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Preparation and Performance Study of Fly Ash Chelate Composite Adsorbent

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ABSTRACT. *This paper uses fly ash as raw material to prepare a new type of fly ash chelate composite adsorbent, and explores the influencing factors in the preparation process of the composite adsorbent to determine the optimal synthesis process. The adsorption performance of the heavy metal nickel ions in the simulated environment was studied. When the composite adsorbent was synthesized using the best process, the adsorption rate of heavy metal nickel reached 97.2% when the adsorption time was 100 minutes.*

KEYWORDS: *fly ash, composite adsorbent, chelation*

1. Introduction

With the rapid development of China's industrial level, the pollution of heavy metal wastewater is becoming increasingly serious. The sources of heavy metal wastewater are wide and the output is too large. Among them, there are dust removal wastewater from non-ferrous metals and other industries, washing wastewater from electroplating plants, pickling wastewater from electrolysis plants and electrolysis, pesticides, drainage from medical and pharmaceutical peripheral enterprises, mines and mine channels, etc. Drainage of various industries, leaching water from waste rock yards, tailings drainage from mining sites, and other industrial wastewater [1]. The forms of heavy metal ions in water can be divided into dissolved and particulate states [2]. Heavy metal ions in the wastewater will be absorbed and enriched by passive plants, etc., and will be transmitted along the food chain. Heavy metal ions in water can easily inactivate proteins and active enzymes, which can cause metabolic disorders in living organisms, and because they cannot be eliminated by natural degradation, and cannot be eliminated by means of biological digestion and metabolism, they remain in the water. Heavy metal ions will cause immeasurable losses to the health and life safety of organisms [3]. For this reason, the country attaches increasing importance to heavy metal pollution in wastewater. The rectification of heavy metal ions in wastewater and the access standards for discharge are more stringent. Therefore, in order to meet the national policy of the industry, we environmentalists need to formulate more effective, fast and affordable ways to handle and dispose of industries and life containing heavy metal ions. Wastewater, thereby reducing the heavy harm of heavy metal ions in wastewater to our living environment. There are currently three methods for the disposal of heavy metal ions in wastewater: chemical, physical-chemical, and biological methods [4]. The most widely used treatment methods in industrial production are chemical and physical methods. In selecting wastewater treatment technology, different treatment methods are mainly adopted according to the origin and content of heavy metal wastewater and its existence in water bodies. The polymer heavy metal chelate commonly used in wastewater treatment is a macromolecule that is easily soluble in water. It has the function of combining with metal ions in water to form a multi-coordination complex. Special functional atoms on the chelate the coordination reaction with metal ions in water will eventually change into a stable molecular configuration of small molecule chelate. The advantages of polymer heavy metal chelate for the treatment of heavy metal wastewater are lower cost and stable properties of the final reaction product. Therefore, industry scholars have paid great attention to the research of polymer heavy metal chelate in recent time, and have achieved certain breakthrough.

Fly ash is also called fly ash in industry [5], which is mainly industrial waste discharged by some power plants. If industrial fly ash is not properly disposed of, it will cause severe pollution and damage to air, land and living organisms once exposed to the environment, and the consequences are simply unthinkable. Therefore, the rational use of fly ash and the reuse of waste resources have become a major subject for scholars. The color of fly ash is mainly gray and gray-black. The gray-black fly ash is formed because the carbon particles in the coal are not completely burned. Fly ash particles have different morphologies and particle sizes. During combustion, due to the tension of the surface of pulverized coal, its particles are basically spherical, the surface is rough, the layers are uneven, and there are fewer micropores. The molecules of the fly ash collide with each other in the molten state to form a porous polymer aggregate with a rough surface. Therefore, the fly ash has a relatively large specific surface area and pore volume, and its adsorption performance for heavy metal ions is correspondingly enhanced. Fly ash is a mixture of inorganic oxides, most of which are inorganic substances in raw coal. The inorganic substances in coal mines are mainly clay ore, and pyrite, quartz and other minerals [6]. Therefore, the material composition of fly ash is mainly SiO_2 and Al_2O_3. Due to the large output of fly ash, and the need for ball milling and other processes, the cost of synthesis is relatively low, so it has certain development prospects in the treatment of wastewater contaminated by heavy metal ions.

2. Experimental part

2.1 Test drugs and instruments

Hydrochloric acid, KH550,$(NH_2(CH_2)_3Si(OC_2H_5)_3$, epichlorohydrin, glutaraldehyde, thiourea, anhydrous calcium chloride, sodium hydroxide, nickel nitrate, potassium iodide, ammonium citrate, ethylenediamine tetraacetic acid Disodium, butanedione oxime, ammonia; the above are analytical grade. The main test instruments are ATY124 electronic balance; VIS-7220 UV-visible spectrophotometer; PHS-3C precision pH meter; DF-101S collector-type constant temperature heating magnetic stirrer; SHA-B constant temperature water bath oscillator.

2.2 Analysis method

Determination of Ni^{2+} concentration: The content of nickel ions in the solution will be determined by the diacetyl oxime spectrophotometry. The experimental principle of this method is: In a slightly alkaline solution, nickel ions can undergo a series of chemical reactions with butanedione oxime, and subsequently form a complex with dissolving properties. The complex is generally burgundy and can form an absorption peak at a wavelength of 530 nm. Therefore, we chose a wavelength of 530nm to measure its absorbance and calculate the adsorption rate.

2.3 Standard curve drawing

Take 6 colorimetric tubes with stoppers, and then add the above-mentioned standard use solution of nickel ion 0, 1.00, 2.00, 3.00, 4.00, 5.00ml, and then add the 50% citric acid prepared Add 2.0 ml of ammonium solution and 1.0 ml of 0.05 mol/L of the above iodine solution, add water to 20 ml, and shake well (if it is not shaken, it will affect the absorbance measurement). Add 2.0 ml of 0.5% diacetyl oxime solution and shake well. Then add 2.0ml of 5% Na_2-EDTA solution, add water to the mark and shake well. After the above solution is left for 5 minutes, then select a 10mm cuvette (other cuvettes of other specifications can also be used, but it must be consistent), measure its absorbance at a wavelength of 530nm, and then make a blank correction. Standard curve corresponding to nickel ion content. The standard curve is shown in Figure 1.

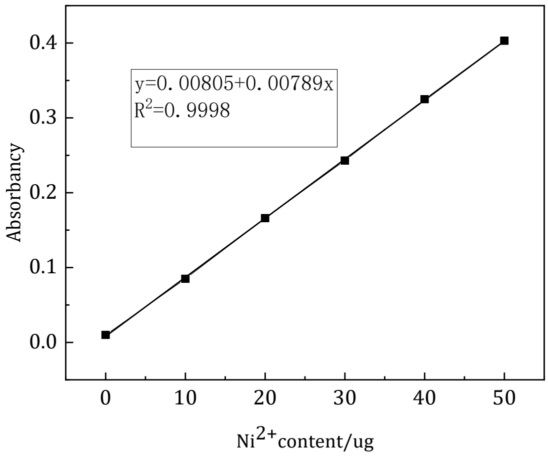

Figure. 1 The standard curve line of Ni^{2+}

2.4 Calculation of adsorption capacity

The calculation method when the adsorption of nickel ions by the chelated composite adsorption material reaches the equilibrium adsorption amount is as follows (1):

$$Vs\ [(C1-C2)/C1]\times 100\% \qquad (1)$$

In formula (1),

Vs is the adsorption rate;

C1 is the concentration of the solution before adding the adsorbent;

C2 is the concentration of the solution after adding the adsorbent.

2.5 Preparation of chelated adsorption material

Put a certain amount of fly ash in a three-necked flask, and then add an aqueous solution of a coupling agent KH550 (or KH560) with a certain concentration gradient. After it is thoroughly mixed with the fly ash, place the three-necked flask in a thermostatic constant temperature in a magnetic stirrer, the temperature was adjusted to 40°C. And magnetically stirred for 2 h. Then, an aqueous solution containing 0.3 g of thiourea was uniformly added to the three-necked flask and the magnetic stirring was continued for 3 h. Add 1g of sodium hydroxide to provide alkaline conditions, and then add 3ml of glutaraldehyde, a cross-linking agent, and magnetically stir for 3h. Then take out the three-necked flask, put it in the oven, adjust the temperature to 353K and dry for 24 hours. Adsorption material.

3. Condition optimization

3.1 Influence of the dosage of coupling agent KH550 on the adsorption effect

Weigh 10g fly ash, a total of six parts, put it in a three-necked flask, and then add an aqueous solution containing 0.1, 0.2, 0.3, 0.4, 0.5, 0.6g of coupling agent KH550, mix thoroughly with the fly ash, and put the three-necked flask in Put it into a collector type constant temperature magnetic stirrer, adjust the temperature to 40 ° C, and magnetically stir for 2h. Then, an aqueous solution containing 0.3 g of thiourea was uniformly added to the three-necked flask and the magnetic stirring was continued for 3 h. Subsequently, an aqueous solution containing 1 g of sodium hydroxide was added to provide alkaline conditions for the subsequent cross-linking reaction. After 5 min, the cross-linking agent glutaraldehyde 3ml was added and stirred magnetically for 3 h. The three-necked flask was taken out, placed in an oven, and the temperature was adjusted to 353 K to dry After 14 hours, the chelated composite adsorbent was removed. Separate 0.5 g of each of the six chelating agents and add them to 100 ml of Ni^{2+} solution with a concentration of 200 mg/L. After shaking at room temperature for 10, 20, 40, 60, 80, and 100 min, respectively, filter and determine the remaining Ni^{2+} in the filtrate. Concentration.

The adsorption performance of chelated composite adsorbent on Ni2+ in simulated wastewater is shown in Figure 2. According to Fig. 2, it can be seen that the adsorption amount of Ni2+ on the final product prepared by using different amounts of KH550 increased rapidly with time, and the adsorption amount of Ni^{2+} remained basically unchanged after 80 minutes. With the increase of the amount of KH550, the adsorption of Ni2+ on the final product increased first and then decreased. When the amount of KH550 reached 0.3, the adsorption rate of Ni^{2+} by the final product reached 93.7%. When the amount of KH550 continued to increase, the amount of adsorption decreased instead. This is because too much KH550 may hinder the contact area between the chelator and heavy metal ions and negatively affect the adsorption. Therefore, when the amount of coupling agent KH550 is 0.3g, the adsorption capacity of the chelating composite adsorbent to Ni^{2+} is the largest. The final product of this group of chelate composites has good overall strength and is not easily soluble in water. As the amount of KH550 increases, the strength of the final product gradually increases. When the amount reaches 0.3g, the amount of KH550 continues to increase, and the final product the intensity changes little.

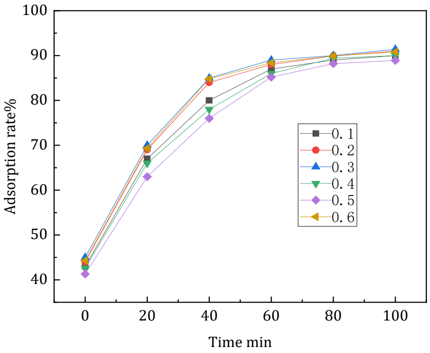

Figure. 2 Effect of KH550 dosage on adsorption of Ni^{2+}

3.2 Effect of the dosage of coupling agent KH560 on the adsorption effect

The effect of the amount of KH560 on the adsorption performance and strength of the final product. The coupling agent KH550 was replaced with KH560. The other reaction conditions were the same. Similarly, the six chelating agents were prepared by adding 0.5g to 100ml, and the concentration was In a 200 mg/L Ni^{2+} simulated solution, shake at room temperature for 10, 20, 40, 60, 80, and 100 min, respectively, and then filter and measure the remaining Ni^{2+} concentration in the filtrate. The adsorption performance of the chelated composite adsorbent for Ni^{2+} is shown in Figure 3. According to Fig. 3, the adsorption amount of Ni^{2+} on the final product with different dosages of KH560 also increased with time, and the adsorption amount remained basically unchanged after 80 min. When the amount of coupling agent KH560 reached 0.4g, the adsorption rate of Ni^{2+} by the chelating agent reached 90.5%. When the amount of KH560 continued to increase, the amount of adsorption decreased instead, for the same reasonKH550. Therefore, when the amount of KH560 is 0.4g, the adsorption capacity of the chelating composite adsorbent to Ni^{2+} is the largest.

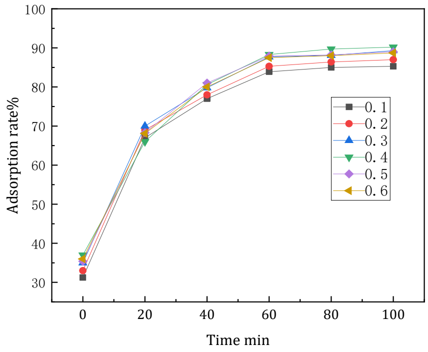

Figure. 3 Effect of KH560 dosage on adsorption of Ni^{2+}

In summary, when the amount of the coupling agent KH560 reaches 0.3 g, the adsorption rate of the chelating composite adsorbent to Ni^{2+} reaches 93.7%. Therefore, considering comprehensively, KH550 is finally selected as the coupling agent for the composite chelating agent, and the optimal dosage is 0.3g.

3.3 Effect of thiourea dosage on adsorption performance and strength of final product

Weigh 10g of fly ash, a total of six parts, put it in a three-necked flask, and then add an aqueous solution containing 0.3g of KH550, mix thoroughly with the fly ash, and then put the three-necked flask into a heat-collecting thermostatic magnetic stirrer the temperature was adjusted to 40 ° C. and magnetically stirred for 2 h. Then, an aqueous solution containing 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 g of thiourea was slowly added to the three-necked flask and the magnetic stirring was continued for 3 h. Subsequently, an aqueous solution containing 1 g of sodium hydroxide was added to provide alkaline conditions for the subsequent cross-linking reaction. After 5 minutes, the cross-linking agent glutaraldehyde 3 ml was added and stirred magnetically for 3 h. The three-necked flask was taken out, placed in an oven, and the temperature was adjusted to 353 K and dried. After 14 hours, the chelated composite adsorbent was removed. In the adsorption experiment, 0.5 g of each of the six chelating agents was taken out and added to 100 ml of a simulated solution of Ni2+ at a concentration of 200 mg / L. After shaking at room temperature for 10, 20, 40, 60, 80, and 100 minutes, the mixture was filtered and finally the concentration of remaining Ni2+ in the filtrate was measured.

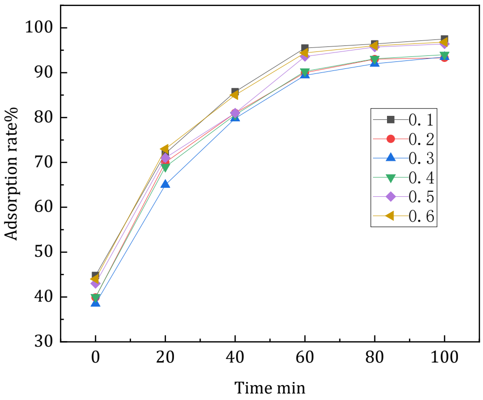

Figure. 4 Effect of thiourea dosage on adsorption of Ni^{2+}

The adsorption performance of the chelated composite adsorbent for Ni^{2+} is shown in Figure 5. According to Fig. 5, it can be seen that the amount of Ni^{2+} adsorbed by the final product added with different amounts of thiourea increased rapidly with the increase of time, and its adsorption of nickel ions remained basically unchanged after 60 minutes. With the increase of the amount of thiourea, the amount of Ni^{2+} adsorption first decreased and then increased. When the amount of thiourea is 0.1, the adsorption rate of Ni^{2+} on the chelate composite material reaches 97.2%. Too much thiourea may reduce the contact area between fly ash and heavy metal ions, which will have a negative impact on the adsorption. However, since thiourea is a chelating agent, the amount of thiourea continues to increase. The effect gradually began to dominate, so the amount of adsorption increased instead. The overall strength of the final product of this group of chelated composites slowly increases and then decreases rapidly with the increase of the amount of thiourea. When the amount of thiourea exceeds 0.4 g, the strength of the final product becomes significantly worse, it is brittle and more soluble in water.

3.4 Effect of reaction temperature on adsorption performance

Weigh 10g of fly ash, a total of five parts, and place them in three-necked flasks. Then add an aqueous solution containing 0.3g of coupling agent KH550. After it is fully mixed with the fly ash, place the three-necked flask in a heat-collection In a constant temperature magnetic stirrer, magnetically stir at a temperature of 303K, 313K, 323K, 333k, 343K for 2h. Then, an aqueous solution containing 0.1 g of thiourea was slowly added to the three-necked flask and the magnetic stirring was continued for 3 h. Subsequently, an aqueous solution containing 1 g of sodium hydroxide was added to provide basic conditions for the subsequent cross-linking reaction. After 5 min, 3 ml of glutaraldehyde, a cross-linking agent, was added and magnetically stirred for 3 h. Finally, the three-necked flask was taken out and placed in an oven and the temperature was adjusted to after drying at 353K for 14 hours, the formed chelate composite adsorption material was removed. Take five parts of the above-mentioned final products and add them to 100ml of Ni^{2+} solution with a concentration of 200mg/L, shake at room temperature for 10, 20, 40, 60, 80 and 100min respectively, filter and determine the remaining Ni^{2+} in the filtrate. Concentration.

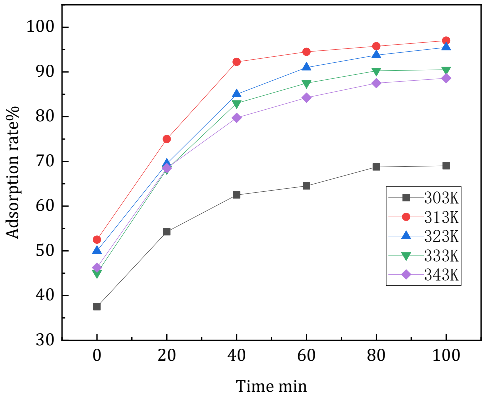

Figure. 5 Effect of reaction temperature on Ni^{2+} adsorption

The adsorption performance of the chelated composite adsorbent Ni^{2+} is shown in FIG. 5. According to Figure 5, it can be seen that when the temperature rises from 303K to 313K, the adsorption amount of Ni^{2+} in the final product increases rapidly, and then continues to increase the temperature, and the adsorption amount slowly decreases. Conducive to the progress of the grafting reaction, which will adversely affect the adsorption. Therefore, the optimal reaction temperature is 313K.

4. Results and discussion

After discussing the experimental conditions of each link, the optimal synthesis process was finally determined: put 10 g of fly ash in a three-necked flask, and then add an aqueous solution of coupling agent KH550, which accounts for 3% of the amount of fly ash, and fully meet the requirements After mixing, the three-necked flask was placed in a heat-collecting constant temperature magnetic stirrer and magnetically stirred for 2 h at a temperature of 313K. Then, an aqueous solution of thiourea with a mass of 1% by mass of fly ash was uniformly added to the three-necked flask, and the magnetic stirring was continued for 3 hours. Then, 3 ml of glutaraldehyde, a cross-linking agent, was added and magnetically stirred for 3 hours. The three-necked flask was taken out and placed in an oven. The temperature was adjusted to 353K and dried for 14 hours. Finally, a fly ash chelate adsorbent was obtained. The experimental results show that it has good mechanical strength, is not easily soluble in water, and has good adsorption performance for Ni^{2+}.

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