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Pharmaceutical Wastewater Treatment Based on Mathematical Model

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The purpose of this paper is to solve the problem of the waste water produced by pharmaceutical industry. However, the general biochemical treatment system is difficult to meet its processing requirements. As the water intake of regulating tank fluctuates greatly, the amount of coagulant is often added according to the experience in the coagulation pretreatment of pharmaceutical waste water, which makes the quality of coagulation effluent unstable. Based on mathematical model, the waste water treatment process of pharmaceutical factory is taken as an example, while the effect of coagulation as pretreatment process on pharmaceutical waste water treatment is analyzed. Meanwhile, a mathematical model is established to judge the dosage of coagulant to prevent water quality fluctuation of coagulation effluent. The experiment ensures that the effluent quality is stable within a range and reduces the impact on subsequent biochemical systems. The results show that the coagulation effect of waste water with high CODcr and high turbidity is greater than that of low load and low turbidity waste water. In addition, coagulation has a fairly good removal effect for turbidity. Based on the above findings, we concluded that the PAC dosage calculated by the model can stabilize the CODcr value of the condensate effluent in the 1600mg/L-1800mg/L range, and complete the stable mission of the effluent CODcr index.

1. Introduction

The pharmaceutical industry has developed rapidly in the past few decades. It has not only brought great economic benefits, but also caused serious environmental pollution. Pharmaceutical waste water has the characteristics of complex pollutant composition, large impact load, high antibiotic content, high chroma and poor biodegradability (Qian et al., 2015). Among all kinds of industrial waste water, pharmaceutical waste water is a serious problem that is difficult to be treated. The environmental pollution caused by it is far more harmful than other industrial waste water (Sirtori et al., 2015).

With the increasingly prominent environmental problems in our country, the state is becoming more and stricter with pollution discharge from enterprises (Huang et al., 2015). *The Standard for the Discharge of Water Pollutants in the Pharmaceutical Industry* was formally implemented in July 2010, which is a standard document in the pharmaceutical industry. The implementation of the new standards covers all the pharmaceutical industry and classification, including extraction, fermentation, bio-engineering, chemical synthesis and drugs. From the content point of view, the formulation of major pollutants emission targets is more stringent. Among them, the emission index of the dichromate index (CODcr) was lowered from 150mg/L to 120mg/L when it was first consulted in 2007. At present, the treatment technology of pharmaceutical waste water includes physical, chemical, biochemical and combined processes (Liu, et al., 2015). Coagulation treatment is a common sewage pretreatment process. The principle is to add chemicals to water to change the surface characteristics of colloidal particles, so that it is difficult to sink. Macromolecules and suspended matter will converge and sink through charge attraction, bridging adsorption, or net capture sweeping (Sarkar et al., 2015). The flocculated floc is then removed from the waste water by filtration and separation. As a pretreatment process, coagulation is usually applied to raw water containing more large molecules and suspended particles, or deeper turbid water. Generally, the removal rate of CODcr is very high, while the turbidity and chroma greatly decrease after coagulation pretreatment (Pal et al., 2016). In order to make the effluent of coagulation stability in a certain

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range and avoid the impact of water fluctuation on the subsequent, a mathematical model is established to solve these problems (Narayanasamy, et al., 2016). The CODcr value of the effluent CODcr also is stabilized within a certain interval after coagulation treatment. At the same time, the consumption of coagulant and flocculant is reduced (Mannina et al., 2016).

In order to study the operation and treatment of chemical synthetic pharmaceutical wastewater (Janus and Ulanicki, 2015.), the two-phase anaerobic membrane bioreactor is proposed (Bozkurt et al., 2015). On the basis of experimental data and ADM 1 and ASM 1 (Goyal and Sharma, 2016), a mathematical model of two phase anaerobic membrane bioreactor for treating chemical synthetic pharmaceutical wastewater is established (Pretel et al., 2016). The characteristics of wastewater water quality and model parameters are also determined (Fernández Bou et al., 2015). Through the study of the mathematical model (Zhao et al., 2015), the reaction process of two-phase anaerobic membrane bioreactor can be better understood (Ghafoori, 2015). In addition, the influence of various factors on the final treatment effect and the limiting steps of anaerobic digestion can also be studied in depth (Puchongkawarin et al., 2015). The experiment can also predict the influence of the influent water quality and water quantity on the treatment effect and the measures needed to adapt to these changes (Bustillo-Lecompte et al., 2016). If the reactor operation is not ideal, a solution through the model is used to ensure that the wastewater treatment plant is in the best running condition (Jian and Zhen, 2015), such as the improvement of water quality (Dionisi et al., 2016), reduction of energy consumption and amount of excess sludge (Shen et al., 2015).

2. Experimental materials and methods

2.1 Experimental instruments and drugs

Instrument: JJ-4A six electric mixer, WGZ-1 turbidity meter, 721G UV spectrophotometer, fast digestion instrument, pH rapid detector, HH420-2B constant temperature water bath, thermometer, 280S electric heating pressure cooker.

Drugs: PAC coagulant (Al_2O_3 27.3%), 0.01mol/L polyacrylamide PAM, HCL solution, Nessler's reagent, 98% sulfuric acid solution, 0.01mol/L NAOH, 0.5g/L of potassium sodium tartrate solution [$C_4O_6H_4KNa$] 0.25mol/L $K_2Cr_2O_7$ solution, H_2SO_4-Ag_2SO_4 solution containing 1% Ag_2SO_4, ferroin indicator, ferrous ammonium sulfate [0.10mol/L (NH_4) $2Fe_2$ (SO_4) 2 - $6H_2O$] 10g/L 50g/L, phenolphthalein solution, K_2S_2O solution, mercury sulfate (Hg_2SO_4) chemically pure 100g/L, ascorbic acid, ammonium molybdate 1.3g/L [(NH_4) $6Mo_7O_{24}$ - $4H_2O$] solution, acid potassium antimony tartaric 3.5g/L [$KSbC_4H_4O_7$ - $1/2H_2O$] solution.

2.2 Water quality test

The coagulation sedimentation test water is taken from the waste water treatment process of a chemical pharmaceutical factory to adjust the tank waste water. The relevant water quality parameters are shown in table 1:

Table 1: The waste water quality coagulation experiment

Water quality project	CODcr(mg/L)	NH_4+-N(mg/L)	pH	TP(mg/L)	Turbidity NTU	Temperature
Detection value	2000-3400	180-210	6.5-8.0	8-14	80-210	18.7 °C

2.3 Experimental procedure

In this paper, the experimental steps of coagulation sedimentation are as follows:

(1) Dosing stage: Water samples was added into the 1000mL beaker. After adjusting the influent pH and temperature, and then coagulant PAC and coagulant aid PAM were added, stirring it at the time of 1min and 250r/min of speed.

(2) Coagulation stage: After 1min rapid mixing, the stirring speed was reduced to 60 r/min, and continued to stir 30min.

(3) Precipitation stage: After 20min stationary, the water sample in the middle of the liquid surface and sediment interface was selected to measure the turbidity and CODcr.

2.4 Establishment of PAC dosing model

In order to make the effluent of coagulation stability in a certain range and avoid the impact of water fluctuation on the subsequent biochemical treatment, the optimum dosage of polyaluminium chloride (PAC) and polyacrylamide (PAM) is calculated by establishing a mathematical model. The CODcr value of the effluent CODcr is stabilized within a certain interval after coagulation treatment. At the same time, the consumption of coagulant and flocculant is reduced.

The waste water used in this paper is taken from the waste water treatment process of this pharmaceutical factory. The waste water in this tank has a large fluctuation. Because of the intermittent production of drugs and many kinds of drugs in the plant, the solubility of pollutants in waste water is higher for many days. Sometimes, the concentration of pollutants in sewage is very low for a number of days. According to the long-term inspection data of the plant, the concentration of CODcr in regulating pond waste water is 1800 mg/L-3400 mg/L. If the coagulation process pursues the maximum removal rate, when the water is adjusted for several days and the influent CODcr concentration is about 3200 mg/L, then the maximum removal rate is about 55% through the test (Kim et al., 2015). That is, the concentration of CODcr is more than 1700 mg/L after coagulation. When the load of the regulating tank is reduced and the influent CODcr concentration is about 1800 mg/L, then the highest removal rate is 31%. That is, the concentration of CODcr is more than 1200 mg/L after coagulation, and the effluent CODcr load is lower than before. The gap between the two can reach 500 mg/L. If we take into account the external factors such as interference, water quality fluctuations and other factors, the actual removal rate of CODcr will be lower. The gap in water output for CODcr is likely to be greater. This will have an impact on subsequent biochemical treatment. Therefore, a mathematical model should be established to find out the relationship between the PAC dosage and the influent CODcr value, so as to ensure the CODcr value of the effluent in an interval range.

3. Experimental results and analysis

3.1 Experiment on the relationship between CODcr, turbidity and PAC dosage

The study shows that it has little effect on coagulation when the initial pH of waste water is 6.5-7.5. When the temperature is between 20 and 30, the coagulation effect is little. In addition, the ratio of PAM/PAC is from 1: 40 to 1: 30, which is more economical for coagulation. When the parameters such as influent, pH and temperature are set in the proper range of coagulation reaction, these factors are not taken into account. The relationship between CODcr, turbidity and dosage of coagulant PAC is studied.

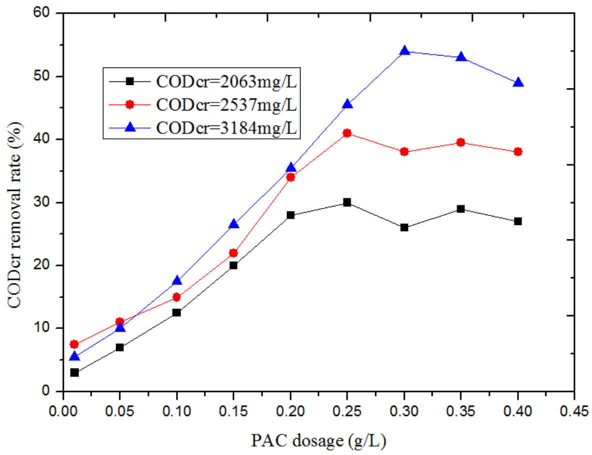

Figure 1: The relation between the removal rate of CODcr and PAC dosage

The CODcr, turbidity and PAC dosing experiments are carried out. The waste water used in the experiment is taken from the waste water treatment process of a pharmaceutical factory. Water samples are three groups of water samples with high and low load in different time periods. The CODcr concentration of water sample in first group is 3184mg/L, and the turbidity is 172NTU. The CODcr concentration of water sample in second groups is 2537 mg/L and the turbidity is 143NTU. The CODcr concentration of water samples in last group is 2063 mg/L, and the turbidity is 105NTU. Coagulation tests are carried out on the three groups of water samples. The test condition is as follows: The regulating water is 6.5-8.0 pH. The temperature is at 20 °C to 25 °C. The ratio of flocculant and coagulant dosage is 1 to 40. It is also accompanied by 1min stir speed 250r/min, 30min slow mixing 60r/min, and the CODcr and turbidity is measured after resting 20min.

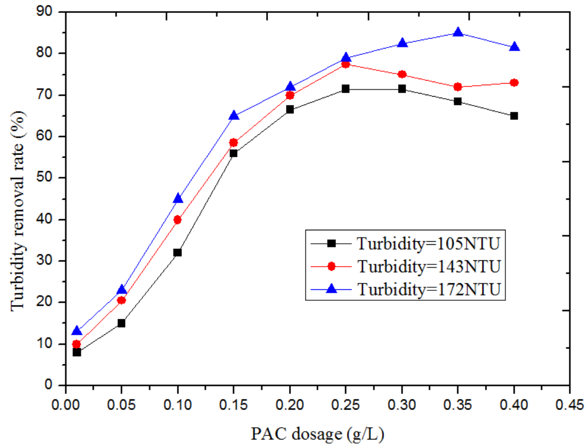

Figure 2: The relation between different turbidity removal rate and PAC dosage

As shown in figure 1 and 2, the PAC dosage has the same trend for the removal of waste water with different concentrations of CODcr and turbidity. With the increase of PAC dosage, the removal efficiency of CODcr and turbidity is better and better. However, when the dosage is more than a certain value and continues to be added, the removal efficiency of CODcr and turbidity will change. However, the removal rate will be reduced. In addition, for the waste water with higher turbidity and higher CODcr load, the coagulation treatment effect is greater than that of low load and low turbidity waste water. CODcr is 3184 mg/L and turbidity is 172NTU. When the dosage of PAC is 0.30g/L, the removal rate of CODcr and turbidity is 53% and 85%. The CODcr concentration of coagulation effluent is 1525 mg/L and turbidity is 25.8NTU. When CODcr was 2063 mg/L and turbidity was 105NTU, then the PAC dosage is 20g/L. Meanwhile, the turbidity removal rate of CODcr is 32% and 66%. The CODcr concentration of coagulation effluent is 1382 mg/L and turbidity 33NTU. Therefore, generally speaking, the waste water with larger CODcr load and turbidity is recommended to be treated with coagulation as a pretreatment, and the removal effect will be better.

3.2 Model parameter selection

The PAC dosing model is established to stabilize the CODcr of the coagulation effluent in a certain range, mainly aiming at the large fluctuation of the water quality in the coagulation intake tank, resulting in inaccurate dosage and instability of the effluent quality of the coagulation. The water samples used in the test are taken from the waste water treatment process of a pharmaceutical factory, and the influent water quality of the tank fluctuates considerably. Through long-term detection and regulation of pond water, water quality is shown in table 2.

As can be seen from table 2, when the CODcr is 3184 mg/L and the turbidity is 172NTU, the waste water can be regarded as a group with poor water quality in the regulating tank. When the dosage of PAC is 30g/L and the highest removal rate is 52%, then the minimum effluent concentration is 1525 mg/L. In addition, after considering the process of flocculation, the influent load CODcr is between 1800 mg/L and 2200 mg/L, and the concentration of coagulation effluent CODcr can be set at 1600 mg/L-1800 mg/L.

The model parameters mainly collect experimental data between CODcr, turbidity and coagulant dosage. The test process is as follows: The waste water is the CODcr pool waste water with high concentration of 3256mg/L and the turbidity of 193NTU, which is diluted into 12 groups for each waste water. The PAC dosage and coagulation test are carried out for each group of waste water. For each coagulation test, the PAC dosage range is 0.15g/L-0.30g/L, and the dosage is increased by 0.01g/L each time. In order to reduce the workload, through the analysis for figure 1, it can be seen that when the CODcr concentration is 2537mg/L-3184mg/L, the amount of PAC addition is at least above 0.2g/L before the application of water quality CODcr within the set range. Therefore, 12 groups of tests are divided into 3 categories. When CODcr is higher than 3000mg/L, the dosage of PAC is between 0.25g/L-0.30g/L. When CODcr is in 2500mg/L-3000mg/L, the amount of PAC is between 0.20g/L-0.25g/L. When CODcr is in 2000mg/L-2500mg/L, the amount of PAC is between 0.15g/L-0.20g/L.The test condition is as follows: The regulating water is 6.5-8.0 pH. The temperature is at 20℃ to 25 °C. The ratio of flocculant and coagulant dosage is 1 to 40. It is also accompanied by 1min stir speed 250r/min, 30min slow mixing 60r/min, and the CODcr and turbidity is measured after resting 20min. For each set of experiments, the CODcr values that we selected is close to the 1600mg/L-1800mg/L value and the corresponding PAC dosage is recorded. The final data are shown in table 3. At the same time, it is also found that the turbidity of the effluent is basically maintained within 30NTU-50NTU range.

Table 2: Changes of CODcr and turbidity of waste water in coagulation experiment

Serial number	Inlet TP(mg/L)	CODcr(mg/L) Influent turbidity	Dosage PAC	Inlet CODcr (mg/L)	Effluent turbidity NTU	CODcr removal rate	Turbidity removal rate
1.	3256	193	0.30	1688	37	48%	81%
2	3184	186	0.28	1640	41	48%	79%
3	3052	172	0.27	1773	31	42%	82%
4	2846	158	0.25	1675	37	41%	77%
5	2753	165	0.24	1697	42	38%	75%
6	2689	157	0.23	1585	36	39%	75%
7	2537	143	0.21	1628	40	36%	72%
8	2463	120	0.20	1732	35	30%	71%
9	2331	129	0.19	1636	45	30%	66%
10	2287	115	0.18	1669	36	27%	65%
11	2137	96	0.16	1712	46	22%	52%
12	2063	105	0.15	1641	48	20%	54%

3.3 Model checking

To verify the reliability of the model, the experimental data are taken into the model and the corresponding amount of PAC and PAM is calculated. At the same time, coagulation tests are carried out for the 6 groups of waste water, in which PAC and PAM dosage are calculated as model values. The experimental conditions are the same as those of previous coagulation tests, and the results are shown in table 3. As can be seen from the table, the amount of coagulation PAC calculated by the model can make the effluent CODcr value between 1600mg/L-1800mg/L. This shows that the model can meet the design requirements.

Table 3: The model calculation PAC dosing quantity corresponding coagulation effluent CODcr values

Serial number	Inlet CODcr (mg/L)	Influent turbidity NTU	Model calculation of PAC dosage (g/L)	CODcr effluent of PAC dosing flocculation test (mg/L)
1	2806	168	0.24	1705
2	2505	141	0.21	1644
3	2284	124	0.18	1663
4	2774	173	0.24	1627
5	2948	162	0.26	1734
6	1938	103	0.15	1635

4. Conclusions

Because the influent water quality, CODcr and turbidity are different in the coagulation pretreatment of pharmaceutical waste water, there is difference in the effluent CODcr after coagulation. The influent CODcr is established to ensure that the effluent quality is within a certain range, which is beneficial for further biochemical treatment of the follow-up stage. Based on the analysis results, the following conclusions can be drawn:

(1) For waste water with large turbidity and high CODcr load, coagulation treatment is more effective than waste water with low load and turbidity. As a pretreatment process, coagulation can play the best effect in waste water treatment process. In addition, coagulation has a fairly good removal effect for turbidity.

(2) The PAC dosage calculated by the model can stabilize the CODcr value of the condensate effluent in the 1600mg/L-1800mg/L range. This keeps the effluent CODcr indicator stable.

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