Treatment of High Concentration Organic Wastewater by Multi-step Flocculation and Adsorption

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Abstract. Acrylic fiber wastewater from acrylic plant was used as feedstock, the feasibility of treatment high concentration organic wastewater by combination method of flocculation and adsorption was investigated through single factor experiment and orthogonal experiment. Experiment results showed that positive ion polyacrylamide presented the best flocculation effect in the experiment of treatment acrylic fiber wastewater by single flocculant. The flocculating effect was improved remarkably by multi-step flocculation and adsorption, and the removal effect of turbidity and COD was increased. The optimum combination order was positive ion polyacrylamide, the polymerization aluminum chloride and the shell polyose, and the removal efficiency of turbidity and COD can reach above 90% and 70.5% after treatment acrylic fiber wastewater by the combination of flocculation and adsorption, respectively.

1. Introduction

Acrylic fiber wastewater contains a large number of organic pollutants, mainly for the remaining raw materials in each section of the production process and various newly synthesized substances[1-2]. Therefore, acrylic fiber wastewater also has high concentration wastewater and high ammonia nitrogen wastewater. The typical characteristics of wastewater, such as high toxicity wastewater and other types of wastewater, were recognized as one of the refractory waste water in the world[3,4]. At present, the treatment methods of acrylic fiber wastewater mainly include[5-9]: flocculation sedimentation, membrane separation, Fenton oxidation, ozone oxidation, internal electrolysis, catalytic degradation and biochemical treatment. Although some achievements have been made in the treatment of acrylic fiber wastewater, the turbidity and COD$_{cr}$ of the treated wastewater still cannot reach GB 8978-1996 "Comprehensive Wastewater Discharge" The requirements of the first-class standard of the Standard for Release[10].

In this paper, the flocculation and adsorption experiments of wastewater from acrylic fibre chemical plant of Fushun Petrochemical Company were carried out. The performances of several flocculants were compared and combined with adsorption. It was hoped to find out a flocculant combination with wide application range, good treatment effect, low dosage and economical and practical use. This study had certain practical significance for promoting the application of flocculation-adsorption method in organic wastewater treatment.

2. Materials and methods

2.1. Experimental materials and equipment
The wastewater used in this experiment was collected from the wastewater purification workshop of Acrylic Fiber Chemical Plant of Fushun Petrochemical Company. The designed influent water quality was pH 6.3-7, SS 140 mg/L, COD$_{cr}$ 1908.6 mg/L and turbidity 84.

The experimental drugs include: ployaluminium chloride (PAC), ployaluminium ferric chloride (PFS) and cationic polyacrylamide (CPAM), which were supplied by Fushun Acrylic Fiber Factory; chitosan, sodium hydroxide, hydrochloric acid, activated carbon, potassium dichromate, ammonium ferrous sulfate, mercury sulfate, and silver sulfate, which were all analytical purities, purchased from Guoyao Pharmaceutical Group Pharmaceutical Co., Ltd.

2.2. Analytical Method
COD$_{cr}$ of wastewater was determined according to the New Standard for the Determination of Chemical Oxygen Demand of Water Quality (HJ828-2017), and turbidity of wastewater was determined by spectrophotometry according to GB13200-1991.

2.3. Experimental Method

2.3.1. Single Flocculant Treatment of Acrylic Fiber Wastewater
The pH value of water sample was adjusted by dilute hydrochloric acid and sodium hydroxide solution, and different amounts of inorganic flocculants such as ployaluminium chloride, ployaluminium ferric chloride, cationic polyacrylamide and chitosan were added. Fast stirring (150 r/min) for a certain time, then slow stirring (60 r/min) for a certain time, so as to appear a good alum, standing until obvious stratification, take the supernatant, determine the COD, turbidity of the treated water. Then the removal efficiencies were calculated, and the effects of pH value, dosage and stirring time on flocculation were investigated.

2.3.2. Multistage Flocculation and Adsorption Treatment of Acrylic Fiber Wastewater
A single flocculant was used to treat acrylic fibre wastewater. The flocculant with good flocculation effect was screened out, and then the wastewater treatment experiment was carried out by combining the flocculant with the adsorption. 1000 mL water sample was put in stirrer, each flocculant was added in beaker under suitable conditions. After flocculation, settle down statically. Take supernatant and inject it into adsorption column composed of activated carbon. Collect the adsorbed water sample and determine its index. This was a one-step flocculation adsorption experiment. On this basis, flocculate and adsorb the water sample again and measure it. Various indicators were compared.

3. Results and discussion

3.1. Single Factor Experiment
Ployaluminium chloride was used to treat acrylic fiber wastewater, with the pH value of 7.5 and the dosage of 700 mg/L. When stirring for 25 minutes, the treatment efficiency was the highest and the flocculation effect was the best. The turbidity and COD removal rates were 82.1% and 34.8% respectively, and the flocculation condition and treatment effect were slightly better than that of ployaluminium ferric chloride. The optimum conditions for treating acrylic wastewater with cationic polyacrylamide were pH 6.8, dosage 6 mg/L and stirring time 10 min. At this time, the floc was large and dense, and the flocculation effect and treatment effect were very good. The optimum conditions for treating acrylic fiber wastewater with chitosan were pH 5.2, dosage 2700 mg/L and stirring time 15 minutes. The flocculation effect was the best, and the removal efficiency of each index can reach more than 30%.

3.2. Multi-step Flocculation and Adsorption Experiment
A single flocculation experiment shows that cationic polyacrylamide was the best flocculant in the four flocculants, the maximum COD removal rate can reach more than 40%, the turbidity removal
effect was also obvious, the floc produced by flocculation was large and easy to settle; next was chitosan, the maximum COD removal rate was close to 40%, but the flocculation effect of chitosan was not ideal and the floc was unstable. It was easy to float on the surface of water samples; inorganic flocculants ployaluminium chloride and ployaluminium ferric chloride were relatively weak, but ployaluminium chloride was slightly better than ployaluminium ferric chloride, so ployaluminium chloride was used as inorganic macromolecule flocculant in the subsequent multi-step flocculation adsorption. Acrylic fiber wastewater was treated by multi-step flocculation and adsorption process. The experimental results were shown in Table 1.

Table 1 Effect of Flocculation and Adsorption Step-by-Step Treatment

| Serial number | Flocculant/ Adsorbent | Turbidity removal rate (%) | Effluent CODcr(mg/L) | CODcr Removal rate (%) |
|---------------|-----------------------|---------------------------|----------------------|------------------------|
| 1             | PAC                   | 82.6                      | 1355.4               | 30.5                   |
| 2             | Activated carbon      | 89.6                      | 984.6                | 48.3                   |
| 3             | Activated carbon      | 91.6                      | 952.3                | 50.1                   |
| 4             | Chitosan              | 93.5                      | 801.8                | 58.3                   |
| 5             | Activated carbon      | 97.1                      | 686.8                | 64.8                   |

From Table 1, it can be seen that the adsorption after each flocculation was very effective for the removal of organic matter, and the COD removal rate increases gradually, which also shows that this method can indeed improve the flocculation effect and the removal efficiency of COD and turbidity. However, it was necessary to consider the regeneration of activated carbon after saturation. Otherwise, the saturation of activated carbon will reduce the adsorption efficiency, thus reducing the turbidity and COD removal efficiency, not only failing to achieve the purpose of removal, but also increasing the organic matter in water samples.

The flocculation and adsorption conditions suitable for multi-step treatment of acrylic fiber wastewater were further explored. The experimental results were shown in Table 2.

Table 2 Effect of multi-step flocculation and adsorption treatment

| Order of addition | Turbidity removal rate (%) | CODcr Removal rate (%) |
|-------------------|---------------------------|------------------------|
| PAC+CPAM+Chitosan | 97.1                      | 70.5                   |
| PAC+Chitosan+CPAM | 94.6                      | 65.5                   |
| CPAM+PAC+Chitosan | 96.1                      | 58.6                   |
| CPAM+Chitosan+PAC | 92.1                      | 63.3                   |
| Chitosan+PAC+CPAM | 95.7                      | 61.0                   |
| Chitosan+CPAM+PAC | 93.5                      | 57.2                   |

The order of flocculant dosage will change the effect of flocculation and adsorption. Although the three flocculants were still used to treat acrylic wastewater, the effect and flocculation state were different because of the different order of flocculant dosage. From the data in Table 2, it can be seen that the removal efficiency of each combination was much better than that of single flocculation, especially after activated carbon adsorption, the removal efficiency of organic matter was obviously improved, the turbidity removal rate was above 90%, and the COD removal rate was also above 57%. The best combination of PAC+CPAM+chitosan in the treatment of acrylic fiber wastewater by multi-step flocculation-adsorption process has good flocculation effect. The concentration of COD was reduced to 580.4 mg/l, and the removal rate reaches 70.5%. The organic matter in the wastewater was obviously removed, and the turbidity was also obviously removed.

Multi-step flocculation and adsorption were better than single flocculation in treating wastewater from acrylic fibre process. The floc alum produced was larger, the amount was larger, the sedimentation was faster and the water quality was clarified. Although the multi-step flocculation-adsorption process can achieve better removal effect for high concentration organic wastewater, there were many factors affecting the experiment. Various components and states of water samples may change after each step of flocculation-adsorption. Therefore, orthogonal experiments were designed to determine the effect of pH value and dosage on the experiment in the actual
multi-step flocculation-adsorption process. The experimental results were shown in Table 3.

| Number | Factor | PAC (A) | CPAM (B) | Chitosan (C) | COD Removal rate % |
|--------|--------|---------|----------|--------------|---------------------|
| 1      | 6.7    | 6.8     | 5.2      | 66.5         |
| 2      | 6.7    | 7.4     | 6.6      | 63.2         |
| 3      | 6.7    | 8.3     | 7.5      | 63.7         |
| 4      | 7.5    | 6.8     | 6.6      | 68.4         |
| 5      | 7.5    | 7.4     | 7.5      | 69.2         |
| 6      | 7.5    | 8.3     | 5.2      | 70.3         |
| 7      | 8.3    | 6.8     | 7.5      | 64.5         |
| 8      | 8.3    | 7.4     | 5.2      | 63.9         |
| 9      | 8.3    | 8.3     | 6.6      | 58.7         |
| K1     | 193.4  | 199.4   | 200.7    |              |
| K2     | 207.9  | 196.3   | 190.6    |              |
| k 3    | 187.1  | 192.7   | 197.4    |              |
| K1     | 64.5   | 66.4    | 66.9     |              |
| K2     | 69.3   | 65.4    | 63.5     |              |
| k 3    | 62.5   | 65.2    | 65.8     |              |
| Gradation R | 6.8 | 2.2     | 3.4      |              |
| Excellent level | 2 | 1       | 1        |              |

From the orthogonal experimental results of the pH values of each flocculant, it can be concluded that the optimum pH values of the actual multi-step flocculation adsorption process were PAC 7.5, CPAM 6.8 and chitosan 5.2, which were consistent with the optimum pH values determined by single factor experiments.

From Table 4, it can be seen that the orthogonal experiment results were basically the same as the single factor experiment results. The dosage of polyaluminium chloride and cationic polyacrylamide has not changed, 700 mg/l and 6 mg/L respectively. However, the dosage of chitosan has decreased to 2250 mg/L, which indicates that with the multi-step experiment, each flocculation and adsorption has a certain change in the water sample solution itself. The optimum conditions of the flocculant to be added after chemical treatment have changed. Therefore, the optimum conditions for the final multi-step flocculation adsorption test were as follows: the dosage of polyaluminium chloride was 700 mg/L, the pH value was 7.5; the dosage of cationic polyacrylamide was 6 mg/L, the pH value was 6.8; the dosage of chitosan was 2250 mg/L, and the pH value was 5.3.
4. Conclusion

Single flocculant treatment of acrylic fiber process wastewater shows that the organic polymer flocculent treatment effect was better than other flocculants, that was, cationic polyacrylamide flocculation effect was the best. The combination of flocculation process and adsorption process can significantly improve the single flocculation effect. The best combination sequence of multi-step flocculation was cationic polyacrylamide, polyaluminium chloride and chitosan. The combination of flocculation and adsorption was used to treat acrylic fiber wastewater. Its removal effect was much better than that of flocculation and adsorption alone. At the same time, the cost of flocculation and adsorption method was low, and it was easy to operate.

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