

The study of Ni (II) removal from aqueous solution by modified sediment

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Abstract. Preparation of high-temperature roasting modified sediment as an adsorbent, to research the effect of adsorption of Ni (II) from aqueous solution through static adsorption test. Through static adsorption experiments, Adsorption kinetics and thermodynamics properties of roasting sediment adsorption of Ni^{2+} were researched. It was observed that the adsorption process was described with the Langmuir and Freundlich theories, and the Freundlich model indicated the best fit to the adsorption process, showing that adsorption is between monolayer and multilayer. The adsorption of the Ni^{2+} onto the roasting sediment was described pseudo-first-order kinetics equation and pseudo-second-order kinetics equation, and the pseudo-second-order kinetics equation showed the best fit to the adsorption process, showing that it is dominated with chemical adsorption. Equilibrium adsorption capacity of roasting sediment for Ni^{2+} was found to be 3.6563mg/g. Thermodynamic parameters indicated (ΔS , ΔH and ΔG) that the adsorption of the Ni^{2+} onto the roasting sediment is endothermic process.

1. Introduction

Nickel is one of the essential elements of the human body [1-2], appropriate amount of intake is beneficial to the health of the human body. However, long-term exposure to drinking water and excessive nickel, will cause serious harm to the human body, and can lead to a variety of lesions. Acute poisoning showed: nausea and vomiting, stomach pain, gastrointestinal mucosa necrosis, severe abdominal pain, bloody stools and other pathological phenomena [3-4]. Chronic poisoning symptoms: neurasthenia, neurological dysfunction, pyramidal damage, Parkinson's syndrome and other pathological phenomena. At present, the treatment methods of nickel at home and abroad are mainly contact oxidation method and ion exchange resin. However, these methods are too expensive, complex process, not easy to promote [5-6]. Adsorption is one of the most effective methods to remove heavy metal ions in wastewater. It is more mature and stable method and simple operation, low cost, technology is mature.

The traditional methods of sludge treatment are landfill, incineration and dumping, but it will cause serious pollution and damage to the environment, it is the law prohibited. Therefore, it is necessary to find a new way of utilization. Dianchi is rich in sediment resources, it contains a large number of organic



sediments and putrefaction, also it has large surface area, It has a certain degree of adsorption, but the adsorption effect is more significant, after high temperature modification of the Dianchi sediment.

2. Experimental part

2.1. Main instruments and reagents

722S visible spectrophotometer; PHS-3C type pH meter; SHZ-82 type constant temperature oscillator; LD4-2A low speed centrifuge; AB204-S electronic analytical balance; XL30SEM-TMP scanning electron microscope.

2.2. Experimental materials and methods

The bottom mud is added to the energy saving box type furnace with the initial temperature of 20 °C and heated at a heating rate of 5 °C/min for 85 minutes to about 450 °C, constant temperature roasting 120min to carbonize, and vibrating sieve machine after cooling, then, select 80 ~ 100 mesh particles for the electric blast oven dry standby.

The surface morphology before and after modification was analyzed by scanning electron microscope (XL30ESEM-TMP). And the results are as follows. As it shown from Fig. a: The crystal structure of the unmodified sediment is smooth and rough, the distance between the pore and larger floc degree is not obvious. As it shown from Fig. b: The crystal structure of the modified sediment was destroyed, higher surface roughness. The pore is well developed and has a wide pore size distribution, a higher degree of flocculation. This makes the sediment has a large specific surface area, which is more conducive to improve the adsorption performance of the sediment.

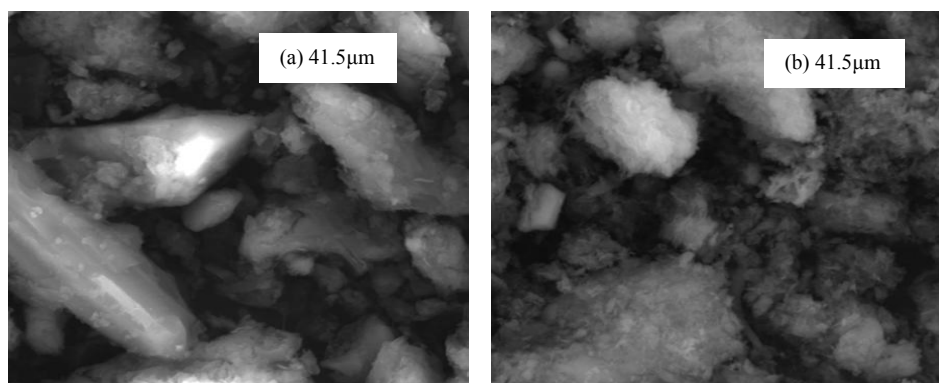


Fig.1 SEM image of sediment before (a) and after (b) modification

Determination of high-temperature roasting modified sediment by using Bruker TENSOR27 infrared spectrometer in Germany. The results are shown in Figure 2.

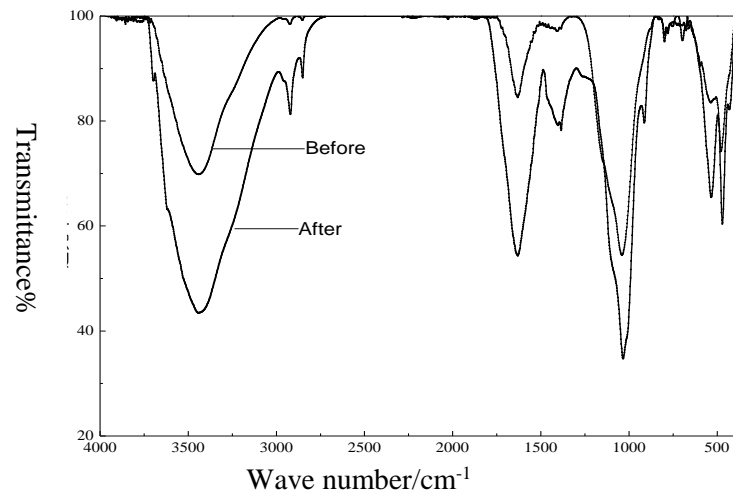


Fig.2 IR spectrum of sediment before and after modification

As can be seen from Fig.2: The original sediment has absorption peak at 3440.95cm^{-1} , this is because of the stretching vibration of O-H. The modified sediment has an absorption peak at 3439.85cm^{-1} , and the peak shape is sharper than -OH. This is due to high temperature roasting caused by amine N-H and OH bands overlap and association. The absorption peak of original sediment at 2919.79cm^{-1} is due to the stretching vibration of saturated hydrocarbon C-H and compared with the modified sediment, the dipole moment changes little^[7]. The modified sediment has an absorption peak at 1630.39cm^{-1} , which is caused by the stretching vibration of C = O. The presence of a peak at 1039.31cm^{-1} is due to the appearance of Si-O-C, and the absorption of $\nu_{\text{Si-O}}$ is due to the presence of Si in the sediment^[8]. The above analysis shows that the high temperature makes the sediment carbonization and evaporation of large amounts of water and change the internal functional groups, so that the adsorption of heavy metal ions is better.

The effects of Ni^{2+} concentration, adsorption time, pH and the amount of adsorbent on the removal of Ni^{2+} from the modified sediments were investigated by static adsorption method. And then take 100ml of a certain concentration of Ni^{2+} water samples, then, weigh a certain amount of roasted sediment into a 250ml Erlenmeyer bottle to close the bottle. Placed in a thermostat at a temperature of 25°C for 120 min. The supernatant was transferred to a centrifuge tube. Centrifuge at 3000 r / min for 15 min. The supernatant was took out in turn. The concentration of residual Ni^{2+} in the water samples after adsorption was determined by the method of spectrophotometric method (GB11910-89). In the course of the experiment, parallel and blank control experiments were carried out. The formula for calculating the saturation adsorption of Ni^{2+} is^[9]:

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (1)$$

c_0 and c_e are the mass concentrations of metal ions in the solution before and after adsorption(mg/L); V is the volume of heavy metal solution(L); m is the addition quality of adsorbent(g). The formula for calculating the removal rate of Ni^{2+} is^[9]:

$$\eta = \frac{c_0 - c_e}{c_0} \times 100\% \quad (2)$$

c_0 and c_e are the mass concentrations of metal ions in the solution before and after adsorption(mg/L).

3. Experimental results and discussion

3.1. Effect of initial concentration on adsorption

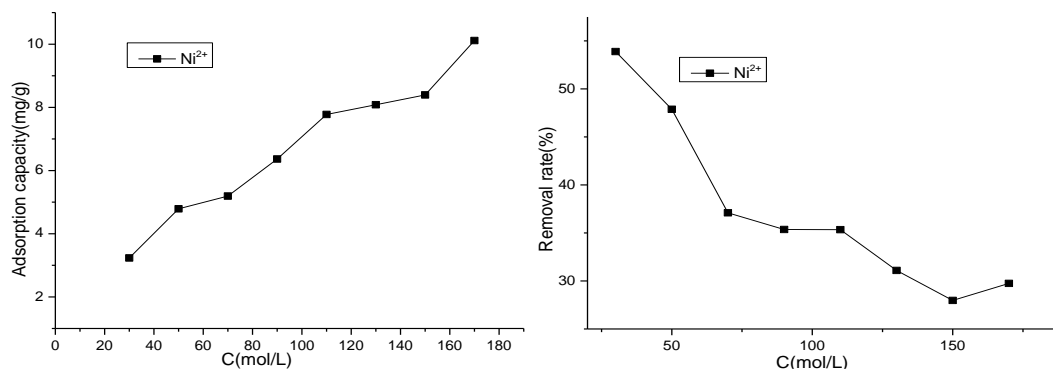


Fig.3 Effect of initial concentration on adsorption

As can be seen from Fig.3: With the increase of ion concentration, the adsorption capacity of modified sediment increased gradually, but the adsorption rate decreased gradually.

This is because the dosage of modified sediment is constant, the surface exchange position is certain, the adsorption capacity is also certain, so the adsorption effect of Ni^{2+} concentration is much lower than the low concentration of adsorption effect. It can be seen that the modified sediment adsorption of low concentration of wastewater is better, the best range is less than 10mg /L.

3.2. Effect of pH on adsorption

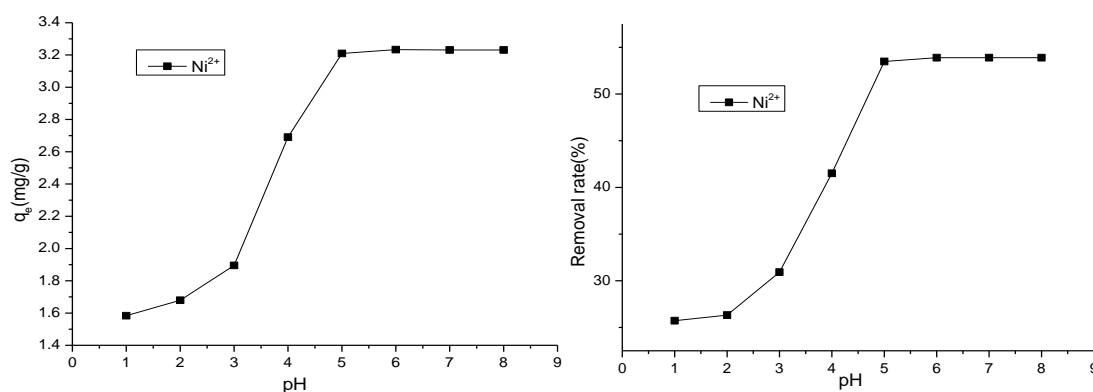


Fig.4 Effect of pH on adsorption

PH is one of the important factors that affect the adsorption and removal rate of heavy metal ions in Wastewater. On the one hand the value of the pH value of the solution directly affects the distribution of the charge on the surface of the adsorbent, thus affecting the combination of ions and adsorbents. As can be seen from the figure, with the continuous increase of the pH value in the system, the removal rate and the adsorption capacity of Ni^{2+} on the whole is gradually increased. When the pH value is low, the adsorption system contains a large number of H^+ , and attached to the surface of the sediment, and Ni^{2+} formation of intense competition, thus affecting the adsorption of sediment; When the pH value increases gradually, the concentration of H^+ will gradually decrease, and the competitive relationship between H^+ and Ni^{2+} will gradually weaken, which is helpful to improve the adsorption capacity of Ni^{2+} . When $pH > 8$, the solution system is mainly OH^- present, OH^- and heavy metal ions Ni^{2+} precipitation reaction occurs, is not conducive to explore the adsorption effect of adsorbents. Therefore, in weak acid

and neutral environment is conducive to improve the removal of heavy metals, thus it can be seen that the solution system is the best pH value range of 5 ~ 8, for comprehensive consideration, in the course of the experiment to select pH=7 as the best results.

3.3. Effect of dosage on adsorption

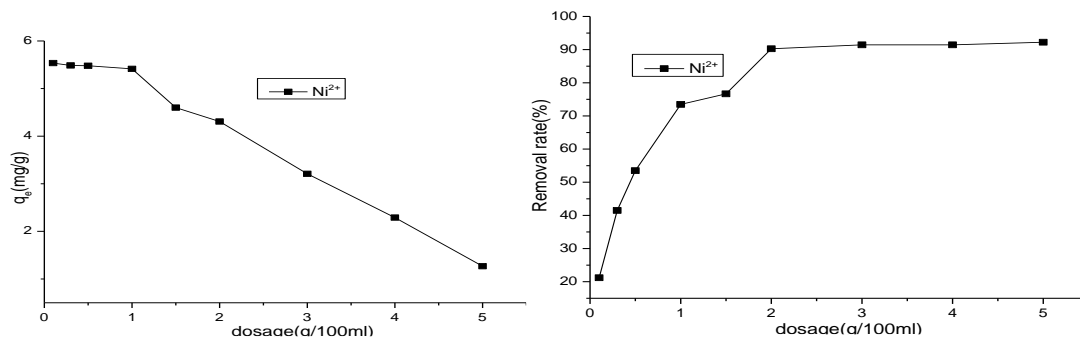


Fig.5 Effect of dosage on adsorption

The dosage of adsorbent is another important factor affecting the adsorption effect. If the dosage of adsorbent is too small, it cannot effectively remove the heavy metal ions in the solution, so it is difficult to meet the emission requirements; if the dosage of adsorbent is too large, it will not only affect the adsorption effect, but also waste the resources and increase the processing cost. It can be seen from the figure that with the increase of the dosage, the removal rate increases gradually, but the adsorption capacity decreases gradually. Comprehensive consideration, the best dosage is 1.0mg/100mL.

3.4. Effect of adsorption time on adsorption

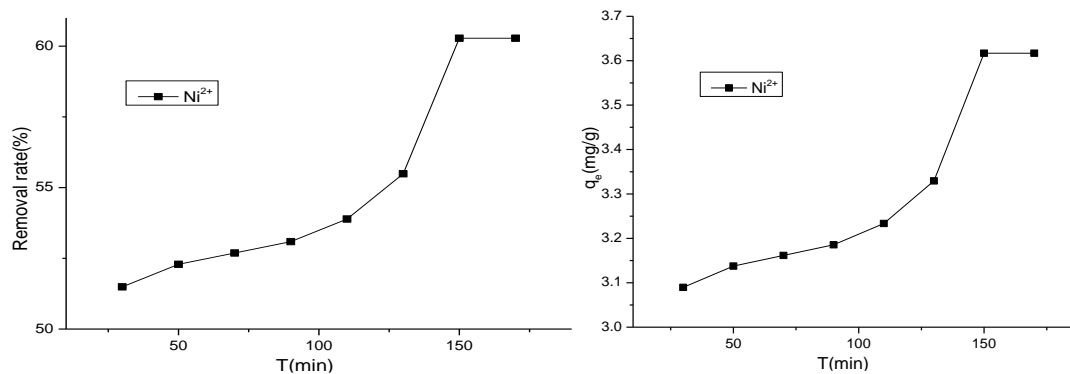


Fig 6 Effect of adsorption time on adsorption

It can be seen from the figure that the sedimentation rate and adsorption capacity of Ni²⁺ modified by high temperature calcination are relatively slow with the increase of time. At 150 min, the adsorption reaches the maximum value and there is almost no analytic phenomenon, which further shows that Ni²⁺ and the adsorption group in the system to maintain a stable adsorption potential, so it is not easy to resolve after adsorption. So the experiment to determine the time is 150min.

3.5. Effect of temperature on adsorption

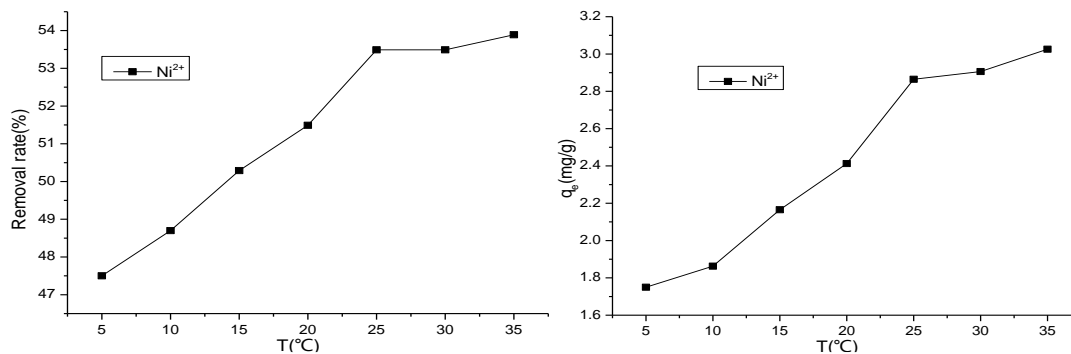


Fig.7 Effect of temperature on adsorption

Since the reaction process has an exothermic and endothermic process, the temperature determines whether the reaction is carried out and the reaction is balanced. Therefore, the temperature is also one of the key factors affecting the adsorption efficiency. It can be seen from the figure that the best temperature is 25°C.

3.6. Adsorption isotherm of modified sediment

Adsorption capacity of high temperature roasting modified sludge adsorption of Ni²⁺ is an important index to measure the sediment adsorption capacity. The adsorption balance between the quantity and the solution in the solid liquid phase system, used to simulate the model of adsorption isotherm and Freundlich isotherm for Langmuir^[10].

$$\text{Langmuir adsorption isotherm: } \frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{b q_m} \quad (3)$$

$$\text{Freundlich adsorption isotherm: } \lg q_e = \lg K_F + \frac{1}{n} \lg c_e \quad (4)$$

c_e is the mass concentrations of metal ions in the solution after adsorption(mg/L); q_e is adsorption capacity(mg/g); q_m is the maximum adsorption capacity(mg/g); K_F and n are constants.

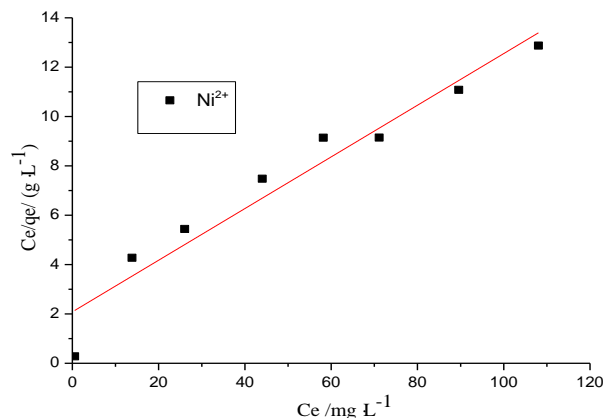


Fig. 8 Langmuir isotherm for adsorption on calcination sediment

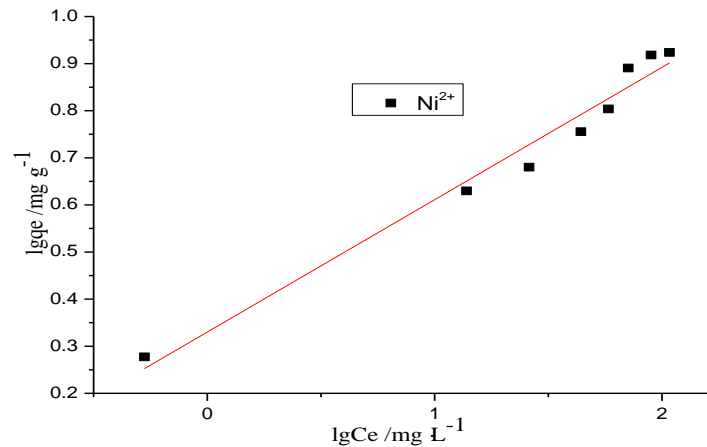


Fig. 9 Freundlich isotherm for adsorption on calcination sediment

Tab.1 Langmuir isotherm and Freundlich isotherm equation parameters for calcination sediment

Heavy metal ion	Langmuir equation			Freundlichequation		
	b	q_m	R^2	$1/n$	K_F	R^2
Ni^{2+}	0.0462	9.6246	0.9331	0.2880	1.9984	0.9679

The adsorption of Ni^{2+} by high temperature roasting modified sediment is in accordance with Langmuir and Freundlich adsorption isotherm equation. The R^2 of Freundlich equation is larger than Langmuir equation, we can see that Freundlich equation fitting effect is better than Langmuir equation fitting effect. This indicates that the adsorption of Ni^{2+} at high temperature roasting sediment is carried out simultaneously between monolayer and multilayer. The $1/n$ of the Freundlich equation is related to the adsorption strength and the value is less than 1, which proves that the adsorption process is easier.

3.7. Adsorption kinetics mechanism

Through the study of adsorption kinetics, the adsorption mechanism can be studied more deeply. The relationship between the adsorption capacity and the adsorption time of adsorbent can be expressed by the adsorption kinetic model. At present, many models have been established in the adsorption kinetics, such as, pseudo first order kinetic model, pseudo two order kinetic model, Elvish equation model, intraparticle diffusion equation model, Weber kinetic model, etc. The pseudo first order kinetic equation, pseudo two order kinetic equation, Elovich equation and the intraparticle diffusion equation are widely used in the study of adsorption mechanism^[11-12].

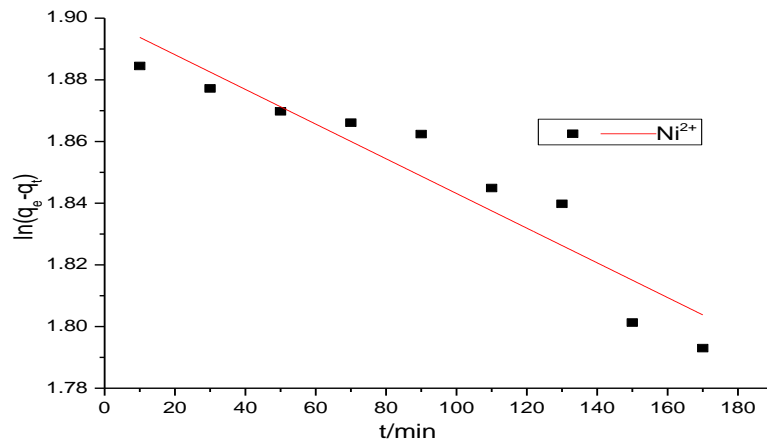
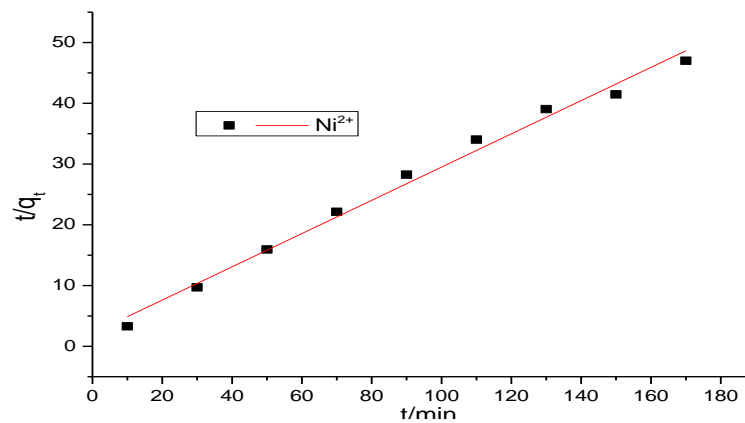
Lagergren pseudo first order adsorption kinetics equation:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Laguerrre pseudo two order adsorption kinetics equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

q_e is the amount of adsorption in equilibrium (mg/g); q_t is the amount of adsorption at time t (mg/g); t is the adsorption time (min); k_1 and k_2 are constants.

**Fig. 10** Pseudo first order kinetic fitting curve**Fig. 11** Pseudo two order kinetics fitting curve**Tab.2** Kinetic parameters

Heavy metal ion	Pseudo first order kinetic equation			Pseudo two order kinetics equation		
	K_1	$q_e (mg / g)$	R^2	K_2	$q_e (mg / g)$	R^2
Ni^{2+}	0.0006	6.6906	0.8812	0.0349	3.6563	0.9896

From the figure and table we can know that the adsorption curve and the fitting curve have some deviation, which indicates that the pseudo-first-order kinetics is not the main factor controlling the adsorption process during the adsorption process, because the main factors that affect the adsorption rate during the adsorption process are not the diffusion of the liquid film. The pseudo two order kinetic coefficient R^2 is closer to 1. The results show that the adsorption of Ni^{2+} in the high temperature roasting sediment is more in accordance with the pseudo two order kinetics model. The chemical bond is the main factor affecting the adsorption of the adsorbent, so the adsorption process is mainly chemical adsorption. According to table 2, the equilibrium adsorption amounts of Ni^{2+} was 3.6563 mg/g, and the difference between the measured values is less. Adsorption effect is ideal.

4. Conclusion

Compared with the original sediment, high temperature roasting to change the internal functional groups of sediment and produce new groups and chemical bond conversion and generation, and the specific surface area also increased several times, increasing the activity of adsorbents, is conducive to adsorb heavy metals. The high temperature roasting sediment adsorption of Ni^{2+} data were fitted with Langmuir and Freundlich adsorption isotherm equation, but the fitting effect is better with the Freundlich adsorption isothermal equation, indicating that the adsorption between single and multilayer. The adsorption kinetics of Ni^{2+} adsorption on high temperature roasting sediment is fitted by adsorption kinetics equation. The adsorption process follows Lagergren pseudo-second adsorption kinetics equation, which indicates that chemical adsorption is the main chemical bond, and the equilibrium adsorption capacity of Ni^{2+} was 3.6563mg / g, and the adsorption effect was ideal.

Acknowledgments

Talent research started--Study on the Performance of Typical Heavy Metal Ion in Modified Sediment of Dianchi Lake Sediment (14119031)

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