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Study on the Adsorption Performance of Amino-grafted Composite Kaolin for Nickel-containing Wastewater

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Abstract: With the rapid development of industrialization, the pollution of nickel-containing wastewater produced by non-ferrous metal smelting is becoming more and more serious. In order to meet the urgent requirements for the discharge of nickel-containing wastewater, effective and economic treatment technologies and materials are pursued. The experiment used natural kaolin as the main raw material was calcined at 500°C and combined with natural zeolite. Through orthogonal test, the calcined kaolin and natural zeolite 2: 1, N-2-aminoethyl-3-aminopropyl trimethoxy silane coupling agent (KH792) was used to modify the composite sample to obtain the modified composite kaolin adsorbent. XRD, SEM, BET and FT-IR were used for characterization before and after modification. It was found that the amino functional groups in KH792 were successfully grafted onto the surface of the composite kaolin. After modification, the specific surface area of composite kaolin increases from $9.522 m^2/g$ to $13.517 m^2/g$, and the pore size expands from 10.022nm to 15.143nm. The adsorption performance of Ni^{2+} and its influencing factors were studied by using modified composite kaolin. Through the study, it was determined that the concentration of Ni^{2+} of 30 ml test water was 80 mg·L^{-1}, and the modified kaolin was added 0.2g and adsorbed for 240 min at 25°C and pH 5.45. The removal rate increased from 54.9% to 99.94%. The adsorption process follows the quasi-second-order kinetic model, and the adsorption isotherm corresponds to the Langmuir model.

Keywords: Kaolin, Adsorption, Heavy Metals, Diamino Modification

1. Introduction

In recent years, heavy metal ion pollution has become more and more serious. Among the adsorption materials for treating heavy metal wastewater, kaolin is popular among enterprises due to its low cost and good adsorption properties, but its pore size and surface bond adsorption capacity are poor, and the effect of adsorbing heavy metal ions in wastewater is limited, so it needs to be modified [1]. To increase the pore size or enhance the surface bond adsorption force to improve the adsorption effect of heavy metal ions. Generally, kaolin modification is divided into acid and thermal alkali modification. For example, Liu used different concentrations of sulfuric acid to modify kaolin, which greatly increases the surface area of kaolin [2]; David Moses Kolade used hot lye to modify kaolin. The properties can also increase its surface area, but these two types of modifications

did not improve the bond adsorption capacity of natural kaolin, and acid-base solutions are prone to secondary pollution [3]. Since Johannsen first summarized the theory of bonding between functional groups and inorganic substances in silane coupling agents [4]. The domestic gradually grafted various functional groups to inorganic substances in order to achieve the purpose of treating metal wastewater. Hong Manshui used carboxyl-containing silane to synthesize materials and is used to adsorb heavy metal ions, and it is found that the adsorption capacity increases with the increase of carboxyl content [5]; Li Hongyu used the functionalization of sulfhydryl groups in heavy metal wastewater adsorption materials for the first time [6]; Chen Feng sheng used amide group-synthesized cationic surfactants for the first time and found that it has strong surface adsorption [7]. This kind of research shows that grafting the surface of natural kaolin with functional groups can improve the adsorption capacity of surface bonding and have a higher removal effect on

metals. The inorganic crystalline microporous structure of natural zeolite has large porosity, good cation exchange and screening capabilities, and the combination of the two to form a composite adsorbent can improve the effect of adsorbing heavy metal ions [8].

In this study, on the basis of kaolin calcining pretreatment, natural zeolite was supplemented to obtain a composite adsorbent with a higher pore size, and then KH792 was used to modify the composite adsorbent to increase the surface bond adsorption capacity, and a larger kaolin-based composite adsorbent was obtained. Adsorbent with specific surface area, pore size and strong bond site adsorption. The prepared adsorbent was used in the experiment of adsorbing Ni^{2+} in wastewater, and the related adsorption model was discussed, which lays the theoretical foundation for the relevant research on the adsorption of Ni^{2+} by grafting kaolin with diamino functional groups.

2. Materials and Methods

2.1. Reagent Materials

The experimental material are natural kaolin, Natural zeolite and N-2-aminoethyl-3-aminopropyltrimethoxysilane coupling agent (KH792), reagents are nickel sulfate sodium hydroxide, hexahydrate, hydrochloric acid, absolute ethanol. The above medicaments were purchased from Sinopharm Chemical Reagent Co. LTD. The required instruments are mainly the Nov AA 330 flame atomic absorption spectrometer in Jena, Germany.

2.2. Experiment Method

2.2.1. Preparation Test

The natural kaolin was calcined at 200~700°C, and after cooling, it was ground, sieved and classified. The kaolin of about 200 mesh was selected for the test. KH792 was hydrolyzed at 40°C for 30 minutes, and a 3-factor 3-level orthogonal test design was selected. Three factors are selected: the ratio of calcined kaolin to natural zeolite, mixing time, and mixing temperature. Among them, calcined kaolin: natural zeolite is 1:0.5, 1:1, 1:1.5; stirring time is 3h, 4h, 5h; stirring temperature is 60°C, 65°C, 70°C. The test results determined that kaolin was calcined at a temperature of 500°C, the ratio of calcined kaolin to zeolite was 1:0.5, and the modification temperature was 70°C and stirred with KH792 hydrolysis solution for 4 hours as the optimal conditions. After the material is filtered and separated by precipitation, the excess KH792 on the surface of the modified kaolin is repeatedly washed with absolute ethanol. Place it in a drying box to make it dry, and the powder obtained by grinding is the final modified composite kaolin adsorption material.

2.2.2. Adsorption Test

Prepare nickel-containing wastewater with nickel sulfate hexahydrate, control the concentration of Ni^{2+} at 10~100 $mg \cdot L^{-1}$, adjust the pH value at 1~6.5 through acid-base solution, take 30mL of nickel-containing wastewater for adsorption test, and control the adsorption time to 0~ 360min, the adsorption temperature is controlled at 10~40°C, the dosage is 0.1~0.35g conditions, by changing the single factor, the residual concentration of Ni^{2+} in the simulated wastewater is measured and the adsorption capacity of the adsorbent is calculated.

2.2.3. Mechanism Analysis

KH792 has a special structure and can react with inorganic substances to form chemical bonds. During the modification process, KH792 undergoes a hydrolysis reaction, and then undergoes a dehydration condensation reaction to form an oligomeric structure. This oligomeric structure then forms a hydrogen bond with the hydroxyl group on the surface of the inorganic material, and further undergoes condensation or dehydration to form a covalent bond through heating and drying. Finally, the amino functional group is grafted onto the surface of the composite adsorbent [9]. as shown in Figure 1.
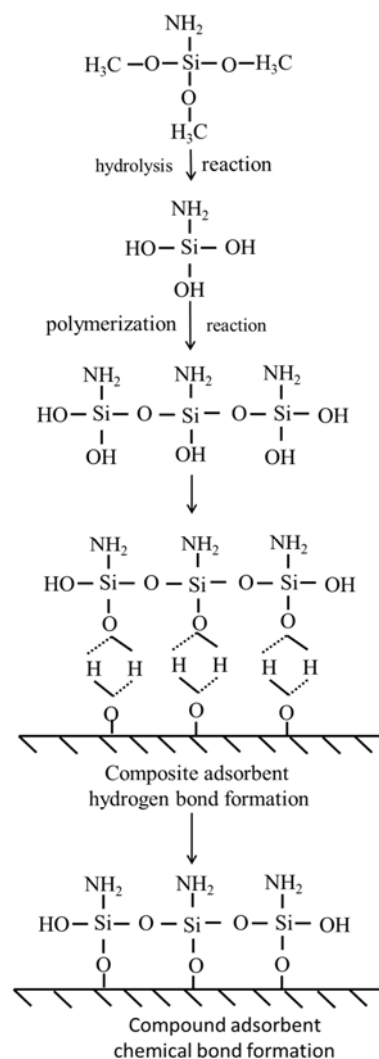

Figure 1. *Modification mechanism of composite kaolin.*

The amino functional group is grafted to the surface of the

composite kaolin, amino group undergoes protonation or deprotonation reaction under the adjustment of pH, and forms a surface complex with Ni^{2+} through coordination, so as to achieve the purpose of adsorbing Ni^{2+} [10]. The specific response is as follows:

$$-NH_2 + H^+ \rightarrow -NH_3^+ \qquad (1)$$

$$-NH_2 + Ni^{2+} \rightarrow -NH_2Ni^{2+}$$

$$-NH_2 + Ni^{2+} + H_2O \rightarrow -NH_2Ni(OH)^+ + H^+ \qquad (2)$$

$$-NH_2 + H_2O \rightarrow -NH_2OH^- + H^+$$

$$-NH_2OH^- + Ni^{2+}(NiOH^+) \rightarrow -NH_2OH^- \cdots Ni^{2+}(-NH_2OH^- \cdots NiOH^+) \qquad (3)$$

(1) Amino protonation/deprotonation reaction.
(2) Surface complex formed by coordination between amino group and Ni^{2+}.
(3) The amino group exchanges with the hydroxyl group in the solution through hydrogen bond, and then reacts with Ni^{2+}.

3. Results and discussion

3.1. Characterization and Performance Analysis

3.1.1. X-ray Powder Diffraction Analysis

Using the x-ray powder diffract meter performs phase scanning analysis on the kaolin powder before and after modification, and the spectrum is shown in Figure 1. It can be seen from the figure that the composite kaolin is mainly composed of kaolinite, quartz and mica, among which the diffraction peak of kaolinite is around 25° [11, 12]. The position and modification of the diffraction peak of the modified composite kaolin It is almost the same as before, and there is no obvious change in the peak shape, indicating that the composite kaolin has not changed the original structure of the material after KH792 modification, but only plays a role in modifying the surface.
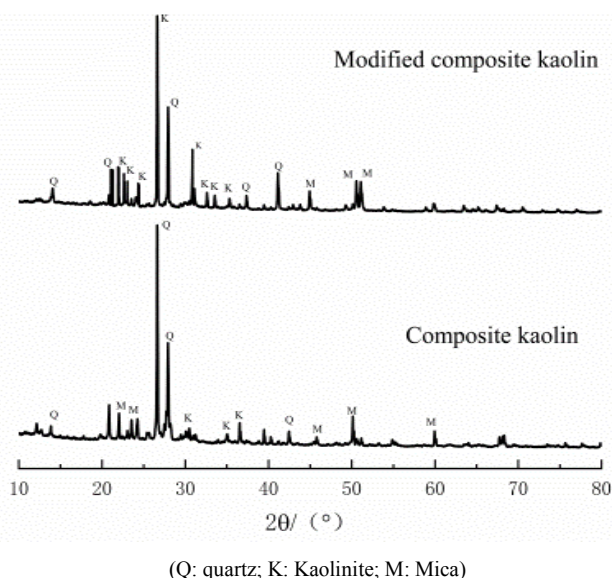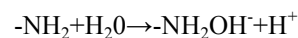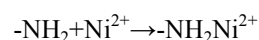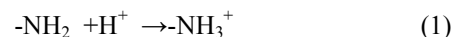

(Q: quartz; K: Kaolinite; M: Mica)

Figure 2. *XRD patterns of composite kaolin before and after modification.*

3.1.2. Scanning Electron Microscope Analysis

The morphology of composite kaolin before and after modification was scanned and analyzed by scanning electron microscope, and the morphological characteristics are shown in Figure 2. From Figure 3a_1, it can be seen that the layers of composite kaolin are scattered, the color is darker, and the gaps between the layers are small. Figure 3a_2 is enlarged and found to be uneven. It can be seen from b_1 that the modified composite kaolin maintains the original layered structure, and the layers become small and dense. After zooming in to Figure 3b_2, it is found that the layered structure of the modified composite kaolin under high magnification is more obvious and brighter than the a_2 layer, indicating that the amino group has been successfully grafted onto the surface of the composite kaolin.
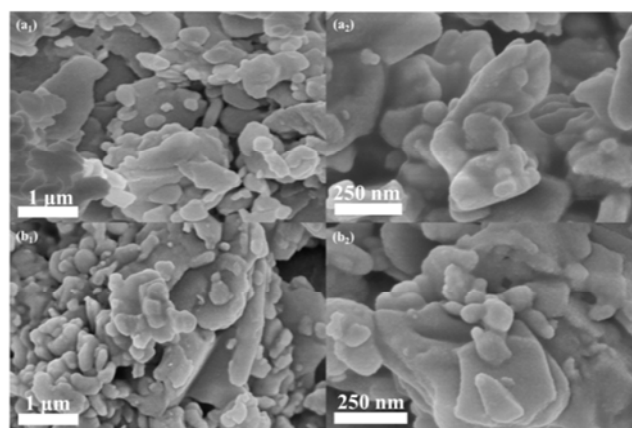
(a_1, a_2 composite kaolin, b_1, b_2 Modified composite kaolin)

Figure 3. *SEM atlas of composite kaolin before and after modification.*

3.1.3. Specific Surface Area and Pore Size Analysis

The specific surface area and pore diameter of the composite kaolin before and after modification were measured by a specific surface area analyzer. The specific data are shown in Table 1.

It can be seen from Table 1 that the modified composite kaolin in this experiment has an increased specific surface area and pore size compared to before modification, which has achieved the purpose of modification.

Table 1. *Specific surface area and aperture.*

sample	Specific surface area (m²/g)	Aperture (nm)
Composite kaolin	9.522	10.022
Modified composite kaolin	13.517	15.143

3.1.4. Infrared Spectroscopy Analysis

The infrared spectrum of the composite kaolin before and after modification is shown in Figure 3. It can be seen from the figure that the peaks of the modified composite kaolin at 474.98, 572.07 and 822.63 cm^{-1} have been strengthened,

indicating that the composite kaolin produced more Si-O-Si during the modification process. Compared with the former, the intensity of the -OH vibration peak and the vibration absorption peak of Si-OH at 1439.11 and 1100.67 cm⁻¹ of the modified kaolin also increased slightly, indicating that the modified composite kaolin produced more silico-hydroxyl groups. In addition, the infrared spectrum of modified kaolin added four peaks at 2350, 2525.56, 2650, and 3427.37 cm⁻¹. It was found that the 3427.37 cm⁻¹ peak was the vibration peak of OH, it can be inferred that a small amount of hydroxyl was produced during the modification of kaolin. It can be seen from the figure, 2350, 2525.56 and 2650 cm⁻¹ are the vibration peaks of the amino group, indicating that the amino functional group has been successfully grafted onto the surface of the composite kaolin [13].
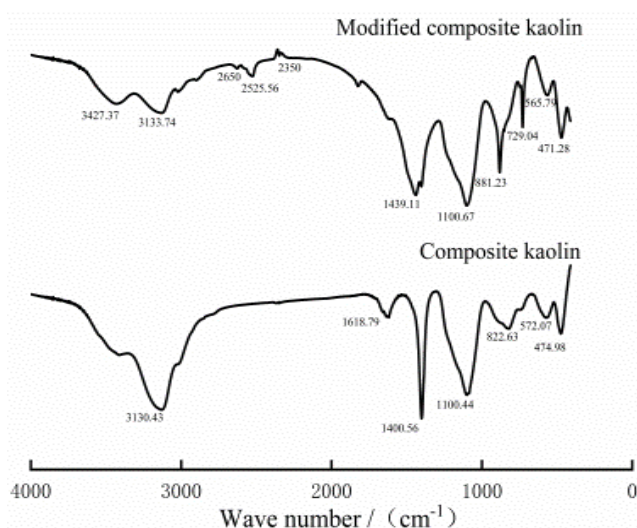

Figure 4. *Infrared atlas of composite kaolin before and after modification.*

3.2. The Influence of Different Factors on the Removal of Ni²⁺ by Adsorbent

3.2.1. Influence of Concentration on the Removal of Ni²⁺ by Adsorbent

The Ni²⁺ wastewater with different concentrations was prepared according to test 1.2.2 conditions, 0.1g modified kaolin was added, the pH was 4.89, the residual concentration of Ni²⁺ was measured after 30 minutes of shaking at room temperature, and the adsorption capacity of the adsorbent was calculated. The results are shown in Figure 4.

In this process, as the initial concentration increases, the Ni²⁺ removal rate is gradually reduced, and the adsorption capacity of the adsorbent is continuously increasing. When the initial concentration is 10 mg·L⁻¹, the removal rate of Ni²⁺ by modified kaolin is the highest, reaching 98.07%, and the adsorption capacity is 2.942 mg·g⁻¹. At this time, the adsorption capacity has not reached the maximum, indicating that there are extra adsorption sites on the surface of the adsorbent [14]. The increase in concentration allows more Ni²⁺ to occupy the site, so that the removal rate gradually decreases and the adsorption capacity gradually increases. When the wastewater concentration increased from 60

mg·L⁻¹ to 80 mg·L⁻¹, the removal rate decreased most significantly.

When Ni²⁺ exceeds 80 mg·L⁻¹, the sites are gradually occupied, and the adsorption capacity increases gradually until it reaches equilibrium. In view of the experimental results of this factor to avoid the subsequent excessive dosing of the adsorbent, the applicable range of this test is 0~80 mg·L⁻¹, with 80 mg·L⁻¹ being the best.
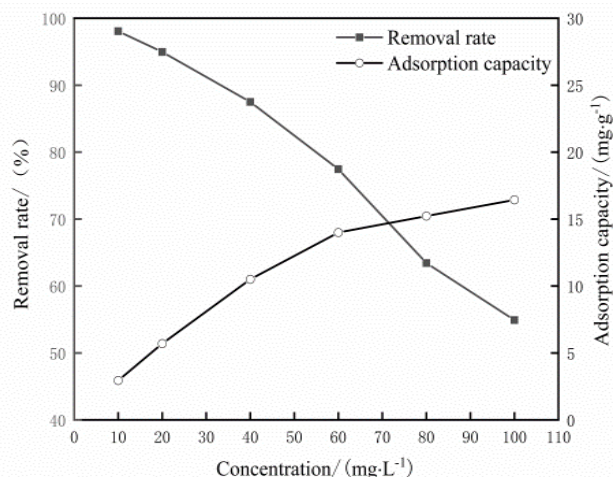

Figure 5. *Effect of concentration on Ni²⁺ removal by adsorbent.*

3.2.2. The Influence of Dosage on the Removal of Ni²⁺ by Adsorbent

According to the conditions of test 1.2.2, only the dosage of the adsorbent was changed for the test, the residual concentration of Ni²⁺ was measured, and the adsorption capacity of the adsorbent was calculated. The results are shown in Figure 5.

As can be seen from the figure, increasing the dosage will increase the Ni2+ removal rate. When 0.1g is added, the removal rate is only 60.78%. Continue to increase, the removal rate increased from 60.78% to 84.25%. Adding 0.3g, the residual concentration of Ni²⁺ has reached the standard, which is 0.03mg·L⁻¹. Increase the dosage again and find that the removal rate is basically in balance. It is because the adsorbent provides too many sites and the amount of Ni²⁺ is limited, so that the overall change in the adsorption capacity tends to decrease. Taking into account the short adsorption time under this factor, combined with the trend graph of removal rate and adsorption capacity, the dosage of adsorbent is about 0.2g.

3.2.3. Effect of Time on the Removal of Ni²⁺ by Adsorbent

According to the conditions of test 1.2.2, only change the adsorption time for the test, determine the residual concentration of Ni²⁺, and calculate the adsorption capacity of the adsorbent. The results are shown in Figure 6.

The process consists of fast adsorption, slow adsorption and stable adsorption. In the first 30 minutes, Ni²⁺ quickly occupied the surface and inside of the adsorbent, and its removal rate and adsorption capacity increased rapidly. When the adsorption time is gradually increased from 30min to 60min, 120min and 240min, the removal rate of Ni²⁺ in the

wastewater by the adsorbent is still increasing, but its rate gradually slows down. The growth rate of the adsorption capacity is still very fast, indicating that the adsorbent has enough adsorption sites for Ni^{2+} in the first 240 minutes. After 240 minutes, the experiment began to adsorb slowly and entered equilibrium adsorption. At this time, Ni^{2+} in the solution occupied all the sites of the modifier, and the removal rate and adsorption capacity reached the maximum, which were 99.94% and 11.99 mg·g^{-1}, respectively. After that, the removal rate and adsorption capacity did not change significantly until 360 minutes. Therefore, 240 minutes is the best time for adsorption.
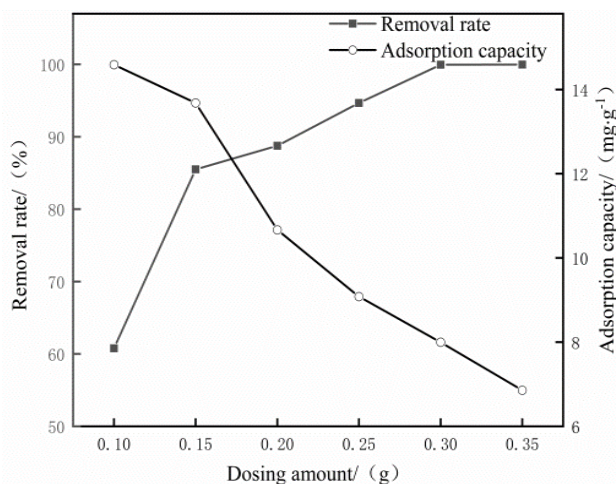

Figure 6. Effect of dosage on Ni^{2+} removal by adsorbent.

3.2.4. The Influence of pH on the Removal of Ni^{2+} by Adsorbent

According to the conditions of test 1.2.2, only change the pH for the test, determine the residual concentration of Ni^{2+}, and calculate the adsorption capacity of the adsorbent. The results are shown in Figure 7.
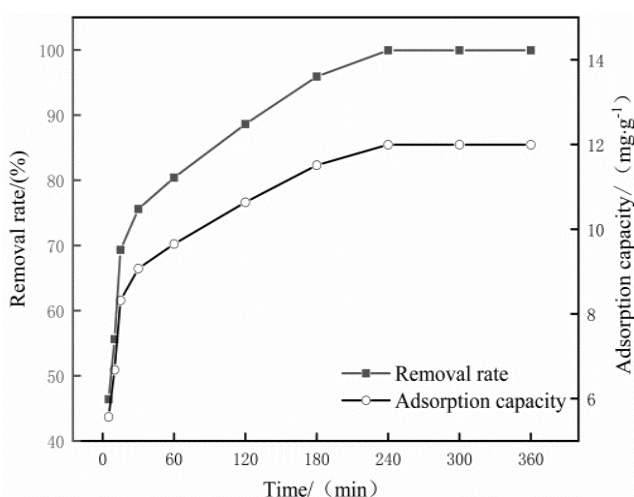

Figure 7. Effect of time on Ni^{2+} removal by adsorbent.

The removal rate of Ni^{2+} increases with the increase of pH When the acidity of the solution is the strongest, the concentration of H+ in the solution is also the maximum. H+

and Ni^{2+} form a certain competitive adsorption relationship [15]. The removal rate is only 36.42% at this time. Increasing the pH significantly increases the removal rate of Ni^{2+} by the adsorbent, indicating that the competitive relationship between H^+ and Ni^{2+} in the solution is weakened, and it is not ruled out that the structure of the adsorbent is destroyed under acidic conditions and affecting its removal rate. When the pH is adjusted to 5.35, the residual concentration of Ni^{2+} is 0.046 mg·L^{-1}. When the pH was adjusted to 6.35, a blue precipitate gradually appeared in the solution. It was inferred that the precipitate was Nickel hydroxide precipitate, and the subsequent pH adsorption was "false adsorption". So the adsorption pH is around 5.35.
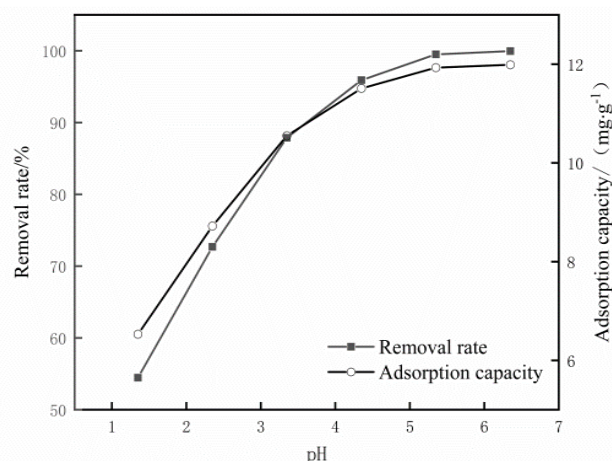

Figure 8. Effect of pH on Ni^{2+} removal by adsorbent.

3.2.5. The Influence of Temperature on the Removal of Ni^{2+} by Adsorbent

According to the conditions of test 1.2.2, only change the temperature for the test, determine the residual concentration of Ni^{2+}, and calculate the adsorption capacity of the adsorbent. The results are shown in Figure 8.
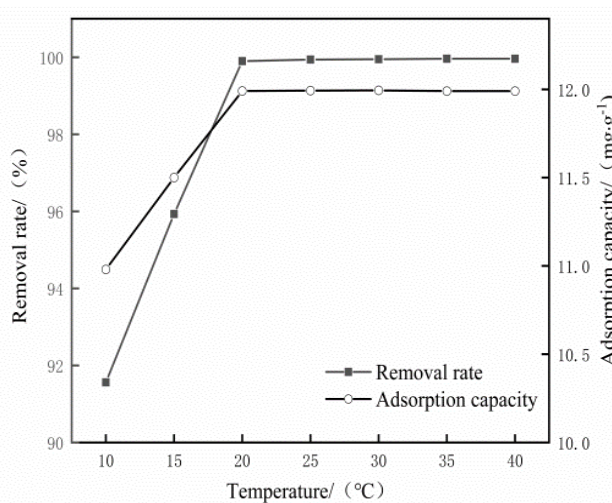

Figure 9. Effect of temperature on adsorption of Ni^{2+}.

When the temperature is between 10°C and 20°C, the removal rate of the adsorbent is significantly increased.

When the temperature reaches 20°C, its residual concentration is 0.055g, which has reached the national emission standard, indicating that the increase in temperature in this environment has accelerated the kaolin The amino functional groups on the surface react strongly to Ni^{2+} in the solution. After that, as the temperature increases, the removal rate curve changes more slowly. It shows that the amino functional group still has a higher affinity for Ni^{2+} with the increase of temperature, but it is not obvious. And the residual concentration of the temperature between 20°C ~ 40°C has reached the standard. In order to save energy, in this experiment, the adsorption temperature is 20°C ~25°C.

3.3. Adsorption Kinetics Study

At room temperature, take 30ml of nickel-containing wastewater with a concentration of 80 mg·L^{-1} and add 0.2g of adsorbent. Discuss the change rule of wastewater Ni^{2+} removal rate with time. Perform quasi-first-order kinetics simulation and quasi-second-order kinetics simulation with the data obtained during the experiment according to formula 3 and formula 4:

$$Q_t = Q_e(1 - e^{-K_1 t}) \qquad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (4)$$

Formula: t—Adsorption time; Q_t —Adsorption capacity at time; Q_e—Equilibrium adsorption capacity; K_1, K_2—Kinetic rate constant.

The simulated parameters are shown in Table 2, and the simulated curve is shown in Figure 9. The adsorption capacity (12.433 mg·g^{-1}) obtained by the quasi-second-order kinetics is closer to the adsorption capacity obtained from the experiment (12.011 mg·g^{-1}), and the fitting parameters are better. It shows that the adsorption process is consistent with the quasi-second-order kinetic model.

Table 2. Kinetic fitting parameters of modified kaolin.

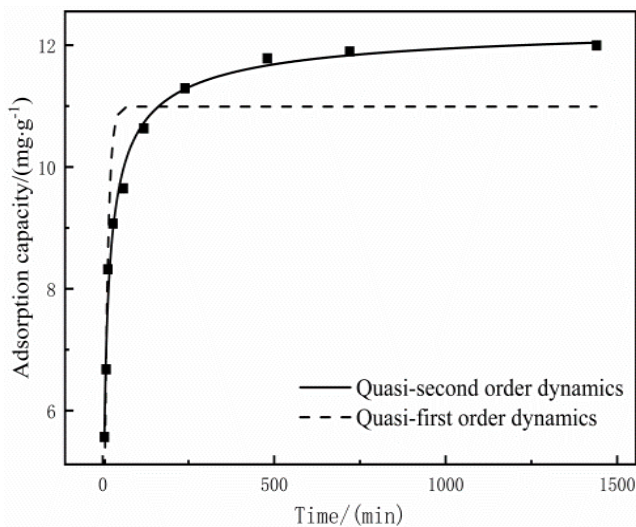| C_0/(mg·L^{-1})	Actual Q_e/(mg·g^{-1})	Quasi-first order dynamics			Quasi-second order dynamics		
		Q_e/(mg·g^{-1})	k_1	r^2	Q_e/(mg·g^{-1})	k_2	r^2
80	12.011	10.991	0.109	0.797	12.433	0.296	0.985

Figure 10. Kinetic fitting curve of modified kaolin.

3.4. Adsorption Isotherm Study

Take three groups of 30ml nickel-containing wastewater with different gradients, add 0.2g adsorbent under the temperature conditions of 298K, 303K, 313K, shake for 2h, centrifuge, measure the residual concentration of Ni^{2+}, and use Langmuir, Freundlich isotherm equation to fit, See formula 5 and formula 6 for details.

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \qquad (5)$$

$$Q_e = K_F C_e^{1/n} \qquad (6)$$

Formula: Q_m—maximum adsorption capacity, mg·g^{-1}; Q_e—equilibrium adsorption capacity, mg·g^{-1}, K_L—Langmuir model constant; K_f—Freundlich model constant.

The simulation curve is shown in Figure 10, and the simulation parameters are shown in Table 3.

Compared with the Freundlich adsorption model, the adsorption process is more consistent with the Langmuir adsorption model. In the process of increasing the temperature, the theoretical maximum adsorption capacity Q_m is also increasing, which can be judged as an endothermic reaction.

Table 3. Isotherm fitting parameters of modified kaolin.

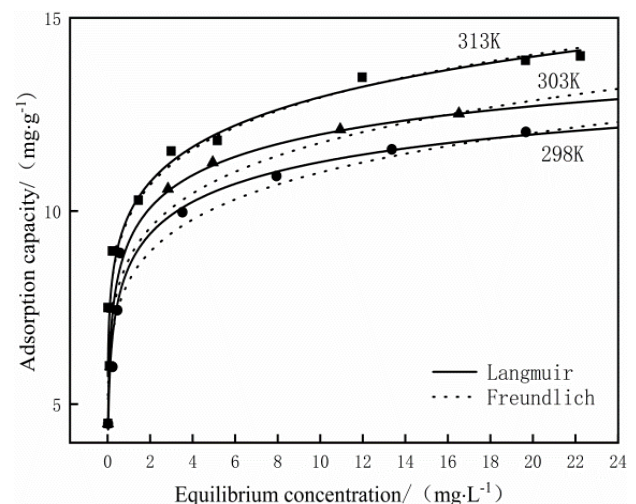| Temperature/(K)	Langmuir model			Freundlich model		
	Q_m/(mg·g^{-1})	K_L	r^2	K_F	n	r^2
298	16.44	1.08	0.967	8.18	0.128	0.951
303	17.45	1.12	0.976	8.75	0.129	0.962
313	19.68	1.65	0.923	8.83	0.119	0.910

Figure 11. Adsorption isothermal fitting curve of modified composite kaolin.

4. Conclusion

(1) The optimal modification conditions of composite kaolin were as follows: The mass ratio of calcined kaolin to zeolite was 2:1 at 500°C, and the modification temperature was 70°C, and the mixture was stirred with KH792 hydrolysate for 4h. The specific surface area and pore size of modified composite kaolin increased by 41.95% and 51.1% respectively.

(2) The optimal adsorption conditions for a 30 ml test water sample with a Ni^{2+} concentration of 80 mg·L^{-1} are 25°C and pH 5.35. The modified composite kaolin is added 0.2g and adsorbed for 240 minutes, and the removal rate is increased from 54.9% before modification to 99.94%. In the influencing factor test, the adsorption time and pH have a greater impact on the removal of Ni^{2+} by the adsorbent, which can be considered as the main factors.

(3) The adsorption behavior is mainly caused by the ion exchange and surface complexation reaction of $-NH^2$ and Ni^{2+} on the surface of the composite kaolin, which conforms to the quasi-second-order kinetic model and Langmuir adsorption model.

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