COAGULATION TREATMENT OF WASTEWATER IN PETROLEUM INDUSTRY USING POLY ALUMINUM CHLORIDE AND FERRIC CHLORIDE

Hamidreza Farajnezhad[1] & Parvin Gharbani[2]
[1]M.Sc. student, Department of chemistry, Ahar Branch, Islamic Azad University, Ahar, Iran
[2] Department of Chemistry, Ahar Branch , Islamic Azad University, Ahar, Iran

ABSTRACT
Removal of pollutants produced by industrial plants is requirement for reuse of water and obtains to environmental standards. Chemical coagulation process is an important and convectional method for wastewater treatment to reduce color, COD and TSS. Choice of a suitable coagulant for maximum contaminant removal and reduction in costs is the most important parameters of wastewater treatment. In this study the feasibility of using poly aluminum chloride instead of ferric chloride in petrochemical wastewater treatment has been investigated. Based on the results of jar test the poly aluminum chloride is more efficiency and the flocculated formed by poly aluminum chloride is larger than flocculated formed by ferric chloride and so separation is desirable. Results show that varying of pH has no significant effect on color removal of petroleum wastewater, so pH=7.5 was chosen as suitable pH.

Keywords: *Poly aluminum chloride, Ferric chloride, COD, Color,TSS.*

1. INTRODUCTION

In Iran, the petroleum industry is one of the most important industries of the country. However, large volumes of wastewater are generated during the process. Different conventional physicochemical and biological treatments have been used to treat the petroleum wastewater. The pollutants in the petroleum wastewater are different salts, surfactants, heavy metals, mineral oils and others. This wastewater can cause serious environmental problems due to their high color, large amount of suspended solids, and high chemical oxygen demand. So, they have to be removed before being discharged into the environment. Because of the nature of the colloidal suspension, these particles will not sediment or be separated with conventional physical methods (such as filtration or settling) unless they are agglomerated through coagulation and flocculation. Colloid particles are removed from water via coagulation and flocculation processes [1].

Coagulation indicates the process which colloidal particles and very fine solid suspensions are destabilized, so that they can begin to agglomerate if the conditions are appropriate. Flocculation refers to the process by which destabilized particles actually conglomerate into larger aggregates so that they can be separated from the wastewater.

The colloids commonly found in wastewater are stable because of the electrical charge that they carry. The charge of colloids can be positive or negative. However, most colloidal particles in wastewater have a negative charge [2]. In addition, coagulation can also produce the removal of particles larger that colloidal particles due to the entrapment of such particles in the flocs formed during coagulation. In most water treatment plants, the minimal coagulant concentration and the residual turbidity of the water are determined by the Jar-Test technique. Besides, physical-chemical treatment allows reducing dissolved, suspended, colloidal and non settable matter as well as coloring from dyes. Coagulation or flocculation process was conducted for the treatment of industrial wastewater to achieve maximum removal of COD, TP and TSS[3]. Aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate were commonly used as coagulants [4].

Therefore, Amudaa and Amoob [5] investigated the effect of coagulant dose, polyelectrolyte dose, pH of solution and addition of polyelectrolyte as coagulant aid and found to be important parameters for effective treatment of beverage industrial wastewater. Besides, Guibal and Roussy [6], pointed that the coagulation and the flocculation of suspended particles and colloids result from different mechanisms including electrostatic attraction, sorption (related to protonated amine groups) and bridging (related to polymer high molecular weight).

Adsorption [7], chemical coagulation [8], microfiltration [9], and photocatalytic processes [10] have been examined for treatment of organics and petroleum constituents in oily wastewaters. Electrocoagulation also may be considered as an alternative treatment method of oily wastewaters, as it has been applied successfully to oil and greasy wastewaters [11-12].

The aim of the present study is to evaluate and compare the effectiveness of ferric chloride and poly aluminum chloride (PAC) as coagulant in pre-treatment of the petroleum wastewater in different experimental conditions. The optimum pH and dosage needed to achieve the best performance of ferric chloride and poly aluminum chloride in coagulation process were determined.

2. EXPERIMENTAL

2.1 Sample Collection and Materials

Sample of petroleum wastewater was collected from a petroleum company, which is situated in Tabriz, Iran.

ferric chloride ($FeCl_3.6H_2O$) and poly aluminum chloride , PAC ($Aln(OH)_mCl(3n-m)$ were purchased from Chlor Pars Company.

2.2. Coagulant preparation

Stock solutions of ferric chloride and poly aluminum chloride should be prepared before starting the experiment. The solutions were prepared by dissolving 10g of each substance in distilled water and the solution volumes were increased to 1 liter. Each 1 ml of these stock solutions was equivalent to 20 mg/L when added to 500 mL of wastewater. They have been prepared in three different concentrations, i.e. 10, 20 and 30 mg/L into distillated water.

2.3 Jar test

A conventional jar test apparatus was used in the experiments to coagulate sample of petroleum wastewater by using ferric chloride and poly aluminum chloride. It was carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. The pH of solution was controlled by adding H_2SO_4 or NaOH. Before fractionated into the beakers containing 500mL of suspension, the samples of petroleum wastewater were mixed homogeneously. Then, the samples were analyzed to measure color, pH, T.S.S and COD for representing an initial concentration. Chemical characteristics of the raw wastewater are given in Table 1.

After the desired amount of poly aluminum chloride and ferric chloride was added to the suspension, the beakers were agitated at various mixing time and speed, which consist of rapid mixing (150 rpm) for 1 minutes and slow mixing (30 rpm) for 10 minutes to coagulation .
After the agitation being stopped, the suspension was allowed to settle for 20 minutes. Finally, a sample was withdrawn using a pipette from the top inch of supernatant for turbidity and COD and TSS measurements which representing the final concentration. All tests were performed at an ambient temperature in the range of 20-23°C. In the experiment, the study was conducted by varying a few experimental parameters, which were PAC dosage (10-30mg/L) and pH (5.5-8.5) in order to study their effect in coagulation and obtain the optimum conditions for each parameter.

Table 1. Chemical characteristics of the raw wastewater

COD	T.S.S	Color	pH
1120 ppm	110ppm	119ppm	7.5

2.4 Analytical analysis

The COD test was performed by Wet Chemical Oxidation method. It is used to measure the oxygen demand for the oxidation of organic matters by a strong chemical oxidant which is equivalent to the amount of organic matters in sample.
Moreover, color removal was measured by using spectrophotometer HACH Model DR/2000. In order to determine TSS, samples were filtered through a weighed standard glass-fiber filter with 0.2 µm diameter. The residue on the filter was dried at 110ºC. The increase in the weight of the filter represents the total suspended solid. pH of wastewater was measured by using a 713 pH meter.

The removal efficiency (% Removal) was calculated from the following formula:

$$\%Removal = \frac{C_0 - C}{C_0} \times 100$$

Where, C_o and C = COD, TSS and color contents of wastewater (mg/L) before and after coagulation treatment, respectively.

3. RESULTS AND DISCUSSION

3.1. Comparison of Different Coagulants

The objective of this study was to compare the two coagulants, i.e., PAC and ferric chloride, that can be used to coagulate the suspension particles in the petroleum wastewater. It was found that the behavior of coagulant may change from wastewater to another according to many factors including pH, kind of coagulant and different constituents of wastewater [13]. Figure 1 show the removal efficiencies for PAC and ferric chloride as coagulants. It was found that PAC had more efficiency in removing color compared with PAC at the specified conditions.

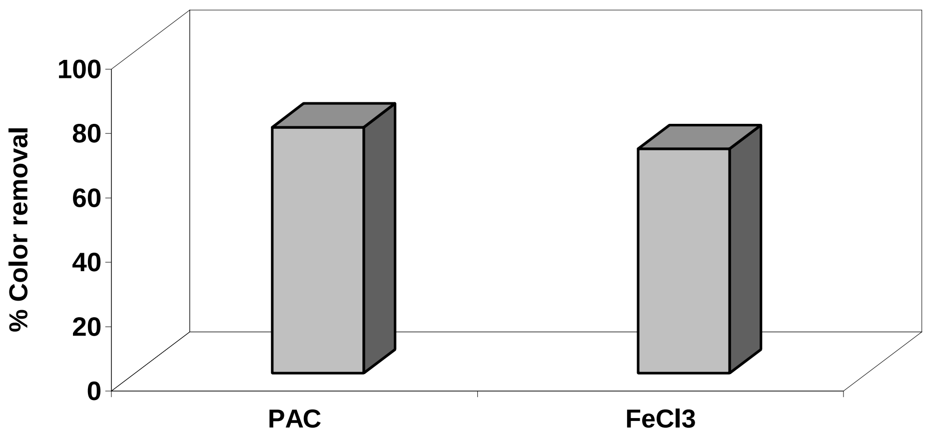

Figure 1. Effect of different coagulants on % color removal.
pH=7.5; [FeCl3]0=30 mg/L; [PAC]0=30 mg/L

3.2. Effect of pH on Treatment Process

The pH is a key parameter in the coagulation process. The optimum value of pH depends on the properties of the water treated, type of the coagulant used and its concentration [13]. To measure the effect of initial pH , the pH of each of sample was adjusted at different value using 1 N of sulfuric acid or sodium hydroxide solutions. Four experiments at initial pH values of 5.5, 6.5, 7.5 and 8.5 are performed.

The results presented in Figure 2 show that PAC has more efficiency for removal of color (86-88%) than ferric chloride (74-79%). But there is no significant change in % of color removal by varying the pH in the case of both coagulants. So, it can be concluded that pH has no effect on the color removal of petroleum wastewater.

Thus pH=7.5 was selected for further tests, because it was the initial pH of the raw wastewater. So, no need for adding chemicals to adjust the pH.

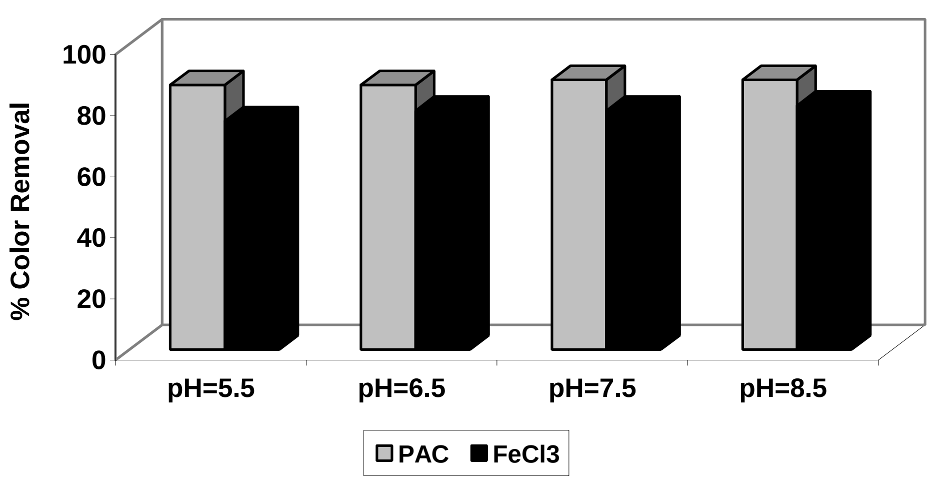

Figure 2. Effect of initial pH on color removal
[FeCl3]0=30 mg/L; [PAC]0=30 L

3.3. Effect of Coagulant Dose

To evaluate of coagulant dosage effect on color removal of petroleum wastewater, three different of coagulant dose (10, 20 and 30 mg/L) were used. As illustrated by Figure 3, the highest efficiency of color removal to such wastewater was achieved using 10 mg/L of ferric chloride (78%) and PAC (88%). It can be deduced that, increasing the coagulant dosage decreased the efficiency of coagulant in removal of color.

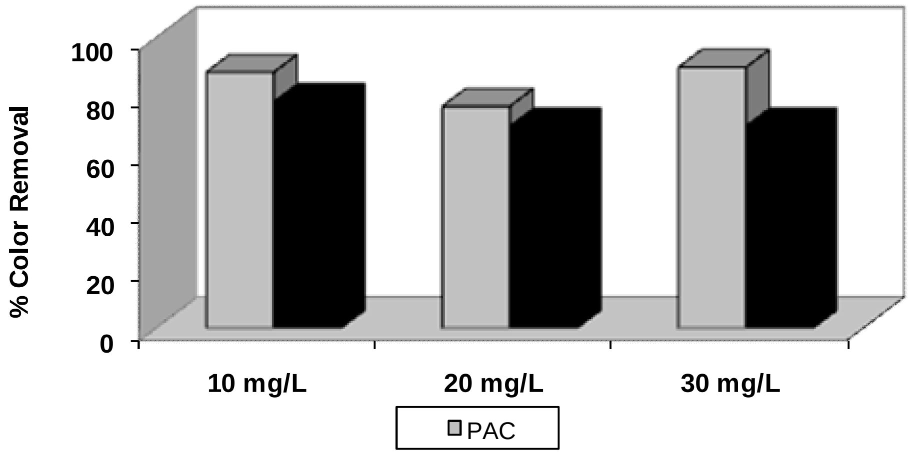

Figure 3. Effect of coagulant dose on color removal
pH=7.5

3.4. COD and TSS Analysis

COD and TSS concentrations of the wastewater were measured, as the two were important in unit process design. The wastewater has an average COD concentration of 1120 mg/L. The concentrations of COD in all the sampling point were higher than the WHO values of 1000mg/L for the discharged of wastewater into stream. High COD concentration observed in the wastewater might be due to the use of chemicals, which are organic that is oxygen demand in nature. Figure 4 shows the removal of COD by ferric chloride and PAC in different concentrations. As shown in both concentrations, PAC (48-72%) reduced the COD more than ferric chloride (44-67%).

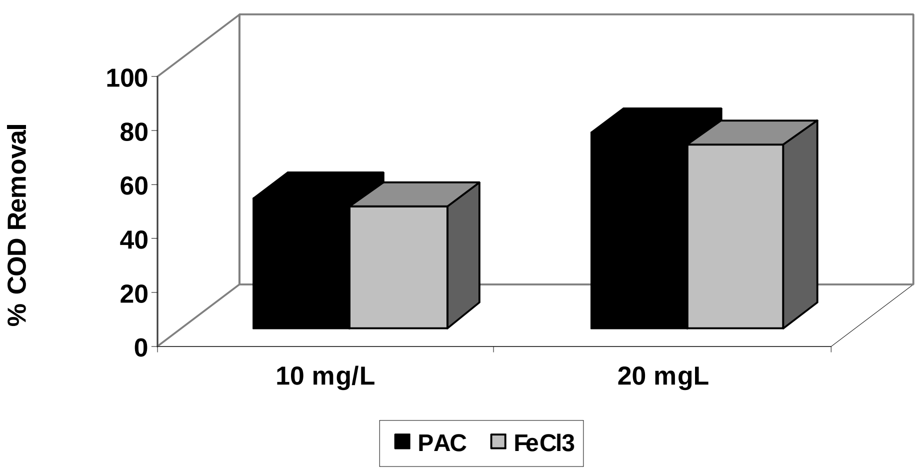

Figure 4: Removal of COD by ferric chloride and PAC in different concentrations
pH=7.5

The other parameters significant study is total suspended solid (TSS). Total suspended solids (TSS) include all particles suspended in water which will not pass through a filter. Literature classified wastewater TSS as follows: TSS less than 100 mg/L as weak, TSS greater than 100 mg/L but less than 220 mg/L as medium and TSS greater than 220 mg/L as strong wastewater. Results of the study show that TSS of raw wastewater from the petroleum

wastewater can be classified as medium and should be treated before discharged into stream (110 mg/L). The total suspended solids (TSS) concentrations of petroleum removed by PAC and ferric chloride is shown in Figure 5.
As shown , using ferric chloride and PAC as coagulant would be improved the removal of TSS 71-76% and 78-81%, respectively.

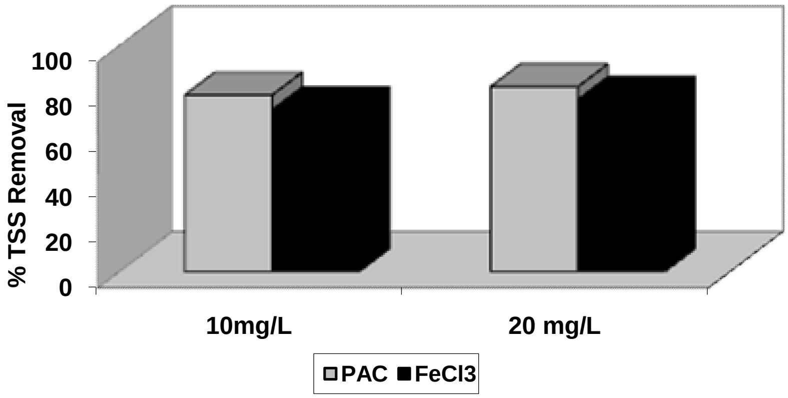

Figure 5: Removal of TSS by ferric chloride and PAC in different concentrations pH=7.5

4. CONCLUSIONS

The focus of this paper was to investigate the potential use of coagulation process for the removal of color, COD and TSS from petroleum wastewater influents using ferric chloride and PAC. The experiments conducted confirm the significant effect of coagulant dosage on coagulation process. Under optimal conditions of process parameters, a coagulant dose of 10 mg/L was efficient to remove 78 and 88% of the effluents' color by ferric chloride and PAC , respectively. Varying of of pH in this work showed negligible differences in the color removal efficiencies and this suggests that the solution pH can be used as optimum pH. The results obtained indicated that the best color removal was achieved at dose concentration of 10 mg/L and pH =7.

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