Evaluation of Alum/Lime Coagulant for the Removal of Turbidity from Al-Ahdab Iraqi Oilfields Produced Water

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ABSTRACT

The removal of turbidity from produced water by chemical coagulation/flocculation method using locally available coagulants was investigated. Aluminum sulfate (alum) is selected as a primary coagulant, while calcium hydroxide (lime) is used as a coagulant aid. The performance of these coagulants was studied through jar test by comparing turbidity removal at different coagulant/ coagulants aid ratio, coagulant dose, water pH, and sedimentation time. In addition, an attempt has been made to examine the relationship between turbidity (NTU) and total suspended solids (mg/L) on the same samples of produced water. The best conditions for turbidity removal can be obtained at 75% alum+25% lime coagulant at coagulant dose of 80 mg/l at pH 6 and 120 min for sedimentation time. At these conditions, the turbidity reading was reduced from 92 to 2.1 NTU.

Key words: coagulation, turbidity, alum, produced water.

تقييم مختثر الشب - النورة في ازالة العكورة من المياه المصاحبة لأنتاج النفط من حقول الأحدب العراقية

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الخلاصة

في هذا البحث تمت دراسة ازالة العكورة من الماء المنتج بطريقة التخثر/ التلبد وباستخدام مخثرات متوفرة محلياً. تم استخدام كبريتات الالمنيوم (الشب) كمخثر رئيسي بينما استخدم هيدروكسيد الكالسيوم (النورة) كمخثر مساعد. تم دراسة اداء هذه المخثرات بطريقة الدفعة وباستخدام فحص الجرة وذلك بمقارنة ازالة العكورة من الماء تحت ظروف مختلفة مثل نسبة المخثر / المخثر المساعد و كمية المخثر و الدالة الحامضية للماء وزمن التركيد. بالاضافة الى ذلك, تم عمل دراسة مختبرية لمعرفة العلاقة بين درجة العكورة (وحدة كدرة) ومجموع المواد الصلبة المعلقة (مليغرام لكل لتر) لنماذج مختلفة من الماء المنتج. بينت النتائج بأن المخثرات المستخدمة اظهرت افضل اداء في ازالة العكورة وان الجرعة الامثل للمخثر هي ٨٠ مليغرام لكل لتر والرقم الهيدروجيني الامثل هو ٦ وافضل زمن التركيد كان١٢٠ دقيقة وان افضل نسبة مخثر/ مخثر مساعد كانت ٧٥% شب مع ٢٥% نورة. تناقصت قراءة العكورة من ٩٢ الى ٢,١ وحدة كدرة عند هذه القيم المثلى.

الكلمات الرئيسية: التخثر, العكورة, الشب, المياه المنتجة.

1. INTRODUCTION

Treating oilfield water can help facilitate additional water management options for operators such as beneficial uses that in the short and long term can potentially provide certain community and economic advantages. Treated produced water has the potential to be a valuable product rather than a waste. A large number of methods were used as treatment technologies such as heat treating, gas flotation, chemical separation, membranes, filtration, and biological degradation. Several methods are available to remove the suspended solids or turbidity (like cuttings, sand, clay particles, and microorganisms) and their methods are filtration, coagulation, gravity separation, and biological treatment, **Arthur, 2005.**

All waters, especially produced water, contain both dissolved and suspended particles. Coagulation and flocculation processes are used to separate the suspended solids portion from the water. The suspended particles vary considerably in source, composition charge, particle size, shape, and density. Correct application of coagulation and flocculation processes and selection of the coagulants depend upon understanding of the interaction between these factors, **,Smita, et al., 2012.**

Turbidity is cloudiness or haziness of water (or other fluid) caused by individual particles that are generally invisible to the naked eye. It is a characteristic related to the concentration of suspended solid particles in water and has been adopted as an easy and reasonably accurate measure of overall water quality, **Tseng, 2000.** World Health Organization (WHO) has set the guideline value for the residual turbidity in drinking water at 5 Nephelometric Turbidity units (NTU), **Connachie, et al., 1999.** Although turbidity purports to measure approximately the same water quality property as total suspended solids, but the later is more useful because it provides an actual weight of the particulate material present in the sample. While a relationship can be established between turbidity and suspended solids, this relationship can and will change spatially and temporally due to variations in solid composition and stream energy, **Rasmussen, 1995.**

For all water types, there are many parameters that affect coagulation performance for turbidity removal including the character and concentration of the particular material, chemical and physical properties of the water, mixing time, mixing speed, and temperature. The common parameters are coagulant type, dose, pH, and settling time, **,Uyak** and **Toroz, 2007.** The coagulation process utilizes what is known as a chemical coagulant to promote particle agglomeration. **Eilbeck** and **Mattock, 1987** presented a list of common coagulants in treating wastewater. They mentioned that the most frequently used coagulants are iron and aluminum salts and especially, for economic reasons, aluminum sulfate and ferric chloride. Coagulants are sometimes assisted with further chemicals, known as coagulant aids. They essentially are polyelectrolytes and lime alkalinity addition, **Kiely, 1997.**

The aim of this work was to study the feasibility of turbidity removal from real produced water from Al-Ahdab Oilfields by alum and lime coagulants. The process was examined for the first time in Iraq under different values of coagulant/ coagulants aid ratio, coagulant dose, water pH, and sedimentation time.

2. MATERIALS

2.1 Produced Water

A volume of produced water obtained for sampling from Al-Ahdab Oilfields, 180 km south-east of Baghdad, was stored in a plastic container for the duration of the study. Samples of this water were analyzed chemically in the Al-Ahdab Oilfields and results are listed in **Table 1.**

2.2 Coagulants

The chemical coagulants used in the present study were aluminum sulfate and calcium hydroxide. Aluminum sulfate (Alum) is selected as a primary coagulant, while calcium hydroxide (lime) is used as a coagulant aid. Alum is a white crystalline solid with the formula $Al_2(SO_4)_3.18H_2O$ with purity of 97.3%wt. Lime is a very fine white powder. It has the chemical formula of $Ca(OH)_2$, purity of 95%wt. The selected coagulants have been chosen in this work due to their physical and chemical properties which give their ability to remove turbidity on their molecular species from the bulk liquid. Also, they are of low cost and are locally available.

3. EXPERIMENTAL PROCEDURE

All coagulation experiments were conducted in six-place conventional jar-test apparatus. Six beakers with 1 liter volume of produced water are used at time of experiment. The study includes the effect of coagulant/ coagulant aid ratio, coagulant dose, pH, and sedimentation time on turbidity removal. Different combinations of coagulant dose (20, 40, 60, 80, 100, and 120 mg/l), pH (3, 4, 5, 6, 7, and 8), and sedimentation time (30, 60, 90, 120, 150, and 180 min) were tested. The pH was adjusted by adding drops of HCl (0.1M) or NaOH (0.1M) prior to the addition of coagulant. To simulate coagulation, flocculation, and sedimentation conditions, rapid mixing at 200 rpm was performed for 3 min, followed by slow mixing for 30 min at 30 rpm and final step (0 rpm) for 60 min settling time, **Degremont, 1979.** After completing the settling time, supernatant was withdrawn with a plastic syringe from near 3 cm below the liquid-air interface for analysis of turbidity and total suspended solids. All the experiments were carried out at ambient temperature of 20-25 C^o.

Total suspended solids (TSS) are that portion of the total solids that are retained on a filter paper (Cellulose nitrate membrane, approximately 0.45 mm pore size). Before sampling, filter papers were prepared by first soaking them in distilled water, drying them at 100 C^o, weighing and recording their weights. Now, a measured volume (100 ml) of produced water is passed through the filter. The filter containing the residue is then dried in an oven for one hour at 100 C^o. The sample is then cooled and weighed. The increase in weight represents TSS. Finally, TSS was calculated by using the equation below, **APHA, 1998.**

$$TSS\left(\frac{mg}{l}\right) = \frac{(A-B)}{C} \times 1000 \tag{1}$$

where A = final weight of the filter (mg), B = initial weight of the filter (mg), and C = volume of water filtered (l). This inexpensive TSS tells much about the produced water character and can be run in less than two hours with fairly inexpensive equipment.

4. RESULTS AND DISCUSSION

4.1 Evaluation of the Percentage Ratio of Coagulant/Coagulant Aid

Different doses of aluminum sulfate (alum) as a primary coagulant with the coagulant aid (lime) were added to the produced water with initial turbidity as 92 NTU, uncontrolled pH as 5.8, coagulant dose as 60 mg/l, and 60 min as sedimentation time. The results are shown in table 2. Examining this table, it is clear that there was an improvement in the turbidity removal when

25% lime were used as a coagulant aid in conjunction with 75% alum compared to alum alone and this can be regarded as the best coagulant. **Lin, et al., 1971** showed that the addition of alum to water releases hydrogen ions and consequently lowers the pH. Unless the hydrogen ions can be removed, the formation of an effective floc, $Al(OH)_3$, is impossible. The hydrogen ions can be removed by the alkalinity in natural water or by the addition of lime. This finding is in agreement with **,Degremont, 1979** and **Kiely, 1997.** They mentioned that if there is insufficient alkalinity in the water with high turbidity, alkalinity is added by means of lime addition, even with small amount, to improve the alkalinity and optimize coagulation.

4.2 Effect of Coagulant Dosage

Coagulant dosage was one of the most important parameters that have been considered to determine the best condition for the performance of coagulant used (75%alum+25%lime) in coagulation/ flocculation process. The effect of coagulant dosage on the removal of turbidity is shown in **Fig. 1**. Coagulant dosage was varied from 0 to 120 mg/l while other parameters were kept constant at pH 5.8 and 60 min for sedimentation time. From **Fig. 1**, it can be seen that the best dose of coagulant was 80 mg/l and the removal efficiency of turbidity was 91.41%. It is noticed that turbidity values are decreasing for coagulant dosage level of 0 to 80 mg/l and gradually increasing for dosage level of 100 to 120 mg/l. This may be explained by: high dose of the coagulant in the suspension caused charge stabilization of colloid particles, due to the adsorption of counter ions (in this case was Al^{+3}). Increasing the dose of coagulant more than 80 mg/l raised the turbidity because the excess adsorption of the counter ions caused the charge of colloidal particles to become positive (i.e. re-stabilization of the colloidal particles). The results obtained in this study are similar to those reported by **Ghaly et al., 2007** who reported that colloidal particles are negatively charged and upon addition of aluminum sulfate to wastewater, the Al^{+3} ions are attracted to these particles. At the point of complete charges neutralization, the colloids begin to agglomerate due to collisions between particles. If excess coagulant is added to the wastewater, the results are a reverse of the net charge on the colloidal particles (from negative to positive). Particle re-stabilization by charge reversal allowed greater amounts of smaller particles to remain in solution, thus increasing the total solids as well as the color intensity of the treated water.

4.3 Effect of pH

In the coagulation/ flocculation process, pH is very important as the coagulation occurs within a specific pH range. An optimum pH range, in which metal hydroxide precipitates occur, should be determined to establish best conditions for coagulation. In this study, a range of pH between 3 to 8 was selected. The results of the study showing the effect of pH on the removal of turbidity are presented in **Fig. 2**. To determine the best pH value, coagulant dosage was maintained at 80 mg/l and 60 min for sedimentation time. The best pH was determined at a value of 6 followed by 5 and 7 and the turbidity removal was 91.09% as shown in **Fig. 2**. It was found that the percentage of turbidity removal was increased at pH from 3 to 6 and then it declined for pH 7 to 8. The obtained results are in accordance with those obtained by **Degremont, 1979** and **Sadeddin et al., 2011,** which indicated that aluminum salts work best in a pH range of 5.5-7.4. Outside this range, a higher concentration of dissolved aluminum is liable to be found.

4.4 Effect of Sedimentation Time

In this experiment, the sedimentation times were varied from 30 to 180 minutes. Other parameters were kept constant at pH 6 and 80 mg/l for coagulant dosage. The effect of sedimentation time on coagulation process is given in **Fig. 3**. From this figure, it can be seen that the turbidity decreased with increasing settling time and it reached equilibrium at 120 min. At this point, removal efficiency of turbidity was 97.72 %. Further increase in time had no effect on turbidity removal. This result explained that almost all flocs produced after the coagulation and mixing process have settled to the bottom of the sludge layer after 120 min. The settling process is mainly affected by the gravity where heavier flocs will settle faster than dispersed particle.

4.5 Turbidity versus Total Suspended Solids

Both turbidity and total suspended solids (TSS) are defined by the method used to measure them. Turbidity is an optical measurement; it depends on the number of particles in the sample and their shape and size. While TSS is a gravimetric measurement, it depends on the total mass of filterable material in the sample, **Rasmussen, 1995, Fig. 4**. The final relationship between turbidity and TSS at Al-Ahdab oilfields produced water was shown in **Fig. 5**. This figure confirms the existence of a strong linear relationship between turbidity readings and TSS concentrations. High coefficient of determination (R^2=0.972) value was obtained for this relationship. From the published NTU-TSS relationship, **Irvine, et al., 2002** and **Hannouche, 2011.** It is seen that it can vary considerably between different aquatic systems and even at different times for the same stream, so there is no universal correlation of turbidity and TSS.

5. CONCLUSIONS

The aluminum sulfate (alum) combination with coagulant aid (lime) provided higher removal efficiencies of turbidity compared to coagulation with alum alone. The added alum to water causes the release of hydrogen ions which lowers the pH.

The best conditions for turbidity removal using a jar test process can be obtained at 75% alum+25% lime coagulant ratio at coagulant dosage of 80 mg/l at pH 6 and 120 min for sedimentation time. This dose caused colloid particles to be charge stabilized, while increasing the dose increase the turbidity where re-stabilization occurs.

At these conditions, the NTU reading was reduced from 92 to 2.1. The TSS-turbidity relationship may be both site and time specific, so the relationship is normally unique for a particular catchment and within a particular period of time.

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Table 1. Analysis of produced water from Al-Ahdab oilfields, date: 2-3-2013.

Parameter	Value	Permissible Limit
pH	5.5-5.9	6.5-8.5
Turbidity (NTU)	92	5
TSS (mg/l)	2520	30
Density (kg/m^3)	1095	_

Table 2. The percentages of the coagulant doses.

Sample No.	Coagulants	Final Turbidity (NTU)	Removal Efficiency (%)
1	100 % alum + 0 % lime	54.4	40.87
2	75 % alum + 25 % lime	12.8	86.09
3	50 % alum + 50 % lime	37.2	59.57
4	25 % alum + 75 % lime	61.4	33.26
5	0 % alum + 100 % lime	73	20.65

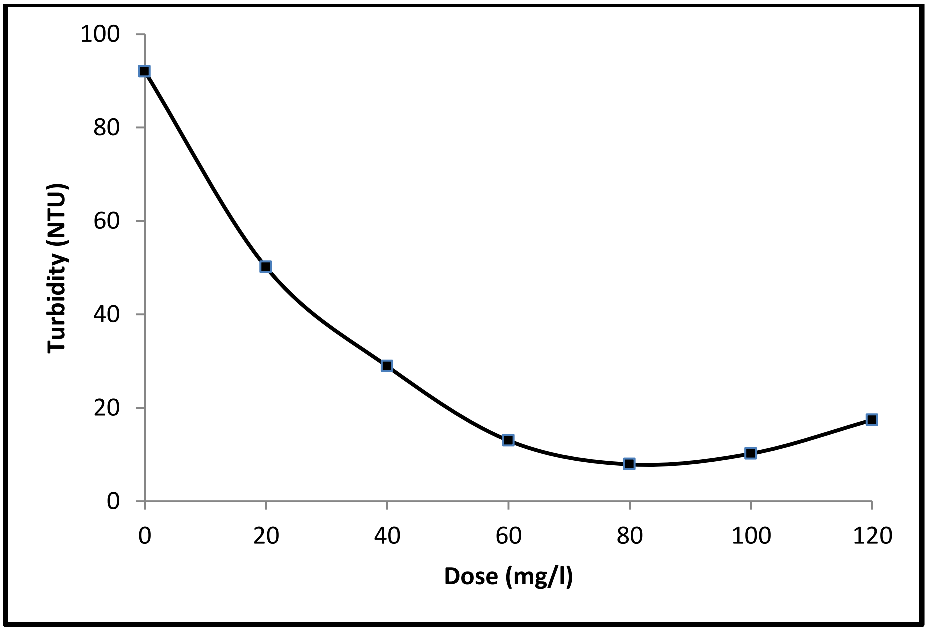

Figure 1 The effect of coagulant dosage on turbidity removal from produced water.

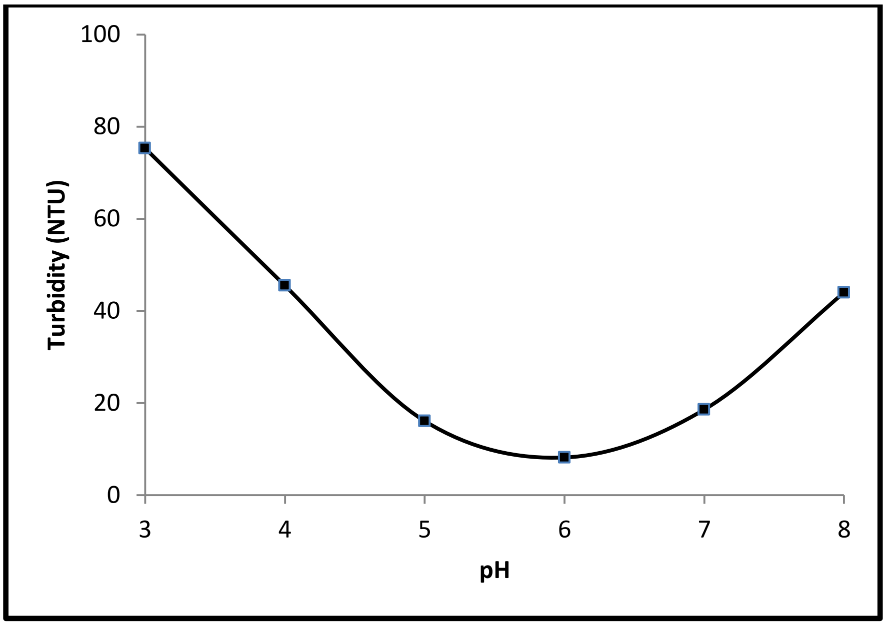

Figure 2. The effect of pH on turbidity removal from produced water**.**

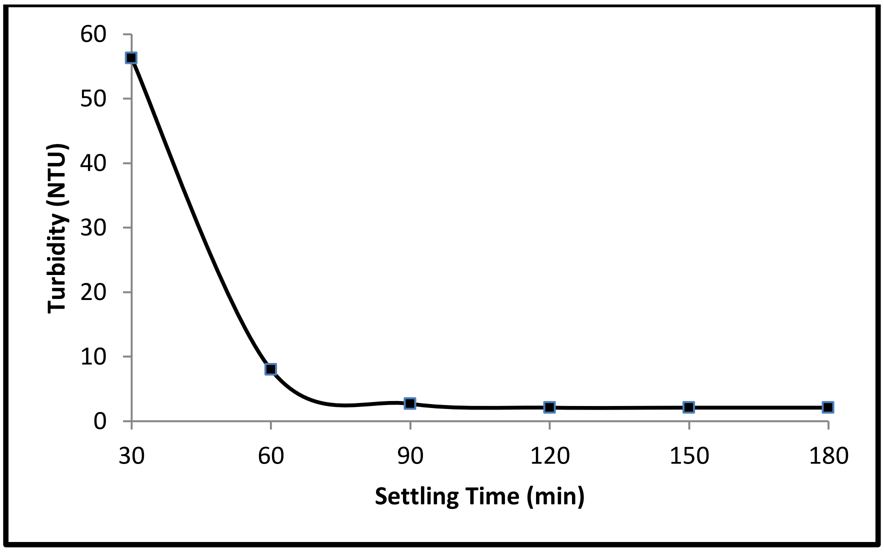

Figure 3. The effect of sedimentation time on turbidity removal from produced water.

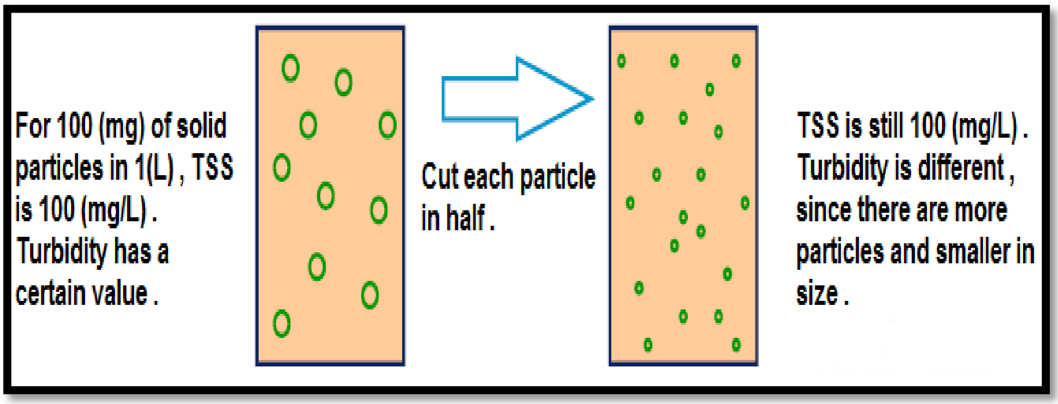

Figure 4. Turbidity compared to TSS**.**

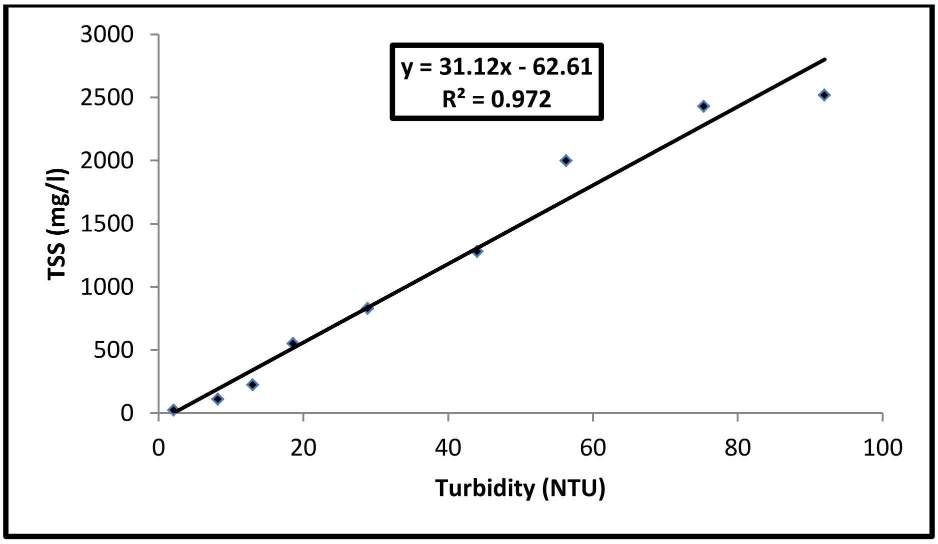

Figure 5. Turbidity-TSS relationship at Al-Ahdab oilfields produced water.