Research on the Adsorption Effects of Biomass by Microstructural Characterization and Intelligent Numerical Computation Method

Yongli Zhang*, Ruiting Li
Technology Institute, Guangzhou College of Technology and Business, Guangzhou, China

*Corresponding author: zhangyongli@gzgs.edu.cn

Abstract. In this paper, sodium sulfide solution as a simulation of sulfur-containing wastewater, using orange peel as adsorbent, through the change of the absorbance of simulated wastewater to analyze the orange peel adsorbent on the treatment effect of simulated wastewater, to explore its optimal experimental conditions. The experimental results show that the adsorbent has a certain adsorption effect on the sulfur compounds in the sulfur-containing wastewater. With the change of the pH value of the adsorption environment, the adsorption rate has changed. The addition of different chemical modifiers in the water will affect the adsorption and effect of orange peel.

Keywords: Biomass, chemical modifiers, adsorption.

1. Introduction
Sulfur exists mostly in the form of H₂S, HS⁻, S²⁻ and other compounds in nature [1], and its toxicity is caused by the transformation of sulfide into hydrogen sulfide. The maximum concentration of hydrogen sulfide allowed in West Germany and the United States is 10 ppm, and there is no danger when the concentration is lower than 10 ppm. When the concentration of hydrogen sulfide reaches 100 mg/L, people will suffer from toxic shock. It can even cause death. In February 1978, a hydrogen sulfide poisoning case occurred in the tannery of Horwin Leather Company in Chicago, USA, resulting in 35 people being poisoned and 8 people dying [2]. With the rapid development of industry, sulfur pollution is becoming more and more serious. Sulphide pollution includes gas sulfide pollution and water sulfide pollution. Sulphide pollution in water is mainly caused by human activities, such as chemical plants and pharmaceutical manufacturing industries, which produce some more sulfur-containing wastewater. Sulphide in wastewater has certain toxic, corrosive and foul odor. Sulfur and its compounds can be subdivided into active and inactive sulfur according to their corrosion resistance properties. Due to this kind of active sulphur itself has strong corrosion resistance, can be directly with other metal pipelines and other related devices produces chemical reaction, structure of normal use for wastewater will produce very big effect to its operation, caused great pollution to the environment, rather than the chemical properties of active sulphur is relatively stable, and it is not easy to direct reaction with the metal. Therefore, the wastewater containing sulfur dioxide in production and daily life must be timely and properly disposed of.
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. Wang Rongrong et al. [3] prepared biological activated carbon by using peanut shell as the main raw material under pyrolysis at 300℃. The adsorption effect of nitrate nitrogen on the surface pollutants of biological activated carbon was investigated by batch homogeneous equilibrium adsorption experiments. The experimental evidence shows that the pH value is an important factor affecting the adsorption of nitrate nitrogen on biological activated carbon, and the pH value<6 is conducive to the adsorption of nitrate nitrogen. When the initial concentration of the solution is higher, the content of the adsorbent of the biological activated carbon is higher, and the maximum content of the adsorbent can be as high as 40 mg/g under the adsorbent system of 800 mg/L.

Ji Xueqin et al. [4] studied the adsorption and mechanism of two groups of rice straw biochar prepared at different pyrolysis temperatures on organic dyes Sunset Yellow and Methylene Blue, and the study showed that the adsorption mechanism of the two dyes was significantly different. Yin Li et al. [5] prepared cow dung derived biochar under 600℃ hypoxia condition and studied its adsorption performance. The adsorption process was fast at first and then slow, and the adsorption equilibrium could be reached after 60 min. Ma Yanmei [14] 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/(mg·g), and the adsorption capacity was very large and the adsorption rate was high.

Physical adsorption has the following characteristics: (1) due to the small adsorption force, the middle of the chemical gas by physical adsorption of small molecules is relatively easy to quickly return to the side of the adsorption gas phase, that is, more easily "desorption"; (2) Generally speaking, the activation process of chemical adsorption may be completely natural and reversible, with almost no sudden chemical kinetic energy to directly activate these substances (even if only the practical need is very small), and the activation rate of adsorption and direct removal of these substances is very fast. That is, it can be considered with great certainty that a chemisorption interaction may occur directly once contact occurs between the adsorption binder and the activated substance; (3) all the physical adsorption chemical reaction absorption process are directly realized a chemical exothermic adsorption reaction, the physical adsorption process released by the "adsorption heat" is far less than any chemical solid adsorption of chemical heat, The heat of adsorption is much closer to the heat of chemical vaporization in the liquid state or the heat of chemical condensation in the solidification state of the physical adsorption mass. (4) for physical and chemical adsorption process is a kind of selective adsorption, or any kind of chemical solids are necessarily can direct any physical adsorption of a gas, only is the number of different things is that the physical adsorption (due to remove adsorbent is greater than the number of small physical adsorption absorption effect of no more than physical application value of practical application); (5) because the adsorption physical mechanical adsorption and chemical condensation are closely interrelated, it must be only when the adsorption temperature is far lower than the removal of adsorbents and substances as high as a boiling point.

Orange skin absorption technology belong to in physical adsorption process of a new type of biomass adsorption technology, it is considered to be a new kind of industrial wastewater treatment technology, compared with other traditional wastewater treatment technology, biomass adsorption technology is mainly embodied in the following advantages: (1) low energy consumption, less capital cost, simple management and disposal of the high efficiency; (2) This product has the function of reducing the emission of low-concentration pollutants; (3) Low requirements for operating environmental conditions;
(4) it can be desorbed and regenerated, and can be reused for many times; (5) raw materials are simple and easy to obtain; (6) renewable, simple steps; The price is low and the environment is friendly. The physical adsorption mechanism has been widely discussed in recent years. Because the specific surface of the activated carbon is composed of a number of micropores, the structure of the pore will directly affect the adsorption capacity, and can be used as the adsorption capacity of the medium pore and large pore channels. However, at the same time, because the activated carbon can display many different types of oxides, there is a selective chemical adsorption between them in the process of adsorption. When heavy metal ions are adsorbed from the air and transferred to the activated carbon, the heavy metal ions and compounds form corresponding chemical characteristics. The pH value of the solution, specific surface area and pore structure of the activated carbon are the main influencing factors. Therefore, the adsorption of heavy metal ions by activated carbon is usually the result of physical and chemical adsorption and the combination of the two.

2. The experiment part

2.1. Main instruments and reagents
Reagents: p-amino-N, N-diethylaniline sulfate (analytical pure); Concentrated sulfuric acid (analytically pure) ferric chloride; Sodium hydroxide (analytically pure); Potassium hydroxide (analytically pure); Sodium chloride (analytically pure); Sodium sulfide crystal (Na₂S·9H₂O); Sodium acetate crystal (analytically pure) (this is blue + pink)

Equipment: 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 were 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. Preparation of ferric chloride solution. The iron trichloride was accurately named in an electronic balance and 100 g was extracted. Then the iron trichloride was put into a small beaker, and an appropriate amount of neutral distilled water was put into a magnetic pot or a magnetic stirrer with high pressure and rapid heating for repeated stirring. Repeated again after blending stir until completely dissolved and can quickly dissolve and then transferred to another to 100 mL of medium capacity in small glass bottle, ferric chloride and a moderate amount of distilled water to water in a beaker rinsed several times, respectively, the remaining liquid in a volumetric flask, finally the capacity to 100 mL of water, configured to 1000 g/L of ferric chloride solution.

2.2.3. Preparation of p-amino-N, N-diethylaniline sulfate solution. 1.5g p-amino-N, N-diethylaniline sulfate was accurately weighed with an electronic balance and put into a 100 mL beaker. Water was added to a magnetic stirrer heated at high temperature to stir and dissolve evenly. The water was completely poured into a 100 mL glass bottle with a small amount of water for several times, and then the beaker was rinsed clean with distilled water. Pour the remaining liquid into a volumetric flask and add water to a constant volume of 100 mL. Pour 50 mL of 1 mol/L sulfuric acid solution and 50 mL of the above solution into a 100 mL volumetric flask, shake well and put in a dark place for use. (This is blue + pink)
3. Results and discussion

3.1. Influence of pH on adsorption effect

PH is one of the important factors affecting the adsorption effect of wastewater. Take a number of 100 mL beakers, take 50 mL of simulated waste water with a measuring cylinder, and pour it into each beaker. Marked as No. 1, 2, 3, 4, 5, 6, 7 and added 0.01 mol/L of sulfuric acid solution to each beaker, controlled as a series of pH gradients of 4, 5, 6, 7, 8, 9, 10, and added 1 g of orange peel powder to each beaker. After standing for 6 h, 10 mL of supernatant was taken, 0.2 mL of chromogener was added, and stood for 20 min. The absorbance at different pH was measured, as shown in Table 1, and the experimental results were shown in Figure 1.

| pH  | Absorbance | Absorption rate (%) |
|-----|------------|---------------------|
| 4   | 2.748      | 41.94               |
| 5   | 1.454      | 69.28               |
| 6   | 0.843      | 82.19               |
| 7   | 0.723      | 84.72               |
| 8   | 0.754      | 84.07               |
| 9   | 0.927      | 80.41               |
| 10  | 1.235      | 73.91               |

Instructions
Original absorbance of simulated sulfur-containing wastewater is 4.733.

The experiment shows that there is a linear relationship between the adsorption rate of orange peel and the pH value when the pH is 4. When pH increased from 4 to 7, the absorbance of the wastewater decreased from 2.748 to 0.723, and the sulfur adsorption rate of the wastewater increased from 41.94% to 84.72%, showing an upward trend. When pH > 7, the absorbance of wastewater increases from 0.723 to 1.235 in the process of increasing the pH value of wastewater from 7 to 11, and the sulfur adsorption rate of wastewater decreases from 84.72% to 73.91%, showing a downward trend. This is because the higher the pH value, the more hydroxide ions, hydroxide ions and sulfur ions have a competitive relationship in the adsorption process. As hydroxide ions increase, the adsorption capacity of sulfur ions decreases, so the adsorption rate decreases and the adsorption capacity becomes weak. The adsorption rate of orange peel reached the maximum when the pH value was 7, because the pH value had an impact on the form of sulfur ions, so it also had an impact on the adsorption results.
3.2. Influence of chemical modifier on adsorption effect

Add 1 g orange peel powder to each beaker, then add 1 mL of different chemical modifiers NaCl, NaOH, C₂H₅OH, and H₂SO₄ with a concentration of 0.5 mol/L to the four beakers respectively. No modifier is added to one beaker. Mix well and label. After standing for 6 h, 10 mL supernate was taken and 0.2 mL chromogen was added. After standing for 20 min, the absorbance under different modifiers was measured, as shown in Table 2, and the experimental results were shown in Figure 2.

### Table 2. Solution absorbance under different chemical modifiers.

| Modifier | Untreated | NaCl | NaOH | C₂H₅OH | H₂SO₄ |
|----------|-----------|------|------|--------|-------|
| Absorbance | 0.631 | 0.297 | 0.701 | 0.458 | 0.427 |
| Absorption rate (%) | 863.67 | 93.72 | 85.19 | 90.32 | 90.98 |

Instructions: Original absorbance of simulated sulfur-containing wastewater is 4.733.

Figure 2. Influence of modifier on the adsorption effect of orange peel.

The experimental results showed that the adsorption and effect of orange peel were different when different chemical modifiers were added in water. When the modifiers added in water were NaCl, C₂H₅OH, and H₂SO₄, the adsorption of orange peel had a positive effect and the adsorption rate increased. The addition of NaOH has a negative effect on the adsorption function, causing an inhibiting effect and a slight decrease in the adsorption rate, which is because the strong alkalinity of NaOH will break the structure of the adsorbent. In conclusion, NaCl has the best modification effect on orange peel adsorbent.

3.3. Structural characterization of orange peel

Wet 0.1 g of orange peel powder with drying time of 10 h, put the adsorbed orange peel powder into the oven and dry it to constant weight, then weigh 0.1 g of orange peel powder after use. The two materials were observed with a scanning electron microscope (SEM) after gold-spraying, and the results are shown in Figure 3 (a) and Figure 3 (b). Is selected as modifier.
Figure 3. SEM image of orange peel powder.

As can be seen from Fig. 3 (a), the surface of the orange peel presents a bumpy structure, with a large number of adsorption gaps and tiny pores, which has a very positive significance for the adsorption reaction. As can be seen from Figure 3 (b), part of the surface of orange peel powder becomes smooth after drying, the adsorption space is relatively reduced, and the adsorption capacity is weakened. However, there are still large adsorption pores on the surface, which still has a certain adsorption capacity.

4. Conclusion
The experimental results show that the orange peel adsorbent has a good effect on the treatment of wastewater containing sulfur. The adsorption rate changed with the change of the pH value of the adsorption environment, and the highest adsorption rate was obtained when the pH value was 7. There are significant differences in the adsorption effect of modified orange peel with different modifiers, and the adsorption effect is better with sodium chloride.

References
[1] Zhu Qiuping, Zhang Meng, Ge Gang, Feng Bing, Wang Qipei, Yao Na. Journal of Nanchang University (Engineering Science), 2020, 42(01): 16-22. (In Chinese)
[2] Wei S L. Review on the treatment and recycling of sulphide waste liquid abroad [J]. Leather Science and Technology, 1983(08): 36-39. (In Chinese)
[3] Rongrong Wang, Xin Lai, Jie Li, Hong Chang, Guilong Zhang. Journal of Agro-Environment Science, 2016, 35(09): 1727-1734. (In Chinese)
[4] Ji Xueqin, Lv Li, Chen Fen, Yang Chunping. Adsorption of organic dyes by straw biochar and its mechanism [J]. Acta Scientiae Circumstantiae, 2016, 36(05): 1648-1654.

[5] Li Yin, Haiyan Zou, Tao Fei, Xiaoyu Xiao, Hui Zhang, Zhongshi He. Adsorption kinetics and thermodynamics of biochar from cow dung on methyl violet in water [J]. Environmental Chemistry, 2017, 36(12): 2650-2657.