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Pretreatment of Wastewater Streams from Petroleum/Petrochemical Industries Using Coagulation

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Abstract

Coagulation-flocculation processes using different types of conventional coagulants, namely, ferric chloride ($FeCl_3$), aluminum sulfate ($AL_2(SO4)_3 \cdot 18H_2O$), lime and ferrous sulfate ($FeSO_4$) were investigated using the Jar-test technique. A further aim is to determine the optimum conditions for the treatment of industrial wastewater effluents i.e. coagulant dosage, mixing rate, temperature and pH control. Under optimal condition of process parameters, coagulation/flocculation process was able to lower the turbidity well below the permissible level (1.8 NTU). The results indicate that ferric chloride had superior efficiency compared with other coagulants with efficient dose of 800 mg/l. The optimal initial pH of the effluents that enhanced the turbidity removal was 8.6. The temperature showed no significant effect on the turbidity removal.

Keywords: Ferric Chloride, Coagulation, Wastewater, Petrochemicals, Pretreatment

1. Introduction

This template, Yanbu Industrial City, at the Red Sea Coast of Saudi Arabia, is considered as one of the major industrial cities in the Kingdom of Saudi Arabia. The city accommodates several large refining and petrochemical plants as well as a broad range of other manufacturing and support enterprises [1]. This inexorable growth in the scale of the petrochemical industries and oil refinery was largely responsible for the remarkable ecological problems at Yanbu Industrial City.

This forces the Saudi government to issue strict legislation concerning the quality of industrial wastewater effluents and the industries are not allowed to discharge any treated or untreated effluent in open channels and even after treatment, the reclaimed water must have to comply with direct discharge standards before discharge to the sea [2]. So the entire industrial sectors send their wastewater effluents to a local wastewater treatment plant to treat their waste effluents to an increasingly high standard. Actually, the treatment system consisting of physical, chemical, and biological units is not enough in its current state to reach the permissible levels of discharge especially for turbidity. However, the focus of this paper is the enhancement of coagulation process in an attempt to comply with turbidity standards for obvious health issues.

Coagulation, adsorption on activated carbon, precipitation, evaporation, ion-exchange, oxidation, and biodegradation and membrane filtration are known as an industrial pollution prevention technology and used for the decontamination of contaminated water and wastewater [3]. According to Renault *et al.* [3], complete treatment will clearly require several steps and it is often appropriate to combine several methods of purification before maximal efficiency is obtained.

Coagulation/flocculation is a widely-used process in the primary purification of water and in industrial wastewater treatment [3-5]. This method has a preference in the primary purification processes mainly due to the ease of operation, high efficiency, cost effective Also, it uses less energy than alternative treatment [5-7].

Coagulants, both inorganic and organic such as aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate are widely used as coagulants in water and wastewater treatment for removing a broad range of impurities from effluent, including organic matter, turbidity, color, microorganism, colloidal particles and dissolved organic substances [4,5,8-10]

Wang et al [11] demonstrated that many factors can influence the efficiency of coagulation-flocculation process such as the type and dosage of coagulant/flocculant, pH, mixing speed and time, temperature and retention time. An appropriate combination of these factors is desirable to obtain a high efficiency of treatment.

Dosta et al [9] and Franceschi et al [12] illustrated the role of the pH in determining the electrical charge of organic and inorganic colloids and considered it as a major factor in the hydrolysis of aluminum salts.

The process usually consists of the rapid dispersal of a coagulant into the wastewater containing solid particles followed by an intense agitation commonly defined as rapid mixing [13]. The coagulant aggregates the particles into small flocs that slowly settle by charge neutralization in negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate (sweep flocculation), thereby facilitating their removal in subsequent sedimentation, floatation and filtration stages [5,6]. Zheng *et al.* [10] reported that the basic prerequisites for an effect- tive coagulant are the charge neutralization capacity and the bridge-aggregation ability.

The aim of this systematic study was to optimize the coagulation-flocculation process and investigate the effect of wastewater initial pH, affects the type of coagulant and coagulant dosage, Temperature and mixing conditions in order to enhance the efficiency of the coagulation—flocculation process especially focusing on the optimal turbidity removal.

2. Materials and Methods

2.1. Wastewater Samples

Wastewater was obtained from the wastewater treatment facility in Yanbu Industrial City. This wastewater is a mixture of industrial wastewater from all the industrial facilities in Yanbu Industrial City. However, most of these industrial facilities are petrochemical companies and refineries. The wastewater was collected from the influent collection well and sent directly to our lab. Wastewater was stored at 4˚C and was equilibrated to room temperature before use. The main characteristics of the wastewater are presented in **Table 1**.

Table 1. Main characteristics of wastewater.

BOD5[1] mg/lit	TSS[2] mg/lit	TDS[3] mg/lit	TS[4] mg/lit	Total hardness mg/lit as $CaCO_3$
57.5	2217	2323	4545	190

[1]After 1/10 dilution; [2]TSS: Total suspended solids; [3]TDS: Total dissolved solids; [4]TS: total solids.

2.2. Preparation of Coagulants

Ferric chloride ($FeCl_3$) was obtained from Loba Chemie (India), Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) was obtained from Panreac Quimica SA (Spain), Ferrous sulfate ($FeSO_4$) was obtained from TechnoPharmChem (india). 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 to be tested.

2.3. Comparison of Different Coagulants

Coagulation and flocculation tests were performed in a standard jar test apparatus (SOLTEQ flocculation test unit, Mode TR 10) consisting of six paddles and equipped with 6 beakers of 1 liter volume. Each beaker was filled with 500 ml of wastewater sample. The performance of the coagulants was compared by adding 50 ml of each one to 500 ml of wastewater without adjusting pHs of the samples. The samples were agitated at a flash mixing speed of 300 rpm for 3 minutes followed by slow mixing speed of 50 rpm for 15 minutes. At the end of the stirring period the flocs were allowed to settle down for 20 minutes. The samples were taken by immersing a pipette 2 cm below the surface of the water. Turbidity, total dissolved solids, and pH were measured using Hach 2100 AN turbidimeter, SevenEasy conductivity meter from Metler Toledo, and pH501 EuTech Instrument, respectively. All the equipment were calibrated before use.

2.4. Effect of pH

To measure the effect of initial pH 7, 1-liter beakers were filled with 500 ml of the wastewater. The pH of each of sample was adjusted at different value using 1 N of sulfuric acid or sodium hydroxide solutions. The pHs tested covered the range from 3 up to 11.5. To each beaker 50 ml of $FeCl_3$ were added. The mixture were rapidly mixed at 300 rpm for 3 minutes, slow mixed for 15 minutes at 50 rpm and allowed to settle for 20 minutes. Samples to be analyzed were taken from the supernatant 2 cm below the level of the liquid.

2.5. Effect of Coagulant Dose

The optimum dose of the selected coagulant was determined by placing different volumes of coagulant (5, 10, 20, 30, 40, 50, 70 ml) in conical flasks. The volume was adjusted to 70 ml in each flask by adding distilled water (65, 60, 50. 40, 30, 20, 0 ml, respectively). This procedure was applied to keep the total volume of the treated samples at the same value. The rapid stirring speed was 300 rpm for 3 minutes and the slow stirring speed was 50 rpm for 15 minutes, followed by 20 minutes of settling.

The effect of coagulant dose on pH of solution was measure by adding different doses of coagulant to 500 ml aliquot of the wastewater, stirring for 2 minutes and then measuring the pH of the different solutions. The effects of rapid and slow mixing speed were studied similarly. The rapid mixing speed was varied from 100 to 350 rpm keeping the slow mixing at a constant value of 50 rpm. The slow mixing effect was studied by varying the speed from 45 rpm to 100 rpm keeping the rapid mixing at a value of 300 rpm.

2.6. 30-Minutes Settling Tests

This experiment as usual with a jar test protocol. Two beakers were filled with 500 ml aliquot of wastewater. 40 ml of FeCl3 were added to each beaker. The mixtures were rapidly stirred at 300 rpm for 3 minutes, followed by slow stirring at 50 rpm for 15 minutes. The two samples were placed in 1-liter cylinder and allowed to settle down without disturbance. The volume of the sludge in the cylinder was observed with time. All the above mentioned tests were performed at room temperature.

2.7. Effect of Temperature

The effect of temperature was tested by adjusting the temperatures of three wastewater samples (500ml each) at three different temperatures (13˚C, 22˚C and 43˚C). To each sample 40 ml of $FeCl_3$ were added. The mixture were stirred rapidly for 3 minutes at 300 rpm, slow-stirred at 50 rpm for 15 minutes, and allowed to settle for 20 minutes. The final temperature was measured to take into account the effect of any change that may have occurred.

3. Results and Discussion

3.1. Comparison of Different Coagulants

The objective of this experiment was to determine the best coagulant that can be used to reduce turbidity to the permissible level for such wastewater. It is well known that the behavior of coagulant may change from wastewater to another according to many factors including alkalinity, pH, and different constituents of wastewater [11, 12]. **Figure 1** depicts the removal efficiencies for different coagulants. It was found that ferric chloride had superior efficiency in removing turbidity compared with other coagulants at the specified conditions.

Final turbidity of 1.8 NTU is well below the permissible level set by governmental agencies in Yanbu Industrial City (15 NTU) for such parameter. Ferrous sulfate at these conditions increased the turbidity of the sample, while lime has negligible effect on turbidity removal.

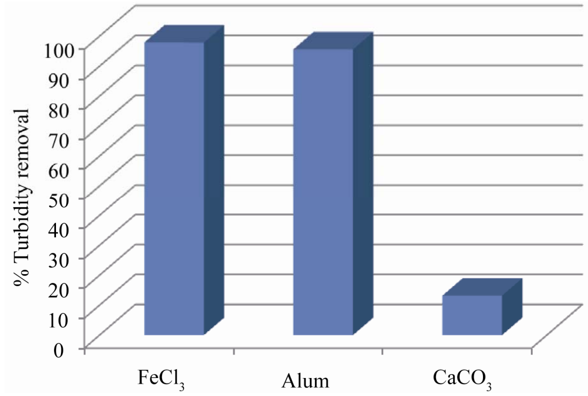

Figure 1. Effect of different coagulants on turbidity removal.

Alum was found to have comparable removal efficiency to $FeCl_3$, but the later was chosen to avoid the hazardous effect of alum.

3.2. Effect of pH on Treatment Process

The pH value is a very important factor in the coagulation process. The optimum value of pH depends essentially on the properties of the water treated, type of the coagulant used and its concentration. Abdulaziz *et al.* [14] attributed the effect of pH on coagulation process as a balance of two competitive forces; (1) forces between H^+ and metal hydrolysis products for interaction with organic ligands that may be present in water, and (2) forces between hydroxide ions and organic anions for interacttion with metal hydrolysis products. The effect of pH can be explained by the study of the reactions involved with the coagulants as depicted below [15]:

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3(\downarrow) + 3CaCl_2 + 6CO_2$$

$$2FeCl_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3(\downarrow) + 3CaCl_2$$

It is clear that the increase of the concentration of alkalinity will shift the reaction to the right direction (product side), i.e. enhancing the coagulation/flocculation process. It can be depicted from **Figure 2** that the optimum initial pH for turbidity removal is 7 and 8.6 giving removal efficiencies of 95.9% and 95.2%, respectively. The later pH was selected for further tests for two reasons. First, it was the initial pH of the raw wastewater. So, no need for adding chemicals to adjust the pH. Second, as illustrated by **Figure 3**, the coagulant dose will lead to a decrease in pH of the solution until it reaches an acidic value, which is not required during coagulation. By the addition of iron chloride ($FeCl_3 \cdot 6H_2O$) as coagulant, the suspended negatively charged solid particles are destabilized.

The removal of solids in water by settling or filtration of the solid particles must be incorporated as flocks and

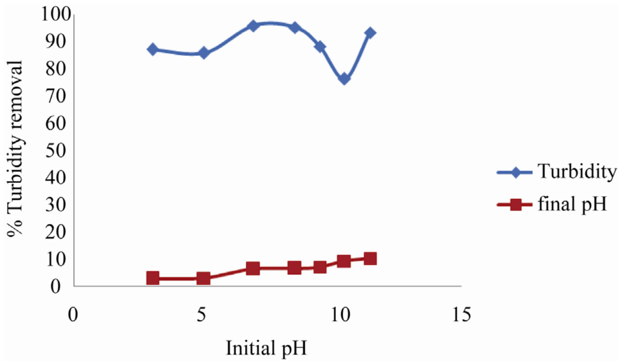

Figure 2. Effect of initial pH on turbidity removal.

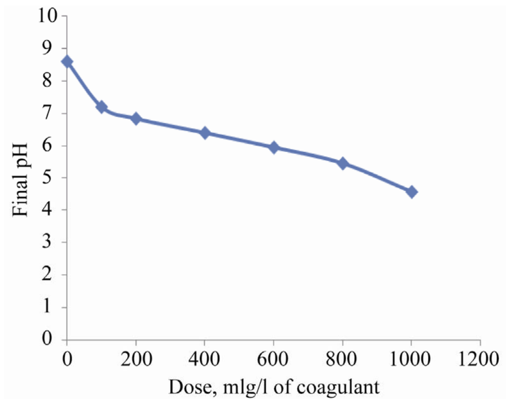

Figure 3. Effect of coagulant dose on solution pH.

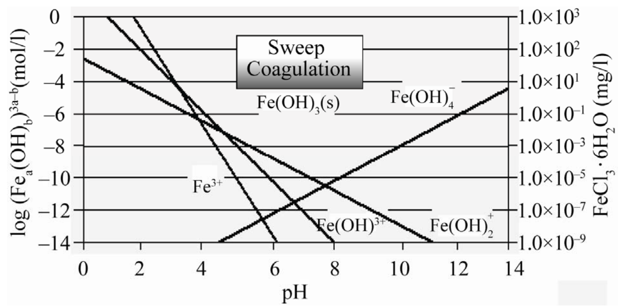

Figure 4. Effect of initial pH on turbidity removal.

these flocks are formed after dosing of the coagulant.

The addition of $FeCl_3 \cdot 6H_2O$, as coagulant, to water will result in formation of $Fe(OH)_3$ which dissociates to form different positively charged ions and negatively charged ions which are produced due to the following hydrolysis reactions [16]:

$$Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^-$$

$$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)^{2+} + H_3O^+$$

$$Fe(OH)^{2+} + H_3O^+ \leftrightarrow Fe(OH)_2^+ + H_3O^+$$

$$2Fe^{3+} + 4H_2O \leftrightarrow Fe(OH)_2^{4+} + 2H_3O^+$$

$$Fe(OH)_3 + OH^- \leftrightarrow Fe(OH)_4^-$$

As the above reactions indicate, in addition to iron hydroxide, the following hydrolyses products of Fe^{3+} are also formed: $Fe(OH)^{2+}$, $Fe(OH)^{2+}$, $Fe(OH)^{-4}$. The concentration of each ion depends on the pH, dose concentration and equilibrium constant for each reaction which is temperature dependant. The calculated dependence of the concentration of each hydrolysis product over wide pH range and different dose concentrations is depicted in **Figure 4**.

The results obtained indicated that the best turbidity removal was achieved at dose concentration of 800 mg/l and pH range between 7 and 8.6 as indicated in **Figures 2** and **5**, respectively. By referring to **Figure 4**, these operating conditions are located in the above dark rectangle. In this region, large amounts of precipitated $Fe(OH)_3$ are formed with the absence of positively charged particles. This is evidence that at these optimum conditions a precipitation coagulation, or sweep coagulation, is the dominant mechanism where colloids are incorporated into neutral (iron) hydroxide flocs.

The measurements presented in **Figure 2** showed that the pH value of water decreases by increasing the dose concentration of $FeCl_3 \cdot 6H_2O$.

As a result of the dosing of iron chloride, OH- ions are removed and the pH will decrease. The magnitude of the pH drop depends on the buffering capacity of the water. The higher the buffering capacity, the smaller the pH drop is. When the pH drop is too large, pH will be increased by dosing a base, such as caustic soda.

It is worthy to notice that, by examining **Figure 4**, the pH value influences the solid particles stabilization in two counter currently directions. At low dosage concentration, increasing the pH leads to an increase in the negatively charged ions (stabilization effect) and a decrease in the concentration of the positively charged ions (destabilization effect). The achieved maximum turbidity removal at high dose concentration over the optimum pH range between 7 and 9 can be explained through the enhancement of precipitation of $Fe(OH)_3$. This forces the sweep coagulation process. This process cannot occur in strongly basic medium or strongly acidic medium.

The observed drop in turbidity removal in strongly basic medium is due to the increased concentration of the negatively charged ions which contributes negatively in the coagulation process by its stabilization effects.

3.3. Effect of Coagulant Dose

As illustrated by **Figure 5**, the highest efficiency of turbidity removal to such wastewater was achieved using 800 mg/l of ferric chloride. This dose resulted in turbidity removal efficiency of 97.5% equivalent to a final turbidity of 2.2 NTU. This high dose can be decreased to half its value (400 mg/l) to produce turbidity removal

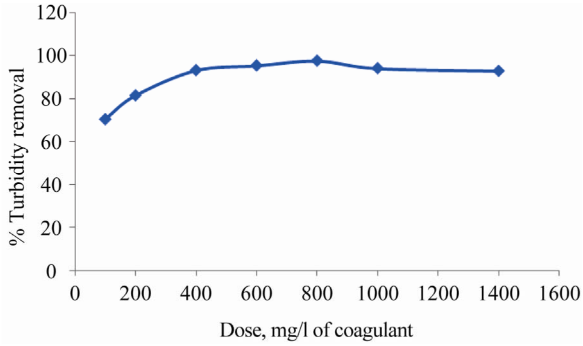

Figure 5. Effect of Coagulant Dose on turbidity removal.

efficiency of 93% (equivalent to final turbidity of 5.9 NTU). This later value can be accepted from a pretreatment process for such wastewater taking into consideration it would go through more treatment processes (two biological treatment processes followed by sand filtration).

3.4. Effect of Mixing and Settling Rates

The effect of agitation rate on the turbidity removal efficiency is illustrated by **Figures 6** and **7**. The highest turbidity removal (98.1%) was achieved at 200 rpm of rapid mixing. However, the other rates produced comparable results. The lowest removal efficiency was obtained at a stirring rate of 350 rpm (95.6%). The next one was at 100 rpm (96.55%). Comparing the later value obtained at the lowest speed with the rate that produced the highest removal efficiency (98.1% at a rate of 200 rpm), it is clear that the negligible difference in removal efficiency suggests the use of the lowest velocity that will save energy. Similar results were obtained for the slow mixing rates. All the tested rates gave comparable removal efficiencies ranging from 98.2% up to 98.7%. These removal efficiencies are equivalent to final turbidities less than 2 NTU. So, the lowest velocity (45 rpm) can be used for a slow mixing step. **Figure 8** illustrates the settling process after flocculation/coagulation. The solid volume reached a value of 13% of its initial value after 90 minutes. The sludge volume index for the produced sludge was calculated to be 190 which is an acceptable value.

3.5. Effect of Temperature

The temperature of Saudi Arabia may reach 50 Degrees Celsius. This high temperature in Saudi Arabia is very common. The average temperature during the winter season is roughly around 8 to 20 degrees Celsius.

However, even in the summers, the nights are really chilly as the desert tends to become cold once the sun sets down. The effect of temperature on the coagulation process was studied at three different temperatures as illustrated by **Figure 9**. It is clear that the temperature does not have a considerable effect within the studied temperature range (13 up to 43˚C). Slight differences were noticed due to this temperature effect. Removal efficient obtained at room temperature 22˚C (96.3%) was the highest compared to 95.4% and 95.8% achieved at 13 and 43˚C, respectively.

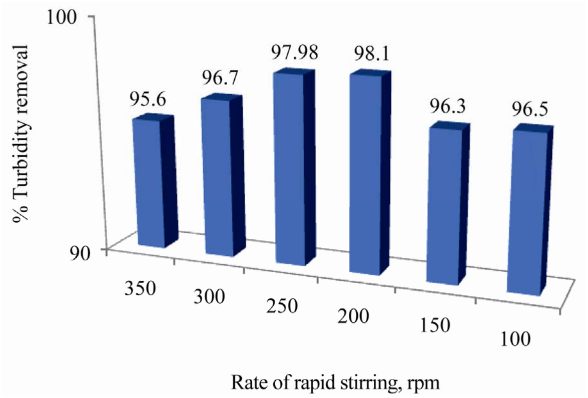

Figure 6. Effect of Rate of Rabid Mixing on turbidity removal.

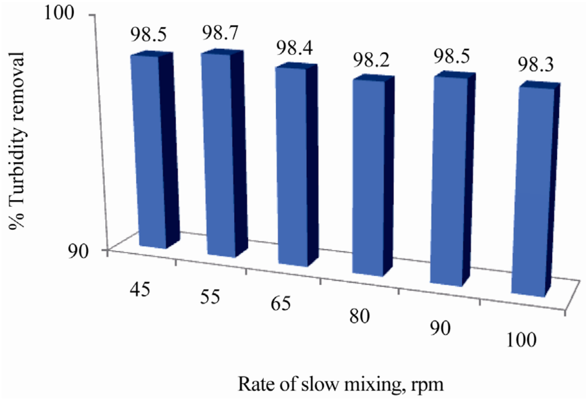

Figure 7. Effect of Rate of slow Mixing on turbidity removal.

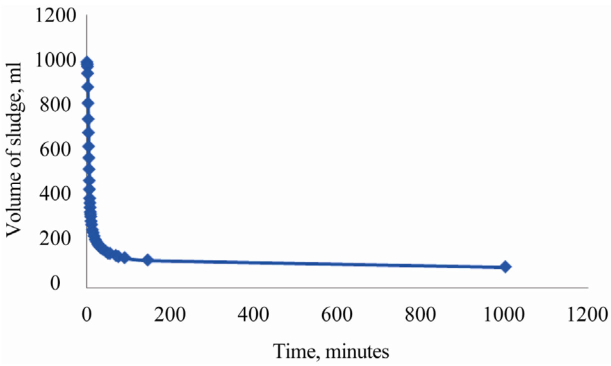

Figure 8. Settling rate of the sludge.

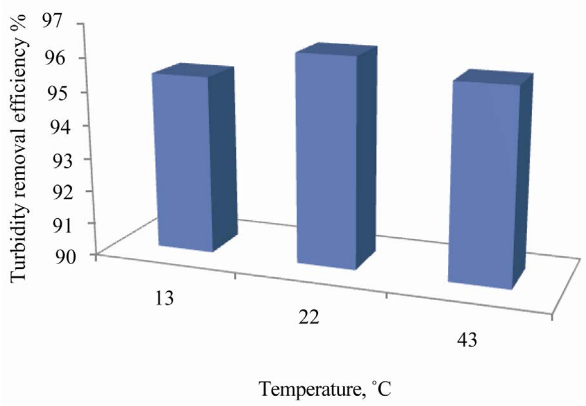

Figure 9. Effect of Temperature on turbidity removal.

4. Conclusions

The focus of this paper was to investigate the potential use of coagulation-flocculation process for the removal of turbidity from industrial wastewater influents using aluminum sulfate and iron salts. The experiments conducted confirm the significant effect of pH on coagulation process.

Increasing pH form acidic range to alkaline range promotes turbidity removal indicating the significant role played by pH in imparting surface charge of organic and inorganic colloids. The optimum pH for the removal of turbidity from industrial effluents under the experimental conditions used in this work was = 8.6.

Under optimal conditions of process parameters, a coagulant dose of 400 mg/l was efficient to remove 93% of the effluents' turbidity.

Rate of mixing range used in this work showed negligible differences in the turbidity removal efficiencies and this suggests that the lowest mixing rate can be used to save energy.

Coagulation-flocculation process has proved an efficient process to remove turbidity from industrial wastewater effluents.

5. Acknowledgement

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