Computer Numerical Simulation and Study on Adsorption Properties of Orange Peel Using Scanning Electron Microscope

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Abstract. In this paper, using orange peel as raw material, based on the adsorption mechanism of orange peel, the adsorption performance of biomass adsorbent on sulfur compounds was studied. Sodium sulfide solution was used to simulate the sulfur-containing wastewater, and it was found that the orange peel biomass had a certain adsorption effect on the sulfur compounds in the wastewater. Through the control experiment, the influence of drying time and dosage of orange peel pretreatment on the adsorption effect was explored, so as to find out the best conditions for orange peel adsorption of sulfur-containing wastewater, and provide a theoretical basis for the treatment of industrial sulfur-containing wastewater.

Keywords: Drying time, dosage, orange peel.

1. Introduction

China is a big fruit production country, in the fruit production is rising at the same time, so the production of waste is also very huge, mainly peel, fruit dregs, stone and so on. Pericarp in the domestic waste accounted for nearly half, weight accounted for a relatively large. The surface of pericarp contains hydroxyl, amino, carboxyl and other functional groups [1], which has high nutritional and rich functional components and has great development potential.

In water treatment, orange peel is one of the most favored pericarps by scholars and researchers. In recent years, there have been many studies on the adsorption of various heavy metal ions in wastewater by pericarps. Porous chemicals such as activated carbon, fiber, ceramic particles mixed with water, or making wastewater by other particles state of chemical filter, this way of adsorption is a common means of wastewater adsorption treatment, its principle is to use the suspended solids in the wastewater, organic chemical particles, metal ions, such as the pollution of chemical adsorption directly in other porous chemicals and remove the quality of the surface. Generally speaking, the higher the concentration of pollutants in adsorption equilibrium, the greater the adsorption capacity. Adsorption method has the advantages of good treatment effect, simple operation and convenient management, but its main disadvantage is the amount of adsorption materials, expensive cost. Ma Zhihao [2] et al. pointed out that Huolong peel, orange peel, banana peel and grapefruit peel all had good adsorption capacity, among which the adsorption capacity of citrus peel was as high as 98%. As one of the important places of origin of citrus in China, data show that in 2018, the output of citrus in China's orchards can reach 20.4%.
Therefore, as a kind of industrial waste in the food industry, red orange peel needs to have the strong characteristics of large recovery output and high efficiency. As an adsorbent, it needs to have the strong characteristics of low price, wide source and renewable. In order to recycle orange peels, it is of positive significance to explore the adsorption performance of orange peels and optimize the adsorption conditions for the transformation of orange peels from waste to treasure, reducing the cost of adsorption and reducing environmental pollution.

In this experiment, orange peel is used as raw material to prepare adsorbents. By exploring its adsorption performance under different preparation conditions and different operating conditions, the adsorption capacity of orange peel on sulfurization wastewater is studied, which provides a theoretical basis for the treatment of industrial sulfur-containing wastewater by orange peel. To provide a new way to build a resource-conserving society, reduce environmental pollution, turn waste into treasure, promote economic development, the reuse of waste is an important way. Among them, agricultural biomass is a natural and renewable resource, which has a very excellent regeneration ability by using agricultural biomass waste resources efficiently. Hu Xuefei et al. [3] studied agricultural straw waste and carried out its application in water treatment through preparation of anion/cationic adsorbent, preparation of biochar and preparation of biochar composite material, indicating that biomass adsorbent can replace activated carbon in the field of water environmental pollution treatment. Ji Haiyang et al. [4] prepared three kinds of new biochar by using the diluted residues after pyrolysis and carbonization at different temperatures under high pressure or low oxygen environment, and experimentally discussed the adsorption characteristics of biological activated carbon on Cd²⁺ solution at various preparation temperatures. The experiment shows that with the rise of carbonization temperature, the specific surface area, pH and ash content gradually increase, and the degree of the surface shape and structure law change rule of biological activated carbon is getting lower and lower. The adsorption reactions of the three novel biological activated carbons on Cd²⁺ conform to the standard second-order kinetic equation, and the adsorption effect of the new biological activated carbons prepared at 700°C is the best.

Wu Fan et al. [5] took orange peel as raw material, prepared different modified adsorbents through alkaline oxidation and Fe (III) load modification, studied the adsorption performance of adsorbents on lead wastewater, and explored the influence of different factors on the adsorption effect of adsorbents. The lead removal rate of unmodified orange peel was 88.57%, and the removal rate of modified orange peel was 93.88%, which was higher than the adsorption capacity of ordinary orange peel. And they're all reusable. The fitting of adsorption isotherm shows that the adsorption effect of orange cortex on lead belongs to a single molecular chemisorption, and chemisorption is the most important adsorption method.

Ma Yanmei [6] et al. studied a series of experiments on the adsorption of orange peel on wastewater containing sulfur, and the experiments showed that the modifier, pH value, temperature, dosage, reaction time and so on all had an impact on the adsorption performance of orange peel, among which the change of pH had a greater impact on the adsorption rate of orange peel. Orange peel has a good adsorption capacity of sulfide, the adsorption capacity of sulfide can reach more than 90%. At the same time, the kinetic analysis of the adsorption of sulfur wastewater by orange peel was carried out, and the quasi-second-order kinetic model was obtained. The average adsorption capacity was 1072 mg/g, the adsorption rate constant was 3.092×10⁻³ g/(mgꞏg), and the adsorption capacity was very large and the adsorption rate was high.

Adsorption is an automatic change in the concentration of molecules at two complementary cross-contact interfaces over time. The adsorption system is composed of adsorption solution agent and other adsorption substances. Adsorbent refers to those who have a certain adsorption performance of the material, they are adsorbed substances called adsorption. The reason adsorbents have the ability to adsorb is that their surface has an excess of energy - "surface free energy". The molecules on the surface are different, so are the molecules on the inside. The molecules on the surface have more activity than those on the inside, which is called the surface free energy.

Adsorption occurs naturally when adsorbents and adsorbents contact, which is an important characteristic of adsorption. According to the laws of thermodynamics, in nature, all actions that reduce
one's energy are spontaneous. For example, heat transfer from the high energy side to the low side as the water level changes from high to low. The result of similar behavior is to reduce the "surface free energy" of the adsorbent itself and spontaneously adsorb. For example, in a compressed air dryer, is the water vapor adsorption process a spontaneous process that does not provide external energy?

The structure of folds and voids inside the orange peel is rich, showing prominent lamellar multilayer, honeycombed and irregular multilayer folds and voids. The characteristics of these voids inside the bark of typical orange trees fully guarantee the connecting function of the orange plant to adsorb tree material and other objects to adsorb plant quality. The adsorption ability of orange peel is mainly due to the active cellulose and semi-active cellulose in it. These small molecules containing cellulose also include a large number of active chemical functional groups on the surface of their structure, such as various hydroxyl groups, carboxyl groups and various polyphenols, fatty types, amino acids, etc. They are believed to be a kind of heavy metal active ions that can be adsorbed by the human body directly through ion exchange, chelation and other ways. Ion exchange is the main mechanism of heavy metal adsorption in pericarp. The concentration or removal of heavy metal ions in solution is carried out by using metal ions in solution to exchange heavy metal ions in the pericarp, and the reaction is reversible and of low yield. The pericarp material can be desorbed and regenerated by heating and acid-base reactions. In Mathematical and Yu's experiments on algal microorganism adsorption, the total amount of calcium and magnesium ions and hydrogen ions released by algal microorganism is equivalent or multiple ions respectively, which can indicate the existence of ion exchange mechanism.

2. The experiment parts

2.1. Main instruments and reagents

Instruments: Electronic Balance (ALC-210.4, Guangzhou Shike Instrument Technology Co., Ltd.); Magnetic heating agitator; Visible spectrophotometer (722S, Haiyi Electric Analytical Instrument Co., Ltd.); Crusher (HL-FS500); Acidometer (PC-110, Shanghai Kuosi Electronics Co., Ltd.); 100 mesh sample screens; (101-0, Beijing Kewei Yongxing Instrument Co., Ltd.); Field Emission Scanning Electron Microscope (Zeiss Supra 55, Carl, Germany). Zeiss Supra 55 was used in this paper to analyze the surface morphology of the sample.

2.2. The experiment to prepare

2.2.1. Pretreatment of orange peel. Clean and peel fresh orange skins with a small amount of high temperature tap water for two times, and then rinse them with a small amount of high temperature distilled water for two times. After natural drying and air drying, the excess moisture on the surface of orange peel can be removed. Dry them three times at high temperature in a blast drying oven at 80°C. After three times of drying to 8h, 10h and 12h in the high-temperature roasting chamber, a part of the orange samples was taken out and crushed with manual crusher and electric crusher. After 100 mesh, the samples were screened, sealed and evenly dried for later use.

2.2.2. Para-aminoxylene photometric method. Take 6 colorimetric tubes of 50 mL, labeled as No.1, 2, 3, 4, 5, and 6, and add 0.1, 0.5, 2.0, 3.0, 5.0, and 8.0 mL of sulfur-containing standard solution to each. Add an appropriate amount of distilled water to the scale on the colorimetric tube and shake it evenly with the sodium sulfide solution to prepare a series of standard sodium sulfide solutions with different labeled concentrations, then add 0.2 mL of color reagent and mix it evenly, and leave it for 20 min. The reagent is shaken by a mixture of 20 mL p-amino-N, N-diethylaniline sulfate solution and 1 mL ferric chloride solution, which must be prepared and used on the ready.

The maximum absorption wavelength of the photometer was set at 665 nm to measure the absorbance of the above-mentioned sodium sulfide solutions with different concentrations, and the adsorption rate was calculated by the following formula.
where: \( W \) is adsorption rate, \( \% \); \( C_0 \) is the initial concentration of sodium sulfide solution, mol/L; \( C_e \) is the residual concentration of sodium sulfide solution after adsorption, mol/L.

3. Results and discussion

3.1. Standard solution curve of sulfur compounds and its regression equation

The concentration and absorbance of sulfur-containing compounds solution are shown in Table 1. The abscissa is the concentration and the ordinate is the absorbance. The standard curve of sulfide solution is shown in Figure 1. The linear regression equation is: \( y = 49.48x - 0.033724 \)

| Concentration of \( S_2O_3^- \)/mol/L | 0.0002 | 0.001 | 0.004 | 0.006 | 0.010 | 0.016 |
|--------------------------------------|-------|-------|-------|-------|-------|-------|
| Absorbance                           | 0.041 | 0.089 | 0.225 | 0.329 | 0.536 | 0.823 |

**Figure 1.** Standard solution curve of sodium sulfide

3.2. Effect of drying time on adsorption of orange peel

Prepare three 100 mL beakers, labeled as No.1, 2 and 3, pour 50 mL of 0.1 mol/L sodium sulfide solution into each beaker with a measuring cylinder, add 1 g of orange peel powder with drying time of 8h, 10h and 12 h respectively, indicate the drying time, and let stand for 6 h. When the time was up, 10 mL supernatant was transferred to the three beakers with pipette gun, and 0.2 mL chromogener was dropped into the liquid, and then the liquid was added. After standing for 20 min, the absorbance and adsorption rate were measured as shown in Table 2 and Figure 2.

| Drying time /h | 8    | 10   | 12   |
|----------------|------|------|------|
| Absorbance     | 0.745| 0.505| 0.758|
| Absorption rate (\%) | 84.26 | 89.33 | 83.98 |

**Table 2.** Absorbance of wastewater under the action of orange peel at different drying time.

Instructions: Original absorbance of simulated sulfur-containing wastewater is 4.733
The results showed that the absorbance of water sample decreased first and then increased with the drying time; When the drying time is 10 h, the absorbance of water sample is the lowest, which is 0.505. At this time, the adsorption rate of the most sulfur-containing wastewater of orange peel adsorbent reached 89.33%, which was higher than 84.26% of drying time of 8 h and 83.98% of drying time of 10 h. It can be seen that when the orange peel is put into the oven after natural air drying and dried for 10 h, the adsorption effect of the adsorbent is the best.

3.3. Effect of orange peel dosage on adsorption
Take 3 beakers, measure 50 mL of simulated sulfur-containing wastewater in the measuring cylinder, pour into each beaker, mark as No. 1, 2, 3, 4, 5, 6, add 0.2 g, 0.6 g, 1 g, 1.4 g, 1.8 g, 2.2 g orange peel powder into each beaker, stand for 6 h, take 10 ml of supernatant, add 0.2 ml developer, stand for 20 min, and measure the absorbance as shown in Fig. 3. The experimental results are shown in Fig. 3.

**Table 3.** Effect of adsorbent dosage on adsorption effect.

| Consumption /g | 0.2 | 0.6 | 1  | 1.4 | 1.8 | 2.2 |
|----------------|-----|-----|----|-----|-----|-----|
| Absorbance     | 0.620 | 0.553 | 0.471 | 0.303 | 0.678 | 0.841 |
| Absorptivity (%) | 86.90 | 88.32 | 90.05 | 93.60 | 85.68 | 82.23 |
| Instructions   | Original absorbance A0 of simulated sulfur-containing wastewater is 4.733. |
The experimental results showed that when the dosage of orange peel powder increased from 0.2 g to 1.4 g, the absorbance decreased and the adsorption rate increased with the decrease of powder dosage. When the amount of orange peel was more than 1.4 g, the absorbance of wastewater increased and the adsorption rate decreased. Therefore, the best amount of adsorption effect is 1.4 g, and the amount of orange peel is 28 g/L. Some of the special possibilities are that with the increase of the actual use of sulfur-containing adsorbent, its ion surface area gradually increases significantly, and it can absorb more of the largest sulfur-containing gas ions under certain use conditions. Under certain conditions, there is a nonlinear relationship between the adsorption rate and the maximum amount of sulfur-containing gas ions, and the adsorbent efficiency should reach the highest value after the ions reach full saturation. However, when the amount is too much, orange peel powder is easy to agglomerate and accumulate at the bottom of the bottle, which affects its adsorption effect to a certain extent.

3.4. Structural characterization of orange peel

Weigh 0.1 g orange peel powder with drying time of 10 h, put the adsorbed orange peel powder into the oven, dry it to constant weight, and weigh 0.1 g orange peel powder after use. After spraying gold, the two materials were observed by scanning electron microscope, and the results are shown in Figure 4 (a) and Figure 4 (b).
It can be seen from Fig. 8 (a) that the surface of orange peel presents an uneven structure with a large number of adsorption gaps and fine pores, which has a very positive significance for the adsorption reaction. It can be seen from figure 4 (b) that after drying, part of the surface of the used orange peel powder becomes smooth, the adsorption space is relatively reduced, and the adsorption capacity is weakened, but there are still large adsorption channels on the surface, which still has a certain adsorption capacity.

4. Conclusion

In this experiment, the adsorption performance of orange peel as adsorbent for sulfide was studied by controlling a single variable. In addition to the experimental factors, the adsorption effect of orange peel in different preparation conditions was compared. The results are as follows: the orange peel powder, which is dried in oven at 80 °C for 10 h after natural air drying, has the best adsorption effect on sulfide; When the input amount of orange peel is 1 g, the adsorption effect is the best. Waste orange peel has good adsorption performance, low price, no pollution and other advantages, and because the material of orange peel is simple and easy to obtain, the proportion of orange peel in solid waste is very high. The research on the optimization of orange peel's adsorption performance provides a new way to turn waste into treasure, and to promote China's economic growth and build a resource-saving society.

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