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Study on Pretreatment Technology of Spent Metalworking Fluids

Zeqi Wu

School of shanghai maritime University, Shanghai 201306, China.

Abstract

For metal processing industry to produce metal cutting waste liquids can be poor biochemical problems, adopt the method of coagulation and advanced oxidation of spend metalworking liquids pretreatment, optimized the coagulant added condition, compare the treatment effect of different coagulants under the condition of advanced oxidation on flocculation of waste liquids after treatment, comparing the UV spectra of water under different processing time. The experimental results show that: The removal rate of COD reaches 75.4% after the coagulation treatment of the cutting waste liquids with 28900mg/L COD by polyaluminum chloride (PAC) and polyacrylamide (PAM). The combination of coagulation and advanced oxidation technology can greatly improve the biodegradability of the wastewater after coagulation, and the B/C changes from 0.261 to 0.569, which provides a better treatment condition for the subsequent biodegradation.

Keywords

Cutting Waste Liquids; Advanced Oxidation; Coagulation.

1. Introduction

Metal cutting fluids are a kind of cooling and lubrication, rust and other industrial liquids, can greatly improve the product quality and production efficiency, are widely used with all kinds of metal machining process, but in the process of repeated use, can make the change of cutting fluids composition, make the cutting fluids lose the original function, produce components of complex cutting waste liquids, If discharged directly into the environment without treatment, it will cause serious harm to the environment. Each MWFs the manufacturer of the cutting fluids composition ratio strictly confidential, and will add some antioxidants in cutting fluids and prevent microbes breeding material, so it is difficult to directly use biological method of processing waste liquids metal cutting, must first to pretreatment, cutting waste liquids to combine physical and chemical method and biological method for spend metalworking liquids s depth processing, processing effect is improved. Adsorption [1] membrane filtration [2,3], advanced oxidation [4], biological [5] aerated filter and other methods are generally adopted for advanced treatment of cutting waste liquids, and the combined treatment of multiple methods has better effect. The combination of coagulation and advanced oxidation for the pretreatment of cutting waste liquids are worth further study. In this paper, a mechanical processing plant in Shanghai was treated with enhanced coagulation, and the effect of different coagulation conditions on the removal of COD was discussed, and the coagulation conditions were optimized. On this basis, advanced oxidation process was used to treat the enhanced coagulant effluent, and the effects of different oxidation time on the biodegradability of wastewater were investigated.

2. Materials and methods

2.1 Materials

The cutting waste liquids were taken from a mechanical processing plant in Shanghai, and the water quality indexes were as follows: COD=29800mg/L, ammonia nitrogen 430mg/L, pH=6.4. There are black suspended solids on the surface of cutting waste liquids, and the oil pollution is more serious.

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NaOH, H_2SO_4: all analytical pure, polyaluminumchloride (PAC), polyacrylamide (PAM) are industrial products, advanced oxidation catalytic film, laboratory self-made, UV lamp 57W, PHS-3EPH meter: Shanghai Ray magnetic instrument factory, Hash DRB200digestiondevice, BODTrak^{TW} II: Hashcompany; UV-Vis Spectrophotometer: Shimadzu Co.

2.2 Methods

In the experiment, six 200mL beakers were added with 100mL water samples in each. H_2SO_4 solution or NaOH solution was used to adjust the pH of the original water samples at room temperature. First, coagulant (PAC) was added to the beakers for rapid stirring at 1600rpm for 6 minutes, and then coagulant aid (PAM) was added for slow stirring at 120rpm for 10 minutes. After standing for a period of time, the supernatant was filtered and the COD value was measured.

After coagulation treatment, 500ml of wastewater was taken and put into the reactor. The aeration rate was 50ml/min, the intensity of UV lamp was 57W, and the distance between the advanced oxide film in the reactor and UV lamp was 2cm

3. Results and discussion

3.1 Influence of pH on flocculation effect of cutting waste liquids

The change of pH of oil-bearing wastewater will affect the surface charge state and electrophoresis speed of colloidal particles in wastewater, which will lead to the change of hydrolysates generated by coagulant. When the pH value decreases, the positive wastewater will adsorb hydrogen ions, resulting in the increase of charge of colloidal particles and the speed of electrophoresis. When the pH value increases, the negative wastewater will adsorb a large number of hydroxide ions, resulting in the increase of charge and the speed of electrophoresis. In conclusion, the influence of pH on the surface charge of particles will cause the change of floc. In this paper, optimization experiments are carried out under different pH conditions to explore the pH value that can produce the best coagulation effect, accelerate the growth of flocs and achieve better flocculation effect. The results are shown in Fig.1.

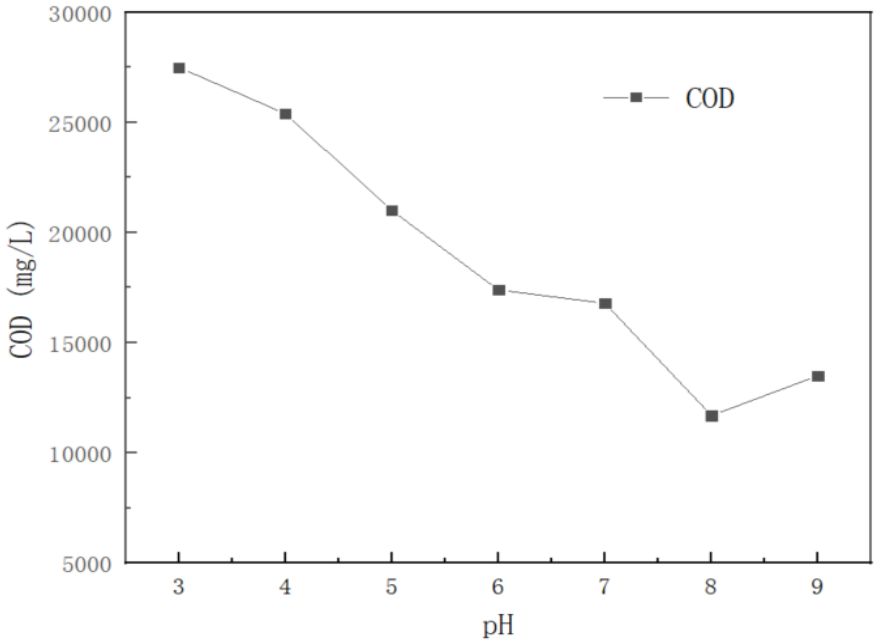

Fig. 1 Relationship between initial pH change and demulsification effect

As can be seen from the change curve in Fig.1, the change of pH value has a significant influence on the flocculation effect. When pH is 4 and 5, flocculent substances appear in the wastewater, which are small in amount and float on the surface of the liquids, and obvious changes are found in the lower

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liquids. This is because PAC mainly exists in the coordination ions of Al^{3+}, and the demulsification effect is not obvious. With the increase of pH, the flocs in the beater gradually increase and the liquids begins to become clear, and the COD value of the wastewater keeps decreasing. When pH=8, the flocs in the beater begin to separate from the wastewater, and then the COD value is the minimum and the demulsification effect is the best. This is because under weakly alkaline conditions, PAC hydrolyzes to generate a variety of complex ions. For example, $[Al(OH)(H_2O)_5]^{2+}$ and $Al_2(OH)^{5+}$, etc., these amphoteric colloid are mostly positively charged and enter the solid-liquids interface through the outer counterion layer of the gel nucleus. Because the organic colloid in the wastewater is usually negatively charged, the repulsion between the colloid is weakened, which is conducive to coagulation [6]. When the pH continues to increase, the COD of wastewater shows an upward trend. This is because when pH is low, H will inhibit the generation of high-priced polyaluminum chloride (PAC) ions; When the pH value is large, it is easy to form with OH- to form Al $(OH)_3$ and other substances [7], so that PAC is not easy to combine with pollutants in wastewater. As a result, the coagulation reaction is not smooth. Therefore, it is considered that the optimal pH value for the wastewater used in this experiment is about 8.0

3.2 Effect of PAC dosage on flocculation of oil-bearing wastewater

When the pH=8 and the PAM=15mL, the dosage of PAC was changed, and the COD values under the PAC dosage of 20, 25, 30, 35, 40 and 45 were measured respectively. The influence of PAC dosage on COD is shown in Fig 2.

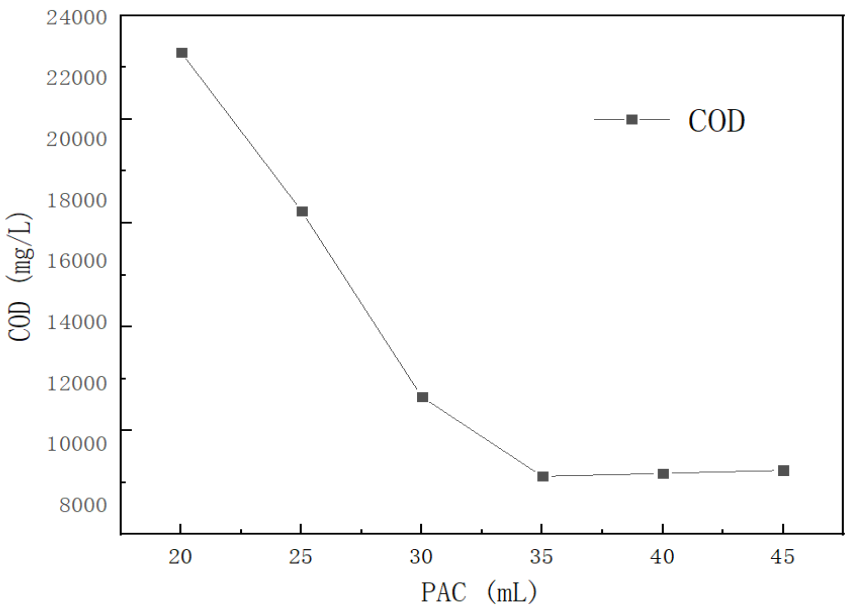

Fig. 2 Relationship between PAC changes and demulsification effect

Aluminum salt has better demulsification effect, which may be caused by the dissociation of coordination water molecules of aluminum ions and the formation of various hydroxyl aluminum ions. Bridges may occur between the hydroxyl groups of each ion to produce multi-nucleated hydroxyl complexes, such as $Al_8(OH)_{14}^{4+}, Al_{13}(OH)_{34}^{5+}$ etc. They can not only neutralize the negative charge on the surface of the colloidal particles, but also make the colloidal particles bridge together when the degree of polymerization is high. It is generally believed that poly $Al_{13}O_4(OH)_{24}^{7+}$ plays a major role in the polymer flocculant PAC [8]. When PAC is added to the solution, it does not need the hydrolysis process similar to that of low molecular flocculant, but is directly adsorbed on the surface of particulate matter, playing a strong role of electric neutralization and bridging bonding. Therefore, PAC can perform faster and stronger demulsification than low molecular coagulants [6]. From 2, it can be seen that with the increase of PAC dosage, wastewater COD removal firstly

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increases significantly and then the growth rate gradually becomes gentle. When the PAC dosage increases to 35mL, the COD removal rate does not increase significantly when the PAC dosage continues to increase. Considering the treatment cost, the optimal PAC dosage is determined to be 35mL.

3.3 Effect of PAM dosage on flocculation of oil-bearing wastewater

When the pH of the spend metalworking liquids are adjusted to about 8 and the dosage of PAC was 35mL, the dosage of PAM was changed, and 15ml, 20mL, 25mL, 30mL, 35mL and 40mL PAM were added respectively. After slowly stirring, the supernatant was filtered, and the COD of the water sample of the supernatant was measured. See Fig3 for the treatment results.

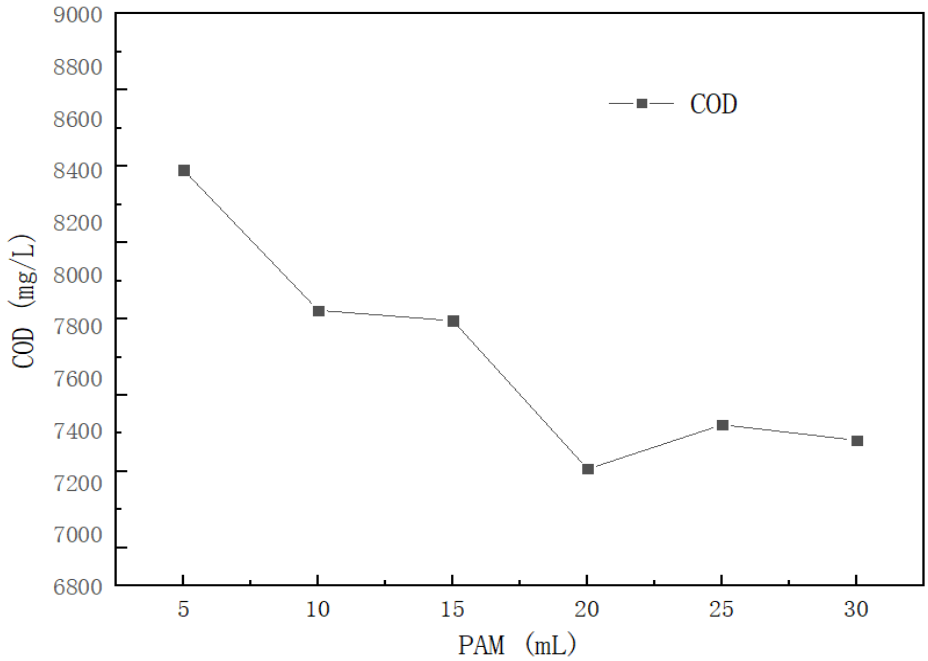

Fig. 3 Relationship between PAM changes and demulsification effect

PAM has the effect of promoting the enlargement and coarsening of the flocculent structure. When PAM is added into the wastewater, the flocculent in the wastewater gradually increases, and can absorb the small suspended particles in the wastewater, reducing the small suspended particles in the beaker. The solid-liquids separation effect is better than that of adding PAC only. As can be seen from the figure, with the increase of PAM dosage, the COD removal rate showed a trend of first increasing and then decreasing. When the dosage of PAM is 20mL, the upper solution is more clear and yellowish in color, while the lower flocs are larger and densier, the water quality is significantly improved, and the COD removal rate is the highest. When PAM is continued to be added, the COD value increases slightly and then decreases, which may be because the increase of cation content in the wastewater leads to the increase of repulsion between colloidal particles. In addition, it is speculated that excessive PAM in water may cause the increase of COD value. As can be seen from the figure, although PAM has little effect on COD removal within the test range, the flocculation sedimentation rate is significantly accelerated and time is saved. Therefore, the optimal PAM dosage of 100mL waste liquids is 20mL, and the effluent COD value at this time is 7250mg/L.

3.4 UV-Vis spectrum analysis of advanced oxidation technology for the treatment of oil-bearing wastewater

UV-Vis spectrophotometry is an analysis method based on the absorption characteristics of organic matter to the ultraviolet light wave with the wavelength of 200~900nm. Compared with the traditional

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COD test method (potassium dichromate oxidation method), it has the advantages of simple and convenient operation [9]. UV_{254} is an index for the evaluation of organic pollutants in water put forward in the 1970s.It refers to the ultraviolet absorbance under the optical path of unit colorimetric dish at the wavelength of 254 nm.

For cutting fluids used in this experiment wastewater effluent after coagulation treatment of water, dropped sharply the macromolecular substances and suspended solids, but the initial raw water pollutant concentration is high, the water still contains a small amount of spend metalworking liquids additives composition [10] (petroleum sulfonate, triethanolamine oleic acid soap, organic silicon, etc.), have certain absorption peak in ultraviolet-visible spectrum. The strength of the ultraviolet-visible absorption spectrum is generally associated with kinds and concentrations of organic matter in wastewater and absorption in the ultraviolet area associated with the degree of sophistication and aromaticity of wastewater, the advanced oxidation system under different periods of oily wastewater by ultraviolet-visible spectroscopy, scanning, analyzing the spectral characteristics of water oxidation under different time, the scan results as shown in fig.4.

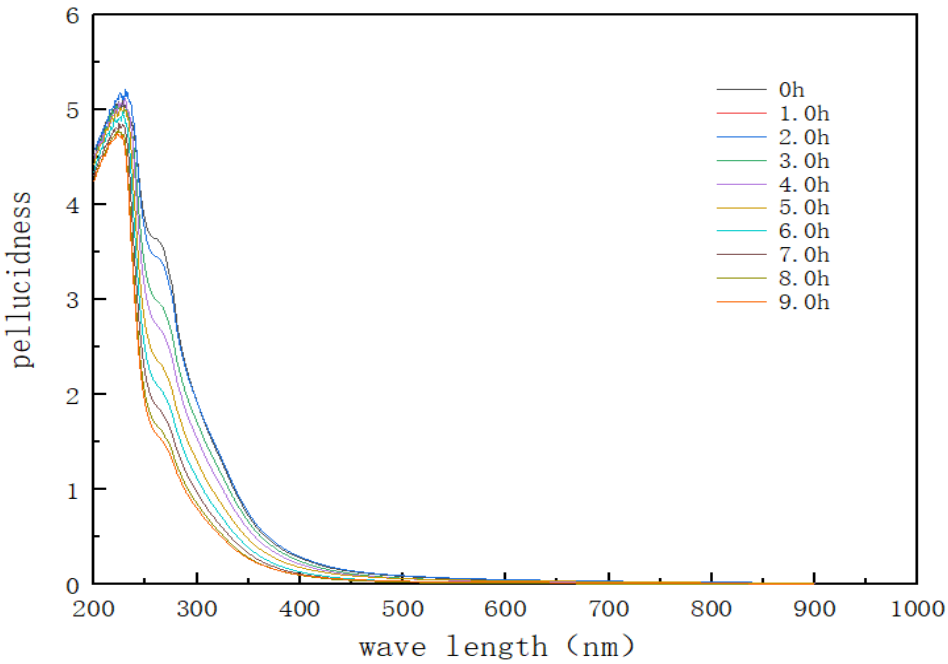

Fig. 4 UV-Vis spectroscopic analysis of effluent of advanced oxidation system at different time

Generally, saturated hydrocarbons have no absorption in the near ultraviolet region, while aromatic hydrocarbons, conjugated systems with double bonds or carbonyl groups, such as lignin, tannin and humus, have obvious absorption or characteristic peaks in the ultraviolet region. Can be seen from the fig.4: as the oxidation reaction continues, advanced oxidation system of the UV-vis spectra of water absorption value as a whole continued to reduce with the increase of reaction time, with the advanced oxidation process of oily wastewater in the molecular structure of macromolecular organic matter, destroy a large extent, decrease of organic matter concentration; In wastewater treatment, before and after UV region significantly lower absorption, can be seen from the diagram, oxidation treatment effluent total dissolved organic matter (DOM) ultraviolet absorption is mainly concentrated in the 200-300 nm, shows that after coagulation treatment of oily wastewater of aromatic compounds [10] polycyclic aromatic hydrocarbons and conjugated system, along with the increase of oxidation time, absorption peak, This indicates that oxidation treatment can destroy these macromolecular substances. Although some soluble organic compounds still exist, their aromaticity and complexity are significantly reduced. Moreover, the B/C ratio at the beginning of the coagulant effluent is changed from 0.261 to 0.569, indicating that the biodegradability is improved [11].

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4. Conclusion

According to the treatment effects of coagulants on cutting waste liquids under different conditions, the most appropriate treatment conditions were screened out by taking COD of the treated waste liquids as the index. In the coagulation treatment, the treatment effect of PAC+PAM combination on cutting waste liquids were better than that of PAC alone. Through comprehensive comparison, it is found that the most appropriate pH in the coagulation method is about 8, the optimal dosage of PAC and PAM in the waste liquids are 350mL/L and 200mL/L, and the COD removal efficiency is 75.4%.

Using the ultraviolet spectrum analyses water quality before and after processing, the results show that through the advanced oxidation process can quickly remove the pollutants in the coagulation after spend metalworking fluids, after oxidation treatment wastewater aromaticity and conjugate system to remove organic matter, tend to be more simple structure, all kinds of organic matter concentration significantly reduced, B/C increase of 0.56, biochemical was improved.

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