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Chemical Precipitation method for Sulphate Removal from Treated Wastewater of Al-Doura Refinery

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KEYWORDS

Al-Doura refinery, chemical precipitation, sulphate, wastewater treatment.

ABSTRACT

Wastewater treatment by Wastewater Treatment Plant, named (INGECO) in Doura refinery suffers from the elevated level of sulphate ion concentrations compared to the recommended EPA [14] specified (250 mg/L). The annual rate, maximum and peak sulphate concentrations that found to be 360; 425 and 550 mg/L respectively. In this study samples prepared from industrial wastewater and the average, maximum and peak sulphate concentrations to be used in chemical precipitation process by using $BaCl_2$ *or Al(OH)3. Results obtained from* $BaCl_2$ *treatment refer to the optimum (dosage, mixing time and mixing speed) to be used in sulphate removal for reuse purpose were (1.5 g/L, 1.2 hr and 80 rpm), (2.25 g/L, 1.5 hr and 90 rpm) and (3.0 g/L, 2 hr and 90 rpm) for each of average, maximum and peak concentrations respectively. Whereas for disposal purpose, were (0.36 g/L, 15 min and 100 rpm), (1.1 g/L, 15 min and 70 rpm), (1.72 g/L, 15 min and 90 rpm) respectively. This process was achieving of highly sulphate removal, but expensive. Whereas the results obtained by using Al(OH)3 indicated unsuitability for treated refinery wastewater treatment of low sulphate concentrations and neutral pH.*

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1. INTRODUCTION

Sulphate ion present in various mineral that are found in soil and rocks sulphate. It forms salts with a variety of alkali and alkaline earth metals such as barium, calcium, magnesium, potassium and sodium. Sulphate may be leached into water from the soil, provided that magnesium, potassium and sodium sulphate salts are very soluble in water. Decaying plant and animal matters release sulphate into water, and numerous chemical products including ammonium sulphate fertilizers contain sulphate in a variety of forms. Treatment of water with aluminum sulphate (alum) or copper sulphate introduces sulphate into water supply. Human activities such as the combustion of fossil fuels and sour gas processing release sulfur oxides to the atmosphere, and rise to sulfuric acid in rainwater (acid rain), and the later results in the return of sulphate to surface waters [15,16]. Although sulphate is non-toxic ion, except at very high concentrations, it exerts a purgative effect:

1) Precipitation of sulphate can cause damage to equipment through the formation of calcium sulphate scale [10].
2) At high concentrations, precipitation of sulphate may affect the efficiency of many industrial processes [9].
3) Sulphate precipitation as gypsum, may impair bad quality to treated water [12].
4) People consuming drinking water containing sulphate in concentrations exceeding 500 mg/L commonly experience cathartic effects, resulting in purgation of the alimentary canal [13].
5) Saline water can impart to salinization of irrigated soils, diminished crop yield and changes in biotic communities [11]. There are different methods to remove sulphate from industrial wastewater. These methods can be divided into physical processes such as membrane filtration, chemical treatment such as precipitation methods and biological sulphate reduction [1-8].

Physical Sulphate removal methods include: (1) Membrane filtration such as RO (reverse osmosis), SRO (Seeded Reverse Osmosis), SPARRO (Slurry Precipitation and Recycle Reverse Osmosis), ED (Electro Dialysis) and EDR (Electro Dialysis Reversal), (2) Ion exchange . Chemical removal Methods include: (1) Gypsum precipitation, (2) Ettringite precipitation such as SAVMIN and CESR (Cost Effective Sulphate Removal), and Barite (barium sulphate) formation. The biological methods are: (1) bioreactors, and (2) constructed wetlands.

2. BARITE FORMATION

Barite ($BaSO_4$) is highly insoluble making it an excellent candidate to remove sulphate ions from wastewater. In this In this process barium salt is added to the sulphate-rich water. The barium salts commonly used include barium carbonate ($BaCO_3$), barium sulphide (BaS), barium hydroxide ($Ba(OH)_2$) and barium chloride ($BaCl_2$) [10]. The reactions that take place are shown in the following reaction equations (1-5) respectively [7].

$$BaCO_3(s) + Na_2SO_4 \rightarrow BaSO_4\,(s) + Na_2CO_3 \quad (1)$$

$$Ba(OH)_2\,(s) + H_2SO_4 \rightarrow BaSO_4\,(s) + 2H_2O \quad (2)$$

$$BaS\,(s) + H_2SO_4 \rightarrow BaSO_4\,(s) + H_2S\,(g) \quad (3)$$

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4\,(s) + 2NaCl \quad (4)$$

$$Al_2(SO_4)_3 + 3BaCl_2 \rightarrow 3BaSO_4\,(s) + 2AlCl_3 \quad (5)$$

A greater quantity of sulphate is recovered when barium sulphide is used, but not as much gypsum is produced. However, toxic hydrogen sulphide gas that has an unpleasant odor is produced. The use of barium hydroxide is proposed for solutions where most metals have already precipitated as metal hydroxides.

Barium salts are expensive, thus, the barium sulphate sludge is often recycled and treated to reduce the costs. As well as, equation (6) is shown aluminum hydroxide ($Al(OH)_3$) interaction with sulphate in water as (Na_2SO_4) that produced aluminum sulfate ($Al_2(SO_4)_3$) sediment of white color.

$$Al_2(SO_4)_3 + 6NaOH \rightarrow 2Al(OH)_3 + 3Na_2SO_4 \quad (6)$$

3. EXPERIMENTS:

After inspection of water quality used in different refinery processes which illustrated in Table I, it is found that the major highly concentration of sulphate in wastewater reach about (2900 mg/L) coming from blow down water of energy units. But when it reach the WWTP, the concentration reduced to less than (600 mg/L) by using ion exchange process, then decreased to average level when mixed with other lesser concentration wastewater into WWTP influent collection basin. There wasn't any specific process to control or remove sulphate to reach the effluent disposal limit in WWTP. Laboratory test results for five years (2008 to 2013) have been analysis as illustrated in figure 1 to determine annual rate and maximum sulphate concentration which found to be (360 mg/L) and (425 mg/L) respectively. Also, peak concentration which possible to reach WWTP for more than (15) days per year considered to be (550 mg/L).

TABLE I: Sulphate concentration in various refinery processes

Water treatment unit	**SO_4 (mg/L)**	
	Influent	***Effluent***
sedimentation basins	(190 – 320)	283
After DMF and ACF		272
After storage tanks when adding chemical substances		300
RO unit	300	(4 – 6)
Water resulting from RO unit (reject)		980
Energy unit – 1	15	15
Energy unit – 1 (reject)		1000
Energy unit – 2 and energy unit – 3	15	0
Energy unit – 2 and energy unit – 3 (reject)		2900
Chiki units (one and two)		120
Hydrogenation units (one and two)		530
Grease unit – 1		155
Grease unit – 2		185
Grease unit – 3		270
WWTP (INGECO) unit	300	360

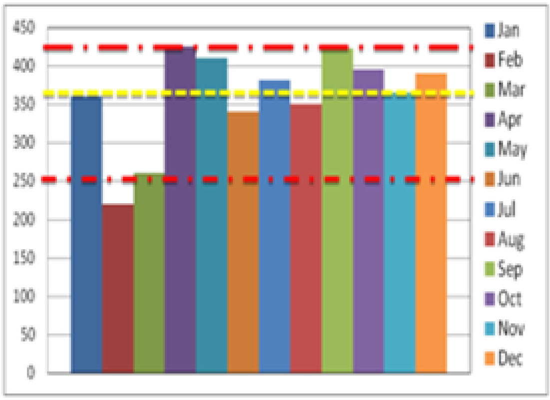

Figure 1: mean monthly rate of treated water sulphate concentration.

Jar test device used to get optimum $BaCl_2$ and $Al(OH)_3$ dosages, mixing times and mixing speeds could be used for sulphate removal from water for disposal or reuse in refinery process (90 min) is considered the reactor detention time used to reach fewer than (10 mg/L) remaining sulphate concentration in water for reuse aim, and (30 min) is considered to reach less than (250 mg/L) for disposal. These considerations are taken in according to (97) runs per each case. Two substances had been used for sulphate removal, first is barium chloride ($BaCl_2$) and second is aluminum hydroxide ($Al(OH)_3$). Prepared samples with average, maximum and peak sulphate concentrations of (360 mg/L), (425 mg/L) and (550 mg/L) respectively had been used in jar test device to determine optimum dosage, mixing speed (N) and mixing time (t_{mix}) needed to use to obtain (100 %) sulphate removal efficiency for reuse (SO_4 < 10 mg/L) and disposal (SO_4 < 250 mg/L) of refinery treated water. (28) treated water samples of (500 ml) each contents (550 mg/L) SO_4 concentration had been prepared to use in jar test device to obtain optimum design parameters, (16) samples for reuse criteria and (12) samples for disposal criteria, (14) samples of treated water in (500 ml) volume each one contents (360 mg/L) SO_4 concentration had been prepared to use in jar test device to obtain optimum design parameters for disposal criteria with extended time to (1.5 hr) rather than (30 min) and fixing mixing speed of (120 rpm).

4. RESULTS AND DISCUSSION

I. Using Barium Chloride ($BaCl_2$):

1):*A*- By fixing Mixing Time (tmix) and Mixing Speed (N) to be (1.5 hr) and (120 rpm) respectively, five vessels for variable ($BaCl_2$) dosages of (0.4, 0.8, 1.2, 1.6 and 2.0 g/L) have been run in the device. Test results obtained were itemized and showed in Figures (2 to 4). Figure 2 illustrates that increasing in $BaCl_2$ concentrations led to decrease SO_4 concentrations to reached a constant value of (6 mg/L), before this lead to increase dissolved chlorides which contributed in increasing of TDS values as appeared from chloride and TDS curves in the same Figure and all other Figures (5, 8, 11, 14, 17, 20, 23, 26, 29, 32, 35, 38, 41, 44, 47, 50 and 53) [18]. Removal efficiencies to reach specified SO_4 reuse concentration of (10 mg/L) are illustrated in Figure 4, which can be concluded that the (100 %) removal efficiency could be obtained from adding (1.5 g/L) dosage of $BaCl_2$, therefore it can be considered that it was the optimum dosage for reuse purpose. While on the other hand, Figure 3 refers to the slightly increasing of pH values with decreasing of temperature values to reach maximum value of (7.3) in (19.4°C) when $BaCl_2$ dosage is (0.8 g/L), then pH tend to be acidic when dosage more than (1.0 g/L) without considerable increasing of temperature. This indicates that the maximum reaction rate has been occurred within (0.8 g/L) dosage. As illustrated from other Figures (6, 9, 12, 15, 18, 21, 24, 27, 30, 33, 36, 39, 42, 45, 48, 51 and 54) of average, maximum and peak SO4 concentrations with variable: the reason temperature affects water's pH is that water molecules have a slight tendency to break down into their constituents, hydrogen and oxygen, as temperature increases. As temperatures increase, a larger proportion of water molecules broke up, releasing a few more hydrogen ions which then decreased the pH of the water. An increase in a solution’s temperature will cause a decrease in its viscosity and an increase in the mobility of the ions in solution. And this increasing may also cause an increase in the number of ions in solution due to dissociation of molecules [17].

B- While in the same N of (120 rpm) and fixed tmix to be (30 min), four vessels for variable ($BaCl_2$) dosages of (0.36, 0.38, 0.40 and 0.42 g/L) have been run in the device. It is found that the optimum dosage of $BaCl_2$ was (0.38 g/L) to reduce sulphate concentration form (360 mg/L) to less than (250 mg/L) as shown in Figure 5. Figure 6 shows pH and temperature behavior curves, temperature drop of one degree with slightly rising in pH values with (0.36 g/L) $BaCl_2$ dosage, but still remaining constant of (23°C) in (0.38 g/L) dosage with the same slightly increasing of pH value, then temperature and pH drop to have the same manner with the other higher dosages, it can considered from pH values. Figure (7) illustrates the SO_4 removal efficiency curve to the specified concentration for disposal. The optimum dosage of $BaCl_2$ to reach (100%) removal efficiency for disposal purpose is (0.36 g/L).

C- Fixing BaCl2 dosage and N to be (1.6 g/L) and (120 rpm) respectively, and with variable tmix of (1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 hr) as shown in Figures (8 to 10). From SO_4 curve of Figure 8 that illustrates the increasing of mixing time from (1.0 – 3.5 hr) which leads to decrease SO4 concentrations until reached maximum sulphate removal of (99.44 %) at (2.5 hr). Figure 9 shows pH and temperature behavior curves that with very slight changes, pH decreased from (7.0) with time until reached (6.7) in (2 hr) then remaining constant acidic. While temperature decreased to reach minimum value of (19.5°C) in (1.5 hr), then slightly raised to be within (20°C) after that. SO_4 removal efficiency curve, it is found that the optimum mixing time for (100%) sulphate removal for reuse purpose is (1.35hr).

D- Fixing $BaCl_2$ dosage and N to be (0.38 g/L) and (120 rpm) respectively, and variable tmix of (7.5, 15, 30 and 60 min) as shown in Figures (11, 12 and 13). Figure 11 illustrates that the mixing time ranged between (15 – 60 min) lead to decrease SO_4 concentrations to reach specified disposal limit at (30 min). Figure 12 shows pH and temperature behavior curves. Figure 13 illustrates SO_4 removal efficiency curve, it is found that the optimum mixing time to reduce sulphate concentration form (360 mg/L) to (250 mg/L) for disposal of treated water is (15 min).

E- Another test was done by fixing $BaCl_2$ dosage and tmix to be (1.6 g/L) and (1.5 hr) respectively, and with variable N to be (80, 120, 150 and 200 rpm). The results obtained are shown in Figures (14, 15 and 16). From SO_4 curve in Figure 14 it is found that the maximum removal of (98.6%) for zero SO_4 concentration have been occurred when N = (150 rpm). It was appeared that the temperature tends to be reduced with increasing of mixing speed until reaching (120 rpm) in slightly acidic solution. The optimum mixing speed (100%) sulphate removal efficiency for ruse purpose was found to be (80 rpm).

F-Fixing $BaCl_2$ dosage and tmix to be (0.38 g/L) and (30 min) respectively, with variable N of (80, 100 and 120), the results obtained are shown in Figures (17, 18 and 19). From SO_4 curve in Figure 17, it is found that the SO_4 concentrations lead to decrease until reaching (250 mg/L) at (100 rpm) in slightly alkaline solution as shown in Figure (18). (100 %) removal efficiency for disposal purpose could be obtained by using (100 rpm) as illustrated from Figure 19.

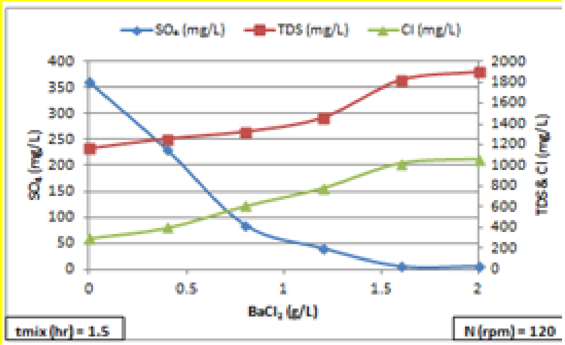

Figure 2: SO_4, TDS and Cl behavior curves by using variable $BaCl_2$ dosages for reuse of treated water.

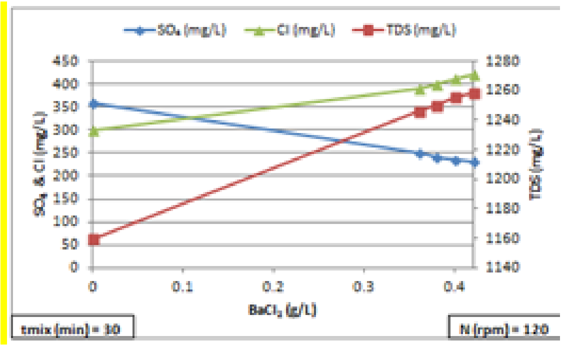

Figure 5: SO_4, TDS and Cl behavior curves by using variable $BaCl_2$ dosages for disposal of treated water.

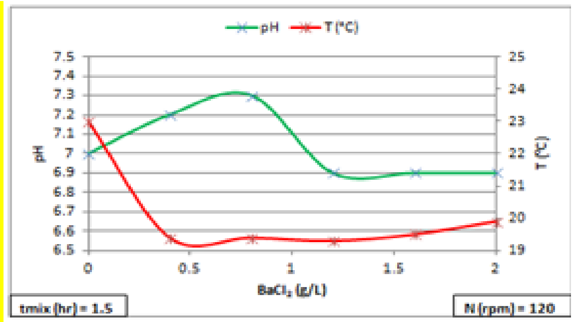

Figure 3: pH and temperature behavior curves by using variable $BaCl_2$ dosages for reuse of treated water.

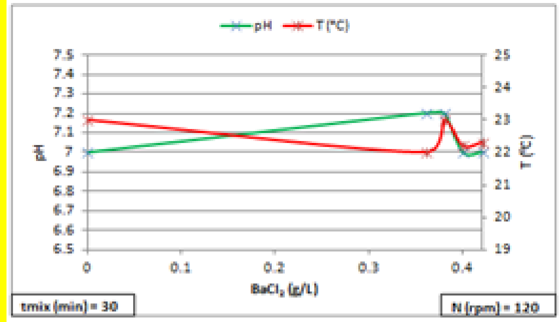

Figure 6: pH and temperature behavior curves by using variable $BaCl_2$ dosages for disposal of treated water.

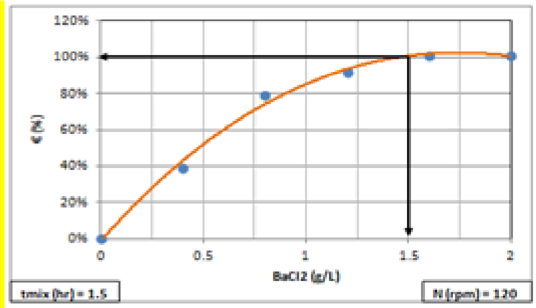

Figure 4: SO_4 removal efficiency curve by using variable $BaCl_2$ dosages for reuse of treated water.

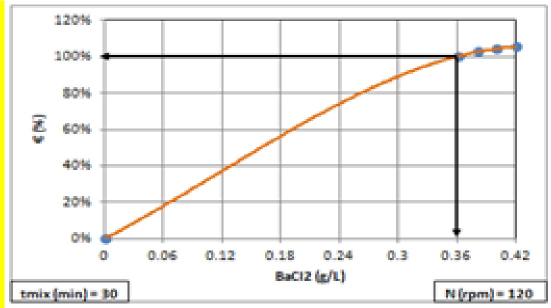

Figure 7: SO_4 removal efficiency curve by using variable $BaCl_2$ dosages for disposal of treated water.

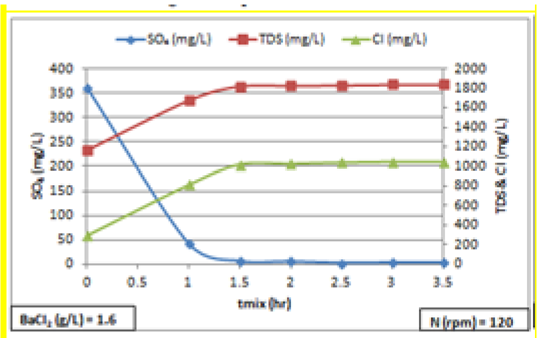

Figure 8: SO4, TDS and Cl behavior curves by using variable mixing times for reuse of treated water.

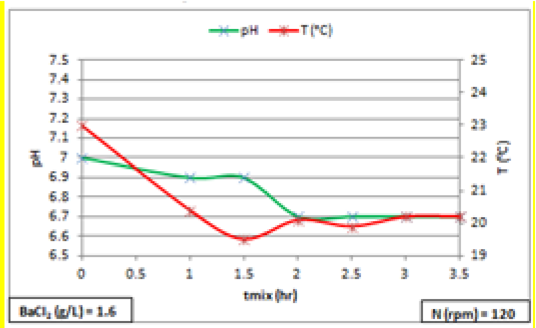

Figure 9: pH and temperature behavior curves by using variable mixing times for reuse of treated water.

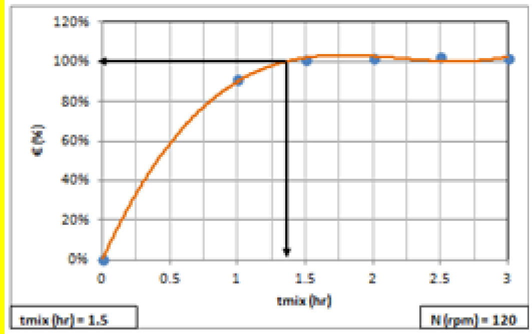

Figure 10: SO4 removal efficiency curve by using variable mixing times for reuse of treated water.

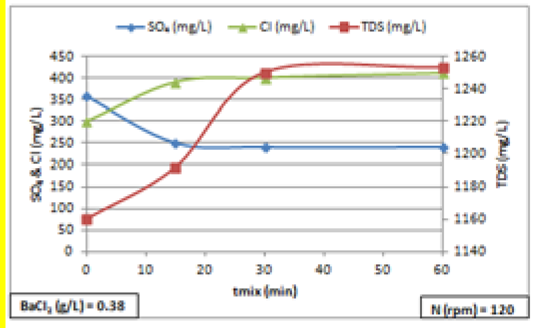

Figure 11: SO4, TDS and Cl behavior curves by using variable mixing times for disposal of treated water.

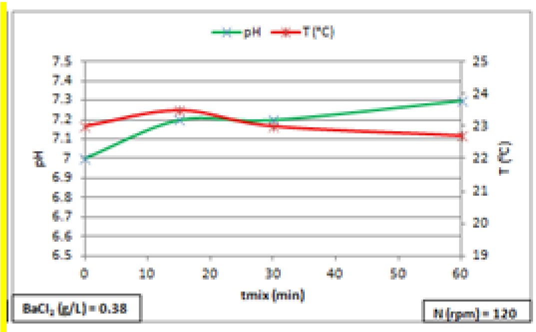

Figure 12: pH and temperature behavior curves by using variable mixing times for disposal of treated water.

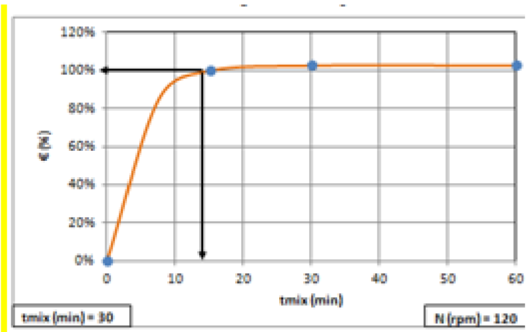

Figure 13: SO4 removal efficiency curve by using variable mixing times for disposal of treated water.

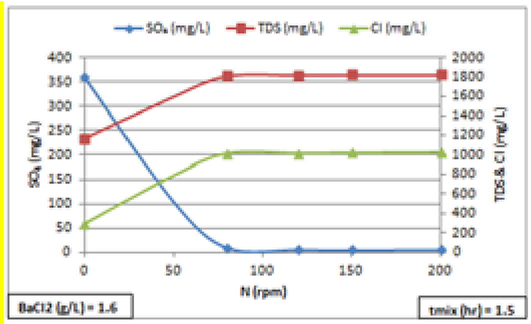

Figure 14: SO4, TDS and Cl behavior curves by using variable mixing speeds for reuse of treated water.

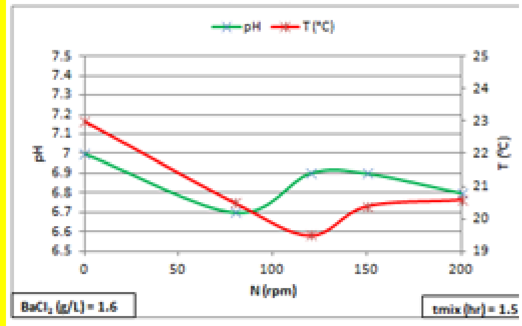

Figure 15: pH and temperature behavior curves by using variable mixing speeds for reuse of treated water

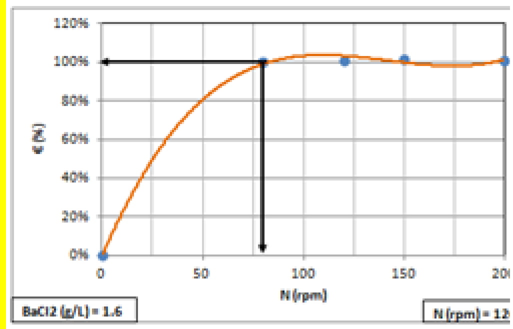

Figure 16: SO_4 removal efficiency curve by using variable mixing speeds for reuse of treated water.

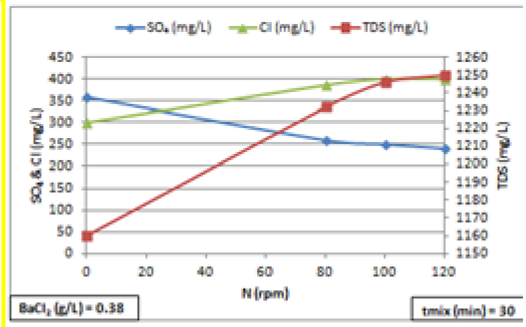

Figure 17: SO_4, TDS and Cl behavior curves by using variable mixing speeds for disposal of treated water.

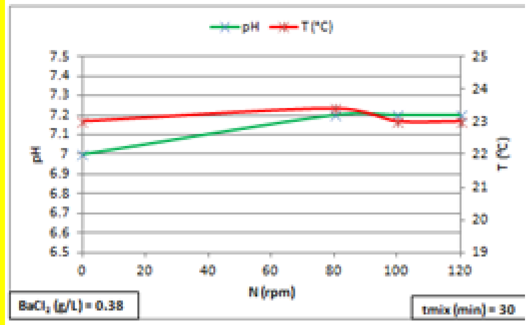

Figure 18: pH and temperature behavior curves by using variable mixing speeds for disposal of treated water.

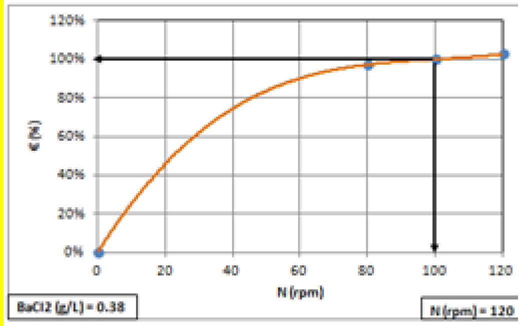

Figure 19: SO_4 removal efficiency curve by using variable mixing speeds for disposal of treated water.

2):*A*- (30) treated water samples of (500 ml) each contents (425 mg/L) SO_4 concentration had been prepared to use in jar test device to obtain optimum design parameters, (18) samples for reuse criteria and (12) samples for disposal criteria. Test results and analysis that obtained from the each run are discussed below:

B- By fixing tmix and N to be (1.5 hr) and (120 rpm) respectively, and with variable $BaCl_2$ dosages of (1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5 and 3.0 g/L), the results obtained are shown in figures (20, 21 and 22). It is appeared from figure 20 that sulphate precipitation was proportional to $BaCl_2$ dosages, when reached (2.5 g/L) the total removal would be (97.65%) and then remaining constant with more dosage. This led to liner increasing of chloride and TDS concentrations until reach (2.0 g/L) of $BaCl_2$ dosage, then curved up in (2.5 g/L) dosage. Therefore, (2.5 g/L) obviously can be considered the optimum dosage could be used for reuse purpose. Figure 21 illustrated that pH tend to decreased with increasing dosages to be an asdic solution with slightly increasing in temperature. It is found that the optimum dosage of $BaCl_2$ is (2.25 g/L).

C- While in the same N of (120 rpm) and fixed tmix to be (30 min) for disposal purpose, and with variable dosages of $BaCl_2$ as (0.9, 1.0, 1.1, 1.2, 1.3 and 1.4 g/L) it is found that (1.2 g/L) led to reduce sulphate concentration form (425 mg/L) to (250 mg/L) as shown in figure 23. Figure 24 illustrated pH curve which indicated that solution tend to be slightly acidic with slightly increasing in temperature. It can observe that the optimum dosage of $BaCl_2$ for (100%) removal is (1.1 g/L).

D- Fixing $BaCl_2$ dosage and N to be (2.5 g/L) and (120 rpm) respectively, and with variable tmix of (1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 hr), the results obtained are shown in figures (26, 27, 28). It is clearly appeared from SO_4 curve in figure 26 that the increasing of mixing time lead to decrease SO_4 to be (10 mg/L) in (1.5 hr), and there are no valuable decreasing for the other extra times. pH and temperatures have the same behaved of variable dosage as showed in figure 27. The (100%) removal efficiency of SO_4 for reuse purpose could be obtained in (1.5 hr) as illustrated from figure 28.

E- In the case of disposal, other test with variable mixing times of (15, 30 and 60 min) and constant $BaCl_2$ dosage and N to be (1.2 g/L) and (120 rpm) respectively had been done. Figure 29 shows it can reach the specified criteria in (15 min). pH and temperature have the same behavior before as showed in figure 30. The removal efficiency was clearly obtained in (15 min) as shown in figure 31.

F- Reuse purpose test with variable mixing speed to be (60, 80, 120 and 150 rpm) and by fixing $BaCl_2$ dosage and tmix to be (2.5 g/L) and (1.5 hr) respectively. From figure 32 it is found that SO_4 reach (15 mg/L) in (80 rpm), then slightly decreased to (10.0 and 8.0 mg/L) when N = (120 and 150 rpm). Solution tends to acidic with slightly increasing in temperature as showed in figure 33. Figure 34 illustrated SO_4 removal efficiency curve, the optimum mixing speed to remove sulphate to (10 mg/L) for ruse of treated water in refinery process is (90 rpm).

G- While by fixing $BaCl_2$ dosage and tmix to be (1.2 g/L) and (30 min) respectively, and with variable N of (80, 100 and 120 rpm). It is found from SO_4 curve of figure 35 that the SO_4 concentrations lead to decrease until reached (< 230 mg/L) at (80 rpm) with ordinary increasing in chlorides concentration and TDS. The temperature will have a slight measurable effect on the pH of water, as the water temperature goes up, pH goes down. The optimum mixing speed to reduce sulphate concentration form (360 mg/L) to (250 mg/L) for disposal of treated water is found to be (70 rpm).

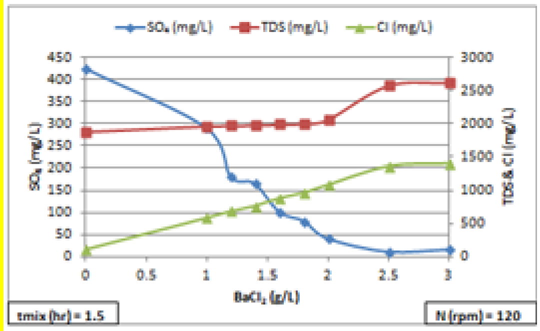

Figure 20: SO_4, TDS and Cl behavior curves by using variable $BaCl_2$ dosages for reuse of treated water.

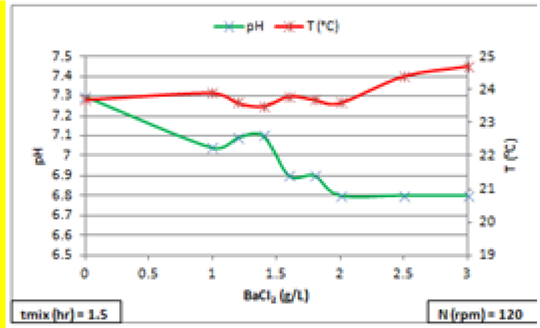

Figure 21: pH and temperature behavior curves by using variable $BaCl_2$ dosages for reuse of treated water.

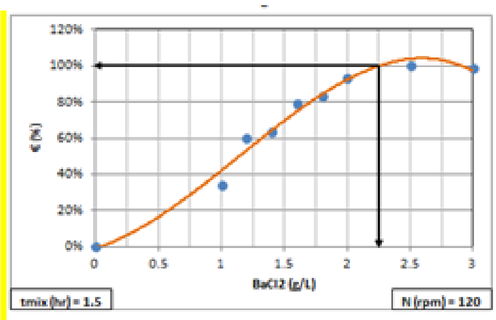

Figure 22: SO_4 removal efficiency curve by using variable $BaCl_2$ dosages for reuse of treated water.

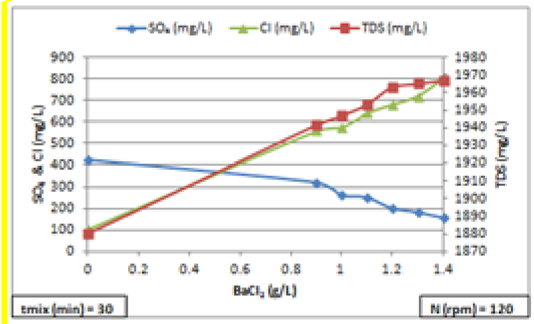

Figure 23: SO_4, TDS and Cl behavior curves by using variable $BaCl_2$ dosages for disposal of treated water.

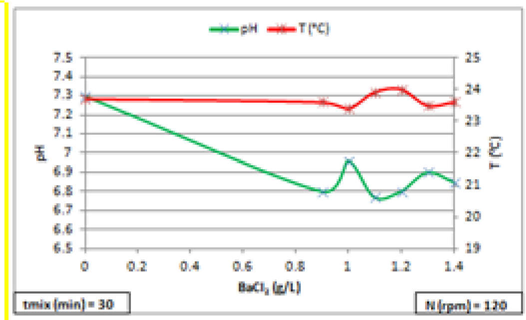

Figure 24: pH and temperature behavior curves by using variable $BaCl_2$ dosages for disposal of treated water.

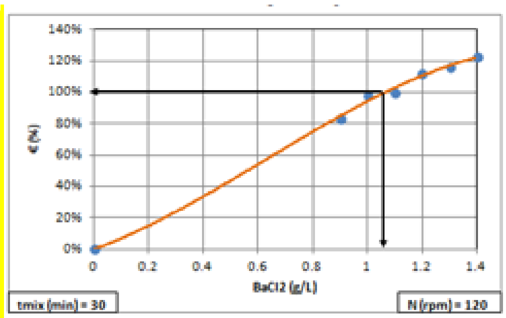

Figure 25: SO_4 removal efficiency curve by using variable $BaCl_2$ dosages for disposal of treated water.

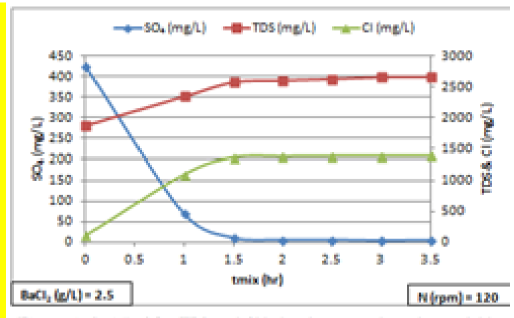

Figure 26: SO₄, TDS and Cl behavior curves by using variable mixing times for reuse of treated water.

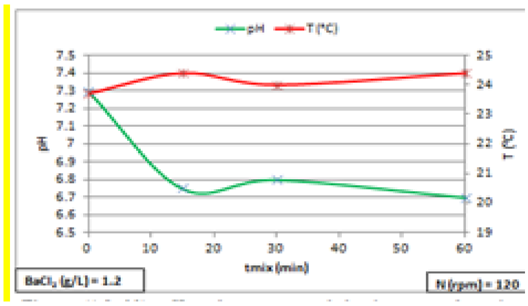

Figure 30: pH and temperature behavior curves by using variable mixing times for disposal of treated water.

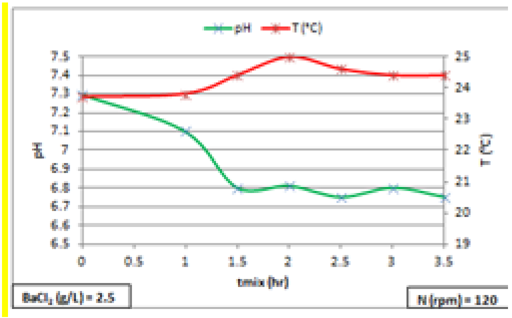

Figure 27: pH and temperature behavior curves by using variable mixing times for reuse of treated water.

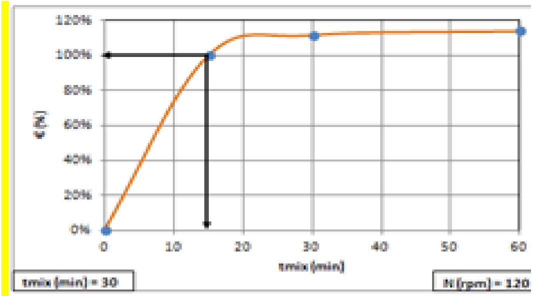

Figure 31: SO₄ removal efficiency curve by using variable mixing times for disposal of treated water.

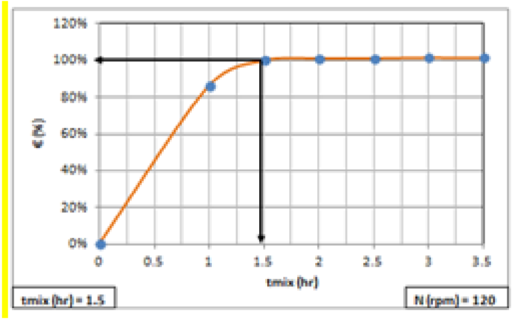

Figure 28: SO₄ removal efficiency curve by using variable mixing times for reuse of treated water.

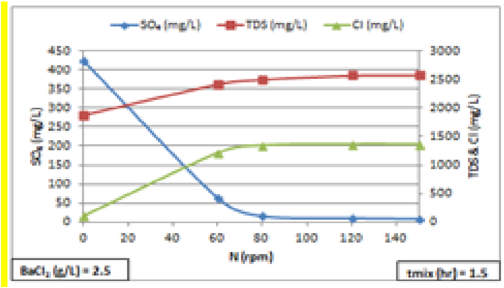

Figure 32: SO₄, TDS and Cl behavior curves by using variable mixing speeds for reuse of treated water.

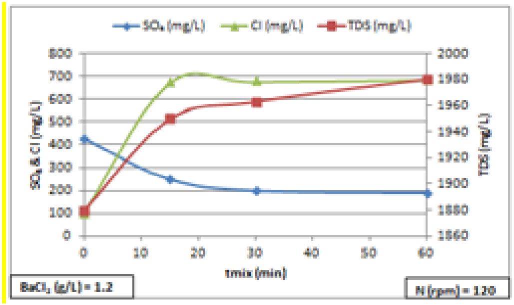

Figure 29: SO₄, TDS and Cl behavior curves by using variable mixing times for disposal of treated water.

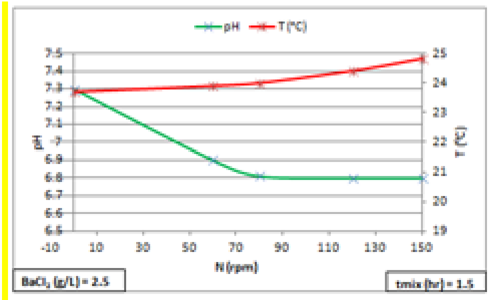

Figure 33: pH and temperature behavior curves by using variable mixing speeds for reuse of treated water.

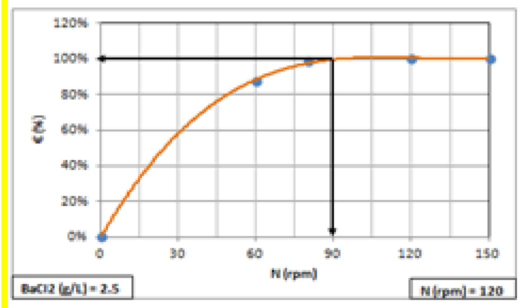

Figure 34: SO_4 removal efficiency curve by using variable mixing speeds for reuse of treated water.

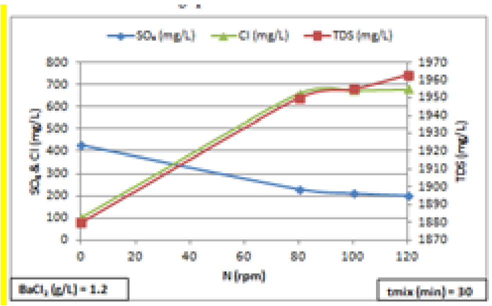

Figure 35: SO_4, TDS and Cl behavior curves by using variable mixing speeds for disposal of treated water.

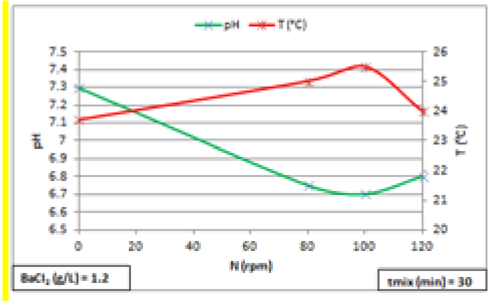

Figure 36: pH and temperature behavior curves by using variable mixing speeds for disposal of treated water.

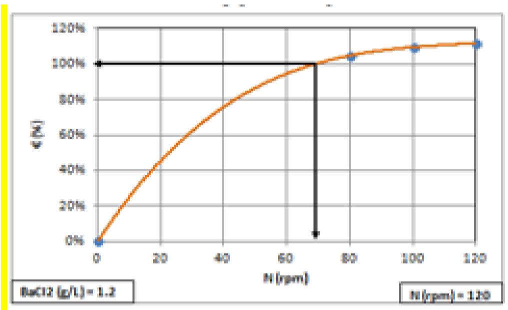

Figure 37: SO_4 removal efficiency curve by using variable mixing speeds for disposal of treated water.

3):*A*- By fixing Mixing Time (tmix) and Mixing Speed (N) to be (1.5 hr) and (120 rpm) respectively, and with variable ($BaCl_2$) dosages of (1.0, 1.2, 1.6, 2.0, 2.5, 3.0 and 3.5 g/L), the results obtained are shown in figures (38, 39, 40). The maximum precipitation of SO_4 has been obtained in (3.0 g/L) to reach (20 mg/L) remaining sulphate, and when dosage increased to the end point of (3.5 g/L) the remaining concentration rise to (40 mg/L) with continues increasing of TDS and Cl concentrations, as showed in SO4 curve of figure 38. This indicated that the maximum valuable dosage of $BaCl_2$ to use in sulphate precipitations was (3.0 g/L) without increasing of mixing speed and time. Figure 39 illustrated that pH decreased to reach neutral point when dosage reach more than (2.5 g/L) and then solution tend to be acidic with slightly increasing in temperature. It couldn't obtained (100%) SO_4 removal efficiency by using this type of substance with any dosage used for reuse purpose to reach specified limit as appeared from figure 40. Total removal efficiency within this criteria could be reached is (98.18%) by using (3.0 g/L) of $BaCl_2$.

B- While in the same N of (120 rpm) and fixed tmix = (30 min) for disposal purpose, and with variable dosage of $BaCl_2$ to be (1.2, 1.4. 1.6, 1.8 and 2.0 g/L), it is found that when dosage to be more than (1.6 g/L) the specified limit of (250 mg/L) could be reached as showed in figure 41. As the water temperature goes up, pH goes down. It is clear from SO_4 removal efficiency curve in figure 43 that the optimum dosage of $BaCl_2$ to reduce sulphate concentration form (360 mg/L) to (250 mg/L) for disposal of treated water is (1.72 g/L).

C- Fixing $BaCl_2$ dosage and N to be (3.0 g/L) and (120 rpm) respectively, and with variable tmix of (1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 hr) as shown figures (44, 45, 46). Figure 44 illustrated smooth curves of SO4, TDS and Cl concentrations with time intervals, in which selected (1.5 hr) reached (20 mg/L) of remaining SO_4, then drop to (2.0 mg/L) when time was (2.0 hr) then slightly increased with more times to reach (12 mg/L) in the end point. Therefore, it can be considered of (2.0 hr) is the optimum time interval to reach minimum SO_4 remaining concentration. Figure 45 showed that the solution tend to be acidic when time increased, with slightly increasing in temperature. It is found that the optimum mixing time to remove sulphate is (2.0 hr) as shown in figure 46.

D- Another test have been done to obtained disposal criteria with variable mixing times to be (15, 30 and 60 min) and by fixing $BaCl_2$ dosage and N to be (1.8 g/L) and (120 rpm) respectively. Figure 47 showed that (15 min) was satisfied removal of more than (310 mg/L) of sulphate in water as appeared from SO_4 curve in figure 46. While pH remaining in alkaline phase with slightly variation in temperature as shown in figure 48. It is clearly appeared from figure 49 that the optimum mixing time for (100%) removal efficiency is (15 min).

E- To determine optimum mixing speed for reuse purpose, constant $BaCl_2$ dosage and tmix of (3 g/L) and (1.5 hr) respectively, with variable N t be (60, 80, 120 and 150) have been taken. Figure (50) showed that the minimum SO_4 remaining concentration reached (15 mg/L) when N = (80 rpm) of (97.3 %) total removal efficiency, and when rising speed more, the concentration slightly increased to reach (24 mg/L) in the end point, with continues increasing in chlorides and TDS values. The water temperature goes up, pH goes down. The optimum mixing speed determined from figure 52 is (90 rpm).

F- Finally to determine optimum mixing speed for disposal purpose, test by fixing $BaCl_2$ dosage and t_{mix} to be (1.8 g/L) and (30 min) respectively, and with variable N of (60, 80, 100 and 120) have been done. The results obtained are shown in figures (53, 54 and 55). As appeared from figure 53 that at (100 rpm) remaining SO_4 concentration was (240 mg/L), while increasing in chlorides and TDS concentration. Figure 54 showed that in this N the solution tend to be neutralized without valuable change in temperature. The optimum mixing speed for (100%) removal is (90 rpm).

Table II and III are illustrated maximum and optimum design parameters recommended to use for remove and reduce refinery treated water sulphate of average, maximum and peak concentrations for reuse and disposal purposes respectively by using barium chloride ($BaCl_2$) substance.

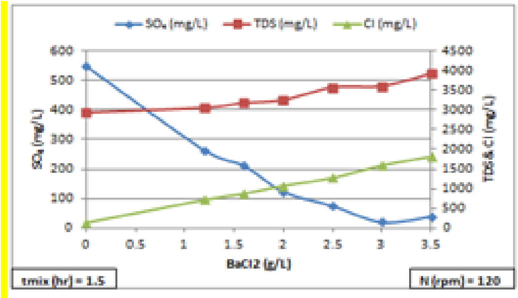

Figure 38: SO_4, TDS and Cl behavior curves by using variable $BaCl_2$ dosages for reuse of treated water.

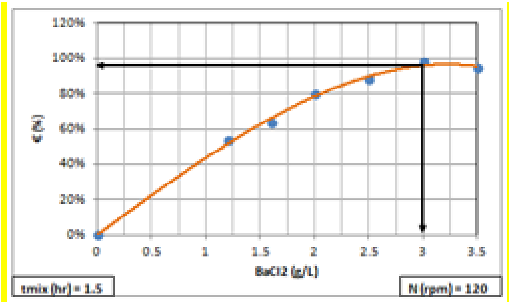

Figure 40: SO_4 removal efficiency curve by using variable $BaCl_2$ dosages for reuse of treated water.

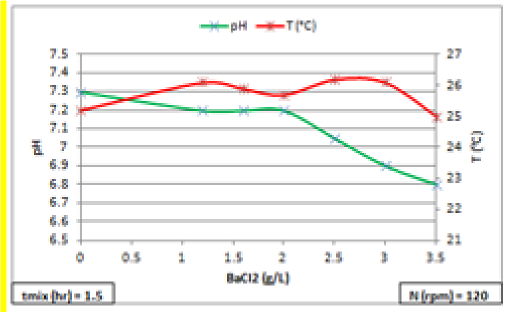

Figure 39: pH and temperature behavior curves by using variable $BaCl_2$ dosages for reuse of treated water.

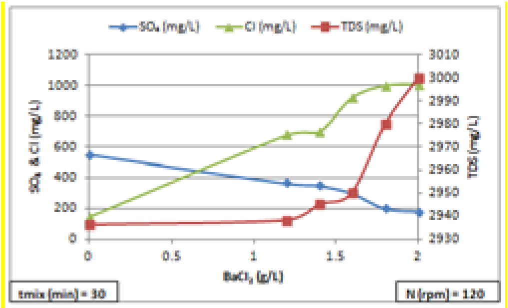

Figure 41: SO_4, TDS and Cl behavior curves by using variable $BaCl_2$ dosages for disposal of treated water.

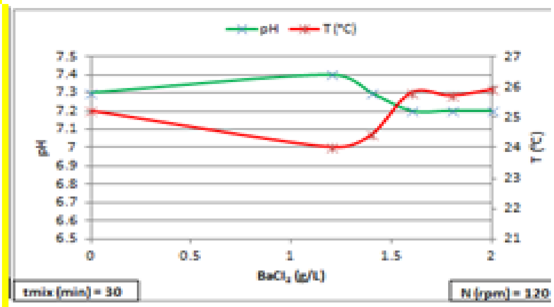

Figure 42: pH and temperature behavior curves by using variable $BaCl_2$ dosages for disposal of treated water.

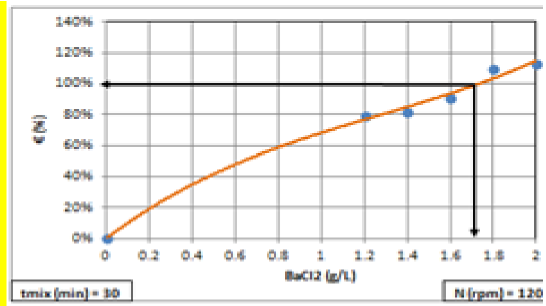

Figure 43: SO_4 removal efficiency curve by using variable $BaCl_2$ dosages for disposal of treated water.

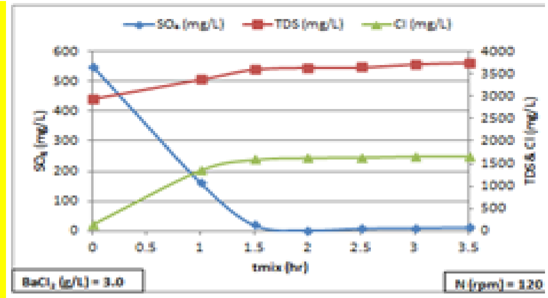

Figure 44: SO_4, TDS and Cl behavior curves by using variable mixing times for reuse of treated water.

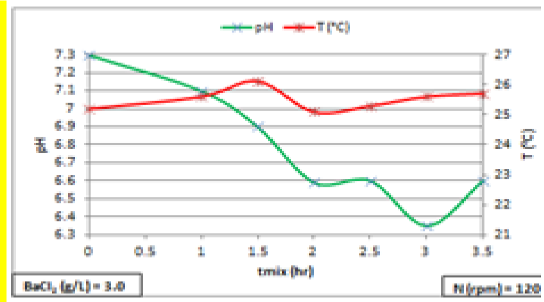

Figure 45: pH and temperature behavior curves by using variable mixing times for reuse of treated water.

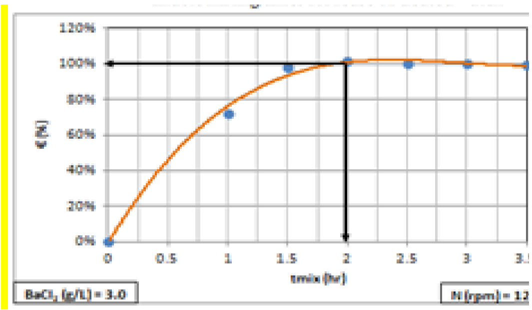

Figure 46: SO_4 removal efficiency curve by using variable mixing times for reuse of treated water.

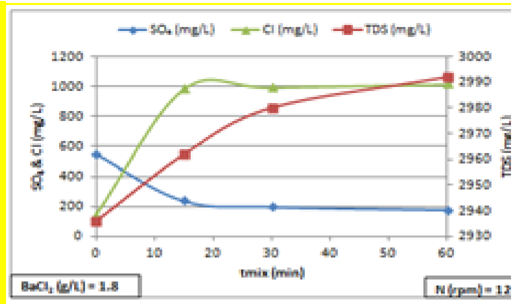

Figure 47: SO_4, TDS and Cl behavior curves by using variable mixing times for disposal of treated water.

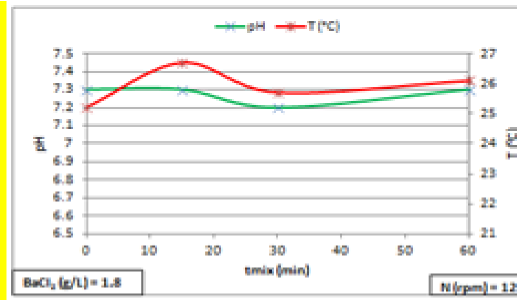

Figure 48: pH and temperature behavior curves by using variable mixing times for disposal of treated water.

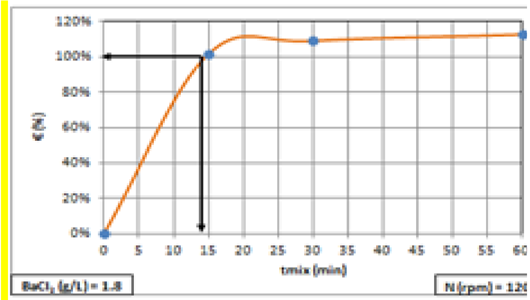

Figure 49: SO_4 removal efficiency curve by using variable mixing times for disposal of treated water.

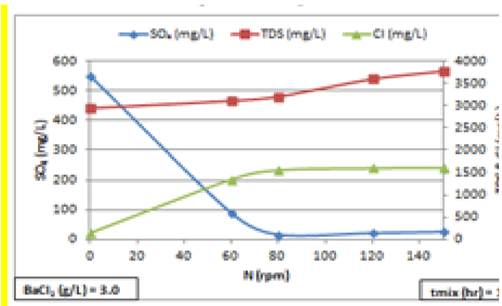

Figure 50: SO₄, TDS and Cl behavior curves by using variable mixing speeds for reuse of treated water.

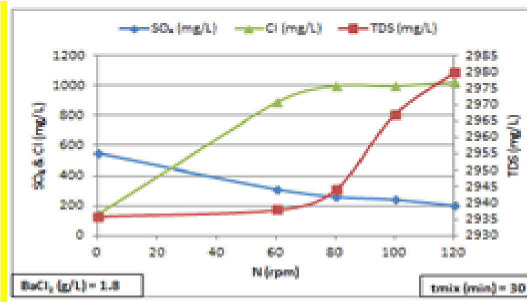

Figure 53: SO₄, TDS and Cl behavior curves by using variable mixing speeds for disposal of treated water.

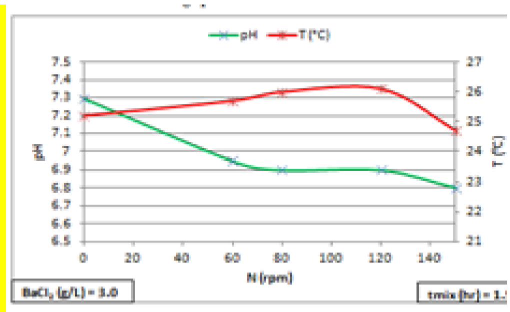

Figure 51: pH and temperature behavior curves by using variable mixing speeds for reuse of treated water.

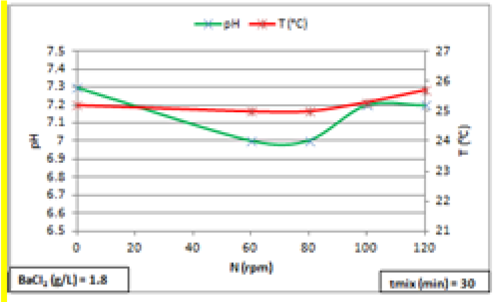

Figure 54: pH and temperature behavior curves by using variable mixing speeds for disposal of treated water.

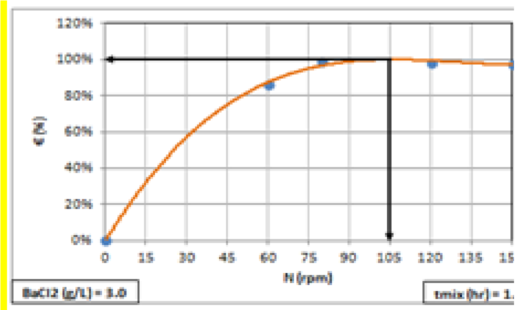

Figure 52: SO₄ removal efficiency curve by using variable mixing speeds for reuse of treated water.

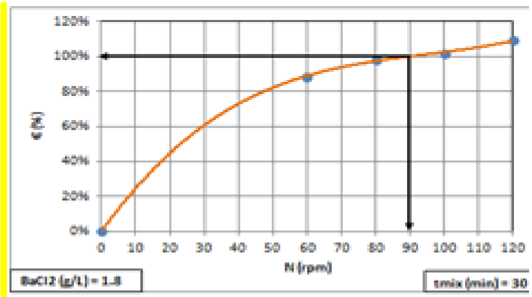

Figure 55: SO₄ removal efficiency curve by using variable mixing speeds for disposal of treated water.

TABLE II: Maximum and optimum design parameters recommended to use for sulphate removal from refinery treated water for reuse by using $BaCl_2$

Influent So4 (mg/L)	$BaCl_2$ dosage (g/L)		Retention time (hr.)		Mixing speed (rpm)		Effluent So4 (mg/L)		Removal efficiency	
	Max.	Opt.	Max.	Opt.	Max.	Opt.	Max.	Opt.	Max.	Opt.
360	1.6 1.6	1.5	2.5 1.5	1.2	120 150	80	2 5	10	99.44 98.61	97.22
425	2.5 2.5	2.25	3 1.5	1.5	120 150	90	3 8	10	99.29 98.12	97.65
550	3 3	3	2 1.5	2	120 80	105	2 15	10	99.64 97.27	99.18

TABLE III: Maximum and optimum design parameters recommended to use for sulphate removal from refinery treated water for disposal by using $BaCl_2$

Influent So_4 (mg/L)	$BaCl_2$ dosage (g/L)		Retention time (hr.)		Mixing speed (rpm)		Effluent So_4 (mg/L)		Removal efficiency	
	Max.	Opt.	Max.	Opt.	Max.	Opt.	Max.	Opt.	Max.	Opt.
360	0.38	0.36	30	15	120	100	240	250	33.33	30.56
425	1.2	1.1	30	15	80	70	230	250	45.88	41.18
550	1.8	1.72	15	15	100	90	240	250	56.36	54.55

II. Using Aluminum Hydroxide $Al(OH)_3$:

Aluminum Hydroxide $Al(OH)_3$had been used in chemical precipitation method that is used in highly sulphate content industrial wastewater for quality assurance. Test results and analysis are discussed below:

1): First run with variable dosages of (Al $(OH)_3$) to be (2.0, 3.0, 4.0, 5.0 and 6.0 g/L). The results are showed in figures (56, 57 and 58). From figure 56 it can observed that SO_4 slightly decreased to (335 mg/L) when dosage was (2.0 g/L), then drop to (230 mg/L) at dosage of (4.0 g/L), and back to increasing to reach (280 mg/L) at (6.0 g/L). While no valuable change in TDS values that slightly increased from (1160 mg/L) to (1195 mg/L) at the end point, and slightly decreasing on Cl concentration to reach (212 mg/L). The pH curve in figure 57 showed that the neutral solution tend to be acidic in the first dosage of (2.0 g/L), and rise to alkaline in second dosage of (3.0 g/L) and remaining constant when dosage increased, without valuable change in temperature. It was clear that the optimum dosage in this case was (4.0 g/L) to reach (100%) removal efficiency of sulphate in water for disposal purpose as shown in figure 58.

2): In the second run, dosages were reducing to be (0.2, 0.4, 0.6, 0.8 and 1.0 g/L). The results shows that the remaining SO_4 had fickle behavior in according to $Al(OH)_3$ dosages, with specific increasing on TDS values and decreasing on chlorides concentrations as shown in figure 59. While pH tend to be slightly alkaline with constant values of (7.3), and temperature drop on degree in the first dosage and still remaining constant as shown in figure 60. From figure 61 it can considered the dosage of (0.23 g/L) is the optimum dosage for (100%) sulphate removal.

The above tests showed that the $Al(OH)_3$ couldn't efficient used in removal of sulphate in treated refinery water for reuse or disposal purposes, because of its unstable behaviors with dosage in specified time for each purposes. Therefore, to have its benefits in refinery process, it suggested to be additional method to use in effluent water pretreatment of refinery process units that produced wastewater with highly sulphate concentrations (such as energy units), to reduce the load coming in INGECO influent basin. Figure 62 showed that SO_4 decreased to reach (1130 mg/L) at (1.4 g/L) then slightly reduce in other dosage to reach (1000 mg/L) at the end point, with slightly increased in TDS and Cl concentrations, without considerable variation in pH and temperature as shown in figure 63. The removal efficiency could be obtained from these dosages could be reach (50%) at (2.0 g/L) dosage as shown in figure 64.

Thus it can be concluded that this substance is not suitable for removal of sulphate from water when sulphate concentration is lesser than (1000 mg/L) and pH = (7.0).

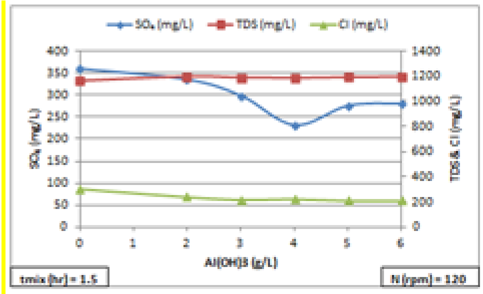

Figure 56: SO₄, TDS and Cl behavior curves by using variable Al(OH)₃ dosages for disposal of treated water.

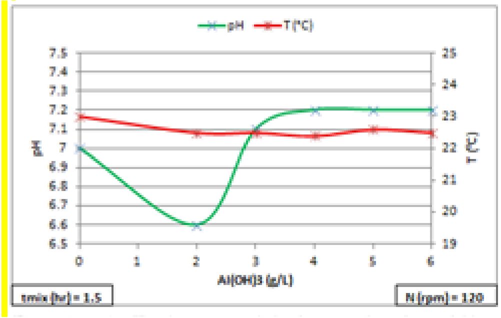

Figure 57: pH and temperature behavior curves by using variable Al(OH)₃ dosages for disposal of treated water.

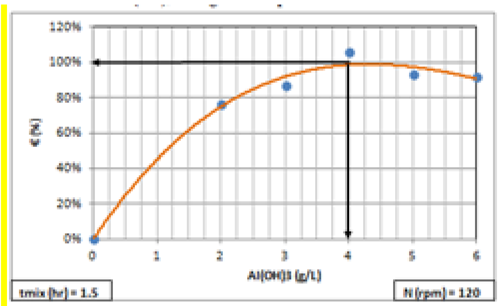

Figure 58: SO₄ removal efficiency curve by using variable Al(OH)₃ dosages for disposal of treated water

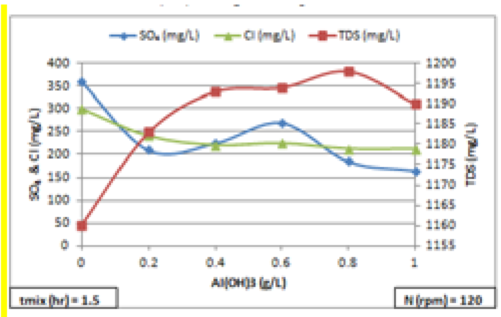

Figure 59: SO₄, TDS and Cl behavior curves by using variable Al(OH)₃ dosages for disposal of treated water.

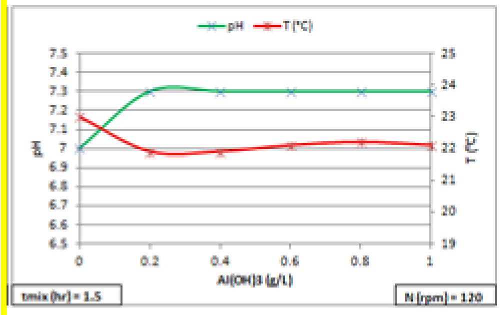

Figure 60: pH and temperature behavior curves by using variable Al(OH)₃ dosages for disposal of treated water.

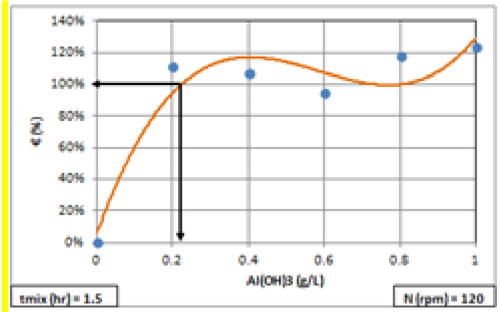

Figure 61: SO₄ removal efficiency curve by using variable Al(OH)₃ dosages for disposal of treated water.

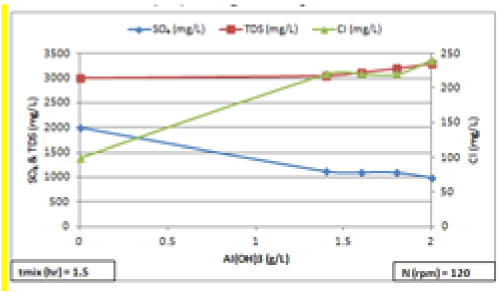

Figure 62: SO₄, TDS and Cl behavior curves by using variable Al(OH)₃ dosages for pretreatment of energy unit effluent water

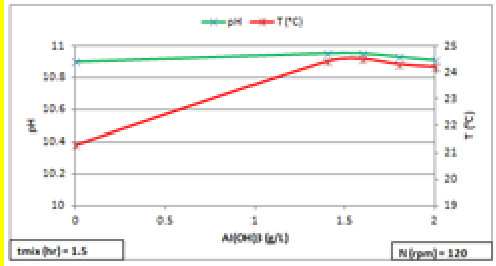

Figure 63: pH and temperature behavior curves by using variable Al(OH)₃ dosages for pretreatment of energy unit effluent water.

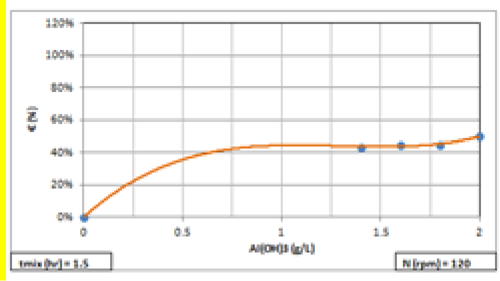

Figure 64: SO₄ removal efficiency curve by using variable Al(OH)₃ dosages for pretreatment of energy unit effluent water.

5. CONCLUSIONS

The inspection of refinery water quality used in various processes that showed in Table I before indicated that the main highly concentration of sulphate in wastewater that reach about (2900 mg/L) was coming from blowdown water of energy units, because of using sulfuric acid for resin regeneration in ion exchange process. The analysis of WWTP effluent water quality historical data indicated that the annual rate, maximum and peak sulphate concentrations are found to be (360 mg/L, 425 mg/L and 550 mg/L), and pH ranged from (7.0 to 7.6). The results by using $BaCl_2$ substance indicated that the maximum and optimum (dosage, mixing time and mixing speed) to use for sulphate removal for reuse purpose at annual rate were [(1.6 g/L, 2.5hr and 120 rpm) or (1.6 g/L, 1.5 hr and 150 rpm)] and (1.5 g/L, 1.2 hr and 80 rpm) respectively, that achieved total sulphate removal about (97.22 %). The results by using $Al(OH)_3$ substance indicated that:

- This substance is not suitable for removal of sulphate from refinery treated water for reuse or disposal purposes.
- 2) The increasing dosage of $Al(OH)_2$ lead to increase chlorides which contribution in increasing of TDS.

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