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CHEMICAL REMEDIATION OF THE EFFLUENTS OF SUEZ OIL PROCESSING COMPANY

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Abstract

The industrial wastewater treatment methods include many types of coagulation process which results from the addition and rapid mixing of coagulant with wastewater to remove suspended or colloidal waste materials. Jar test technique was used in this work where coagulants as aluminum sulphate, ferric chloride and polyacrylamide are added by a suitable percentage of each individually to predict the optimum doses of the previous coagulants. Generally the optimum dose for aluminum sulphate which affects the values of the measured parameters was 100 mg/L. The measured parameters which used to test the quality of treatment are chemical oxygen demand, suspended solids, total dissolved solids, conductivity and dissolved oxygen. The results showed that the optimum dose for ferric chloride was 75 mg/L for the treatment of the previous mentioned parameters. However, the best effective dose of coagulant aid was 30 mg/L where the oxygen content was changed to a maximum value of 5.34 mg/L while, chemical oxygen demand was varied to a minimum value of 145.61mgO_2/L.

Moreover, the doses of coagulant aid were positively significant correlated to dissolved oxygen values($r=0.892$, $p\leq.0.05$) and negatively correlated to chemical oxygen demand($r=-0.855$, $p\leq.0.05$), which reflects the high efficiency of the coagulant aid in reducing the organic wastewater.

Keywords*:* Remediation, industrial effluents, Alum, Ferric chloride

Introduction

The solution chemistry of aluminum (Al) is complex and includes the formation of both mononuclear and binuclear hydroxyl complexes. Aluminum also forms very strong complexes with fluoride and humic substances (humic and fulvic acids). Industries have always been a major source of water pollution [1].

Many industries displace of their process wastewater, cooling water and other liquid wastes into surface water or adding them to a municipal sewer, which lead to a water body. The wastes may be in the form of liquid, solid and gas; these waste materials must properly collected, treated and disposed in the manner that they will cause no current or future public health or environmental problems. Industrial wastewaters vary enormously in compostion, strength, and volume from industry to industry. Some wastewaters may be acidic or alkaline; contain oxygen depleting organic materials, nutrient salts, or suspended solid that can settle in receiving waters.

The industrial wastewater treatment methods include many types of treatments; these are:

1. Neutralization for the industrial wastewater which has a high or low pH reading to a more acceptable pH value.
2. Oxidation –reduction processes for industrial pollutants to become less toxic or more degradable.
3. Sedimentation process as many industrial wastewaters contain appreciable amounts of suspended solids; therefore, can cause problems in sewer system where may settle out or cling to pipe. The settling of suspended solids occurred by using flocculants.
4. Flotation is essentially the reverse of sedimentation process; it is used for the wastewater which contains solids or immiscible liquids that are lighter than water. They float to the surface in the flotation tank, where they can be skimmed off 5-coagulation process by the addition and rapid mixing of coagulant with wastewater to remove suspended or colloidal waste materials that are too small to be effectively removed by gravity separation
5. Activated carbon treatment in which the adsorption can be used to remove industrial organic contaminants that are difficult to remove by other processes.
6. Ion exchange resin which is a chemical treatment process used to remove unwanted ionic species from wastewater.

On the other hand, the coagulation and flocculation processes of water are influenced by a number of factors such as temperature, pH, period and degree of agitation during flocculation as well as the characteristics of the coagulant used. Various coagulants are in common use; the most popular coagulants are aluminum sulphate or alum [$Al_2 (SO_4)_3.14H_2O$] and iron salts (ferric chloride, ferrous sulphate and ferric sulphate).These coagulants work by providing charge destabilization and producing insoluble hydroxide and phosphate floc[2] as shown in the following equations:

$Al_2(SO_4)_3.14H_2O + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4 + 14H_2O + 6CO_2$ (1) O_4

$Al_2(SO_4)_3.14H_2O + 2(PO_4)^{-3} \rightarrow 2AlPO_4 + 3(SO_4)^{-2} + 14H_2O$ (2)

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

$2FeCl_3 + 2(PO_4)^{-3} \rightarrow 2FePO_4 + 6Cl^-$ (4) O_4

Coagulant aids are used to improve coagulation by promotion layer with more rapidly settling flocs. Polyelectrolyte (anionic, cationic and non ionic) are large molecular weight polymers which are long molecules and can link particles together. Coagulation/flocculation process is used for combining small particles into larger aggregates .It is an essential component of accepted water treatment practice. However, aluminum can become toxic when water - pH drops to the value of 5.5, where the maximum aluminum dosing based on toxicity in fish [3]. The commercial alum is added to water where a series of hydrolysis reactions occur before precipitation of $Al(OH)_3$,and the same occur for iron salt [4] according to the following :

$Al^{+3} + H_2O \rightarrow Al^{+2}(OH) + H^+$ (5)

$Al^{+2}(OH) + H_2O \rightarrow Al^+(OH)_2 + H^+$ (6)

$Al^+(OH)_2 + H_2O \rightarrow Al(OH)_3 + H^+$ (7)

This paper deals with treatment of the outlet (wastewater) of oil processing company by using a simple chemical method which can be applied in the location. Jar test technique will be used in this work where the coagulants (aluminum sulphate, ferric chloride and polyacrylamide) are added by a suitable percentage of each individually to predict the optimum doses of each of the above named coagulants. Understanding of such coagulants can be useful for evaluating the chemical method to be used.

Material and methods

1-Equipments: A stirring or mixing device (jar test) was used to provide controlled agitation equivalent in degree to plant scale flocculates ; it is usually provided by speed30-400 r.p.m stirring paddles (model SWI, USA), six jars of 1.5-2liters, and glass funnels, filter papers and

Multimeter; WTW (Wissenshaftlich Technische Werkstatten, GMBH-Germany) was used for measuring of pH, conductivity, salinity, total dissolved solids, dissolved oxygen and turbidity.

2-Solutions: A-Aluminum sulphate solution was prepared by dissolving 1 g of alum (Aldrich) [$Al_2(SO_4)_3.14H_2O$]] in 100 mL distilled water;(1 mL of this solution equals10 mg of aluminum Sulphate).

B-Ferric chloride solution was prepared by dissolving 1gm of ferric chloride (Aldrich) in 100 mL distilled water; (1 mL of this solution equals10 mg of ferric chloride).

C-Polyacrylamide solution was prepared by dissolving 1gm of powder polyacrylamide in 100 mL distilled water.

3-Sampling: A large sample of wastewater of oil Company (20liter) was collected to permit at least four series of jar tests.

4-Procedure: pH, conductivity, salinity, total dissolved solids, dissolved oxygen and turbidity were determined for untreated wastewater of oil company .Where 1 L portion of untreated wastewater of six jars was placed in the stirring equipment. Then, the stirrer was operated and during agitation doses of alum or ferric chloride were added quickly to the six jars with different doses from 25to 150 mg/L. Agitation process was continued for 20 min or for the period of time provided for flocculation; then coagulant aid (polymer) was added. The time of the first appearance of visible floc in each of six portions of the treated samples was observed. After the slow mixing period, the paddles were withdrawn and settling of floc particles was observed. The bulk particles were leaved for settling in the bottom of the jar tests for a period of 30min [5]. Finally, the pH and other parameters were determined for the supernatant water above the floc in each portion using Miltimeter; WTW.

Results and discussion

The characters of untreated and treated wastewater of Suez oil processing company were presented in Tables (1-3). The results treatment indicate variations in pH, suspended solids, dissolved oxygen, total dissolved solids and electrical conductivity as compared with their values before treatment. Evidently, the addition of alum leads to general decrease in the values of above mentioned parameters except for dissolved oxygen which show some increase. It is important to consider possible changes in pH values as the result of dissolution of more carbon dioxide gas into tested solution (stirring of batch experiment) as well as the hydrolysis reactions which occur before precipitation of $Al(OH)_3$ as indicated in equations 5-7 .In addition to, the regression analysis revealed that alum doses correlated negatively with pH readings(r=-0.978,$p \leq 0.05$). Generally the optimum dose for aluminum sulphate which affects the values of the measured parameters is 100 mg/L.Furthermore the floc size formation increases with increasing , alum dose up to 100 mg/L, where the rate of settlement is faster than floc formation[6] .This can be supported by a significant negative correlation between alum doses and suspended solid values

(r=-0.873,$P \leq 0.05$) as shown in Table (4) .So, it is noticed that the suspended solids value increases again and concentration of dissolved oxygen decreases when comparing to the lighter floc formation doses. This is mainly due to the idea that the concentration of Al complexed by humic substances has shown to be a function of solution of $[Al^{+3}]$,$[H^{+}]$,ionic strength and concentration of organic matter[7].

On the other hand, the effect of different doses of ferric chloride on the quality of the treated wastewater is given in Table (2). indicate that, the optimum dose is 75 mg/L for treatment the previous mentioned parameters; but with the increase of the dose of ferric chloride more than75 mg/L ,the efficiency of treatment become less effective. Also,the results revealed a major advantage of ferric chloride as coagulant for improving floc characteristics. Furthermore, ferric chloride was negatively correlated to both of suspended solids($r = -0.86$, $p \leq 0.05$)and total dissolved solids ($r = -0.524$, $p \leq 0.05$) as indicated in Table (4),which provides an evidence supporting the observed results . The floc was large, dense and heavy until reaching the dose 75 mg/L. n addition, the formation of floc become smaller and lighter with increasing Fed_3 dose of ferric chloride above 75 mg/L. On the other hand, the effect of coagulantaid doses (polycrylamide) on water quality is collected in Table (3).The doses of coagulant aid were increased from 10mg/L to 60mg/L by increment rate10mg/L.From look at the Table (3) indicate that, the best effective dose of coagulant aid is 30 mg/L where the oxygen value is changed to a maximum value of 5.34 mg/L and chemical oxygen demand changed to a minimum value of 145.61 mgO_2/L Moreover, the doses of coagulant aid was positively significant correlated to dissolved oxygen values (r=0.892,$p \leq .0.05$)and negatively correlated to chemical oxygen demand (r=-0.855, $p \leq .0.05$).This reflects the high removal efficiencies of organic wastes using the coagulant aid as an advanced treatment step. However, as the coagulant aid dose increases to higher values it becomes less effective for treatment of wastewater as indicated in Table (3).Therefore the presence of higher doses of coagulant aid in solution prevents the particle aggregation and decreases the settling rate of these particles.Ultimately, this increases the total concentration of colloidal bound contaminants in the treated water [8].

Conclusions

Alum represents the most popular remediation technique for removing suspended solids and total dissolved solids from the aquatic environment. Furthermore, the optimum dose for using alum was100 mg/L and for ferric chloride was 75 mg/L while, the best effective dose polyaerylamide was 30 mg/l. However, as the coagulant aid dose increases to higher values it becomes less effective for treatment of wastewater. In the same context, the comparison among the results of the three coagulants used in effluent treatment indicated that polyacrylamide has more advantages for treatment of wastewater than alum and ferric chloride. This result open the way to the developing countries for applying the previous recommended chemical method for treatment of the disposal wastewater of oil refineries. Also, it must take into account the literature data on removal efficiencies of the proposed chemical treatment methods with regard to the environmental point of view.

Table 1: The results of coagulant and flocculation test using alum doses

Parameter	Raw	Alum dose mg/l					
		25	50	75	100	125	150
COD (mg O_2/L)	630.54	597.6	529.04	488.52	337.72	339.2	340.10
pH	10.2	10.1	9.56	8.52	7.05	6.82	6.01
S.S (mg/L)	923.70	823.00	712.00	659.75	620.00	632.75	650.75
TDS (mg/L)	45491	45430	44135	43960	43400	44345	44453
Cond. (μs/cm)	64900	63900	63050	63080	62000	26500	62900
DO (mg/L)	1.80	2.35	3.02	3.13	3.61	3.60	3.6
Salinity (‰)	44.86	44.8	44.5	42.11	41.16	43.20	43.21

Where:

COD (chemical oxygen demand)

S.S (Suspended) solids

TDS (Total dissolved salts)

Cond. (conductivity)

Do (Dissolved oxygen)

Table 2: The results of coagulation and flocculation test by using ferric chloride doses (mg/L)

Parameter	Raw	Alum dose mg/L					
		25	50	75	100	125	150
COD (mg O_2/L)	630.54	545.36	418.02	231.12	234.10	235.51	238.38
pH	10.2	9.57	8.24	7.54	7.22	6.46	6.32
S.S (mg/L)	923.7	735.51	663.11	495.56	496.13	508.19	523.51
TDS (mg/L)	45491	44940	44807	42414	44128	44562	44485
Cond. (µs/cm)	64900	64200	64000	62020	63040	63660	63550
DO (mg/L)	1.80	2.90	3.80	4.15	4.12	4.11	4.10
Salinity (%)	44.86	44.8	43.9	42.11	43.31	43.52	43.61

Table 3: The results of coagulant and flocculation test by using polymer doses (mg/L)

Parameter	Raw	Alum dose mg/L					
		10	20	30	40	50	60
COD (mg O_2/L)	630.54	419.5	354.05	145.61	174.87	181.86	185.91
pH	10.2	9.59	9.61	9.42	9.40	9.33	9.30
S.S (mg/L)	923.7	500.1	301.0	211.0	215.0	220.1	232.0
TDS (mg/L)	45491	44730	44660	44037	44107	44457	44639
Cond. (µs/cm)	64900	63900	63800	62910	63510	63770	63770
DO (mg/L)	1.80	3.0	4.01	5.34	5.33	5.32	5.32
Salinity (%)	44.86	44.01	44.01	43.2	43.6	43.70	43.71

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