

Extraction of Calcium and magnesium ions from Water-Treatment-Plant Sludge for Reusing in industrial water Treatment

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ABSTRACT:

Possibilities for reusing the recovered calcium and magnesium salts coagulant in industrial wastewater treatment was investigated by choosing the power station liquid and solid wastes. Power station is one of the industries with high significance for water pollution in our country.

The analysis of sludge and waste water collected from water treatment basin revealed that it has been enriched by calcium and magnesium ions. The aim of this work is to extract calcium and magnesium ions in the form of CaO , MgO from water treatment sludge and ion exchange waste water, where CaO is hydrated to Ca(OH)₂ and used as lime in the water softening processes. The extracted salts were characterized by using chemical analyses and X-ray; while the chemical analyses of water and sludge were carried out according to the standard methods.

The calcium and magnesium salts recovered by acidification of these sludges and alkalization of precipitate salts have shown good results in the treatment of wastewaters from industrial water produced by water treatment plants.

Key words: extraction of calcium and magnesium, waste water, sludge, water treatment.

1-INTRODUCTION:

Sludges produced from water treatment contain colloidal iron, alum, calcium and magnesium hydroxides (**Conio et al. 1994**), colloidal or dissolved organic matter, clay, silt and microorganisms. Due to the presence of metal hydroxides, they are often called hydroxide sludges. Different studies have been carried out in France (**Forzini, 1990**), in Great Britain (**Skinner et al., 1996**) in Sweden (**Report, 1998**) and in Denmark (**Report, 1998**) about reuse of drinking sludges.

The recovery of coagulant (metal hydroxides) has high economic advantage and recommended as a suitable treatment option for the disposal of water works sludge (**Stendahl et al., 2005**). Sludge produced from water treatment contains colloidal iron hydroxides (**Conio et al., 1994**), colloidal or dissolved organic matter, clay, silt and microorganisms. Due to the presence of metal hydroxides, they are often called hydroxide sludge (**Vaebi et al 2001., Stendahl et al., 2005**). Different studies have been carried out in France (**Forzini., 1990**), in Great Britain (**Skinner et al., 1996**)for the reuse of sludge in the treatment of industrial waste water. Other research works have also been reported (**Zhang et.al 2011, Jimenez et.al., 2006 ,Xu GR et.al., 2008 and Xu GRet.al., 2009**).

Most of the water treatment plants dispose their sludges removed during raw and industrial water treatment processes to the land after draying. However, these wastes are today recognized as an industry-wide pollution problem. In most water treatment facilities, coagulation is a process that generates the bulk of the residual materials and the type and amount of coagulant used can have a significant effect on the amount of residue produced by the plant (**AWWA, 1998**). There upon,

recovery of used coagulants has been proposed as a suitable treatment method for the disposal of water works sludge's.

In order to introduce a better way of controlling water plant wastes, possibilities for reclamation of coagulants from coagulation sludges and use the recovered coagulants in industrial water treatment have been investigated in this study.

2-MATERIALS AND METHODS:

2-1.Source of Sludge containing calcium ion:

Sludge was collected from raw and industrial waste basin of water treatment plant. The dry sludge used in this investigation was collected from industrial water treatment plant, and mainly consists of Ca , Mg , Si, Fe, and other trace elements. Figure (1) illustrates the schematic diagram of water treatment plant including all steps of treatments and sludge production. Also the typical image of dry sludge is shown in figure (2):

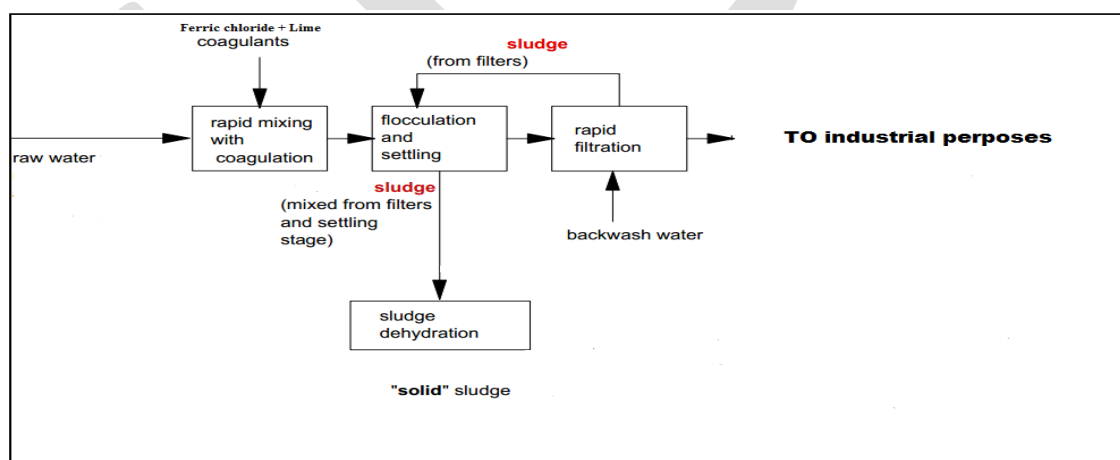


Fig. 1. Production of solid sludge in a water treatment plant

2-2.Source of cation and anion exchange waste water:

Waste water collected from ion exchange plant during regeneration. There are two kinds of water one of them is during cation exchange regeneration (CR) and the other is during anion exchange regeneration (AR). (CR) is acidic in nature and containing calcium and magnesium ions. (AR) is alkaline in nature and containing hydroxide ions. Table (1) shows the chemical analysis of cation and anion Waste Water:



Figure (2): typical image of water treatment dry sludge.

Table (1): Chemical analysis of Cation and Anion Waste Water.

Cation Regeneration waste water (CR)		Anion Regeneration waste water (AR)	
Analysis	Value	Analysis	Value
pH	3.55	pH	12.8
Total hardness mg/l (as CaCO ₃)	2475	Total alkalinity mg/l (as CaCO ₃)	11150
Calcium hardness mg/l(as CaCO ₃)	1350	Sodium mg/l as Na	5990
Magnesium hardness mg/l(as CaCO ₃)	1125	Sulphate mg/l as SO ₄ ²⁻	1750
Sodium mg/l as Na	678	Chloride mg/l as Cl ⁻	6255
Iron mg/l as Fe	1.9		

2-3. Chemicals:

- Commercial lime and ferric chloride.
- All chemicals that used in the analysis in this work were of laboratory chemical grade.

2-4. Sludge analysis:

Solution cations: sodium, potassium, magnesium, and calcium were analyzed using a Dionex Ion Chromatograph.

Floccations in dry sludge were measured using EPA method 3050B (Acid digestion for metals analysis of soils, sediments, and sludges). For this experiment, water treatment sludge was dried at 105°C and the known amount of dried sludge was removed and underwent acid digestion. The prepared samples were quantified using Atomic Absorption Spectrometer.

2-5. Water analysis:

The following series of water examination and chemical analysis were carried out according to the standard method of ASTM Book of Standards (ASTM, 2001).

- Total hardness, Calcium and magnesium hardness and alkalinity of water determined in (mg/l) as CaCO_3 by titration.
- Turbidity removal was measured in nephelometric turbidity units (NTU) using Helige digital direct reading turbidimeter.
- Conductivity of water was measured in microsiemens (μs) using conductivity meter model 32 Yellow springs instrument Co. Inc. U.S.A.

- Total suspended solids (TSS) was measured by filtered the waste water samples through a weighed standard filter with 0.2 μm diameter. The residue on the filter was dried at 110°C. The increase in the weight of the filter represents the total suspended solid.

- pH of wastewater was measured by accumet pH meter model 810Fisher scientific.

- The organic matter expressed as KMnO_4 was determined by consumption of KMnO_4 in acidic solution.

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

$$\% \text{Removal (Reduction)} = C_0 - C / C_0 \times 100$$

Where, C_0 and C = COD, BOD, TSS, Organic matter, turbidity calcium and magnesium contents of wastewater (mg/l) before and after coagulation treatment, respectively.

-Total solids (TS), total suspended solids (TSS), COD and BOD were measured according to slandered method of test ([ASTM, 2001](#)).

- X-ray analysis of dry salts: The dry salts of calcium and magnesium were analyzed by using; Energy Dispersive X-ray System., ISIS Link Instrument P/C. Oxford Co.

-Atomic absorption for the determination of calcium and magnesium of sludge and water:

The calcium and magnesium ion were determined by using atomic absorption spectrometer Solar S-4 S- Series Thermo Electron Corporation UK.

2-6.Extraction of calcium and magnesium salts:

A calculated amount of acidic solution (CR) was added to 100 gram of sludge and undergoes acid digestion at 80°C for one hour then filtered. The calcium and magnesium salts of filtrate were quantified using Atomic Absorption Spectrometer. The filtrate was separated and used as calcium and magnesium supplier.

The alkaline anion waste water (AR) was added slightly to 100 ml of filtrate. The pH of filtered water was increased by this adding until reached to (8.5- 9.5) at this point iron hydroxides was precipitated and isolated by filtration through filter paper. Furthermore addition of (AR) leads to increase pH to 10.5 at this point calcium hydroxide was precipitated and isolated by filtration through filter paper. The more addition of (AR) leads to increase pH to 11.5 at this point magnesium hydroxide precipitated and isolated by filtration. Both of two precipitates were heated at 650°C to produce calcium and magnesium oxide and used as (Lime) softer in the water clarification processes. Figure (3) showed the typical image of extracted salts at pH 10.5 and 11.5.

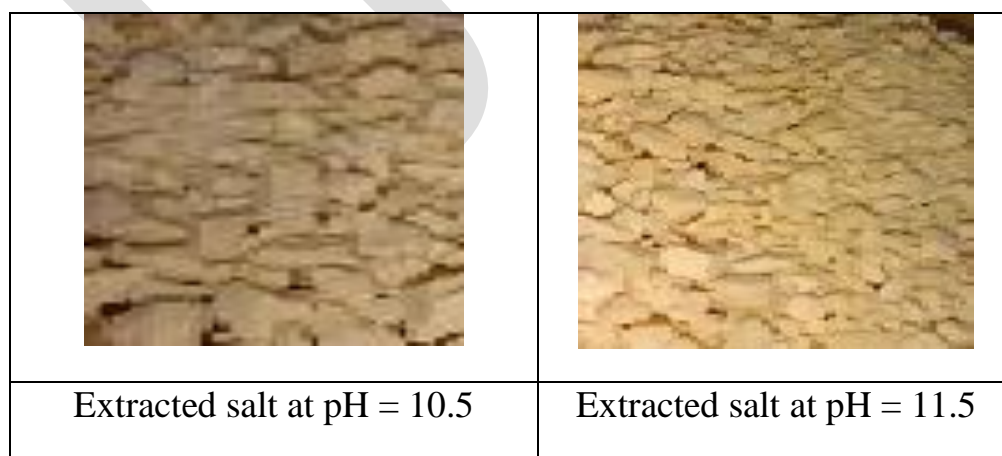


Figure (3) typical image of extracted salts at pH 10.5 and 11.5

2-7. Water samples preparation in clarification processes:

Jar test method is the best way to simulate clarification and permits the comparison of various chemicals combination for determining the optimum chemical program to establish the correct order of addition. The most critical measurements in jar test are coagulation and/or flocculants dosages, flock size, settling characteristics, flock forming time, and finished water clarity. The flocculator in the aforementioned jar test method contains six (1 liter) beakers in conjugation with multiple stirrers. Each beaker was filled with one liter of raw water and stirred at 100 rpm. The different doses of coagulant were added rapidly and stirred for 3 minutes. The stirring rate was then reduced to 50 and 20 rpm for a period of 5 and 10 minutes respectively to allow complete flock formation, and then stirring was stopped. The relative settling rate, flock size and supernatant clarity were recorded. After a settling period of 15 minutes, 250 ml of supernatant water were siphoned-off for further analysis.

The samples were then titrated for total hardness, calcium hardness, and alkalinity. In addition pH and magnesium hardness were determined. Figure (4) showed the formation of precipitate in the jar tester.

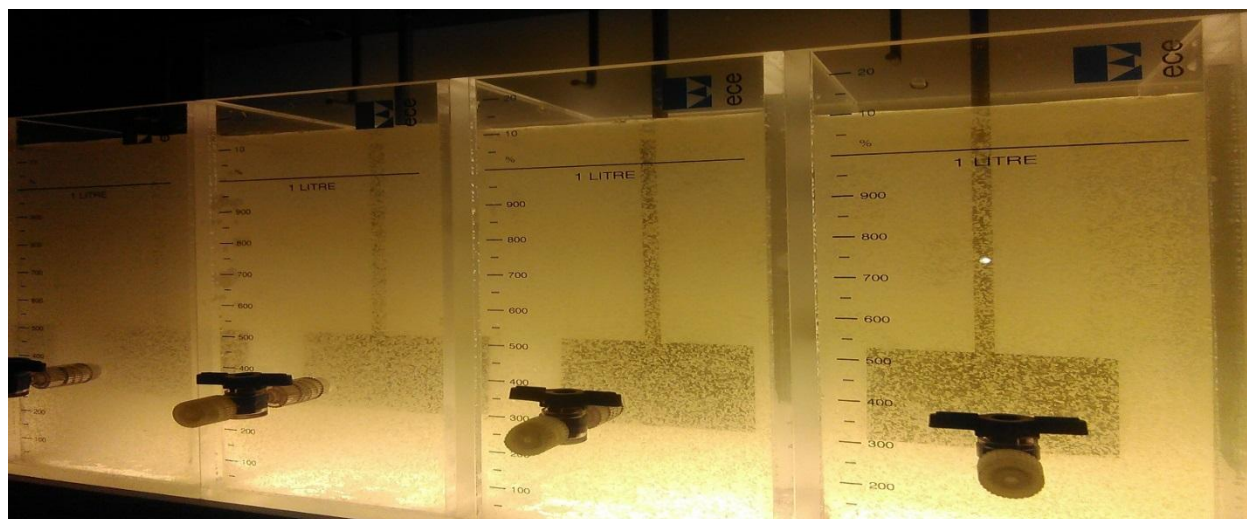


Figure (4) the jar tester during the formation of precipitate and flocks.

3-RESULTS AND DISCUSSION:

3-1.Precepitation of calcium and magnesium salts from waste water:

The above mentioned anion regeneration waste water (AR) which contains sodium (carbonate, bicarbonate and hydroxide) can provide an excellent condition for precipitation of calcium and magnesium salts when added to the filtrate solution produced from digestion processes of sludge by cation regeneration waste water (CR). The addition of (AR) to the filtrate were studied in accordance to change the pH value and to provide maximum precipitation level. Figure (5) show pH change by increasing the amount of (AR). The results indicate that the (pH) increase with increasing (ml) added of (AR) as can be seen from figure (5). This increment of pH leads to increase the precipitation level of calcium and magnesium salts. The precipitation profile of calcium and magnesium salts during the addition of anion waste water (AR) to the filtrate was sown in figure (6). The results indicate that the maximum removal of calcium salts from filtrate solution obtained at pH value between 10-11, while magnesium salts was between 11-12.

The percentage removal reached to 75% and 90 % for calcium and magnesium salts respectively figure (7).

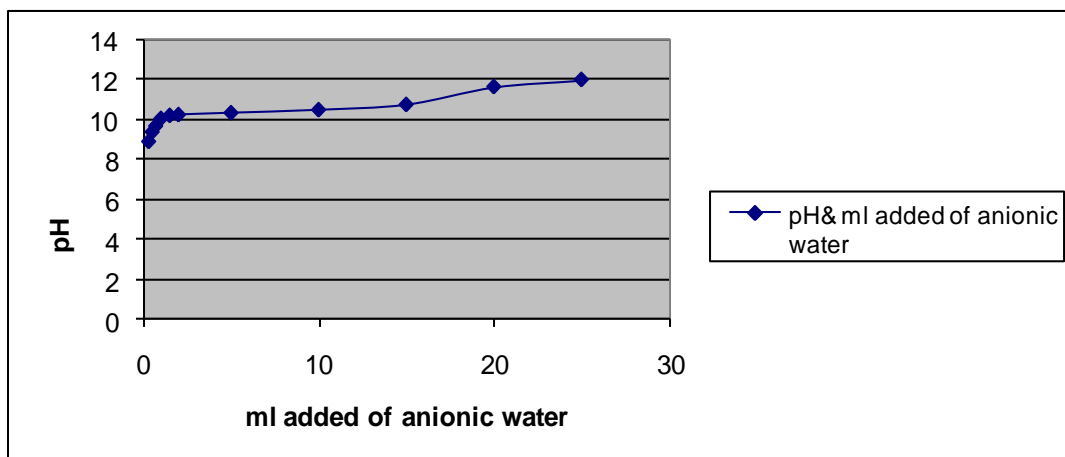


Figure (5) show pH change by increasing the amount of (AR)

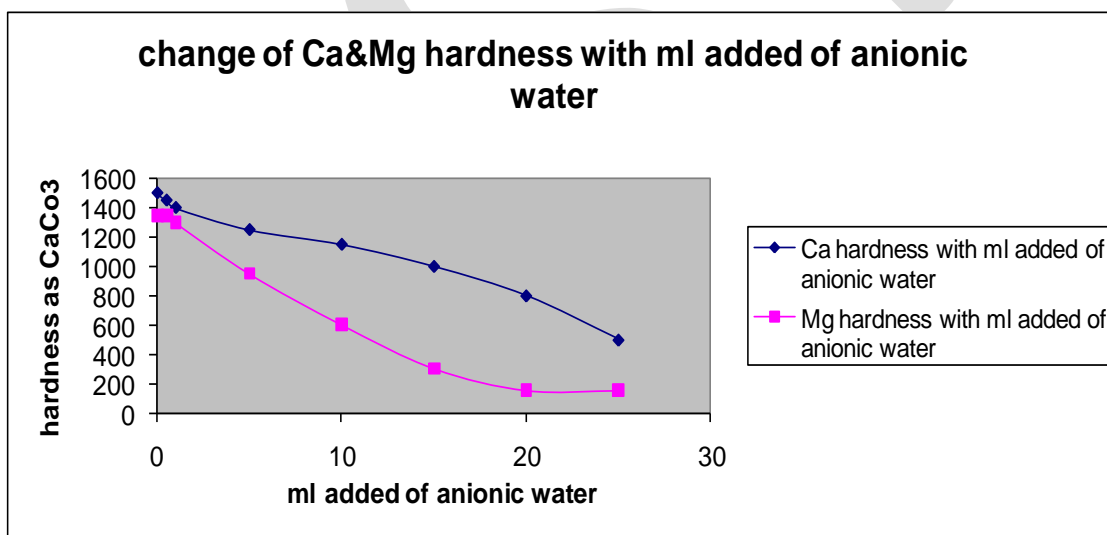


Figure (6) show the precipitation profile of calcium and magnesium salts during the addition of anion waste water (AR) to the filtrate.

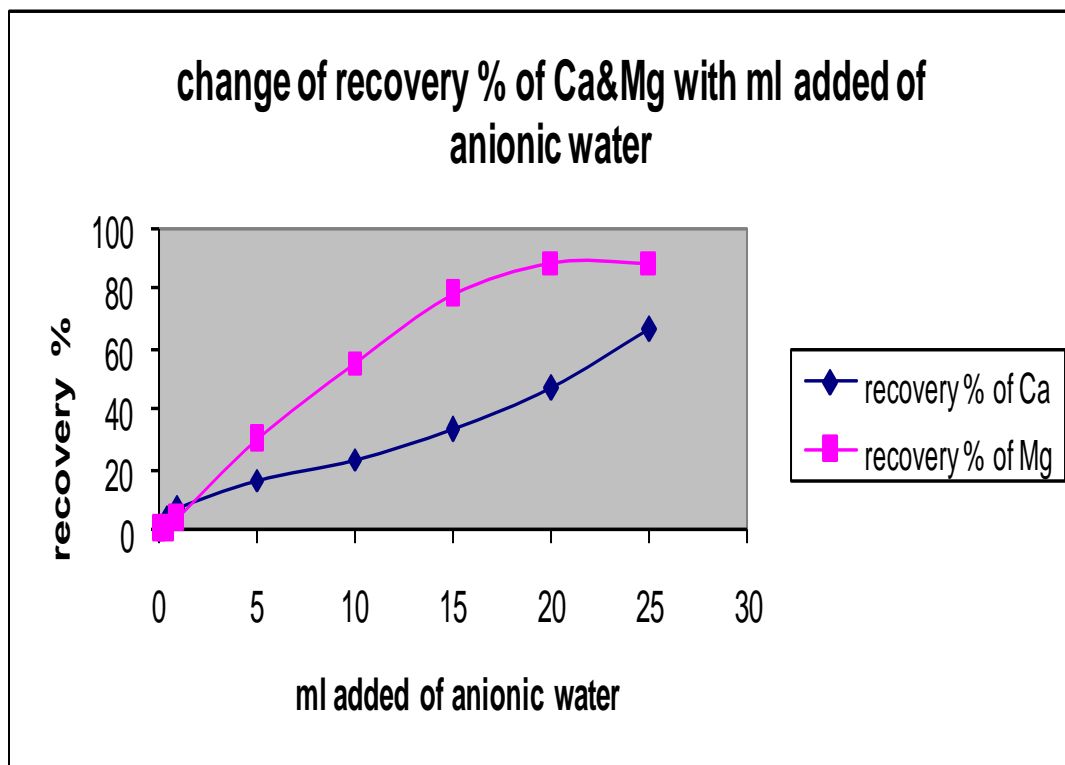


Figure (7) Calcium and magnesium percentage recovery

3-2.Nature of the extracted salts:

The extracted calcium and magnesium salts were introduced to investigation as follow:

3-2-1-1.X-ray analysis of extracted salts:

The extracted salts at pH (10.5) and (11.5) were analyzed by using; Energy Dispersive X-ray System. The results are shown in figures (8 and 9). It is clearly seen that for salt extracted at pH (10.5) the main peak in the chart was for calcium ion .Also for the salt extracted at pH (11.5) the main peak was for magnesium ion.

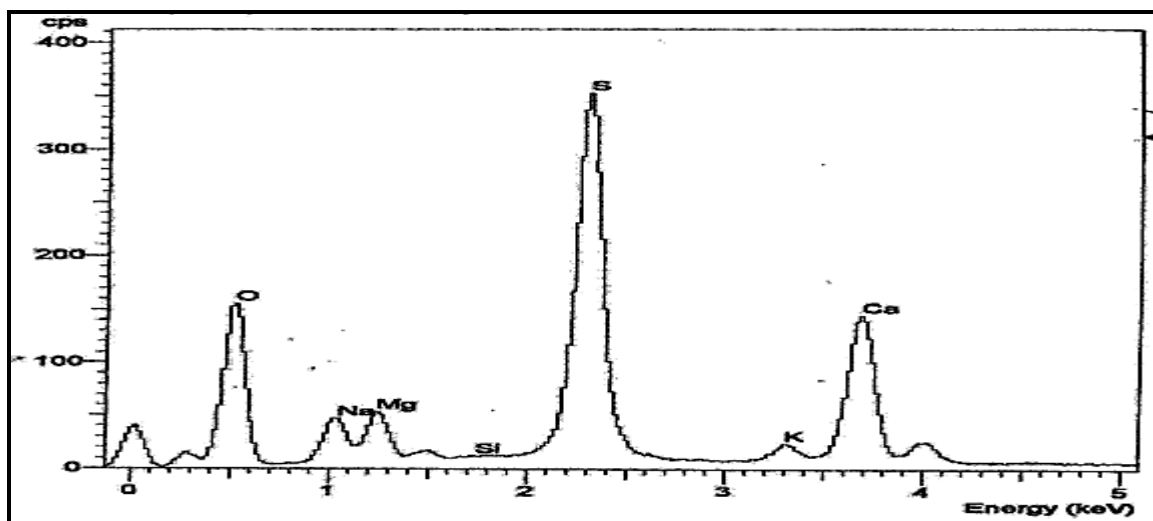


Figure (8) X-ray of the precipitated salt at pH = 10.5

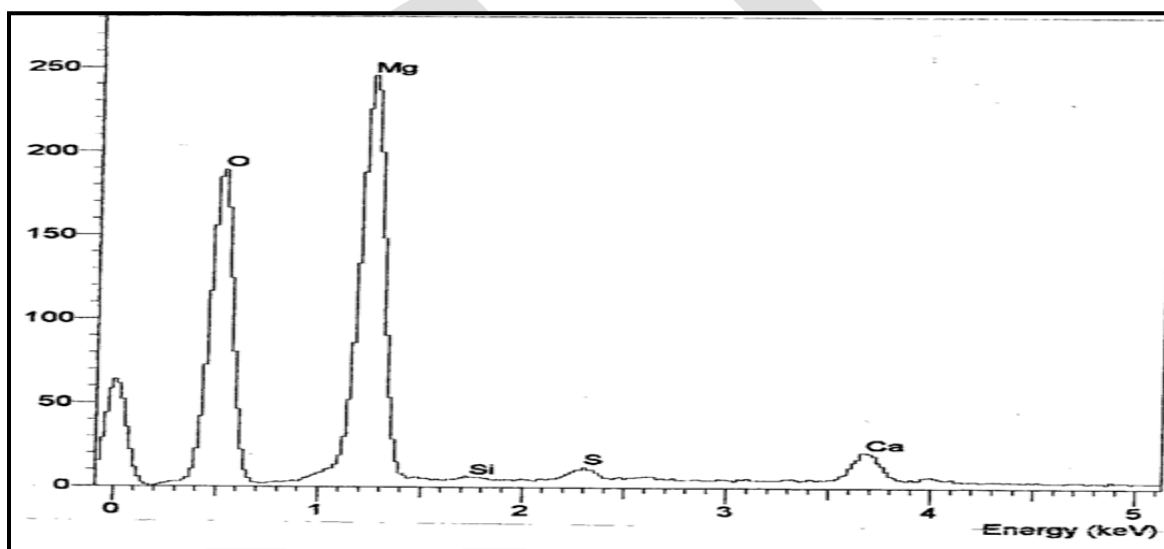


Figure (9) X-ray of the precipitated salt at pH = 11.5

3-3: Effect of Using Ferric Chloride in Clarification Process:

Ferric chloride can be used as a coagulant especially in industrial purposes. Ferric chloride forms flocs with a size larger than that formed by alum. Therefore, it was preferable in the treatment of industrial water.

The steps of evaluation of ferric chloride in the clarification process was carried by changing its dose from 15-55 mg/l. the change in the water parameter by changing ferric chloride dose was determined. Table (2) showed such results.

Table (2): Effect of different doses of ferric chloride on the quality of water.

Parameter	Raw Water	Ferric chloride Dose (mg/l)				
		15	25	35	45	55
pH	8.30	7.55	7.48	7.45	7.41	7.30
Conductivity ($\mu\text{S}/\text{cm}$).	308	343	348	352	359	365
Turbidity (NTU).	4.95	1.15	0.95	0.93	0.96	0.98
Total. alkalinity (ppm)	170	158	156	152	149	145
Total .hardness as CaCO_3 (ppm)	155	151	149	145	153	154
Calcium hardness as CaCO_3 (ppm)	96	93	93	93	95	96
Chlorides (ppm as Cl^-).	37	41	43	47	49	53
Organic matter (mg/l as KMnO_4)	17	13.70	13.31	13.22	13.35	13.35

It is clearly seen from the above mentioned results shown in table (2) that the best clarification conditions which gives lowest turbidity by using ferric chloride was achieved at (35 mg/l ferric chloride).

3-4: Effect of addition of extracted salts on the softening of clarified water by ferric chloride

3-4-1: Addition of extracted salt at pH 10.50(CaO)

Figure (10) show the effect of addition of extracted salt at pH 10.50 with different dose from (0 - 80 mg/l) with clarified water by using (35 mg/l ferric chloride).

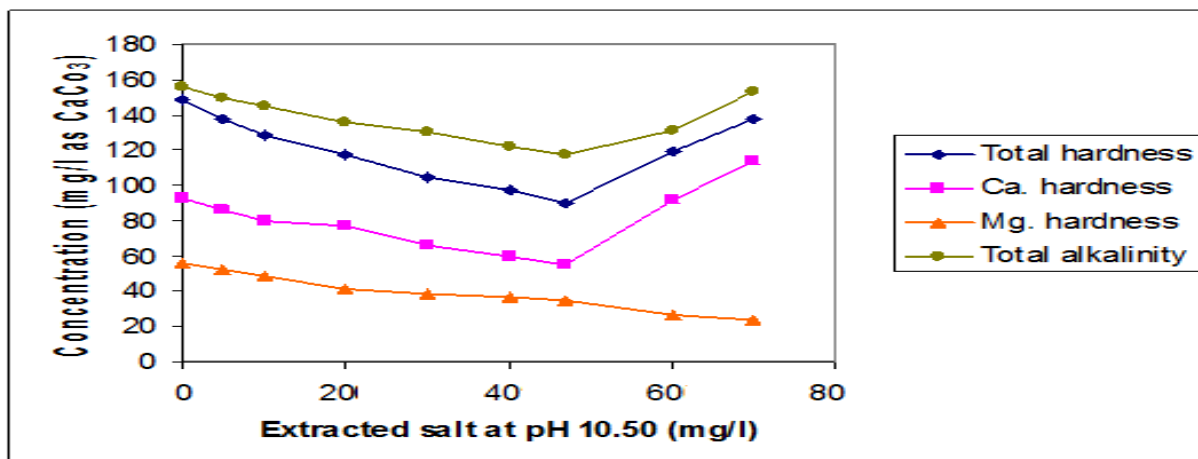


Figure (10) Effect of addition of extracted salt at pH 10.50 on the quality of clarified water by ferric chloride.

As can be seen from Figure (10), the total hardness reached a minimum value of approximately 90 mg/L as CaCO₃ for the extracted salt at pH 10.50 dosage of 50 mg/l.

When concerning calcium hardness first decreased in concentration to a minimum of 55mg/L as CaCO₃ for an extracted salt at pH 10.50 dosage of 50 mg/l and then after that continued to increase in concentration with an increase of extracted salt at pH 10.50 dose. This increase in calcium hardness was observed due to the addition of excess extracted salt pH 10.50 and the absence of alkalinity caused by carbonates.

For magnesium hardness there is a decrement in its value with the increment of extracted salt at pH 10.50. Also the alkalinity decreased to a minimum value at approximately 50 mg/l of extracted salt at pH 10.50 and increased thereafter. This is due to the addition of extracted salt at pH 10.50 and the precipitation of species, which consumes alkalinity that causes the initial decrease.

At extracted salt dosages higher than 50 mg/l the alkalinity increases due to the addition of the excess extracted salt.

For every addition of extracted salt at pH 10.50, free OH^- ions are released; therefore an increase in OH^- ions is responsible for an increase in pH.

3-4--2: Addition of extracted salt at pH 11.50 (MgO).

Figure (11) show the effect of addition of the extracted salt at pH 11.50 with different dose from (0 to 80 mg/l) with clarified water by using (35 mg/l ferric chloride).

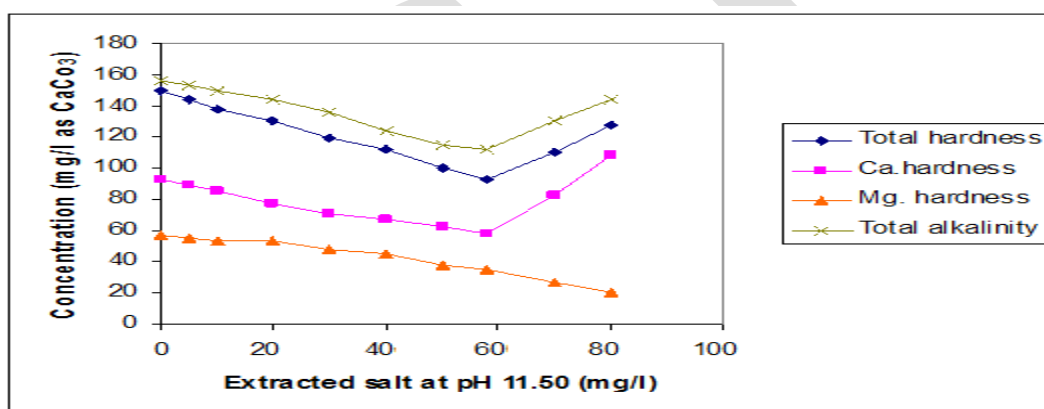


Figure (11): Effect of addition of extracted salt at pH 11.50 on the quality of clarified water by 35mg/l ferric chloride

As can be seen from Figure (11), the total hardness reached a minimum value of approximately 93 mg/l as CaCO_3 for an extracted salt at pH 11.50 dosage of 60 mg/l.

For calcium hardness first decreased in concentration to a minimum value of 60mg/l as CaCO_3 by increasing the extracted salt at pH 11.50 dosages of 60 mg/l and then after that continued to increase with the increase of extracted salt. Also

for magnesium hardness there is a decrement in its value with the increasing of extracted salt dose.

For the alkalinity it is decreased to a minimum value at approximately 60 mg/l of extracted salt and increased thereafter.

3-4-3: Effect of commercial lime on the softening of clarified water by using ferric chloride

Figure (12) shows the effect of addition of commercial lime with different dose from (0 - 80 mg/l) with clarified water by using (35 mg/l ferric chloride).

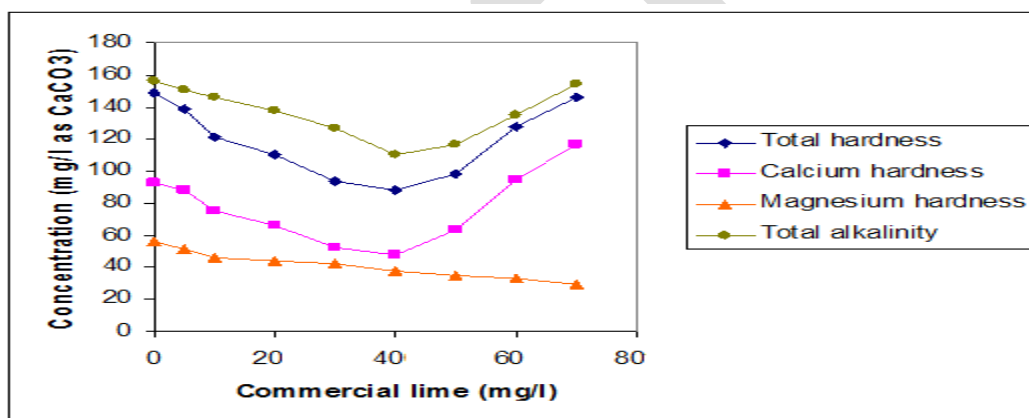


Figure (12): Variation of hardness and alkalinity for varying commercial lime during softening of clarified water by 35mg/l ferric chloride.

Figure (12) shows the same behavior of extracted salts with clarified water by ferric chloride where in the case of using commercial lime, the total hardness reaches a minimum value of approximately 90 mg/l as CaCO₃ for a commercial lime dosage of 40 mg/l. Calcium hardness concentration first decreases to a minimum value of 50 mg/l as CaCO₃ for the dosage of 40mg/l and then starts to increase by increasing the dose above 40 mg/l. Also the increment of commercial lime dose is accompanied by decrement in magnesium hardness. Also the

alkalinity decreased to a minimum value 110 mg/l as CaCO_3 at approximately 40 mg/l of commercial lime and began to increase thereafter. This is due to the addition of commercial lime and the precipitation of species, which consumes alkalinity that causes the initial decrease. At commercial lime dosages higher than 40 mg/l the alkalinity increased.

3-5-Coagulation and Precipitation:

The above mentioned data showed that the optimum dose of each extracted slat was 50 and 60 for (CaO) and (MgO) respectively. Therefore the extracted (CaO) having the lowest dose of addition was chosen to complete the study. The dose of extracted calcium oxide was kept constant at 50 mg/l, different doses of coagulant ferric chloride verses the measured turbidity , organic matter, BOD, COD and TSS after precipitation for samples from the raw water of Nile River was studied. Figure (13) as present the turbidity for the samples treated with ferric chloride, shows that the best turbidity removal 85%, took place at dose 35mg/l + 50 mg/l of extracted (CaO) while the turbidity removal at 35mg/l of commercial ferric chloride alone reach to 79% . The trend of the measurement shows more stable reading from dose of about 35 ppm than that of the low doses. At the same dose of 35 and 50 mg/l of ferric chloride and CaO respectively the organic matter removal reached to 65% then kept constant by increasing ferric chloride dose as can be seen from figure (14). The same trend was observed at 35 and 50 mg/l ferric chloride and CaO for each of BOD, COD and TSS which give percentage reduction reached to 50, 39 and 48 respectively as can be seen from figures 14, 15, 16 and 17. These figures also showed that for all testes the percentage reduction of turbidity, organic matter, BOD, COD and TSS have less values when using 35 mg/l of commercial ferric chloride alone.

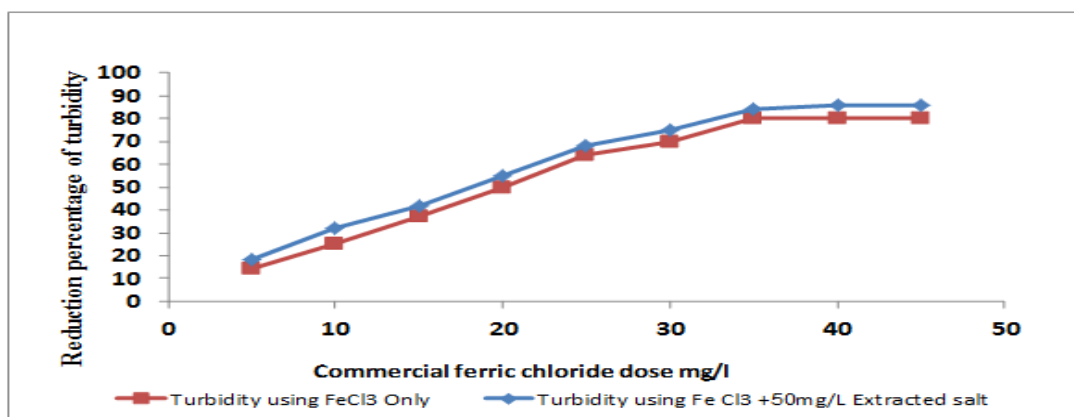


Figure (13) Variation of percentage reduction of turbidity by increasing ferric chloride dose at 50 mg/l of extracted CaO.

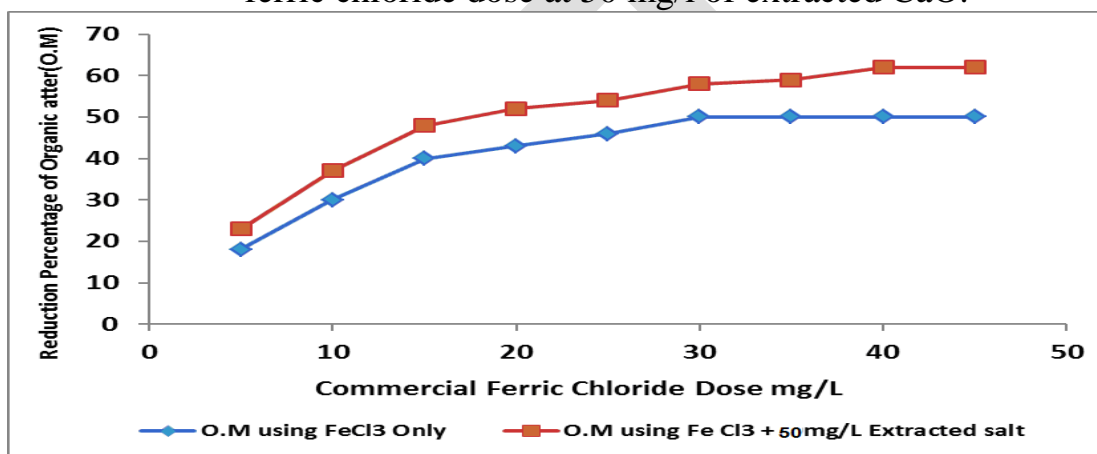


Figure (14) Variation of percentage reduction of organic matter by increasing ferric chloride dose at 50 mg/l of extracted CaO.

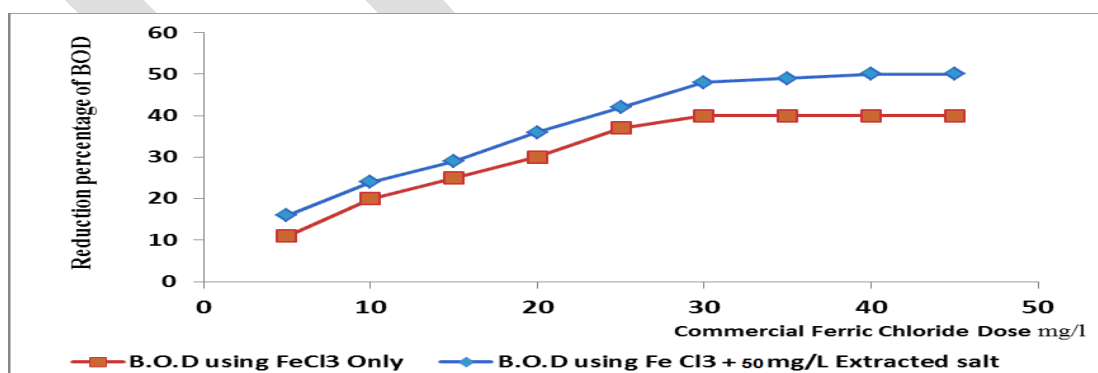


Figure (15) Variation of percentage reduction of (BOD) by increasing ferric chloride dose at 50 mg/l of extracted CaO.

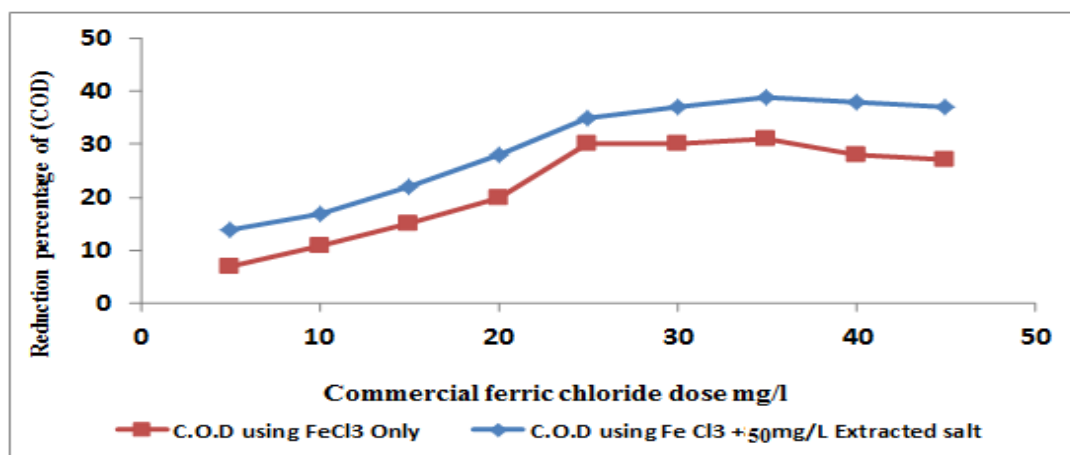


Figure (16) Variation of percentage reduction of (COD) by increasing ferric chloride dose at 50 mg/l of extracted CaO.

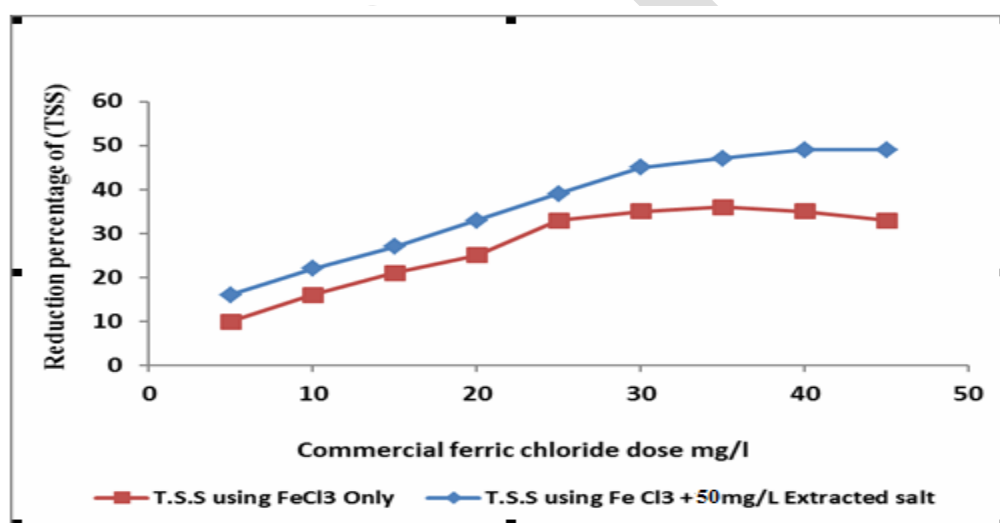


Figure (17) Variation of percentage reduction (TSS) matter by increasing ferric chloride dose at 50 mg/l of extracted CaO.

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