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Low-Cost RSAC and Adsorption Characteristics in the Removal of Copper Ions from Wastewater

Yan Liu, Qin Chen and Rajendra Prasad Singh * 

School of Civil Engineering, Southeast University, Nanjing 210096, China; liuyian@seu.edu.cn (Y.L.); 220191095@seu.edu.cn (Q.C.)

* Correspondence: rajupsc@seu.edu.cn

Abstract: Adsorption is a typical method for treating copper-containing wastewater. Fly ash and steel slag both have a good adsorption performance, and activated clay is added in this study, too. In this study, the performance of residue and soil adsorption composite (RSAC) particles for copper ion adsorption was discussed through the substrate ratio and the influence mechanism, to achieve the win-win effect of industrial waste reuse and copper ion wastewater treatment. The results indicated that adsorption time, dosage, initial copper ion concentration, coexisting ions, and temperature showed different effects on the adsorption, respectively. Additionally, the adsorption kinetic study showed the removal of copper ions by adsorption of RSAC particles was in accordance with quasi-primary kinetic model and quasi-secondary kinetic model. The adsorption thermodynamics study shows the adsorption process of $\Delta G^0 < 0$, $\Delta H^0 > 0$ and $\Delta S^0 > 0$, indicating that the process of copper ion adsorption by RSAC particles was spontaneous, heat-absorbing, and entropy-increasing. The research demonstrates that RSAC particles have a certain adsorption capacity for copper ion.

Keywords: water pollution; adsorption; copper ions; adsorption mechanism; adsorption kinetics; thermodynamics



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1. Introduction

Water contamination through heavy metal ions is an environmental problem of great concern [1]. Adsorption is one of the most efficient methods to remove noxious heavy metal ions, especially for wastewater with large volumes and low heavy metal ion concentrations [2]. Adsorption is spontaneous and the basic principle is that the surface energy of substances could change the concentration at the phase interface. Adsorption usually relies on some adsorbent materials with a large specific surface area and a high surface energy to remove heavy metal ions [3,4]. Adsorption has two major advantages: the reaction rate is fast, and no other reagents are needed. Therefore, adsorption is regarded as an important and promising method for addressing heavy metal ions such as copper in wastewater.

The key issue of adsorption is the adsorbent. Adsorbents with good adsorption performance have such qualities as: a fast adsorption reaction rate, stable physical and chemical properties, good solid–liquid separation, an economical cost, easy recovery and regeneration, and reusability [5]. However, industrial adsorbents could not meet all of these qualities. Therefore, the core of the adsorption method focusing on treating wastewater with heavy metal ions is to find efficient adsorbents at a low cost [6,7].

Currently, common adsorbents in the water treatment domain include activated carbon, fly ash, etc. Activated carbon has a large surface area, fast filtration rate, stable structure, large adsorption capacity, a wide range of applications, and good adsorption performance. However, activated carbon has a short service life, high sludge treatment cost, and low recycling performance [8,9]. Fly ash, a waste product from power plants that use coal as the main fuel, has a loose and porous structure. It can intercept pollutant molecules and bind pollutants to the active sites on the surface by a chemical bond, resulting in

excellent adsorption [10]. Whereas, Andersson et al. [11] have also considered fly ash a low-cost material for adsorption. It has been found that steel slag has a good adsorption effect on copper, nickel and zinc ions, which mainly relies on the generation of hydroxide complexes [12]. Under optimal conditions, the adsorption efficiency of modified steel slag for uranium was 98% [13]. Activated white clay is an adsorbent made from clay minerals by inorganic acidification and other means, and dried by water rinsing. It is mainly made of bentonite clay as a raw material; its appearance is presented as a milky white powder, which is a non-toxic, tasteless, odorless, strong adsorption; and it can adsorb colored substances and organic matter [14]. Bentonite is considered to be an excellent adsorbent for Cu^{2+} , and the maximum adsorption capacity was 248.9 mg/g [15].

The residue and soil adsorption composite (RSAC) particle consists of solid waste and natural minerals. The raw materials used in the preparation of RSAC granules are fly ash, steel slag, activated white clay, bonding agent, and porogenic agents. The main raw materials are fly ash, steel slag, and activated white clay, the first two of which are industrial waste substrates [16].

2. Materials and Methods

2.1. RSAC Preparation

The fly ash used in this study was obtained from a power plant in Nanjing, China, and the steel slag was from a steel mill in Nanjing, China. Table 1 presents the main physical properties of the fly ash and the steel slag, Table 2 provides the particle size distribution of the fly ash and the steel slag, and Table 3 provides the chemical composition of the fly ash and the steel slag as measured by X-ray fluorescence analysis (XRF).

Table 1. Physical properties of waste substrates.

Waste Substrates	Density (g/cm ³)	Specific Surface Area (m ² /g)	Particle Size (μm)	Color
Fly ash	2.91	580	150 or more	Grey
Steel slag	2.10	3653	210 or more	Brown

Table 2. Particle size distribution of waste substrates.

Fly ash particle size (μm)	>3350	3350~880	880~325	325~212	<212
Proportion (%)	7.45	12.76	42.93	23.55	11.87
Steel slag particle size (μm)	>1400	1400~180	180~45	<45	-
Proportion (%)	2.49	7.68	32.40	57.36	-

Table 3. Chemical composition of waste substrates (%).

Chemical Composition	Fly Ash	Steel Slag
CaO	1.31	55.0
Fe ₂ O ₃	4.39	21.5
Al ₂ O ₃	45.9	1.51
SiO ₂	44.4	13.4
MgO	0.261	3.65
MnO	0.026	1.75
SO ₃	0.666	0.512
V ₂ O ₅	0.038	0.417
TiO ₂	1.26	0.296
Na ₂ O	0.094	0.077
ZnO	0.021	-
CuO	0.02	-

Additionally, the physical properties and the chemical composition of the activated white clay used in this experiment are presented in Tables 4 and 5.

Table 4. Physical properties of activated white clay.

Ingredients	Density (g/cm ³)	Particle Size (Through 75 µm Sieve)	Moisture (%)	Free Acid (as H ₂ SO ₄)	Color
Activated white clay	0.7–1.1	≥95%	12	≤0.2%	pale

Table 5. Chemical composition of activated white clay.

	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃
Content (%)	50–70	10–16	1–6	2–4

The binder used in the experiments was 525R ordinary silicate cement, which has the characteristics of a slow thickening rate, fast setting, and high strength. It can significantly improve the early strength of the composites [17]. The porogenic agent used in the experiment was a plant-based foaming agent. It is made by a saponification reaction with rosin and sodium hydroxide as the main raw materials, and it has a light yellow-brown viscous liquid appearance. The use of a plant-based foaming agent makes the adsorbent structure loose and porous, which can enhance the adsorption performance of RSPRC particles [18]. After comprehensive consideration of the adsorption and mechanical properties, the following substrate proportioning methods were set, which are shown in Table 6.

Table 6. Ratio of base material to binder for different groups (%).

Groups	Fly Ash	Steel Slag	Activated White Clay	Bonding Agent
Group I	65	15	10	10
Group II	70	10	10	10
Group III	65	10	15	10
Group IV	60	10	20	10

After the groups of adsorbents were maintained and shaped, static adsorption tests were performed. The results of the experiments are shown in Table 7 and Figure 1. The RSAC particle morphology and the residual liquid shape were observed after the completion of static adsorption experiments.

Table 7. Copper ion removal by different groups of adsorbents.

Groups	Initial Copper Ion Concentration (mg/L)	Residual Copper Ion Concentration (mg/L)	Removal Rate (%)
Group I	100	28.92	71.08
Group II	100	31.04	69.96
Group III	100	25.54	74.46
Group IV	100	18.48	81.52

The properties of the RSAC particles in each group were observed after the adsorption of copper ions. The residuals of Groups I, II, and III were clear, the RSAC particles were not abnormal, and the hardness did not change significantly. The residuals of group IV were somewhat turbid, with slight precipitation, the surface of RSAC particles showed signs of shedding, and the hardness decreased.

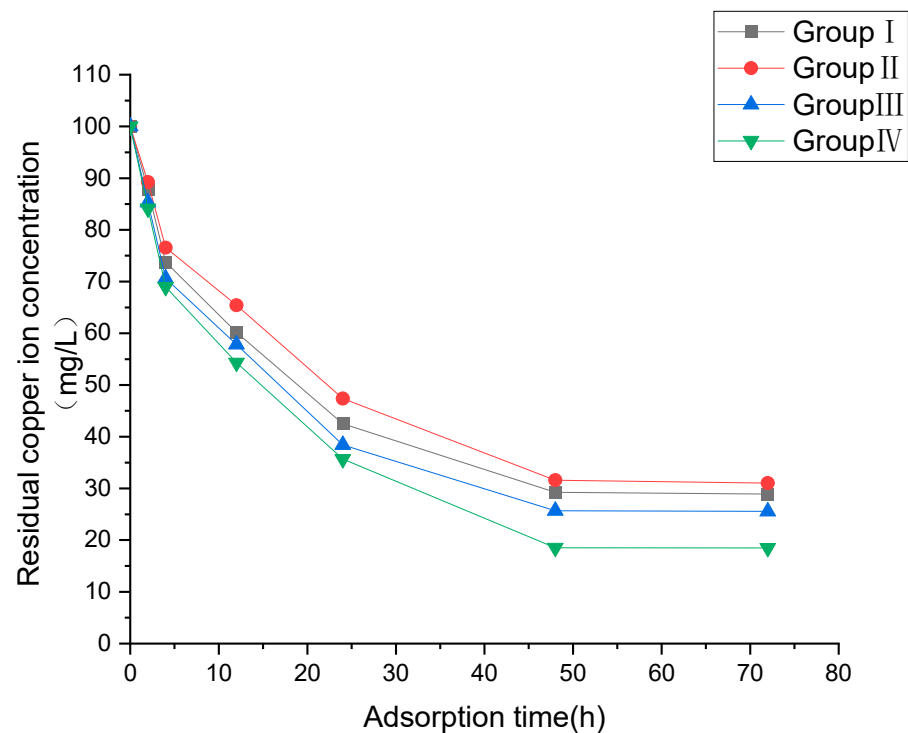


Figure 1. Comparison of adsorption effect of different groups of adsorbents.

Although Group IV had the best adsorption effect on copper ions, it was found that the residual solution had slight precipitation and the strength of the RSAC particles was reduced to break easily. On balance, Group III with the second highest removal rate was selected as the best ratio for the subsequent experiments. The process flow of the pellet is shown in Figure 2.

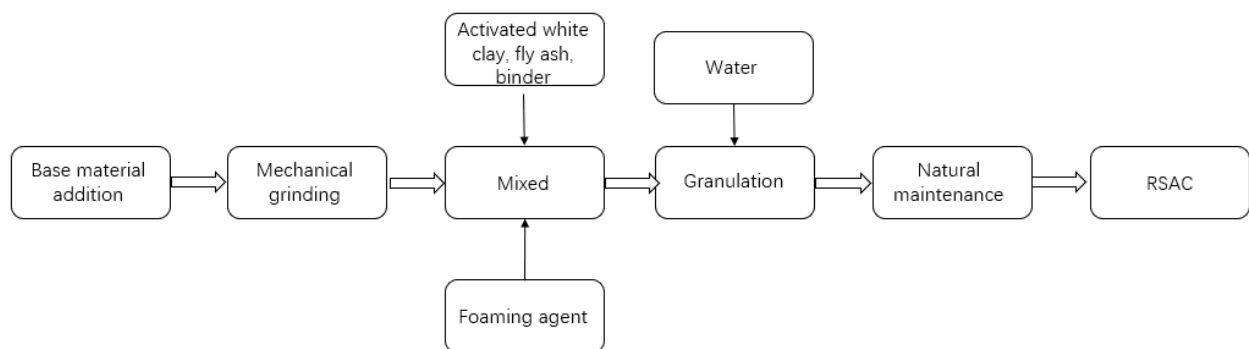


Figure 2. Experimental RSAC pellet fabrication process.

2.2. Determination of Copper Ion Concentration

2.2.1. Measurement Methods

The method used for the determination of copper ion concentration was the bisgly-oxal oxaldihydrazone spectrophotometric method (GB/T 5750.6-2006). The measurement instrument used was a 752 UV-Vis spectrophotometer, which had a minimum detection mass concentration of 0.04 mg/L. At pH 9, copper ions (Cu^{2+}) could react with bis (cyclohexanone oxaldihydrazone) and acetaldehyde. The reaction product is a purple bis (acetaldehyde oxaldihydrazone) chelate, and the copper ion concentration is determined by the relationship between absorbance and copper ion concentration in direct proportion.

2.2.2. Reagents for Experiments

The reagents for the experiments were: copper sulfate (CuSO_4), acetaldehyde solution ($W(\text{CH}_3\text{CHO}) = 40\%$), ammonium chloride (NH_4Cl), ammonium hydroxide (NH_4OH), ammonium citrate ($(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$), ethyl alcohol ($\text{C}_2\text{H}_6\text{O}$), and bis(cyclohexanone)oxaldihydrazone (BCO). All reagents were supplied by Sinopharm Chemical Reagent Co., Ltd., Nanjing, China. All solutions in these experiments were prepared with analytical grade water ($R = 18 \text{ M}/\text{cm}$) using grade A glassware unless otherwise stated.

2.2.3. Determination Procedure

Absorb 25.0 mL water sample in 50 mL glass plug colorimetric tube; another 50 mL colorimetric tube 5, respectively, adding copper standard solution 0 mL, 0.50 mL, 1.00 mL, 1.50 mL, and 2.00 mL, diluted with deionized water to 25 mL.

Absorbing 2.0 mL ammonium citrate solution, adding each colorimetric tube, mixing evenly and adjusting pH to 9.0 with (1 + 1) ammonia. Then, 5.0 mL ammonia-ammonium chloride buffer solution was added and mixed evenly. Then, 5.0 mL BCO solution and 1.0 mL acetaldehyde were added successively. Finally, deionized water was added to the scale and mixed evenly.

Heat for 10 min in a 50°C water bath, remove, and cool. After cooling to room temperature (standing for 20 min), under the condition of wavelength of 546 nm, the absorbance of the sample to be tested and the standard series was determined using a colorimetric dish with an optical path of 1 cm and deionized water as the reference.

The standard curve was plotted with the copper ion concentration of the standard series as the abscissa and the corresponding absorbance as the ordinate. The corresponding copper ion concentration was determined from the standard curve according to the absorbance of the water sample to be measured.

The results of the standard series measurements are presented in Table 8.

Table 8. Measurement results for the standard series.

Absorbance A	0.019	0.020	0.374	0.563	0.751
Copper ion concentration (mg/L)	0	2	4	6	8

The standard curve was plotted as shown in Figure 3 and the linear regression equation (Equation (1)):

$$y = 0.0914x + 0.016, R^2 = 0.9997 \quad (1)$$

2.3. Copper Ion Removal Effect Examination Index

The adsorption effect of RSAC particles on copper ions is mainly reflected in two aspects, namely the copper ion removal rate and the adsorption amount. Removal rate (η) and adsorption amount (Γ) are used in this paper to investigate the copper ion removal effect and the adsorption performance of RSAC particles, respectively.

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

$$\Gamma = \frac{(C_0 - C_e) V}{m} \quad (3)$$

In Equations (2) and (3), η is the removal rate of copper ions (%), C_0 is the initial copper ion concentration of the solution (mg/L), C_e is the concentration of copper ions in solution at equilibrium (mg/L), Γ is the amount of copper adsorbed per unit mass of adsorbent (mg/g), V is the volume of the solution (L), and m is the mass of adsorbent (g).

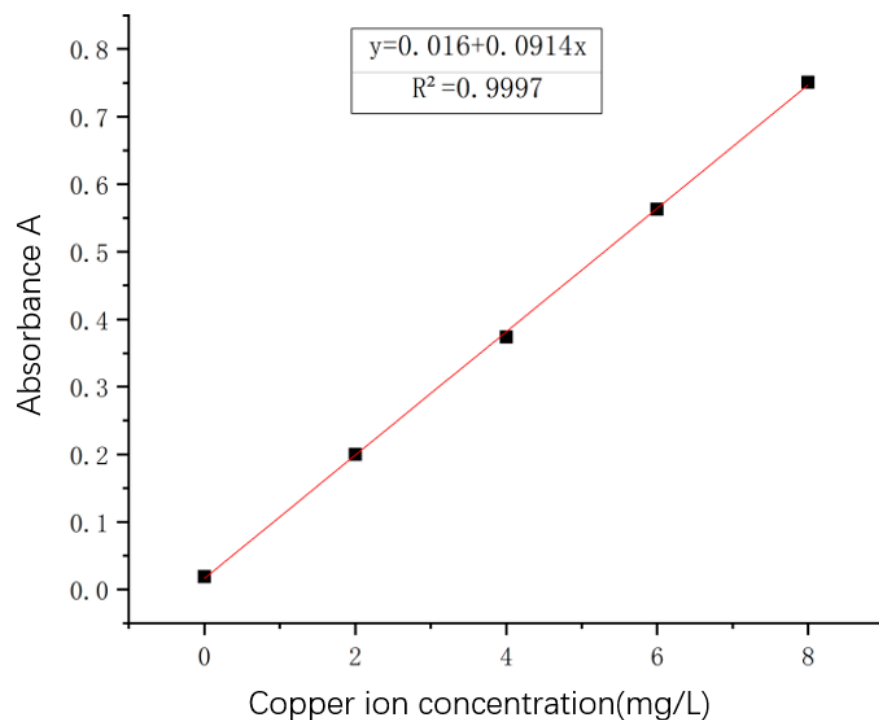


Figure 3. Copper ion standard curve.

2.4. Effect of Time on Adsorption

RSAC particles were weighted and divided into five groups: 2, 4, 6, 8, and 10 g. The groups were put into conical flasks, respectively, with 150 mL of 100 mg/L copper ion solution. Then, all the samples were mixed at room temperature (25 ± 1 °C). The concentration of residual copper ion in the supernatant of each sample was measured at a specific time and the relationship was investigated.

2.5. Effect of Dosage on Adsorption

The same samples were prepared and oscillated at room temperature (25 ± 1 °C). The concentration of residual copper ions in the supernatant of each sample was measured when the adsorption time reached 48 h.

2.6. Study of Initial Concentration on Adsorption

A series of 10, 50, 100, and 150 mg/L copper ion solutions were prepared separately. Then, a 5 g RSAC adsorbent was added into the solution series. Finally, the copper ion concentration in the supernatant of each sample was measured when the static adsorption time reached 2, 6, 12, 24, 48, and 72 h.

2.7. Study of Coexisting Metal Cations on Adsorption

A series of 150 mL of 100 mg/L copper ion solutions were prepared with the coexistence of Na^+ , Mg^{2+} , Ca^{2+} , and Fe^{3+} , respectively. To each sample 5 g RSAC particles was added and then mixed at room temperature (25 ± 1 °C). The copper ion concentration in the supernatant of each sample was measured when the adsorption time reached 48 h.

2.8. Study of Ambient Temperature on Adsorption

Three groups of 150 mL solutions with 10, 40, 80, 120, 160, and 200 mg/L copper ion were prepared. To each sample was added 5 g RSAC particles. The three groups were mixed at 15 °C, 25 °C, and 35 °C separately. To each sample was measured a copper ion concentration of the supernatant when reaching adsorption equilibrium.

The Freundlich and Langmuir models are often used to describe the adsorption behavior in solid–liquid systems [19]. Therefore, the adsorption isotherms of the Freundlich and the Langmuir models were plotted using nonlinear fits based on the experimental results of heavy metal ion adsorption by RSAC particles.

The expression for the Langmuir model equation is (Equation (4)):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (4)$$

In Equation (4), q_e is the adsorption equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L), $q_{\max}$ is the maximum adsorption capacity (mg/g), and K_L is the Langmuir adsorption constant.

The expression for the Freundlich model equation is (Equation (5)):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

In Equation (5), q_e is the adsorption equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L), K_F is the Freundlich adsorption constant, and n is a constant related to the adsorption capacity.

2.9. Kinetic Study of Copper Ion Adsorption by RSAC

Currently, quasi-primary and quasi-secondary kinetic models are often used to describe the adsorption kinetic behavior of adsorbents in solid–liquid static adsorption systems [20].

The expression for the quasi-level kinetic model equation is (Equation (6)):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

In Equation (6), q_e is the amount of solute adsorbed on the adsorbent surface at adsorption equilibrium (mg/g), q_t is the amount of solute adsorbed on the adsorbent surface at the specified moment (t) during the adsorption process (mg/g), and k_1 is the adsorption rate constant (h^{-1}).

The expression for the quasi-secondary kinetic model equation is (Equation (7)):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad (7)$$

In Equation (7), q_e is the amount of solute adsorbed on the adsorbent surface at adsorption equilibrium (mg/g), q_t is the amount of solute adsorbed on the adsorbent surface at the specified moment (t) during the adsorption process (mg/g), and k_2 is the adsorption rate constant ($\text{g}/(\text{mg} \cdot \text{h})$).

A 150 mL sample of a 100 mg/L copper ion was prepared and 5 g RSAC particles were added. Then, the sample was mixed at room temperature (25 ± 1 °C). The rest copper ion concentration was measured at different times to calculate the adsorbed copper ion. The experimental data of static adsorption of copper ions were fitted to the curve using quasi-primary and quasi-secondary kinetic models in turn.

2.10. Thermodynamic Study of the Adsorption of Copper Ions by RSAC

The thermodynamic equations are as follows (Equations (8) and (9)):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K_0 \quad (8)$$

$$\ln K_0 = \Delta S^0 / R - \Delta H^0 / RT \quad (9)$$

In Equations (8) and (9), T is the thermodynamic temperature (K), ΔH^0 is the enthalpy change of adsorption (kJ/mol), ΔG^0 is the free energy of adsorption (kJ/mol), ΔS^0 is the change in entropy of adsorption [$\text{J}/(\text{mol} \cdot \text{K})$], R is the molar volume constant $8.314 \text{ J}/(\text{mol} \cdot \text{K})$, and K_0 is the adsorption partition coefficient, usually taken as the Langmuir constant K_L . Using the isothermal adsorption experimental data of RSAC particles at

different temperatures, the adsorption equilibrium coefficient K_0 was calculated [21]. A straight line could be fitted by using the inverse of the temperature $1/T$ as the horizontal coordinate and $\ln K_0$ as the vertical coordinate for the graph.

3. Results and Discussion

3.1. Adsorption Experiments

3.1.1. Effect of Adsorption Time

The concentration of the residual copper ion in the supernatant of each sample as a function of adsorption time is shown in Figure 4. The residual copper ion concentration showed a similar trend for different dosage amounts. At the beginning of the adsorption reaction (0–12 h), the residual copper ion concentration decreased significantly with the increasing time; at the middle of the adsorption reaction (12–48 h), the residual copper ion concentration decreased slowly with time; at the end of the adsorption reaction (48–72 h), the adsorption equilibrium state was reached. The reason for this trend could be that the initial adsorption occurs mainly on the surface and in the pores of RSAC particles. In the initial adsorption stage, there are many active sites on the surface and in the pores of RSAC particles so copper ions could occupy the active sites rapidly and show the characteristics of a fast adsorption rate [22]. With the extension of time and the increase of adsorption capacity, the active sites become fewer [23]. It was also found that there were large functional groups on the surface of FA and MFA, such as O-H, C=C, and Si-O-Si, which played a crucial role in the process of adsorption of heavy metal ions [24]. It could be inferred that the adsorption equilibrium time of copper ions on RSAC particles is 48 h. This is consistent with the experimental results to explore the optimal ratio of RSAC particles. Therefore, the adsorption time could be set as 48 h in the subsequent static adsorption experiments.

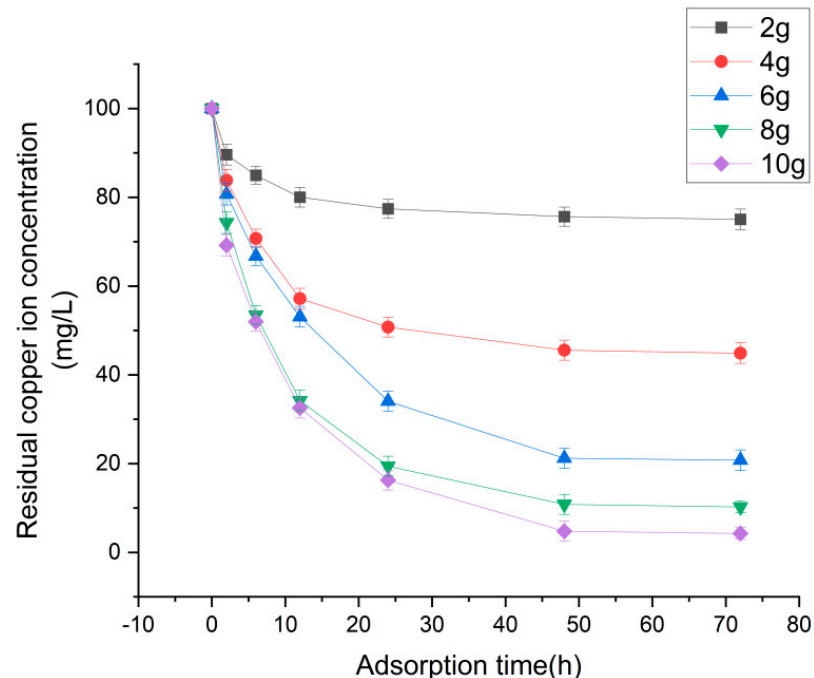


Figure 4. Effect of adsorption time on the adsorption of copper ions by RSAC particles.

3.1.2. Effect of Adsorbent Amount

Figure 5 shows the correlation between adsorbent amount and copper ion adsorption. Firstly, the copper ion removal rate increased continuously with the increase of the RSAC particle amount, but the slope decreased at the same time. Meanwhile, the adsorption amount per unit mass of RSAC particles showed a different trend: the adsorption amount per unit mass of RSAC particles increased at the beginning stage and decreased after

reaching a specific point with the increase of the adsorbent amount. The two trends indicated that there was a balance point between efficiency and performance. The amount aimed best removal rate may lead to inefficient usage of RSAC particles: the adsorption capacity per mass of RSAC particles was only 1.43 mg/g at 10 g, which indicated that the adsorption performance of RSAC particles was not fully utilized. The reason may be that the copper ion removal rate increased because of the increase of RSPRC particle amount, the increase in contact area, and the increase in the number of adsorption sites [25].

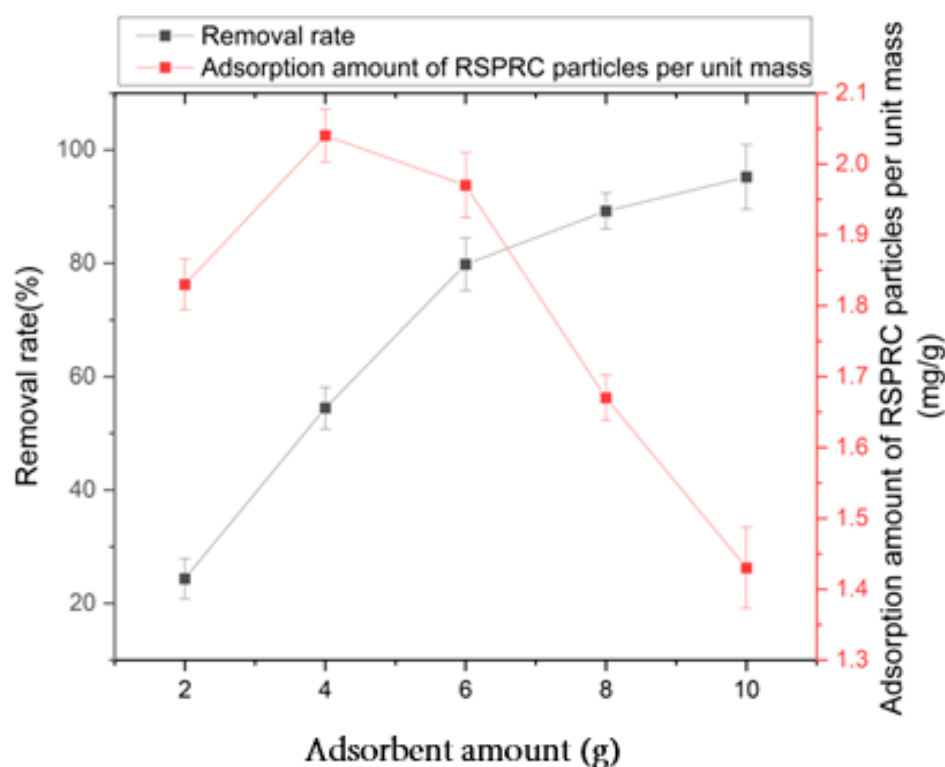


Figure 5. Effect of adsorbent amount on the adsorption of copper ions by RSAC particles.

The adsorption amount of copper ions per unit mass of adsorbent showed a different trend. This may be due to the fact that when the concentration of copper ions in the solution is constant and the adsorbent dosage is low, the adsorption sites are not significant in driving the diffusion and adsorption reaction caused by the atmosphere of copper ion concentration. With the increase in the dosage, the total adsorption sites provided to copper ions in the solid-liquid system increased and the adsorption amount per unit mass of RSPRC particles also increased [26]. Considering economic factors, the dosage of 5 g/150 mL was chosen as a balance point and used in the subsequent experiments.

3.1.3. Effect of Initial Concentration

The relationship between the initial concentration and the residual concentration of copper ions is shown in Figure 6. The removal rate of copper ions and the adsorption amount per unit mass of RSAC particles in each sample after adsorption for 72 h is presented in Table 9. As shown in Figure 6, a high initial copper ion concentration led to a corresponding steep adsorption curve and a fast adsorption rate compared with a low initial concentration sample in the pre-sorption stage. This could be attributed to high initial copper ion concentration providing a sufficient driving force for mass transport, which could make ions occupy the active site on adsorbents rapidly, facilitating the adsorption of copper ions by RSAC particles [27,28].

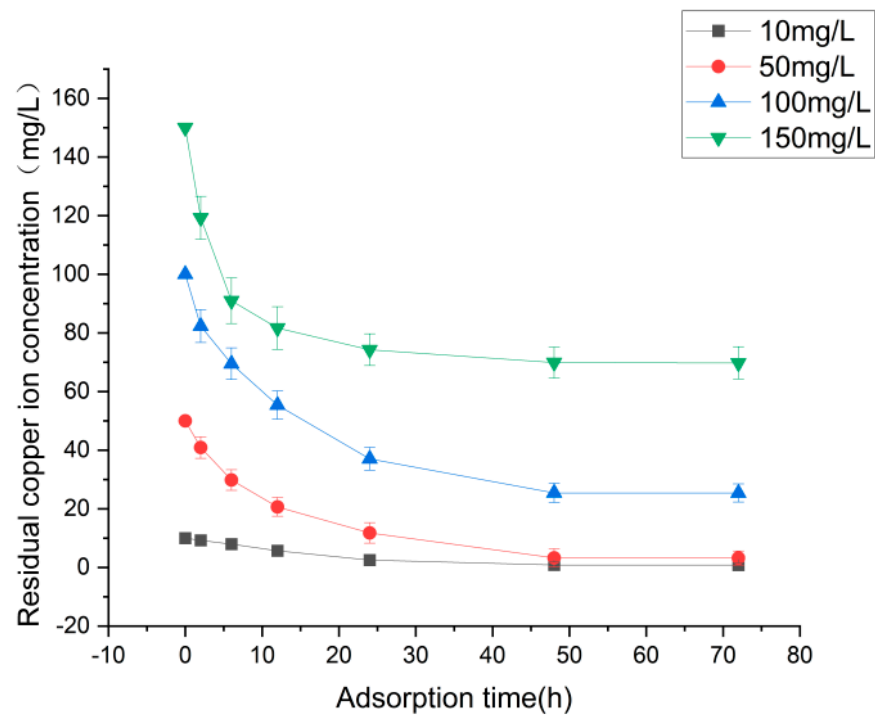


Figure 6. Effect of initial concentration on the adsorption of copper ions by RSAC particles.

Table 9. Copper ion removal for different initial concentrations.

Initial Concentration (mg/L)	Removal Rate (%)	Adsorption of RSAC Particles per Unit Mass (mg/g)
10	91.90	0.28
50	93.58	1.40
100	74.61	2.24
150	53.50	2.41

3.1.4. Effect of Coexisting Metal Cations

Figure 7 shows the relationship between the metal cation concentration and the effect on the removal of copper ions. The results revealed that the adsorption removal rate of copper ions by RSAC particles fluctuates in a small range with the increase of Na^+ concentration, which indicated that Na^+ has a weak competitive behavior against RSAC particles. The adsorption removal rate of copper ions by RSAC particles decreases with the increase of Mg^{2+} and Ca^{2+} concentration, which indicated that Mg^{2+} and Ca^{2+} may have some effect on the removal rate. The adsorption removal rate decreased significantly with the increase of Fe^{3+} concentration, from 74.65% to 62.47%, which indicated that Fe^{3+} had a significant inhibitory effect on the adsorption of copper ions.

The experimental results may be interpreted as that metal cations can replace the original cations in the RSAC particles by ion exchange into the adsorbent surface and pore channels, affecting the adsorption of copper ions on the RSAC particles by changing the adsorbent environment [29]. A higher charge number of the metal cation may result in a stronger ability to replace the original cation [30]. Ion exchange and surface adsorption may be involved in the adsorption process of copper [31].

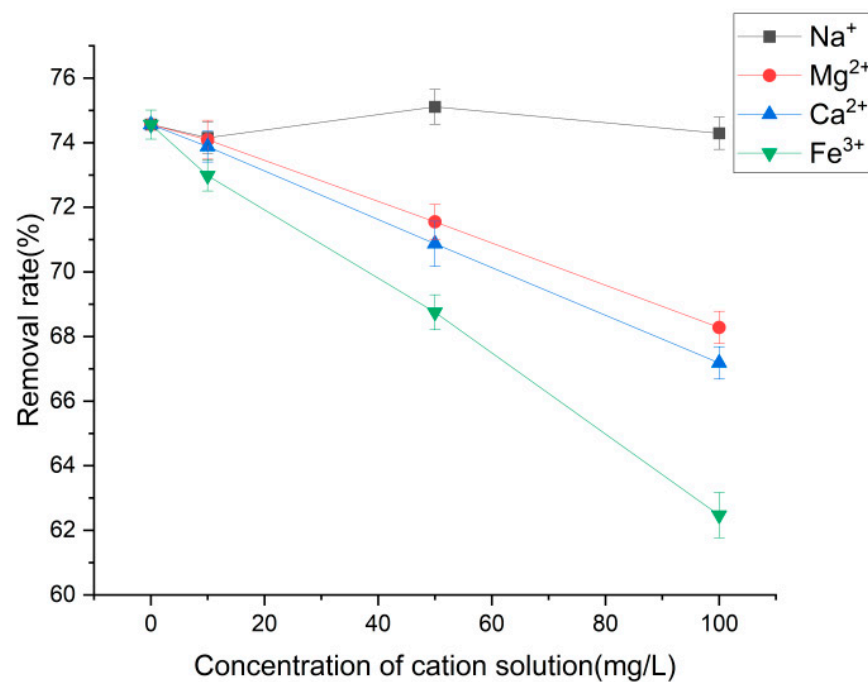


Figure 7. Effect of metal cations on the adsorption of copper ions by RSAC particles.

3.1.5. Effect of Ambient Temperature

The fitted curves at 25 °C are shown in Figure 8. The fitting parameters can be obtained from the adsorption isotherm. It can be observed from Table 10 that the fit coefficients R^2 of both Langmuir and Freundlich models are greater than 0.95 at different temperatures, which indicates that both models could well express the isothermal characteristics of the adsorption of copper ions by RSAC particles. This also implies that the adsorption isotherm characteristics of the adsorbent for copper ions could fit two or more adsorption isotherm models under certain conditions [32]. Based on the Langmuir model, the K_L and the q_{max} which increase as temperature increases indicates that the intermolecular binding and the adsorption capacity may increase as temperature increases. Based on Freundlich model, the low $1/n$ value indicates that the adsorption process could undertake easily. Meanwhile, the K_F which represents the adsorbability increases as temperature increases [33]. The two models show that the adsorption of copper ions by RSAC particles is a heat-absorbing process. This could be explained from different aspects. Firstly, the copper ion needs the energy to approach the RSAC particles and overcome the resistance from the liquid film of the particles to reach the internal active sites. Secondly, the physical adsorption may release heat since the intermolecular force (Van der Waals force) between adsorbates and adsorbents contributed to the main effect during adsorption, which made the molecular kinetic energy decrease by releasing thermal energy [34]. Another study also found that the adsorption process of fly ash involves physical adsorption [35]. In conclusion, chemisorption is an endothermic reaction while physical adsorption is an exothermic reaction, and the adsorbed thermal is more than the released thermal, causing the increase in temperature to promote the adsorption reaction, which is consistent with previous research conclusions [36,37].

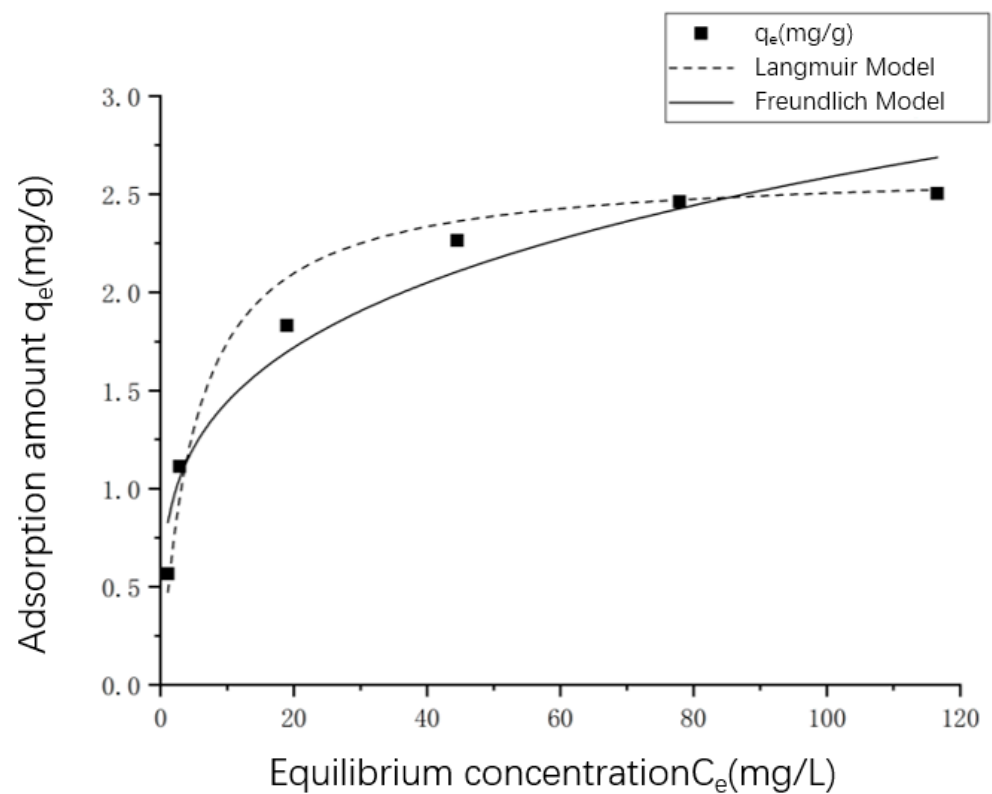


Figure 8. Adsorption isotherm of copper ions (25 °C).

Table 10. Parameters for the adsorption isotherm model fit.

Temp. (°C)	Langmuir Model			Freundlich Model		
	K_L	q_{max}	R_L^2	K_F	$1/n$	R_F^2
15	0.138	2.438	0.974	0.737	0.248	0.960
25	0.196	2.633	0.967	0.805	0.253	0.952
35	0.254	2.862	0.954	0.874	0.262	0.956

3.2. Kinetic Study of Copper Ion Adsorption by RSAC

The fitted curves are shown in Figure 9 and the fitted parameters of the two kinetic models are shown in Table 11. As shown in Figure 9, the adsorption amount of copper ions by RSAC particles increases rapidly with the increase of adsorption time in the early stage of the adsorption reaction. The increase of adsorption amount decreases gradually to almost 0 in the middle and the late stage of the adsorption reaction, which means the adsorption reaches the equilibrium state. In the preliminary stage of adsorption reaction, the adsorbent mainly adsorbs copper ions at the solid–liquid interface [38]. After the preliminary stage, copper ions diffuse from the adsorbent surface to the internal micropores and lattice, reach and are fixed by the internal surface active-sites, thus the adsorption rate decreases slowly [39]. Another study found that the adsorption of fly ash involves both boundary-layer diffusion and intraparticle diffusion [11]. Kai-sung Wang et al. also found fast surface adsorption was followed by a slow intra-particle diffusion adsorption of fly ash [40]. The adsorption process of copper ions by RSAC particles can reach the equilibrium state at 48 h.

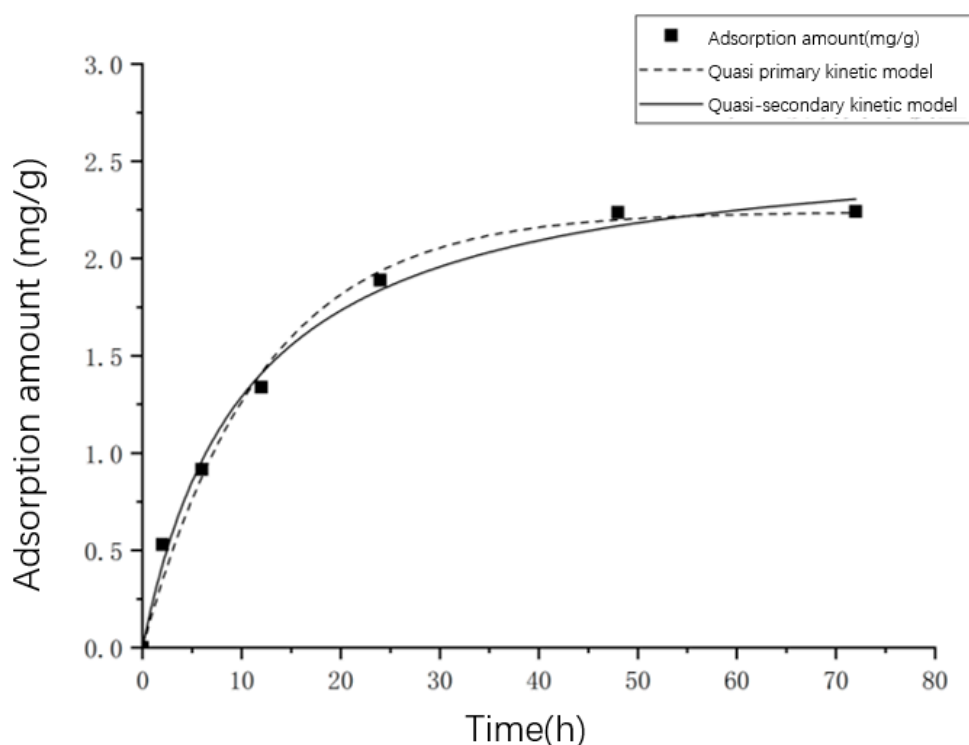


Figure 9. Adsorption kinetic curve of copper ions (25 °C).

Table 11. Sorption kinetic model fitting parameters.

Initial Concentration (mg/L)	Quasi-One Dynamical Model			Quasi-Secondary Dynamical Model (QSDM)		
	q_e	k_1	R_1^2	q_e	k_2	R_2^2
100	2.241	0.0713	0.990	2.640	0.0955	0.993

The R^2 of both models is greater than 0.95 and the difference between them is not significant (Table 11), which indicates that both kinetic models could describe the adsorption process of copper ions on RSAC particles well. It could be further inferred that the adsorption process of copper ions on RSAC particles is a mixed control: both surface diffusion and internal fine pore diffusion are important.

3.3. Thermodynamic Study of the Adsorption of Copper Ions by RSAC

As shown in Figure 10, the intercept and the slope of the straight line were calculated by ΔS^0 and ΔH^0 ; then, we proceeded to calculate the different temperatures of ΔG^0 , and Table 12 presents the various thermodynamic parameters obtained. The adsorption free energy ΔG^0 of copper ions adsorbed by RSAC particles at different temperatures is negative, and the absolute value of ΔG^0 increases gradually with the increase of temperature (Table 12). This indicates that the adsorption of copper ions in solution by RSAC particles is a spontaneous reaction and the spontaneity increases with the increase of temperature [41]. The enthalpy change ΔH^0 during the adsorption of copper ions by RSAC particles is positive, which indicates that the adsorption process is a heat absorption reaction and therefore the increase in temperature contributes to the adsorption [42]. As presented in Table 5, the maximum adsorption capacity of copper ions increases with the increasing temperature, which also confirms that the adsorption of copper ions by RSAC particles is a heat absorption reaction.

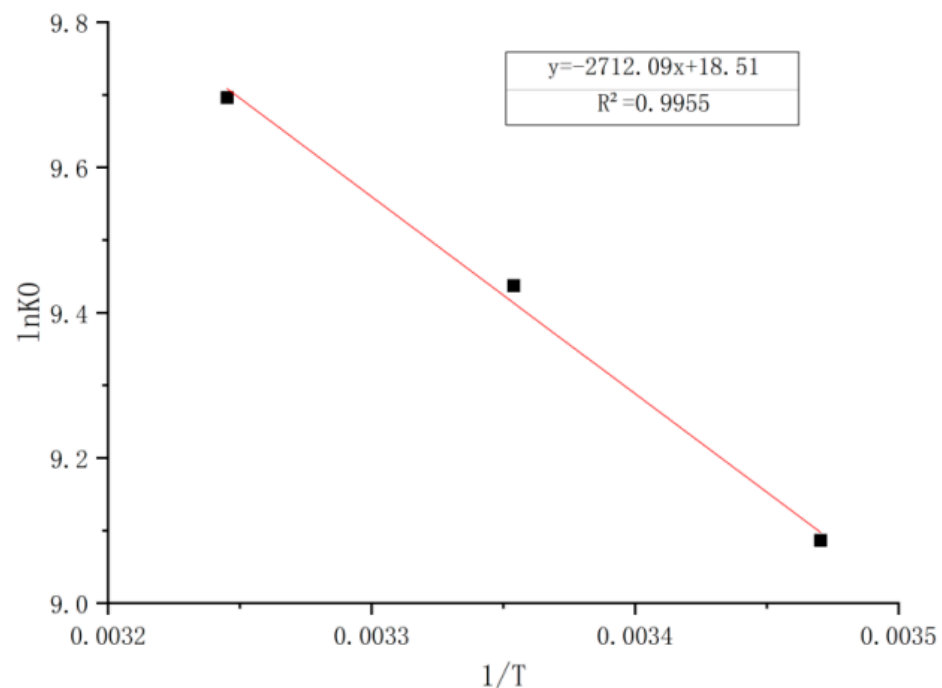


Figure 10. Relationship between $\ln K_0$ – $1/T$ for the process of copper ion adsorption by RSAC particles.

Table 12. Thermodynamic parameters of copper ion adsorption on RSAC particles.

Temp. (K)	$q_{\max}$ (mmol/g)	$K_L \times 10^{-3}$ (L/mol)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol-K)	R^2
288.15	0.0381	8.832	−21.79			
298.15	0.0411	12.544	−23.33	22.55	153.89	0.9955
308.15	0.0447	16.256	−24.87			

4. Conclusions

This study aimed to prepare and to apply RSAC to remove copper ions from wastewater and to discuss the influence mechanism and the microstructure for adsorption by RSAC particles. One of the more significant findings to emerge from this study is that the adsorption of copper ions in a solution by RSAC particles is a spontaneous, heat absorption reaction. The mechanism of copper ion removal by RSAC particles includes an ion exchange reaction and chemical precipitation in addition to physical adsorption. The second major finding is that metal cations can replace the original cations in the RSAC particle ion exchange, change the environment of the adsorbent, and affect the adsorption of copper ions on RSAC particles. This study has also indicated that both Langmuir and Freundlich models can well describe the isothermal characteristics of the adsorption of copper ions by RSAC particles. Both the quasi-primary kinetic model and the quasi-secondary kinetic model can describe the adsorption process of copper ions on RSAC particles well. It can be further inferred that the adsorption process of copper ions on RSAC particles is a mixed control, and both surface diffusion and internal fine pore diffusion are important.

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