal removal, and studied the influencing factors of the selective adsorption for multiple ions. Furthermore, adsorption isotherm models and kinetics were investigated.

Experimental

Materials and Instruments. All reagents were of analytical grade and all solutions were prepared in deionized water. The Amberlite IRP-69 and Dowex 50WX2 200-400 (H) resins were purchased from Suzhou Ketong Biological Pharmaceutical Technology Co. Ltd and Shanghai J&K Chemical Ltd. The properties of Amberlite IRP-69 and Dowex 50WX2 200-400 (H) are showed in Table 2. Sulfuric acid and sodium hydroxide were purchased from Chinasun Specialty Products Co. Other chemicals, $Fe_2(SO_4)_3$ (M=399.88 g/mol), $CoSO_4\cdot7H_2O$ (M=281.10 g/mol), $CuSO_4\cdot5H_2O$ (M=249.69 g/mol), $ZnSO_4\cdot7H_2O$ (M=287.56 g/mol), and KCl (M=74.5 g/mol) were purchased from Suzhou Industrial Park Instrument Co. Ltd.

The pH of the aqueous solution was controlled by sulfuric acid (30 g/L) and sodium hydroxide (30 g/L) and was tested by pH meter. The metal concentration was measured by direct coupled plasma atomic emission spectrometer (ICP-OES, 710-ES, Varian). The resins were dried in a vacuum drying oven at 30 ℃.

Table 2. Properties of Amberlite IRP-69 and Dowex 50WX2 200-400 (H)

Name	Amberlite IRP-69	Dowex 50WX2 200-400 (H)
Type	Strong acid cation	Strong acid cation
Active group	$-SO_3H$	$-SO_3H$
Particle size (mm)	0.6-0.8	0.2-0.4
Lonic form	H^+	H^+
Effective pH range	0-14	0-14
Thermal resistance	463 ℃	277 ℃
Structures		

Preparation of Resins. Firstly, the resins need to be treated before the adsorption experiments. 2.0 g resin was washed twice with 20 mL sulfuric acid (30 g/L) to remove the possible metal complex residuals, then washed again with deionized water to adjust the resins back to be neutral. The resins were filtered and put in the vacuum drying oven at 30 ℃ until the weight was constant. The treated resins were then ready for the experiments.

Single-metal Adsorption. In a single-metal system, 10 mg/L synthetic solution of Fe(III) was prepared with $Fe_2(SO_4)_3$. 100 mL above synthetic solution and 20 mg Dowex 50WX2 200-400 (H) or Amberlite IRP-69 resin were added into a 150 mL conical flask with the magneton. The mixture was then stirred at 25 ℃ for 100 min in an oil bath (pH = 2). The 20 mL liquid after reaction was taken for concentration test. The resin was then filtered and dried.[21]

The adsorption ratio $a\%$ was calculated by the following equation:

$$a\% = \frac{C_0 - C}{C_0} \times 100\% \tag{1}$$

where C_0 (mg/L) is the initial metal concentration and C (mg/L) is the final metal concentration after the reaction.

Multi-metal Adsorption. In multi-metal systems, The Co(II)-Cu(II)-Zn(II) multi-metal system (2-MMS) was prepared with $CoSO_4\cdot7H_2O$, $CuSO_4\cdot5H_2O$, and $ZnSO_4\cdot7H_2O$ in aqueous solution. The Fe(III)-Co(II)-Cu(II)-Zn(II) multi-metal system (32-MMS) was prepared with $Fe_2(SO_4)_3$, $CoSO_4\cdot7H_2O$, $CuSO_4\cdot5H_2O$ and $ZnSO_4\cdot7H_2O$ in aqueous solution. The Fe(III)-Co(II)-K(I) multi-metal system (321-MMS) was prepared with $Fe_2(SO_4)_3$, $CoSO_4\cdot7H_2O$ and KCl in aqueous solution. The above adsorption processes in multi-metal systems proceeded in 100 mL aqueous solution containing metal ions with Dowex 50WX2 200-400 (H) or Amberlite IRP-69 (contact time = 100 min, pH = 3, T = 25 ℃, ions concentration is 10 mg/L for each metal). The ion concentrations in the solution were analyzed by ICP-OES, and the adsorption ratio a% was calculated by eq. (1).

Results and Discussion

Fe(III) Adsorption in Single-metal System. Effect of

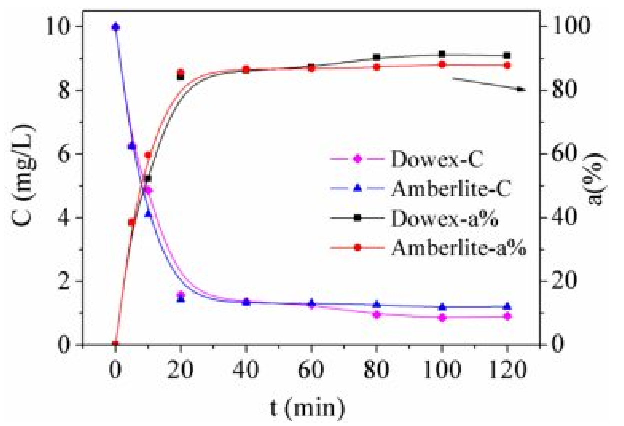


Figure 1. Effect of contact time on adsorption of Fe(III) (iron concentration = 10 mg/L, 25 ºC, 20 mg/100 mL, pH = 2).

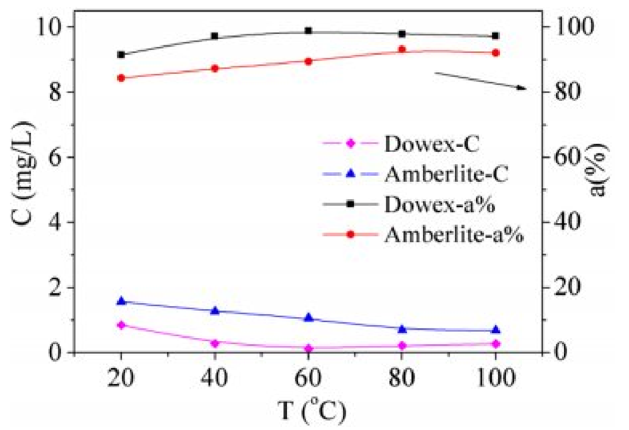


Figure 2. Effect of temperature on adsorption of Fe(III) (iron concentration = 10 mg/L, 20 mg/100 mL, pH = 2, 100 min).

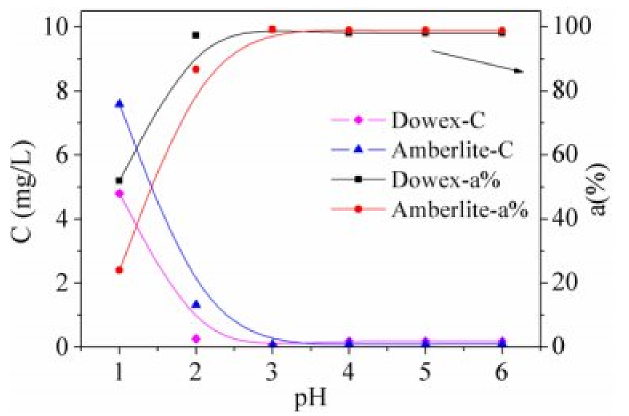


Figure 3. Effect of pH on adsorption of Fe(III) (iron concentration = 10 mg/L, 20 mg/100 mL, 100 min, 60 ºC for Dowex resin, 80 ºC for Amberlite resin).

Contact Time: The influence of contact time was investigated regarding the adsorption reaction involving 20 mg Dowex 50WX2 200-400 (H) or Amberlite IRP-69 in 100 mL Fe(III) solution (10 mg/L). As showed in Figure 1, with the increase of contact time, the adsorption ratio of Fe(III) increased. The adsorption curve then tends to level off. This can be described as attainment of adsorption equilibrium. It is difficult to have more adsorption under these experimental conditions as most active sites in the resins were already occupied by Fe(III).[22] The adsorption reaction was a fast process of ion exchange, consequently, the adsorption ratio (a%) was over 80% for Dowex 50WX2 200-400 (H) in the first 20 min, and 91.4% in 100 min at which it achieved an equilibrium state.

Effect of Temperature: The effect of temperature on adsorption of Fe(III) by Dowex 50WX2 200-400 (H) and Amberlite IRP-69 was also studied in the experiments. The temperatures were changed from 20 to 100 ºC while all other conditions were invariable. The remnant Fe(III) concentration and adsorption ratio are shown in Figure 2. When the temperature was under 60 ºC the adsorption ratio of Dowex 50WX2 200-400 (H) increased, which can be described by the fact that the adsorption process was more favored than desorption at lower temperature when the adsorption amount was within the maximum capacity of resin. While the temperature was above 60 ºC it decreased slightly because that some Fe(III) was released from the resin with the increasing temperature. Consequently, the optimum temperature was found to be 60 ºC for Dowex 50WX2 200-400 (H) and 80 ºC for Amberlite IRP-69, and Dowex 50WX2 200-400 (H) shows a better affinity for Fe(III) with the effect of temperature.

Effect of pH: A series of experiments were performed using Dowex 50WX2 200-400 (H) and Amberlite IRP-69 to remove Fe(III) under different acidic conditions. The impact of acidity on the adsorption was examined under the optimum conditions obtained from the previous experiments. This study varied the pH values in the range 1 - 6 and the Fe(III) concentration of the solution were measured by ICP-OES. The results are shown in Figure 3. The investigation in the effects of pH demonstrated a distinct influence on the adsorption. The Fe(III) adsorption ratios of two resins were found to be quite low in the very acidic conditions. Then the ratio increased rapidly until it plateaued with a maximum recovery of Fe(III) at about 98% with a pH = 3. The resins in solutions with lower pHs showed poor adsorption capacity because the extremely acidic conditions inhibit the stripping process of protons from the $-SO_3H$ group, thus reducing the ion exchange efficiency of the resins.

Effect of Resin Dosage: The effects on the amount of resin have also been studied in this work. The results are shown in Figure 4. It was apparent that the adsorption of Fe(III) was affected greatly as the resin dosage increase. The adsorption ratio increased along with the quantity of resin, which is because the larger surface area and adsorption sites were provided by more resins, enhancing the removal of Fe(III). When the resin dosage was 50 mg in the 100 mL aqueous solution, the maximum adsorption of iron was 99.9% for Dowex 50WX2 200-400 (H) and 99.3% for Amberlite IRP-69. Meanwhile, the Fe(III) was almost completely adsorbed with 50 mg Dowex 50WX2 200-400 (H).

Effect of Iron Concentration: Different Fe(III) concentrations usually have different influences on the adsorption ratio. Figure 5 demonstrates the effects of changing Fe(III) concentration from 10 to 80 mg/L. The results show that the adsorption ratio kept close to 99.9% as the Fe(III) concentration was below 40 mg/L for Dowex 50WX2 200-400 (H). A higher concentration is not favorable for Fe(III) adsorption by the two resins. This is because with more Fe(III), the availability of sites provided by the limited resins is not sufficient. Fe(III) ions were residual in the solution, resulting in the lower adsorption ratio. It can be seen that Fe(III) was easily removed from the aqueous solution by ion exchange but cannot be separated efficiently by precipitation or membrane filtration at lower concentrations.

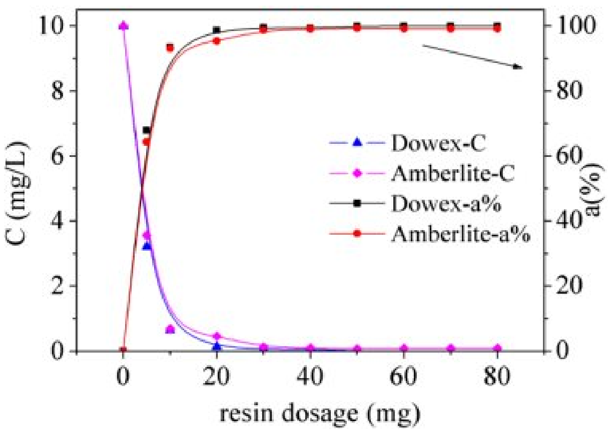


Figure 4. Effect of resin dosage on adsorption of Fe(III) (iron concentration = 10 mg/L, 100 min, pH = 3, 60 ℃ for Dowex resin, 80 ℃ for Amberlite resin).

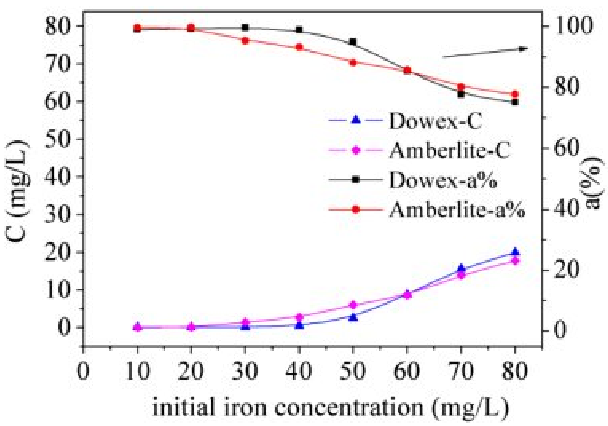


Figure 5. Effect of iron concentration on adsorption of Fe(III) (50 mg/100 mL, 100 min, pH = 3, 60 ℃ for Dowex resin, 80 ℃ for Amberlite resin).

Adsorption Isotherms. Comparing the absorption ratio of Fe(III) with Dowex 50WX2 200-400 (H) and Amberlite IRP-69 in different conditions, it is found that Dowex 50WX2 200-400 (H) showed better adsorption capacity for Fe(III) with the optimum conditions. The adsorption mechanism of the Fe(III) with strong acid cation resin can be represented as the formula (2), and a process of Fe(III) adsorption is displayed in Figure 6.

$$3(HSO_3R) + Fe^{3+} \rightarrow Fe(SO_3R)_3 + 3H^+ \quad (2)$$

As shown in Figure 6, the Fe(III) is adsorbed by the functional group with H^+ being released when going through the resin. The Langmuir and Freundlich isotherm models were introduced to understand the mechanism of Fe(III) adsorption by Dowex 50WX2 200-400 (H) and Amberlite IR-120. The adsorption capacity[23] at equilibrium Q_e (mg/g) was calculated as follows:

$$Q_e = (C_0 - C_e)V/m \quad (3)$$

where V (mL) is the volume of the solution, m (mg) is the weight of the resin dried, and C_e (mg/L) is the equilibrium concentration.

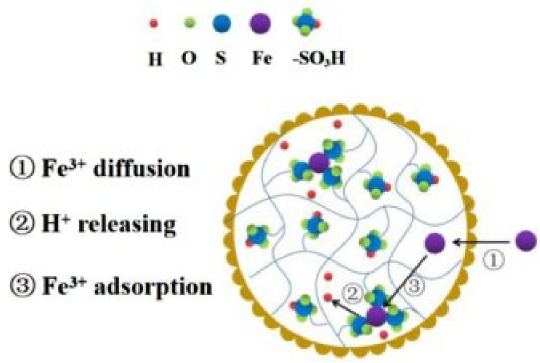


Figure 6. Process of Fe(Ⅲ) adsorption with strong acid cation resin.

The Langmuir model was described as eq. (4).

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \tag{4}$$

where b (L/mg) is Langmuir constant related to the affinity and Q_m (mg/g) is maximal adsorption capacity.

The Freundlich model was described as eq. (5).

$$\lg Q_e = \frac{1}{n}\lg C_e + \lg K \tag{5}$$

where n is Freundlich constant and K is Freundlich binding constant.

The adsorption data is shown with the model fit using the two isotherms with resins adsorption of Fe(III) in Figure 7(a, b). The model parameters were obtained by regression and indicated in Table 3. It was proven that Langmuir isotherm represents a better fit of Fe(III) adsorption than the Freundlich isotherm. Therefore, the Langmuir model was sufficient to describe the adsorption of Fe(III) within the range of the errors permitted.

The Langmuir adsorption isotherm indicates that the adsorption is monolayer and there is no other molecular coating, which is consistent with the experimental results of Fe(III) concentration effects on adsorption ratio. More ions cannot be adsorbed with the increasing of ion concentration because the active sites are completely occupied. It also demonstrates that the probability that an ion is absorbed at one site is independent of whether adjacent spaces have been occupied by other ions. Therefore, the Fe(III) adsorption ratio would increase with the increasing time until equilibrium state.

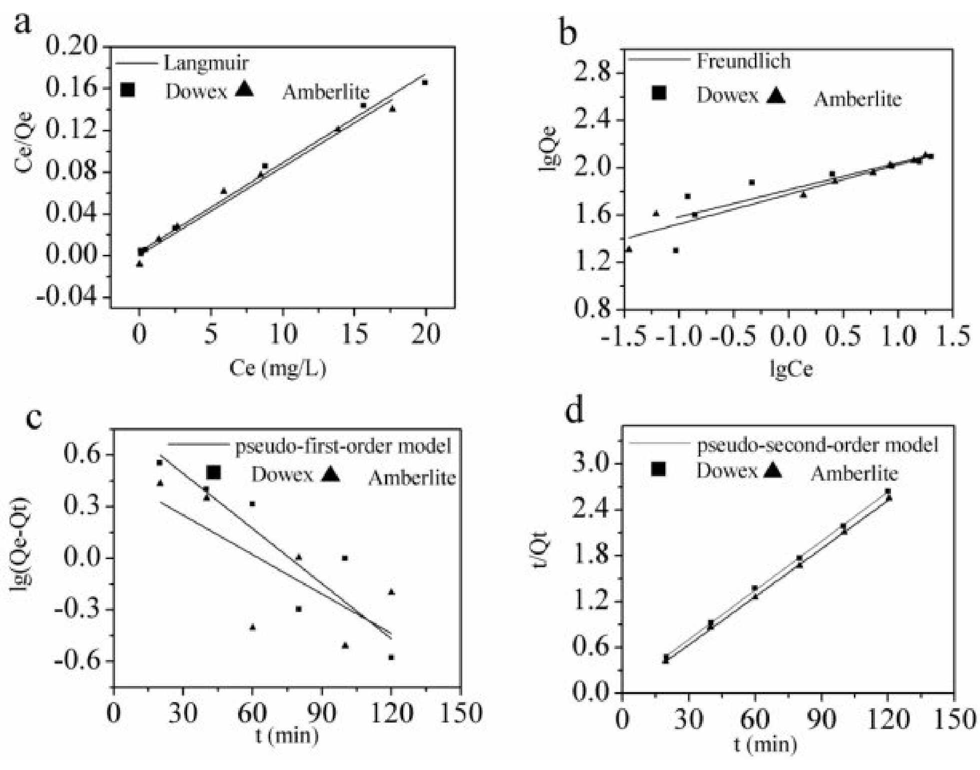


Figure 7. Adsorption model (Langmuir-a, Freundlich-b); The kinetics (pseudo-first-order model-c, pseudo-second-order model-d) for Fe(III) adsorption.

Table 3. Parameters of Langmuir and Freundlich Models for Fe(III) Adsorption

Resin	Adsorption isotherm	R^2	b	K	n
Dowex 50WX2 200-400 (H)	Langmuir	0.994	2.214		
	Freundlich	0.665		65.19	4.36
Amberlite IRP-69	Langmuir	0.977	0.812		
	Freundlich	0.927		58.24	3.99

Adsorption Kinetics. The adsorption kinetic behavior of Fe(III) by Dowex 50WX2 200-400 (H) and Amberlite IRP-69 was described with the pseudo-first-order model and the pseudo-second-order model.[24,25]

The pseudo-first-order model was described as eq. (6):

$$\lg(Q_e - Q_t) = \lg Q_e - k_1 t \tag{6}$$

The pseudo-second-order model was described as eq. (7):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{7}$$

where Q_e (mg/g) is adsorption capacity at equilibrium, Q_t (mg/g) is adsorption capacity at the time t, k_1 (min^{-1}) is rate constant of the pseudo-first-order model, and k_2 (g·mg^{-1}·min^{-1}) is rate constant of the pseudo-second-order model.

The pseudo-first-order model and the pseudo-second-order model were fitted in Figure 7 (c, d) and the parameters are revealed in Table 4. Depending on the experimental data, it was found that the correlation coefficient (R^2>0.999) of the pseudo-second-order model is higher than that of pseudo-first-order model, and the equilibrium adsorption capacity calculated by pseudo-second-order model ($Q_{e,cal}$) is closer to the experimental one ($Q_{e,expl}$). These two points illustrate that the pseudo-second-order model fits well the adsorption of Fe(III) by Dowex 50WX2 200-400 (H) and Amberlite IRP-69.

Selective Adsorption in Multi-metal Systems. Co(II), Cu(II), and Zn(II) Adsorption in 2-MMS: The adsorption of Co(II), Cu(II), Zn(II) by Dowex 50WX2 200-400 (H) and Amberlite IRP-69 resins from aqueous solution in different conditions was also explored in this study. The aim was to evaluate the influencing factors and the adsorption behaviors of resin for multiple metals. The results in 2-MMS are shown in Figure 8. It is found that pH, resin dosage and initial concentration of metal ions have greater effects on the adsorption ratios of the three ions. The adsorption ratios of each metal

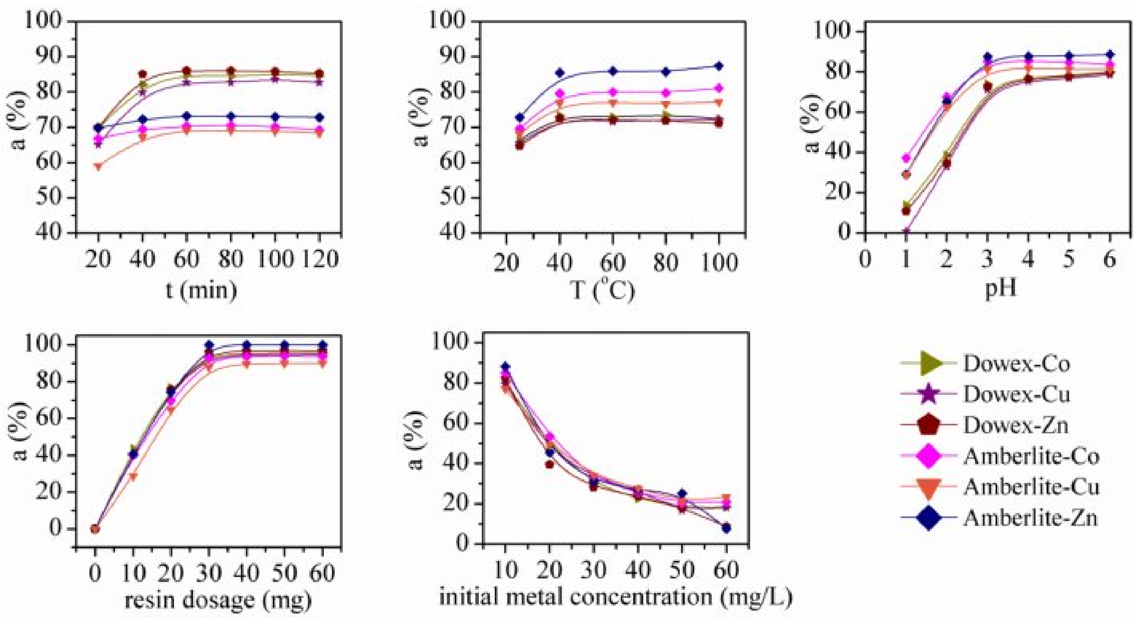


Figure 8. Adsorption ratio of Co(II), Cu(II), Zn(II) with different contact time, temperature, pH, resin dosage and initial concentration in 2-MMS.

Table 4. Parameters of Pseudo-first-order and Pseudo-second-order Models for Fe(III) Adsorption

Resin	Kinetic model	R^2	k_1 (min^{-1})	k_2 (mg^{-1}·min^{-1})	$Q_{e,cal}$ (mg/g)	$Q_{e,exp}$ (mg/g)
Dowex 50WX2 200-400 (H)	Pseudo-first-order	0.786	0.011		6.5	45.7
	Pseudo-second-order	0.999		0.0075	46.7	45.7
Amberlite IRP-69	Pseudo-first-order	0.424	0.0077		3.0	47.6
	Pseudo-second-order	0.999		0.0169	47.8	47.6

increased with increase of pH and resin dosage but decreased with increased initial metal concentration. This is coincident with the conclusion obtained from Fe(III) adsorption in single-metal system. It is also found that for each experimental factor changed, Dowex 50WX2 200-400 (H) and Amberlite IRP-69 have similar adsorption ratios for each metal, and both resins did not exhibit obvious selectivity for individual metal ions in 2-MMS. This may be due to the same valence state of the three ions, which affects the selectivity of the resins.

Fe(III), Co(II), Cu(II), and Zn(II) Adsorption in 32-MMS. In order to explore the adsorption behaviors for metals with different valence in multi-metal systems, and to further verify that the selectivity of the resin is related to the valence state, Fe(III), Co(II), Cu(II), and Zn(II) adsorption in 32-MMS was carried out, and the respective adsorption ratio of four ions is shown in Figure 9(a, b). The adsorption results described as: Fe(III) > Co(II) = Cu(II) = Zn(II). Both resins exhibit the same adsorption selectivity for Co(II), Cu(II), and Zn(II) in 32-MMS, which is consistent with the results of previous studies. The resins showed a much better selectivity for Fe(III) in the same conditions. It confirmed that the valence state of metals really affects the selectivity of the resin. Metal ions of the same valence state lead to the similar adsorption ratio, and metal ions of higher valence state are more selectively adsorbed by resins. Therefore, the Fe(III) reached adsorption equilibrium first with increasing of the resin dosages, after which Co(II), Cu(II), and Zn(II) followed.

Comparing the results of Co(II), Cu(II), and Zn(II) adsorption in 2-MMS and in 32-MMS by Dowex 50WX2 200-400 (H) and Amberlite IRP-69 in Figure 9(c, d). The results showed that the ratios of Co(II), Cu(II), and Zn(II) adsorption in 2-MMS were higher than those in 32-MMS, and the adsorption ratio of each metal in 32-MMS was reduced by about 20% than those in 2-MMS. The above results can be explained as "competitive adsorption" when multiple metal ions coexist in the solution, which is expressed that a negative effect on the adsorption ratio of the metal in the original system happened when one or more metal ions were added to the solution. This is because when two or more metal ions are mixed in the solution, each metal ion competes for the functional groups on resins at the same time, creating "competitive adsorption". Therefore, the adsorption ratio of each metal decreased with the limited amount of functional group.

Fe(III), Co(II), and K(I) Adsorption in 321-MMS. The adsorption of Fe(III), Co(II), and K(I) in 321-MMS by Dowex 50WX2 200-400 (H) and Amberlite IRP-69 in 100 mL aqueous

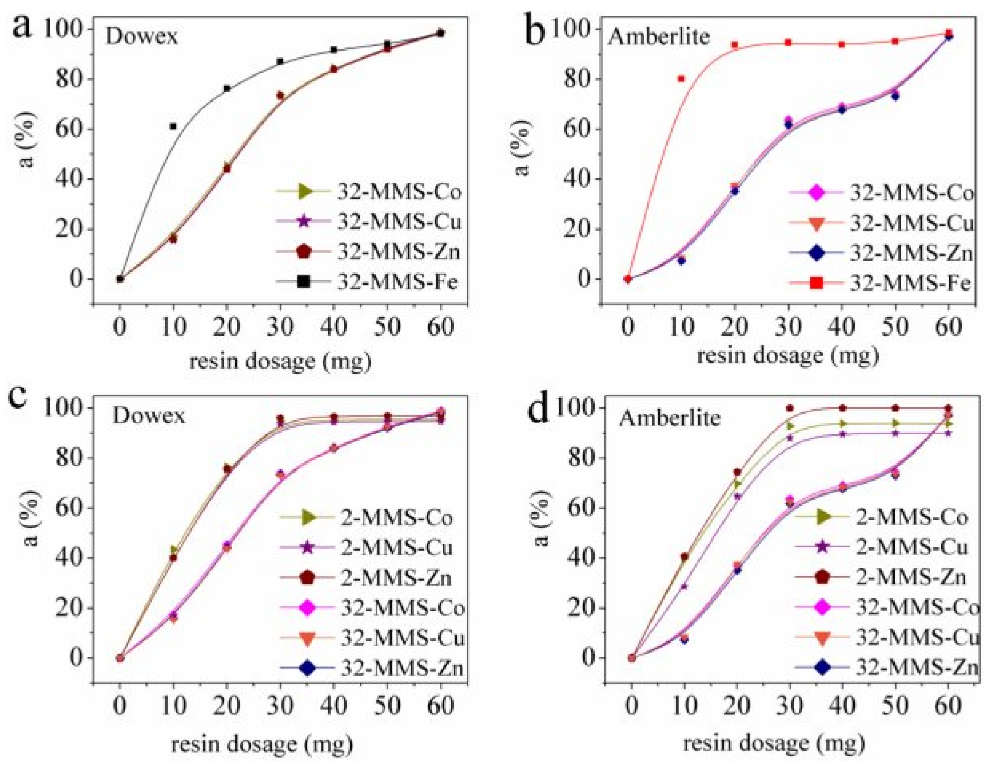


Figure 9. Comparison of adsorption ratios of Fe(III), Co(II), Cu(II), Zn(II) in multi-metal systems.

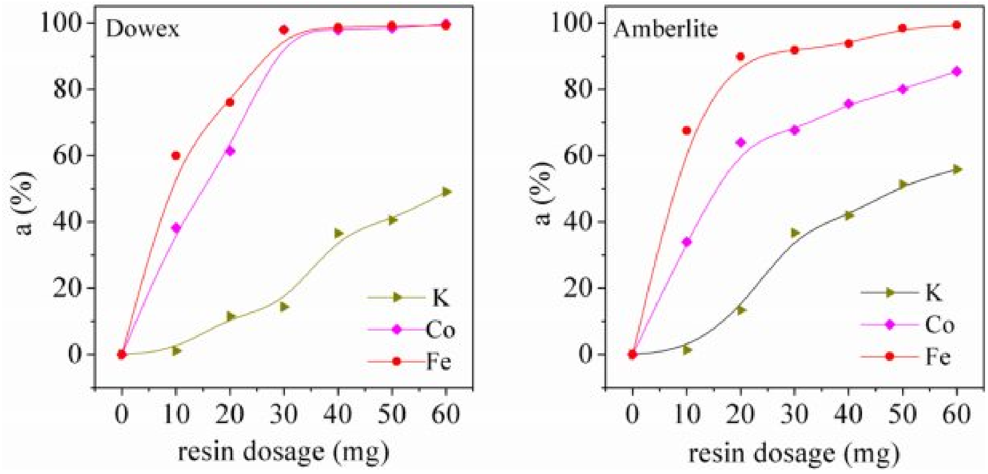


Figure 10. Selective adsorption ratio of Fe(III), Co(II), K(I) in 321-MMS.

solution was further studied. The three metals are in different valence states. The aim is to verify that the higher valence state of metals, the higher adsorption ratio, and the better selectivity of resins. The results are shown in Figure 10. The adsorption ratio of each metal with the same amount of resins in the aqueous solution is: Fe(III) > Co(II) > K(I). The selectivity of resin for ferric iron is greater than that of divalent cobalt, and the adsorption of divalent cobalt is greater than that of monovalent potassium, which is due to the different adsorption force by functional groups. Three equivalents of H^+ from $-SO_3H$ group were consumed for exchange when one equivalents of Fe(III) was adsorbed, and it is easy to form a stable structure of three chemical bonds. However, a monovalent or divalent ion requires fewer functional groups when adsorbed, and with a weak adsorption force, it is difficult to bond or easily to fall off after being adsorbed. Combining the results from 32-MMS, it is confirmed that ions with different valence states result in different adsorption ratios, and the high-valence metal ions are selected preferentially than low-valence metal ions.

Conclusions

Adsorption of Fe(III), Co(II), Cu(II), Zn(II), and K(I) was studied to investigate the adsorption behaviors and mechanism in single-metal and multi-metal systems. The influencing factors of contact time, temperature, pH, resin dosage, and metals concentration were investigated to enhance the adsorption ratio of resins. The results showed that Dowex 50WX2 200-400 (H) had a stronger affinity and higher selectivity for Fe(III). This occurred when the contact time was 100 min ([Fe(III)] < 40 mg/L, resin amount = 50 mg, pH = 3.0, 60 ℃), with the maximum adsorption ratio for Fe(III) being over 99.9%. Mechanism studies showed that Langmuir isotherms model and pseudo-second-order-kinetic equation fit well in the Fe(III) adsorption of single-metal system. Due to the simple operation, mild reaction conditions, and high selectivity of Dowex 50WX2 200-400 (H) and Amberlite IRP-69, the adsorption can be applied to the separation of Fe(III) from aqueous solution.

The results in multi-metal systems showed that Dowex 50WX2 200-400 (H) and the Amberlite IRP-69 resins reveal a weak affinity for the three metals and the similar adsorption ratios for the metal ions of the same valence state. It is proved that the resins demonstrate higher selectivity for metal ions of higher valence. The new findings and adsorption rules will benefit the treatment of industrial wastewater and recovery of metals from spent catalysts.

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References

1. K. Petya and R. Djingova, *Anal. Chim. Acta*, **464**, 7 (2002).
2. J. Yu, J. D. Zheng, Q. F. Lu, X. Wang, X. M. Zhang, Q. Z. Wang, and W. Yang, *Polym. Korea*, **41**, 480 (2017).

3. A. N. Nikoloski, K. L. Ang, and D. Li, *Hydrometallurgy*, **152**, 20 (2015).
4. L. L. Tavlarides, J. H. Bae, and C. K. Lee, *Sep. Sci. Technol.*, **22**, 581 (1987).
5. M. Amara and H. Kerdjoudj, *Desalination*, **168**, 195 (2004).
6. K. Sarangi, P. K. Parhi, E. Padhan, A. K. Palai, K. C. Nathsarma, and K. H. Park, *Sep. Purif. Technol.*, **55**, 44 (2007).
7. Y. Zhang, Q. Liu, and L. Li, *Hydrometallurgy*, **164**, 154 (2016).
8. P. P. Sun, T. Y. Kim, B. J. Min, H. I. Song, and S. Y. Cho, *Mater. Transact.*, **56**, 1863 (2015).
9. M. D. Víctor-Ortega, J. M. Ochando-Pulido, and A. Martínez-Ferez, *J. Ind. Eng. Chem.*, **36**, 298 (2016).
10. R. Chiariza, E. P. Horwitz, S. D. Alexandrators, and M. J. Gula, *Sep. Sci. Technol.*, 2**2**, 581 (1997).
11. C. Lasanta, I. Caro, and L. Pérez, *Chem. Eng. Sci.*, **60**, 3477 (2005).
12. T. H. Nguyen, S. H. Sohn, and M. S. Lee, *Mater. Transact.*, **54**, 1750 (2013).
13. A.-A. S. Aboul-Magd, S. A.-R. Al-Husain, and S. A. Al-Zahrani, *Arab. J. Chem.*, **9**, S1 (2016).
14. L. Duclos, L. Svecova, V. Laforest, G. Mandil, and P. X. Thivel, *Hydrometallurgy*, **160**, 79 (2016).
15. P. P. Sun, T. Y. Kim, B. J. Min, and S. Y. Cho, *Mater. Transact.*, **56**, 738 (2015).
16. A. Dabrowski, Z. Hubicki, P. Podkoscielny, and E. Robens, *Chemosphere*, **56**, 91 (2004).
17. S. Edebali and E. Pehlivan, *Powder Technol.*, **301**, 520 (2016).
18. S. Veli and B. Pekey, *Fresenius Environ. Bull.*, **13**, 244 (2004).
19. A. Demirbas, E. Pehlivan, F. Gode, T. Altun, and G. Arslan, *J. Colloid Interface Sci.*, **282**, 20 (2005).
20. M. S. Lee and M. J. Nicol, *Hydrometallurgy*, **86**, 6 (2007).
21. Y. Fan, X. Wang, and M. Wang, *Hydrometallurgy*, **136**, 31 (2013).
22. G. Karthikeyan, N. M. Andal, and K. Anbalagan, *J. Chem. Sci*., **117**, 663 (2005).
23. M. Parijaee, M. Noaparast, K. Saberyan, and S. Z. Shafaie-Tonkaboni, *Korean J. Chem. Eng.*, **31**, 2237 (2014).
24. Q.T. Bui, Y. S. Jeon, D. Kim, and J. H. Kim, *Polym. Korea*, **40**, 275 (2016).
25. H.-Y. Li, C. Li, M. Zhang, K. Wang, and B. Xie, *Hydrometallurgy*, **165**, 381 (2016).