Experimental Study on the Effect of pH on the Flocculation Demulsification Efficiency

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Abstract. 40 mg/L of artificial emulsified oil water was processed with Al₂(SO₄)₃, FeCl₃ and PAC and PAM as flocculants. Determined the feasible dosage and settling time of each flocculant, researched the effect of pH on the demulsification of different flocculants. The results showed that the demulsification effect of four kinds of flocculants is all affected by pH, and the effect of inorganic flocculant was significantly affected by pH. The maximum removal rates of aluminium sulphate and polyaluminium chloride were 62.0% and 80.7% at pH 7. However, the maximum removal rates of Iron trichloride and polyacrylamide were 77.6% and 85.2% at pH 8.

Introduction

Emulsified oil waste water mainly comes from crude oil extraction, petrochemical, metallurgical, mechanical processing, metal surface treatment process [1]. The emulsifier molecules form a strong facial film in the oil-water interface because of directional adsorption, which increases the effective thickness of the diffuse double layer and the width and gradient of the potential distribution of the electric double layer, the emulsified oil dispersed in water highly uniformly and stably, so the key of emulsified oil treatment is demulsification [2]. Based on the stability mechanism of emulsified oil, the flocculant has the function of demulsification, and the factors that affect the demulsification effect are the types, dosage, reaction time and reaction time, pH and so on [3]. The experiments are carried out by using Al₂(SO₄)₃, FeCl₃, poly aluminium chloride (PAC) and nonionic polyacrylamide (PAM) as the four common flocculants, and use the UV spectrophotometry to determine the content of emulsified oil [4], determine the effective dosage and the settling time of different flocculants, and to explore the effect of pH on the demulsification of different flocculants.

Experimental Materials and Instruments

Test reagent: FeCl₃ (AR), Al₂(SO₄)₃ (AR), PAC(AR), PAM (AR), Na₂SO₄(AR), HCl (AR), H₂SO₄ solution (1:3), distilled water, CH₃(CH₂)₃CH₃ (the absorbance at 225 nm and 254 nm wave strengths was less than 0.1 S), Tween-80 (AR), light diesel oil.

Experimental equipment: electronic balance (FA2204N), ultraviolet visible spectrophotometer (T6), pH tester (PHS-3C), constant temperature magnetic impeller (85-2), coagulation experiment impeller (TA6-4), air aerator (S-4000B).
The Experiment of Demulsification

Preparation of Oily Water Sample

Oily water sample: Taken 200 mg of Tween80 to a certain amount of deionized water and stir until completely dissolved, add deionized water to 1000 mL, get Tween80 solution of 200 mg/L. Take 40 mg diesel oil into a certain amount of Tween80 solution of 200 mg/L, stir well and constant volume to 1000 mL, stir the mixed liquor fully with variable speeds. The impeller stirs 30 min in the speed of 1000r/min initially, then, increase the speed to 8000r/min and stirs 3min, after it, stop stirring and place it stably for 24 hours until the solution is clear and has no oil separating out. The oily water sample whose concentration is 40 mg/L is obtained. The pH is 7. The sample`s temperature in the experiment is 25°C, and it keeps stability within 3 days[5].

Oil Standard Curve Drawing

Standard oil: Take a certain amount of the sample and add some petroleum ether in it to exact it(add 25mL-30mL of petroleum ether to 1L sample ).Add the Anhydrous sodium sulfate to the leaching liquor for dehydration, then filter it to a distilling flask. With the method of distilling, the large part of petroleum ether or ether is recycled. Transfer a small amount of residual liquid into a constant evaporating dish, and use 10 mL-20 mL of petroleum ether to wash the distillation flask, then the lotion is also transferred to the evaporating dish. Put the evaporating dish to a 70 °C water bath to dry, and then put it into a 700 °C oven to bake to a constant weight. This oil is regarded as standard oil.

Oil standard stock solution: Weighing 0.1 g standard solution into the weighing bottle(The error should be smaller than 0.2mg), dissolve it with heptane, transfer them to a volumetric flask of 100 mL, use the heptane to dilute it, then get the oil standard reserve solution of 1.00g/L.

Oil standard solution: Absorb 20ml of the oil standard stock solution, inject it into a volumetric flask of 100ml, dilute it with heptanes, then we will get the oil standard solution of 200mg/ L.

Oil standard curve: According to the above method, dilute the solution step by step in proper order, the standard solution is obtained of 40.0 mg/L, 20.0 mg/L, 10.0 mg/L, 5.0 mg/L, 2.5 mg/L, 1.25 mg/L, 0.5 mg/L separately. Under the wavelength of 226 nm, determine the absorbance by comparing the10 mm quartz cuvette and the light petroleum, after the blank correction, the standard curve is shown in Figure 1.

![Figure 1. Standard curve.](image)

The Feasibility Experiment of Flocculation Demulsification

Determination of the Effective Dosage Flocculant for Demulsification. Take the prepared 40mg/L emulsified oil water samples for 50 mL, put it in the coagulation
experiment impeller, add different amount of flocculant (Al₂(SO₄)₃, FeCl₃, PAC, PAM) into the sample, set up the coagulation reaction procedure: the mixing speed is 800r/min and the mixing time is 30s in the stage of mixture; the mixing speed of the first reaction stage is 400r/min and the reaction time is 5 min; the mixing speed of the second reaction stage is 100r/min and the reaction time is 10min, after it, put the samples still for 2.0 hours, take the supernatant to measure the absorbance, calculate the removal rate of emulsified oil. Removal efficiency of emulsified oil under different dosage of flocculant is shown in Figure 2.

Four kinds of flocculants all have good effect on the removal of emulsified oil, the feasible concentration and the removal rate of emulsified oil as followed: the dosing concentration of Al₂(SO₄)₃ is 2.5 mg/L, the removal rate is 61.7%; the dosing concentration of FeCl₃ is 3.0 mg/L, the removal rate is 72.4 %; the dosing concentration of PAC is 1.5 mg/L, the removal rate is 78.2%; the dosing concentration of PAM is 0.5 mg/L, the removal rate is 82.9%.

**Determination of Feasible Flocculant Settling Time.** According to the experiment result of the 2.1.1, take many pieces of prepared 40mg/L emulsified oil water samples of 50ml, put it in the coagulation experiment impeller, add Al₂(SO₄)₃ of 2.5 mg/L, FeCl₃ of 3.0 mg/L, PAC of 1.5 mg/L, PAM of 0.5 mg/L to the samples respectively, set up the coagulation reaction procedure the same as 2.3.1, after the reaction, take the supernatant to measure the absorbance with the settling time respectively are 15 min, 30 min, 45 min, 60 min, 90 min, 120 min, 150 min, calculate the removal rate of emulsified oil. Removal efficiency of emulsified oil under different settling time conditions is shown in Figure 3.

The effect of settling time on the removal rate of emulsified oil is approximately the same. At the beginning, with the increase of settling time, the removal rate of
emulsified oil increases, but after a certain period of settlement, the removal rate is slowed down and no longer increases. The dosing settling time and the removal rate of emulsified oil are obtained as followed: the settling time of Al$_2$(SO$_4$)$_3$ is 30min, and the removal rate is 62%; the settling time of FeCl$_3$ is 60min, and the removal rate is 73.6%; the settling time of PAC is 60min, and the removal rate is 80.6%; the settling time of PAM is 90min, and the removal rate is 84.7%.

**Effect of pH on Demulsification of Different Flocculants.** Take many pieces of prepared 40mg/L emulsified oil water samples of 50ml, put it in the coagulation experiment impeller, set up the coagulation reaction procedure the same as 2.3.1. According to the experiment result of the 2.3.2, under the conditions of different dosage and settling time, carry out the Flocculation and demulsification as followed: the addition amount of Al$_2$(SO$_4$)$_3$ is 2.5 mg/L, the settling time is 30min; the addition amount of FeCl$_3$ is 3.0 mg/L, the settling time is 60min; the addition amount of PAC is 1.5 mg/L, the settling time is 60min; the addition amount of PAM is 0.5 mg/L, the settling time is 90min.

In the process of demulsification of each kind of flocculant, the pH of the solutions should be controlled respectively to 4, 5, 6, 7, 8, 9, 10, 11, 12, after the reaction take the supernatant to measure the absorbance, calculate the removal rate of emulsified oil. The influence of pH for removal of emulsified oil is shown in Figure 4.

![Figure 4. The influence of pH for removal of emulsified oil.](image)

With the increasing of the pH, the removal rate of four kinds of flocculants to emulsified oil showed a trend of increasing first and then decreasing, which refers that in a certain PH may have the best effect on flocculating demulsification. The effects are showed as followed, the pH of Al$_2$(SO$_4$)$_3$ is 7, the removal rate is 62%. The pH of FeCl$_3$ is 8, the removal rate is 77.6%. The pH of PAC is 7, the removal rate is 80.7%. The pH of PAM is 8, the removal rate is 85.2%.

**Analysis of the Effect of pH on Flocculating Demulsification to Different Flocculants**

**Effect of pH on Flocculating Demulsification of Al$_2$(SO$_4$)$_3$**

When we add Al$_2$(SO$_4$)$_3$ to the samples, it can supply a large number of highly charged ions in the samples, which plays a role in the compression of the double layer, reducing the number of the same charge of dispersed particle, destructing the adsorbed film on the oil water interface, which causes that the suspended particles of emulsified oil is unstable and the particles are condensed to increase the particle size, then the floc and alum will appear. When the floc grows to a certain volume, it is removed from the water
phase because of gravity, so as to realize the removal of emulsified oil in water[6]. When the pH of is smaller than 3, the solution of $\text{Al}_2(\text{SO}_4)_3$ exists in the solution in the state of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. With the increasing of the pH, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ will perform the coordination water molecule dissociation, which is also called hydrolysis process, and produce various hydroxyl aluminum ions. With the increasing of the pH continuously, the hydrolysis was carried out step by step from mononuclear single hydroxyl to mononuclear three hydroxy. Under alkaline conditions, the precipitate of $\text{Al(OH)}_3$ will appear in the sample.

**Effect of pH on Flocculating Demulsification of FeCl$_3$**

Ferric iron in aqueous solution is in the form of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, and various forms of polynuclear hydroxyl complexes may be formed, the hydrolysis reaction varies if the pH changes. Further condensation reaction of the two polymer produce a more advanced polymer, because of the bridging of the hydroxyl that forms $[\text{Fe}_2(\text{HO})_2(\text{H}_2\text{O})_6]^{4+}$ and $[\text{Fe}_3(\text{HO})_4(\text{H}_2\text{O})_3]^{5+}$ and so on. The result of hydrolysis step by step is to produce the precipitate of $\text{Fe(OH)}_3[7]$. Under the condition of weak alkaline, the hydrolysis product of FeCl$_3$ has more positive charge than $\text{Al}_2(\text{SO}_4)_3$’, which has stronger electric neutralization ability and can effectively compress the double electric layer, so it has better demulsification effect [8]. But, it will produce the precipitation of $\text{Fe(OH)}_3$ under the alkaline conditions.

**Effect of pH on Flocculating Demulsification of PAC**

The hydrolysis polymerization of PAC was significantly affected by pH. At a low pH, the hydrolysis of PAC shows a monomer form. In neutral range, PAC turns to $[\text{Al}_7(\text{OH})_{17}]^{4+}$ and $[\text{Al}_6(\text{OH})_{13}]^{3+}$, and it has the best effect. At a high pH, PAC turns to $\text{Al(OH)}_3$ and $\text{Al(OH)}^4$. The pH continues to rise, $\text{Al(OH)}_3$ will hydrolyze under the alkaline conditions: $\text{Al(OH)}_3+\text{OH}^- = \text{AlO}^2^- + 2\text{H}_2\text{O}$, thus it reduces demulsification effect[9].

**Effect of pH on Flocculating Demulsification of PAM**

PAM has a long molecular chain, and it can be bridged with dispersed emulsion particles in solution. It also has a strong flocculation effect. PAM is bridged by the colloidal particles formed by coagulation, which forms a large and tough floc, which has good demulsification effect [10]. The hydrolysis flocculation reaction of PAM is less affected by pH, and it has good demulsification effect under neutral and weak alkaline conditions.

**Conclusion**

The feasibility of four kinds of flocculants and the removal rate of emulsified oil are as followed: the concentration of $\text{Al}_2(\text{SO}_4)_3$ is 2.5 mg/L, the settling time is 30 min, the Maximum removal rate is 62% at pH 7; the concentration of FeCl$_3$ is 3.0 mg/L, the settling time is 60 min, the maximum removal rate is 77.6% at pH 8; the concentration of PAC is 1.5 mg/L, the Settling time is 60 min, the maximum removal rate is 80.7% at pH 7; the concentration of PAM is 0.5 mg/L, the settling time is 90 min, the maximum removal rate is 85.2% at pH 8.

The demulsification effect of different flocculants is affected by pH, and the effect of inorganic flocculant is significantly affected by pH. $\text{Al}_2(\text{SO}_4)_3$ and PAC has the best
flocculating demulsification effect at pH 7, and FeCl₃ and PAM has a good oil removal rate at pH 8.

References


