Research on the properties of modified water treatment agent for white pulp of pomelo peel

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Abstract. A water treatment agent for white pulp of pomelo peel was developed using commercial Pomelo as raw material, which laid a foundation for the further development and utilization of Pomelo Peel. Indeed adsorption Cu$^{2+}$, Fe$^{3+}$ as an index, the effect of modification on the basis of single factor experiment research on the use of sodium hydroxide concentration, pH, adsorbent, adsorption process the time required to the influence of factors such as the adsorption effect, orthogonal experiment as the main experimental method to determine the modification of pomelo peel white pulp desorption process using the adsorption effect of again. The results showed that the modified water treatment agent had higher adsorption efficiency for Cu$^{2+}$ and Fe$^{3+}$ in water, and had favourable reabsorption ability, it can be reused and has higher adsorption efficiency. The developed water treatment agent for white pulp of Pomelo Peel has laid a foundation for the adsorption of Cu$^{2+}$ and Fe$^{3+}$ in water, the efficient utilization of white pulp of pomelo peel and the invention of production equipment.

1. Introduction
Pomelo belongs to rutaceae plants, the main producing area is southern China. POMELO is a kind of fruit rich in vitamins needed by the human body, but the white pulp which is discarded after eating Pomelo can not be fully utilized, causing a lot of waste. The quality of Pomelo peel accounts for about 20% of the weight of pomelo, the annual yield of grapefruit in our country is about two million tons, and the resulting discarded pomelo peel has a mass of about four hundred thousand tons. [1-2] The main components of pomelo peel are pectin, cellulose, lignin, etc. [3] These substances react with metals, such as complexation, which can be used for the treatment of heavy metal liquid waste. Through appropriate chemical modification, the adsorption performance of grapefruit peel can be further improved. [4-6] The modification can improve the pore structure of the daughter skin and increase the active functional groups, thereby enhancing the adsorption activity and the adsorption performance. [7-11]

Currently lack of fresh water has become a worldwide primary problem, and the increase in sewage discharge has exacerbated the water shortage situation. [12-14] For example: Cu$^{2+}$ sewage has caused the content of Cu$^{2+}$ in the soil to exceed the standard. This situation has greatly affected the national economy. [15] Water treatment agent plays an important role in the purification of sewage. [16-18] The 2007 statistical bulletin published by the Organisation for Economic Co-operation and Development (OECD) pointed out that the development of water use in more than 30 countries has increased. In 25
years, the total population of these 30 countries has increased by 20% , Irrigated area increased by 5%, public water consumption increased by 29%, these data also determine the increasing demand for water. [19-21]

In this experiment, sodium hydroxide was used to modify the grapefruit peel, as a Cu\(^{2+}\) ion adsorbent in water, which provided a reference for the treatment of Cu\(^{2+}\) pollution. Using commercially available fresh and mature grapefruit as raw materials, the research on the adsorption and repeated adsorption of Cu\(^{2+}\) in water after partial modification treatment of grapefruit white flesh was determined. Through the single factor test and orthogonal reaction test, the adsorption capacity and repeated absorption capacity of the modified pomelo skin white crumb were determined.

2. Material and Craftsmanship

2.1. Materials and reagents
Materials: The peel of fresh commercially available white pomelo is selected, cut into pieces, dried at 70 °C to constant weight, and then crushed it. The crushed citron peel is passed through a 60-mesh sieve to leave powder and placed in a dry box for use. [22]

Reagents: Sodium hydroxide, absolute ethanol, anhydrous copper sulfate, ferric chloride, sodium chloride and other reagents used in the experiment are all commercially available analytical pure.

2.2. Instruments and Equipment
GZX – 9070MBE type electric blast drying oven (Shanghai Boxun Industrial Co., Ltd. Medical Equipment Factory); LD210-2 electronic balance (Shenyang Longteng Electronics Co., Ltd.); digital precision pH meter (Shanghai Precision Scientific Instrument Co., Ltd.); A3 atomic absorption Spectrophotometer (Beijing General Analysis General Instrument Co., Ltd.); SHZ-DIII Yuhua brand circulating water vacuum pump (Gongyi Yuhua Instrument Co., Ltd.); TG16-WS centrifuge (Hunan Xiangyi Laboratory Instrument Development Co., Ltd.); JJ-1 precision booster electric mixer (Shanghai Pudong Physical Optical Instrument Factory); Chinese herbal medicine grinder (Tianjin Taosite Instrument Co., Ltd.).

3. Experimental process

3.1. Selection of grapefruit
Choose fresh grapefruit in season. After peeling, remove the yellow outer skin and then soak in deionized water to prevent the influence of external dirt.

3.2. Pretreatment
The flesh part of white grapefruit skin after peeling placed in a thermostatic oven at 70 °C, dry to a constant weight (about 18 h), use a Chinese herbal medicine grinder to crush the citron peel white flakes, and then pulverize through a 60 mesh sieve, Then weigh and label the spare.

3.3. Modification
Take 70 g of sieved pomelo peel powder, add 100 ml of absolute ethanol and 100 ml of 0.3 mol/L sodium hydroxide solution and stir with an electric stirrer for 1 h, then perform suction filtration to a colorless transparent gelatinous state and place it at 60 degrees Celsius Constant temperature oven drying.

3.4. Adsorption test and spectroscopic data inspection
Add 1 g/L CuSO\(_4\) solution to the modified pomelo peel powder, respectively, after 35 minutes of treatment, filter and take the supernatant, centrifuge at 10400 r/min for 10 minutes using a high-speed centrifuge, and take the supernatant to measure with an atomic spectrophotometer Absorption peak at 452 nm.
3.5. Repeated absorption treatment
Soak the treated citron peel powder in 20 g/L sodium chloride solution for 40 min to desorption, and then suction filter it with deionized water for 3 to 5 times for spare.

3.6. Repeated adsorption test and repeated spectroscopic data inspection
Add 1 g/L of FeCl$_3$ solution to the treated citron peel powder, stir for 30 min and then filter to take the supernatant, and then use a high-speed centrifuge to centrifuge at 10400 r/min for 10 min to take the supernatant for use. An atomic spectrophotometer measures the absorption peak at 508 nm.

4. Results and analysis

4.1. Single factor test and results

4.1.1. Influence of concentration of modified solution. At an initial concentration of Cu$^{2+}$ of 1 g/L, an adsorption time of 35 min, a system pH of 8, and an adsorbent dosage of 7 g, the effect of modified grapefruit peel powder modified at different concentrations of sodium hydroxide on its adsorption capacity was investigated. As shown in the results of Figure 1, the removal rate of the adsorbent from the concentration of sodium hydroxide from 0.1 mol/L to 0.3 mol/L is significantly improved when the modification, and the removal rate of the adsorbent when the concentration of sodium hydroxide exceeds 0.3 mol/L There is no obvious increase, but there is a downward trend as the concentration continues to increase. In this case, the high concentration of sodium hydroxide has destroyed the original structure of the grapefruit peel powder to a certain extent.

![Fig.1 relationship between Cu$^{2+}$ removal rate and concentration of modified solution](image_url)

4.1.2. Effect of system Ph. When the amount of adsorbent used is 7 g, the initial concentration of Cu$^{2+}$ in simulated wastewater is 1 g/L, and the adsorption time is 35 min, the system pH is 1 to 11, respectively. The purpose is to determine the effect of the pH value of the adsorbent on the adsorption
capacity of the adsorbent under certain conditions. As shown in the results of Figure 2, when the pH value is between 1 and 7, the removal rate increases significantly. The analysis shows that there is a competition for adsorption between H$^+$ and Cu$^{2+}$ in the acidic system. When the pH is between 7 and 8, it tends to be stable. After the pH value is greater than 8, the pH value continues to increase and the removal rate declines, because with the continuous increase of OH$^-$ in the system, it reacts with Cu$^{2+}$ to form a copper hydroxide blue precipitate, which is not conducive to the adsorption, so it is concluded that when the system pH=8, the Cu$^{2+}$ removal rate of the adsorbent reaches the maximum.

![Fig.2 Effect of pH value on Cu$^{2+}$ ion removal rate](image)

4.1.3. Effect of adsorbent usage on Cu$^{2+}$ removal rate. Under the condition that the initial concentration of Cu$^{2+}$ is 1 g/L, the adsorption time is 35 min, and the system pH is 8, the amount of adsorbent is 5 g to 10 g to examine its effect on the adsorption capacity. As shown in the results of Figure 3, when the dosage of adsorbent is from 5 g to 7 g, the removal rate increases significantly, but when the dosage of adsorbent is greater than 7 g, the removal rate does not increase significantly and approaches a steady state, which is due to the adsorption in the system. Saturated so as to form a dynamic balance. Therefore, the adsorption effect is the best when the amount of adsorbent is 7 g.
4.1.4. Effect of adsorption time. The amount of adsorbent used was 7 g, the initial concentration of Cu$^{2+}$ in the simulated sewage was 1 g/L, the system pH was 8, and the adsorption time was 5 min, 15 min, 25 min, 35 min, and 45 min, respectively. The purpose was to investigate the influence of the change of adsorbent adsorption time on the adsorption capacity of adsorbent under certain conditions. As shown in the results of Fig. 4, as the adsorption time of the adsorbent increases, the removal rate of Cu$^{2+}$ continues to increase, but the adsorption rate continues to decrease. When the adsorption time reaches 35 min, the removal rate of Cu$^{2+}$ reaches the maximum, and then the removal of Cu$^{2+}$ The rate maintains a dynamic equilibrium, and 35 min is the optimal adsorption time for Cu$^{2+}$. 

![Fig.3 effect of adsorbent dosage on copper Cu$^{2+}$ ion removal rate](image-url)
4.2. Orthogonal test

4.2.1. The relationship between the concentration of the modified solution, the amount of adsorbent used, the pH value of the system and the adsorption time. Through the orthogonal test, the influence of the concentration of the modified solution, the amount of adsorbent used, the pH value of the system and the adsorption time on Fe$^{3+}$ adsorption was determined.

Test factors: Modified solution concentration (A), adsorbent usage (B), system pH (C) and adsorption time (D), this test mainly considers the influence of these four factors, each of which sets three Level (see Table 1), using L9 (3$^4$) orthogonal combination design to determine the most suitable factors for the maximum desorption and adsorption (see Table 2)

![Fig.4](image)

**Fig.4** The influence of adsorption time of copper Cu$^{2+}$ ion removal rate

| Level | Element | A:(mol/L) | B:(g) | C:(pH) | D:(min) |
|-------|---------|-----------|-------|--------|---------|
| 1     |         | 0.2       | 6     | 6      | 30      |
| 2     |         | 0.3       | 7     | 7      | 35      |
| 3     |         | 0.4       | 8     | 8      | 40      |

*Table 1 4 factor 3 level*
Table 2. Orthogonal tests and results

| A:(mol/L) | B:(g) | C:(pH) | D:(min) | Horizontal combination | Cu\(^{2+}\) removal rate |
|-----------|-------|--------|---------|------------------------|---------------------------|
| 1         | 0.2   | 6      | 6       | 30                     | A\(_1\)B\(_1\)C\(_1\)D\(_1\) | 38.45%                    |
| 2         | 0.2   | 7      | 7       | 35                     | A\(_1\)B\(_2\)C\(_2\)D\(_2\) | 42.83%                    |
| 3         | 0.2   | 8      | 8       | 40                     | A\(_1\)B\(_3\)C\(_3\)D\(_3\) | 56.66%                    |
| 4         | 0.3   | 6      | 7       | 40                     | A\(_2\)B\(_1\)C\(_2\)D\(_2\) | 59.89%                    |
| 5         | 0.3   | 7      | 8       | 30                     | A\(_2\)B\(_3\)C\(_1\)D\(_1\) | 64.94%                    |
| 6         | 0.3   | 8      | 6       | 35                     | A\(_3\)B\(_1\)C\(_3\)D\(_3\) | 62.73%                    |
| 7         | 0.4   | 6      | 8       | 35                     | A\(_2\)B\(_3\)C\(_1\)D\(_2\) | 62.17%                    |
| 8         | 0.4   | 7      | 6       | 40                     | A\(_3\)B\(_1\)C\(_3\)D\(_3\) | 62.53%                    |
| 9         | 0.4   | 8      | 7       | 30                     | A\(_3\)B\(_1\)C\(_3\)D\(_1\) | 63.69%                    |

It can be seen from Table 6 that the influence of the four factors on the adsorption amount after desorption is: A>B>C>D, that is, the concentration of the modified solution>used amount of adsorbent>pH value>adsorption time, and the optimal combination is: A\(_1\)B\(_3\)C\(_3\)D\(_2\). According to the above conditions for the experimental verification of the adsorption capacity, the scheme A\(_3\)B\(_2\)C\(_3\)D\(_2\) was selected for three parallel tests. The Cu\(^{2+}\) removal rate of the scheme A\(_3\)B\(_2\)C\(_3\)D\(_2\) was measured to be 65.37%, and A\(_1\)B\(_3\)C\(_3\)D\(_2\) could be determined as the best scheme.

4.2.2. 3.2.2 The effect of the amount of desorbent adsorbent, the concentration of desorbent, the time of desorption and the time of adsorption

Through orthogonal experiments, the main factors affecting the adsorption of desorbed dose, desorbed solution concentration, desorbed time and adsorbed time on Fe\(^{3+}\) adsorption: the amount of desorbed adsorbent (A), the concentration of desorbed solution (B), the desorbed time (C) and the adsorption time (D), this experiment mainly investigated the influence of these four factors, each factor established three levels (see Table 3), using L9 (3\(^4\)) orthogonal combination design to determine the maximum desorption and adsorption reached the maximum Appropriate factors (see Table 4).

Table 3. 4 factor 3 level

| Level | A:(g) | B:(g/L) | C:(min) | D:(min) |
|-------|-------|---------|---------|---------|
| 1     | 5     | 15      | 30      | 20      |
| 2     | 7     | 20      | 40      | 30      |
| 3     | 9     | 25      | 50      | 40      |

Table 4. Orthogonal tests and results

| A:(g) | B:(g/L) | C:(min) | D:(min) | Horizontal combination | Fe\(^{3+}\) removal rate |
|-------|---------|---------|---------|------------------------|---------------------------|
| 1     | 5       | 15      | 30      | 20                     | A\(_1\)B\(_1\)C\(_1\)D\(_1\) | 47.62%                    |
| 2     | 5       | 20      | 40      | 30                     | A\(_1\)B\(_3\)C\(_3\)D\(_3\) | 53.66%                    |
| 3     | 5       | 25      | 50      | 40                     | A\(_3\)B\(_3\)C\(_3\)D\(_3\) | 58.47%                    |
| 4     | 7       | 15      | 40      | 40                     | A\(_2\)B\(_2\)C\(_2\)D\(_2\) | 59.89%                    |
| 5     | 7       | 20      | 50      | 20                     | A\(_2\)B\(_1\)C\(_1\)D\(_1\) | 63.84%                    |
| 6     | 7       | 25      | 30      | 30                     | A\(_3\)B\(_1\)C\(_3\)D\(_3\) | 61.24%                    |
| 7     | 9       | 15      | 50      | 30                     | A\(_3\)B\(_1\)C\(_3\)D\(_2\) | 61.97%                    |
| 8     | 9       | 20      | 30      | 40                     | A\(_3\)B\(_3\)C\(_3\)D\(_3\) | 62.36%                    |
| 9     | 9       | 25      | 40      | 20                     | A\(_3\)B\(_3\)C\(_3\)D\(_1\) | 62.96%                    |

It can be seen from Table 8 that the influence of the four factors on the adsorption amount after desorption is: A>B>C>D, that is, the amount of desorbed adsorbent>desorbed liquid
concentration>desorbed time>repeated adsorption time, and the optimal combination is: A₂B₂C₃D₁. According to the above conditions for the experimental verification of the adsorption capacity, the scheme A₂B₂C₃D₁ was selected for three parallel experiments. The Fe³⁺ removal rate of the scheme A₂B₂C₃D₃ was measured to be 63.84%, so that A₂B₂C₃D₁ was determined as the best scheme.

5. Conclusion
In this study, fresh commercially available white pomelo was used as a raw material, and its white flesh was chemically modified using chemical methods to determine the influencing factors of its modification conditions, the effects of its secondary utilization and the influencing conditions of external factors. In the single-factor experiment, the best modification conditions were determined by optical inspection: the amount of adsorbent was 7 g, the pH of the system was 8, the concentration of modified sodium hydroxide was 0.3 mol/L, and the adsorption time was 35 min. The removal rate of Cu²⁺ was 65.37%. In the orthogonal test, the effect of secondary utilization and the influence of external factors were determined by optical inspection to determine the optimal modification conditions. The removal rate of Fe³⁺ was 63.84%, and provided a new direction for the development of water treatment agents. This study laid the foundation for the efficient use of pomelo skin white flesh and the invention of production equipment.

References
[1] Tian Xiaoju. Research progress of comprehensive utilization of citron peel[J]. Beverage Industry, 2015, 18(04): 50-54.
[2] Bao Jinyong, Zhao Guojian, Yang Gongming. Current status and prospects of fruit peel utilization in my country [J]. Food Research and Development, 2005(06): 186-191.
[3] Wang Qiong, Fu Hongyuan, He Zhongming, Jiang Zhaohui, Wang Ping. Adsorption and removal of arsenic in water by FeCl₃ modified grapefruit peel[J]. Journal of Environmental Engineering, 2017, 11(04): 2137-2144.
[4] Zhen Baoqin. Study on the treatment of copper-containing wastewater by corncob[J]. Yunnan Chemical Industry, 2005(05): 23-25.
[5] Zhang Ying, Liang Yanqiu. Adsorption of Cu ion by yuzu peel powder[J]. Liaoning Chemical Industry, 2015, 44(02): 116-118.
[6] Wang Chuanling, Yu Min, Lan Yuqing. AlCl₃ modified grapefruit peel absorbs and removes chromium ions in water[J]. Shandong Chemical Industry, 2018, 47(16): 188-191.
[7] Hongyuan, Zeng Ling, Xie Zhihao. Adsorption and removal of hexavalent chromium and arsenic in water by grapefruit peel[J]. Environmental Engineering, 2016, 34(S1): 299-302.
[8] Guo Yanhua, Liu Yanxiang, Liu Li, Wu Wangxi, Zhang Yuanfang. Preparation of yuzu peel biosorbent and its application for the adsorption of heavy metal lead ions [J]. Journal of Jianghan University (Natural Science Edition), 2017, 45(05): 411-417.
[9] Zhou Yin, Hu Changwei, Li Jianlong. Study on the mechanism of grapefruit peel adsorption of methylene blue in aqueous solution [J]. Environmental Science Research, 2008(05): 49-54.
[10] Zhang Zhigang. Study on the adsorption performance of grapefruit peel to hexavalent chromium in water[J]. Journal of Fujian Institute of Technology, 2014, 12(06): 557-561.
[11] Yu Rui, Hu Xin, Ding Zhumong, Zhang Yufeng, Yin Daqiang. Adsorption of Cr₃⁺, Cu₂⁺ and Ni²⁺ on peanut shell, soybean shell and grapefruit peel[J]. Environmental Pollution And Prevention, 2013, 35(09): 43-48+53.
[12] Shannon Mark A, Bohn Paul W, Elimelech Menachem, Georgiadis John G, Mariñas Benito J, Mayes Anne M. Science and technology for water purification in the coming decades.[J]. Nature, 2008, 452(7185).
[13] Schwarzenbach René P, Escher Beate I, Fenner Kathrin, Hofstetter Thomas B, Johnson C, Annette von Gunten Urs, Wehrli Bernhard. The challenge of micropollutants in aquatic systems.[J]. Science, 2006, 313(5790).
[13] Yu Wei, Huang Mu, Li Aimin, Yang Hu. Research on multifunctional natural polymer water treatment agent[J]. Environmental Chemistry, 2018, 37(06): 1293-1310.
[14] Huang Huijuan. Grafted polypropylene nonwoven fabric adsorption and electrodeionization technology combined to treat heavy metal ion wastewater [D]. Suzhou University, 2016.
[15] Huang Mu. Preparation of flocculation/bacteriostatic dual-functional starch modified flocculant and its water treatment performance [D]. Nanjing University, 2016.
[16] METCALF I, EDDY H. Wastewater Engineering Treatment and Reuse 4th Edition [M]. Beijing: Tsinghua University Press, 2003.
[17] Zhang Lizhu, Zhao Lei. Water treatment agent: formulation·preparation·application [M]. Beijing: Chemical Industry Press, 2010.
[18] Song Xutong. International comparison of sustainable water development [J]. China Water Supply and Drainage, 2008, 24(24): 5-8.
[19] Song Xutong. Analysis of urban water development and efficiency in my country [J]. China Water Resources, 2005(13): 40-43.
[20] Song Xutong, Xu Junyi. Analysis of urban water development and efficiency in my country [J]. Construction Science and Technology, 2004(06): 40-41.
[21] Chen Jie. Study on the adsorption of modified grapefruit peel powder to copper ions in wastewater[J]. Chemical Engineering Management, 2017(11): 222.