Efficiency of different coagulants for removing organic load and cadmium from wastewater of Alexandria eastern treatment plant

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This study aims to investigate the Removal Efficiency (RE) of different chemical coagulants for removing the organic load and cadmium from wastewater. The addition has been conducted with the wastewater before entering the sedimentation tanks of the Eastern Treatment Plant (ETP), Alexandria General Organization for Sanitary Drainage (AGOSD).A laboratory investigation has been carried out using Jar test with various coagulants (Lime, Alum, FeCl3 and Lime + 5% sea water) at different dosages. Different parameters including pH, BOD5, COD and SS were experimentally determined. All aspects concerning the chemistry of these coagulants to the wastewater have been taken into consideration and discussed. It was found that the influence of the pH plays a major role in reducing levels of BOD5, COD, SS and Cd especially at higher pH (8-10) as in the case of lime or lime + 5% sea water treatments. The processes of precipitation with alum and iron chloride were similar. Both, of them, have a strong tendency to form insoluble complexes with Cd which enhanced its removal from wastewater. The statistical analysis, of the experimental data, showed that lime salt + 5 % sea water appeared to be the most promising candidate as a chemical precipitant since it produce less amount of sludge than using lime only.

يهدف البحث إلي دراسة تأثير إضافة المرسبات الكيماوية إلي المخلفات السائلة فى إزالة الأحمال العضوية و عنصر الكادميوم وقد تمت إضافة الكيماويات إلي المخلفات السائلة قبل دخولها إلي أحواض الترسيب الخاصة بمحطة التنقية الشرقية التابعة للهيئة العامة للصرف الصحي لمدينة الإسكندرية .ولقد أجريت الدراسة المعملية باختبار مروبات مختلفة وبجرعات مختلفة مثل : الجير، الشبة ، كلوريد الحديديك، الجير مضافا اليه 5% من مياه البحر وذلك باستخدام جهاز (Jar test) وتم قياس الخواص الآتية :الأس الهيدروجيني ،الأكسجين الحيوي الممتص، الأكسجين الكيماوي الممتص والمواد العالقة .وقد نوقشت النتائج ووجد ان الأس الهيدروجيني يلعب دورا مؤثرا فى خفض تركيز عنصر الكادميوم خاصة عند القيم المرتفعة للأس الهيدروجيني من 8 إلي 10 وذلك عند إضافة المروب (الجير) وعند إضافة المروب (الجير مضافا اليه 5% من مياه البحر). قد وجد تطابقا فى السلوك الترسيبي فى حالة إضافة الشبة وإضافة كلوريد الحديديك فكلاهما لديه قابلية لتكوين مركبات غير قابلة للذوبان مما يزيد ويقوى عملية إزالة عنصر الكادميوم. وقد تم تحليل النتائج تحليلا إحصائيا. وخلصت الدراسة إلي ان المروب (الجير مضافا اليه 5% من مياه البحر) كان اكثر المروبات تحقيقا لهدف الدراسة من الناحية العملية وهى تقليل الحمأة الناتجة من المعالجة وكذلك من الناحية الاقتصادية بالمقارنة بالمروبات الأخرى.

Keywords: Chemical precipitation, Coagulants, Cadmium removal, Organic load removal

1. Introduction

Heavy metals are of special concern because they are health hazard, non-degradable and persistent. The tremendous increase in the use of heavy metals in industries over the past few decades has inevitably resulted in an increased flux of metals substances in aquatic environment. Heavy metals can enter the aquatic environment either from point sources such as industrial sewage effluent or from diffuse sources which include road and agriculture run off and aerial deposition [1-2]. Most of these metals occurred in the form of complexed salts, oxides or hydroxides [3]. Understanding the mode of metal interaction with wastewater particulates is essential to design the pretreatment process, management, development and selection of alternatives for municipal wastewater treatment and ultimate solids disposal, reuse and discharge

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of the effluent [4]. It is obvious that the sewage water contains considerable amounts of potentially toxic heavy metals such as cadmium, chromium, copper, nickel, lead and zinc [5]. Recent surveys of wastewater discharge have shown that more than 85% of the applied heavy metals have been accumulated in the sediment of aquatic system and especially in the surface few centimeters [6].

Mechanisms of metal removal in waste water treatment plants have been widely discussed, for example, precipitation and / or adsorption on suspended solids during primary sedimentation [7]. In the hydroxide precipitation technique; heavy metals are removed by adding NaOH or Ca(OH)2 to adjust the wastewater pH to the point where the metal hydroxides exhibit a minimum solubility. In general, the solubility of metal hydroxide in solution decreases with increasing pH to a minimum value (the isoelectric point). Metal hydroxide precipitates can be removed from solution by coagulation, flocculation and sedimentation / filtration operations [8].

One of the most toxic heavy metals is, cadmium which finds its way to the water bodies through wastewater from metallurgical alloying, ceramics electroplating photography, pigment works, textile printing, chemical industries, lead mine drainage and Ni/Cd battery production [9, 10]. Furthermore, cadmium enter water through industrial discharges or the deterioration of galvanized pipes[11]. The percentage of cadmium removed is increased as the pH is increased up to an optimum point between pH 7 and 10 and then is decreased. In higher pH solution, the percent of cadmium removed diminishes [12]. The permissible limit of Cd in treated effluent, set up by Food and Agriculture Organization (FAO 1992) for irrigation use was 0.01 mg/L [6, 13].

This research aims to (i) provide information on the current efficiency of the primary sedimentation tanks of Alexandria General Organization for Sanitary Drainage (AGOSD) of the Eastern Treatment Plant (ETP) in regard to the decrease in heavy metals as well as Chemical Oxygen Demand (COD) , Biological Oxygen Demand (BOD5) and Total Suspended Solids (TSS) ,(ii)Study the efficiency of chemical flocculation or precipitation by using chemical coagulants such as Lime, Alum, Ferric Chloride salts, as well as sea water lime mixture on reducing heavy metals COD, BOD5 and TSS in wastewater, and (iii) recommend the use of a better coagulant treatment with optimum dosages that can meet the international standard criteria and also to meet the economical considerations and consequently, good environmental considerations.

2. Materials and methods

To achieve the mentioned goals, an experimental program was carried out. This required obtaining wastewater samples from inlet and effluent of the primary sedimentation tanks of ETP of GOSD of Alexandria city (Egypt).

Different coagulants with different dosages table 1 were tested by using jar test in this study. The experimental work was divided into five separate groups and carried out as follows: (i) without chemicals addition, (ii) with the addition of different lime dosages of 150, 200, 250, 300 and 350 mg/l, (iii) with the addition of different alum dosages of 150, 200, 250, 300 and 350 mg/l, (iv) with the addition of different ferric chloride dosages of 45, 60, 75, 90 and 105 mg/l, and (v) with the addition of different lime dosages of 150, 200, 250, 300 and 350 mg/l plus 5% of sea water by volume.

Table 1
The used coagulants and dosages

Coagulants		Dosage range (mg/L)
Common name	Chemical formula	
Alum	$Al_2(SO_4)_3,18H_2O$	150,200,250,300,350
Ferric chloride (as Fe)	$FeCl_3$	45,60,75,90,105
Lime	$Ca(OH)_2$	150,200,250,300,350

Lime+5%Seawater	150,200,250,300,350

Coagulant lime+5% seawater was prepared by the addition 5% of seawater (Bicarbonate 140, Calcium 400, Chloride 19×10^3, Iron(III)0.01, Magnesium 1.35×10^3, Potassium 380, Silica 6, Sodium 10.5×10^3, Sulphate 2.65×10^3 ppm) to the prepared solution of 20 g/l of lime.

2.1. Bench test

Bench test was conducted where samples of wastewater were stirred at 100 rpm for 5 minutes, followed by gentle stirring at 25 rpm for 15 minutes. The coagulants were added just before the flash mixed (100 rpm).

2.2. Jar test experiments

Jar test experiments were divided into four sets of runs, each of them represented the working coagulants. The detailed procedural steps are as follows: (i) for each run, six 1L jars, each containing one liter of wastewater sample from point no.1 (influent of primary sedimentation tanks), (ii) dose jars no. 2 to no. 6 with varying dosages of chemical selected covering the initial ranges listed in table 1, Jar no.1 received no chemical and considered as initial term in the results after well mixing (iii) use standard arbitrary timing sequence ensuring adequate mixing, 5 minutes fast mix (100 rpm) followed by 15 minutes slow mix (25 rpm) and then allowed for 30 minutes settlings (iv) after settling period of 30 minutes, samples were drawn from the midpoint of the supernatant layer from each settle jar and (v) these samples, as well as the well mixed raw samples, were analyzed for pH, Suspended Solids (SS) COD, Biochemical Oxygen Demand (BOD5) and Heavy Metals (HM). Atomic Absorption spectrometer spectra (AA) Varian 220 was used to measure heavy metals concentration. All the parameters were detemined in accordance with standard methods [14].

2.3. Statistical analysis

All data were analyzed using a SAS statistical package through an IBM personal computer. Two way ANOVA was carried out to compare the means of different treatments

3. Results and discussion

3.1. Efficiency of primary sedimentation tanks

The characteristics of influent and effluent wastewater and the efficiency of primary sedimentation tanks (without salt addition in removing heavy metals and reducing the organic load presented in the influent wastewater of the plant) is shown in table 2. It is clear from table 2 that the values of removal efficiency of the primary sedimentation tanks of ETP of AGOSD are very low since it reached only 35.9, 28.5, 39.9, 4.67 and 22.2% for COD BOD5, SS, TS and Cd, respectively. These values are low when compared with those recommended by Metcalf and Eddy, 1991 [13].

3.2. Effect of coagulants

Different parameters were measured for every additional coagulant used at different dosages. The results obtained are outlined in the following paragraphs.

3.2.1. Effect of lime coagulant

The addition of lime coagulant dosages increased the pH of the wastewater from 7.48 to 9.48 which indicates the formation of Ca (OH)2 and CaCO3 system which act as the coagulant and form a lime gel type . This

Table 2
The characteristic of the influent and effluent wastewater of primary sedimentation tanks

pH		COD			BOD_5			SS			TS			Cd		
Inf *	Eff**	Inf mg l^{-1}	Eff mg l^{-1}	R.E.*** %	Inf mg l^{-1}	Eff mg l^{-1}	R.E. %.	Inf mg l^{-1}	Eff mg l^{-1}	R.E. %	Inf mg l^{-1}	Eff mg l^{-1}	R.E. %	Inf mg l^{-1}	Eff mg l^{-1}	R.E. %

7.46	7.36	348	223	35.9	221	158	28.5	184	110	39.9	1521	1405	4.67	0.009	0.007	22.2

increase in pH led to a significant effect on COD, BOD5, SS and Cd reduction as shown in table 3, table 4 and fig. 1. The effect of lime coagulant starts at dosage of 200 mg/l. Lime addition generally improved the RE of COD, BOD5 and SS around 17.3, 18.5 and 21.1% respectively over the sedimentation tanks of the ETP.

It was found that the optimum dosage of lime coagulant on cadmium removal is 150 mg/l at pH 9.14 with removal efficiency of 71.4%. The superior performance of lime was reached at dosage of 300 mg/l at pH 9.48 with 85.7% removal efficiency. Obviously, it is reported that the pH plays significant role in cadmium removal efficiency since its precipitation starts at pH 8.2. [3, 7, 8, 9 and 10].

3.2.2. Effect of alum

The addition of alum [Al2 (SO4)3.18 H2O] was effective in reducing the organic load of the effluent as shown in fig. 2 and table 3. The optimum dosage of alum coagulant to improve the removal efficiency of COD, BOD5 and SS ranged between 250 and 300 mg/l.

It was found that the wastewater of the Eastern Treatment Plant (ETP) usually contains calcium and bicarbonate alkalinity especially after the aeration phase which enhances coagulation by evolving CO2 deducing to inter particle bridging and sweep coagulation phenomena. The insoluble aluminum hydroxide is a gelatinous floc that settles with suspended materials [15].The results of alum addition generally improve the

Table 3
The effect of coagulants addition on the characteristics of the effluent wastewater

Coagulants	Tests									
	pH		COD			BOD_5			SS		
	Inf	Eff	Inf mg l^{-1}	Eff mg l^{-1}	R.E. %	Inf mg l^{-1}	Eff mg l^{-1}	R.E. %	Inf mg l^{-1}	Eff mg l^{-1}	R.E. %
Lime (300mg/L)	7.48	9.48	401	188	53.2	213	113	47.0	209	81.0	61.0
Alum (300 mg/L)	7.48	6.5	401	188	53.1	213	95.6	55.2	209	82.5	60.6
Lime + 5% Seawater (300 mg/L)	7.48	9.4	401	177	56	213	105	51.0	209	81.8	61.0
$FeCl_3$ (90 mg/L)	7.48	6.83	401	191	52.3	213	100	52.3	209	81.0	61.3

* Inf: Influent.
** Eff: Effluent.
*** R.E.: Removal Efficiency.

Table 4
The effect of coagulants addition on the characteristics of cadmium reduction

Cd conc. In Raw waste water	Lime				Alum				Lime + 5% Seawater				$FeCl_3$			
	150 mg l^{-1}		300 mg l^{-1}		150 mg l^{-1}		300 mg l^{-1}		150 mg l^{-1}		300 mg l^{-1}		150 mg l^{-1}		300 mg l^{-1}	
Inf mg l^{-1}	Eff mg l^{-1}	R.E. %	Eff mg l^{-1}	R.E. %	Eff mg l^{-1}	R.E. %	Eff mg l^{-1}	R.E. %	Eff mg l^{-1}	R.E. %	Eff mg l^{-1}	R.E. %	Eff mg l^{-1}	R.E. %	Eff mg l^{-1}	R.E. %
0.021	0.006	71.4	.003	85.7	0.005	76.2	.002	90.5	.006	71.4	.003	85.7	0.005	76.2	.002	90.5

* Inf: Influent.

** Eff: Effluent.
*** R.E.: Removal Efficiency.

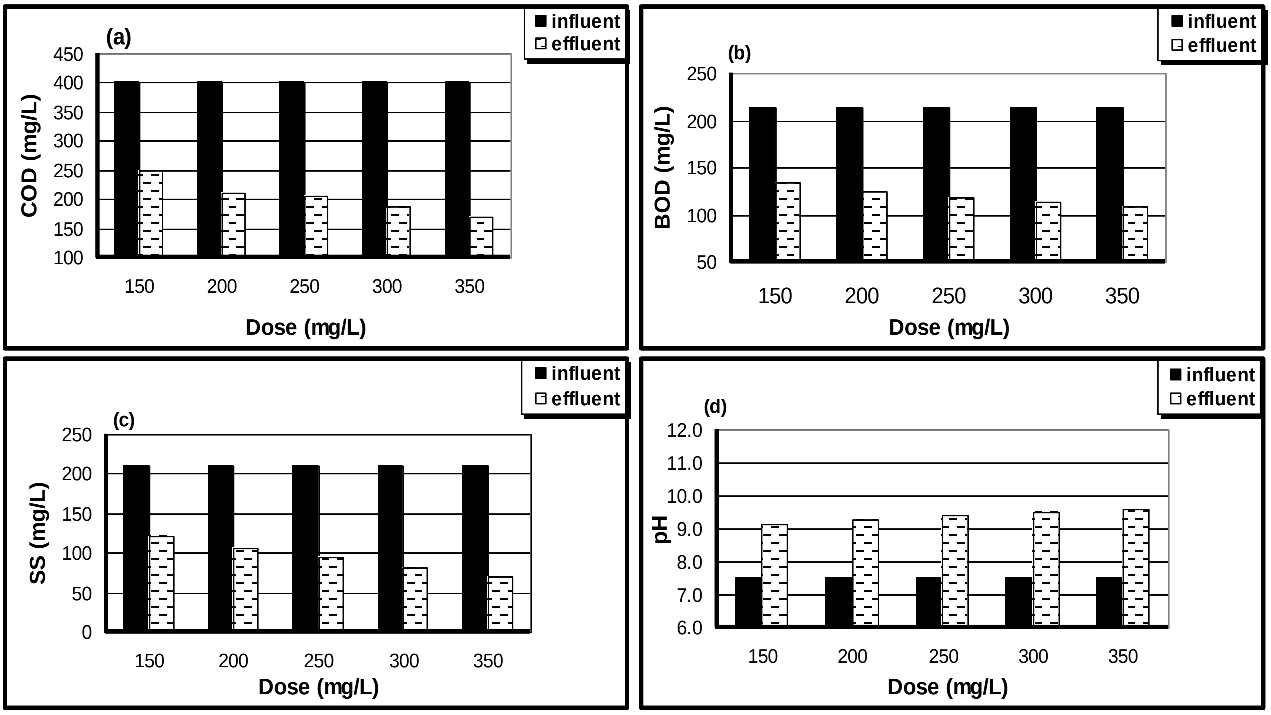

Fig. 1. The relation between lime dose application (mg/L) on the average values of COD, BOD, SS and pH.

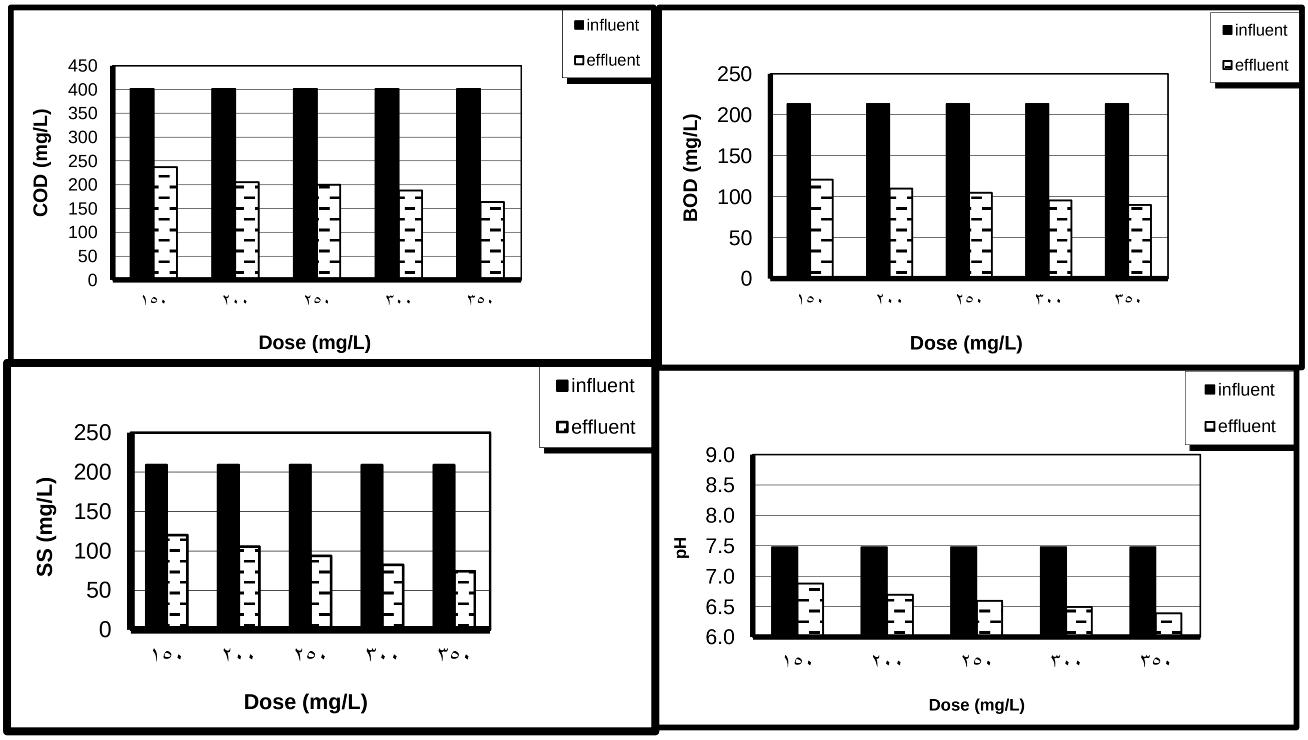

Fig. 2. The relation between alum dose application (mg/L) on the average values of COD, BOD, SS and pH.

removal efficiency RE for COD, BOD5 and SS which were around 18.1, 26.9 and 20.7% over the sedimentation tanks of the ETP for dosage 300 mg/l. table 4 shows that optimum alum dosage was 150 mg/l where 76.2% removal efficiency for Cd was achieved at pH value 6.88. At alum dosage 300 mg/l, the average cadmium removal efficiency was 90.5% at pH value 6.5. It has been reported that Cd is coprecipitated with Al(OH)3 at the acid reaction produced by the alum coagulant [3, 7- 10].

The difference between the average removal efficiency of Cd by using lime and alum dosage is only about 5%. This means that using lime coagulant should be considered as a suitable coagulant for the chemical sedimentation system because its usage is more economic than alum.

3.2.3. Effect of ferric chloride

The addition of ferric chloride (FeCl3) led to a decrease in organic load (COD, BOD5 and SS) as shown in fig. 3. It is clear that the ferric chloride dosage of 90 mg/l demonstrated satisfied performance in reducing of COD, BOD5 and SS where pH value is 6.83.

Addition of ferric chloride salt to the aerated wastewater leads to the formation of insoluble ferric hydroxide as a bulky gelatinous floc similar to the alum floc. It is clear that the dominant system is bicarbonate system where pH is greater than 6.4, and the presence of CaCl2 enhances the flocculation and precipitation process. The results in fig 3 and table 3 showed that ferric chloride addition improved the removal efficiency of COD, BOD5 and SS around 16.4, 23.8 and 21.4% respectively over the sedimentation tanks of the ETP for dosage 90 mg/l.

With regard to cadmium removal, the chosen dosages were 45 and 90 mg/l for ferric chloride. Table 4 shows that ferric chloride dosage of 90 mg/l resulted in increasing cadmium removal efficiency up to 90.5%. The optimum dosage FeCl3 was 45 mg/l where the removal efficiency was 92.6% at pH 7.23. Because of the similarity of behavior for both alum and ferric chloride in cadmium precipitation, the results of cadmium removal efficiency by the two salts are approximately similar. The Cd is rather coprecipitated with the hydroxides of Al or Fe formed in coagulant treatment.

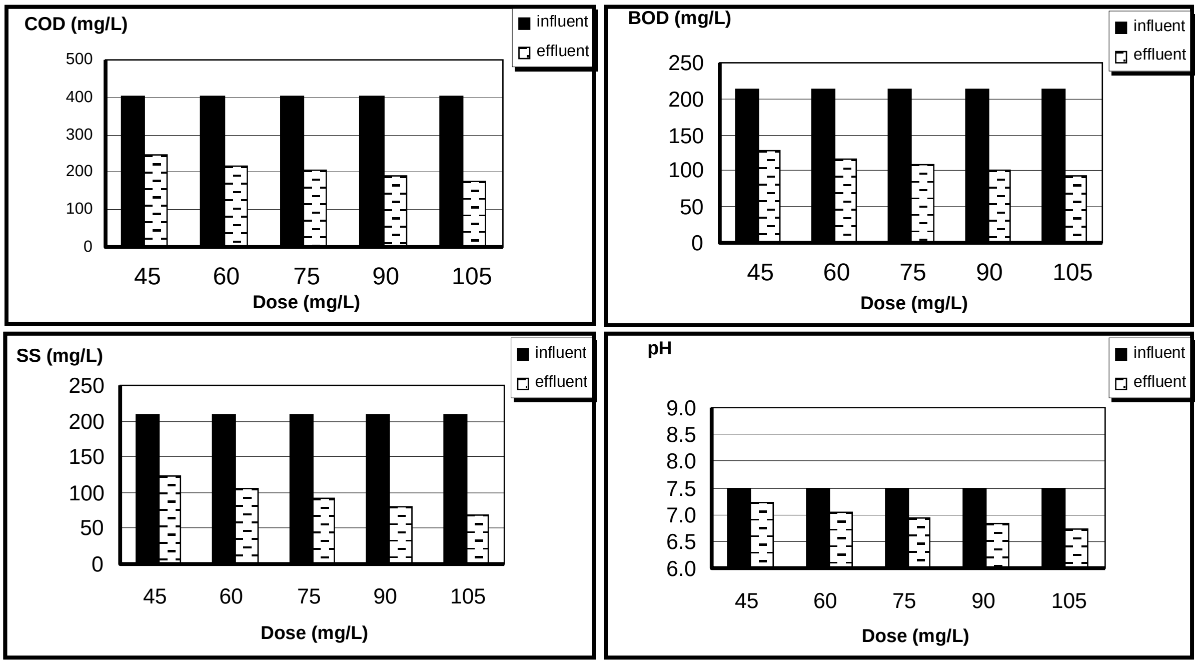

Fig. 3. The relation between ferric chloride dose application (mg/L) on the average values of COD, BOD, SS and pH.

3.2.3. Effect of lime plus 5% sea water

Using Lime plus 5% sea water by volume, coagulant was effective in decreasing effluent organic load as shown in fig. 4 and table 3. The removal efficiency by lime + 5% sea water was better than by lime alone. The differences between the two treatments are about 5% for the lime+5% sea water. The influence of the increased electrolyte-concentration lead de to shrinking in the double layer, hence improved coagulation. Furthermore, the lime dosages will be reduced which consequently reduce sludge quantity production. The results of lime + 5% sea water treatment improved the removal efficiency (RE) of COD, BOD5 and SS around 20.1, 22.5 and 21.1 %, respectively over the sedimentation tanks of the ETP for dosage 300 mg/l.

Table 4 shows that increasing lime +5% sea water dosages from 150 mg/l to 300 mg/l led to increasing cadmium removal efficiency from 71.4% to 85.7% Comparing cadmium removal efficiency by using lime dosages only, there is similarity in the results which obtained by using lime +5% sea water dosages. The presence of magnesium in the sea water functions as an auxiliary coagulant, whereby the pH of 9-10 would save Ca(OH)2. The formation of CaCO3 plus MgCO3 would produce gel type including hydroxides at the high pH values above 9 which would coprecipitate Cd with these gel flocs[11,13].

4. Conclusions

Based on the observations and the results obtained from this study, the following points are conducted:

- Current efficiency of sedimentation tanks of ETP of AGOSD for COD, BOD5, TS, SS and Cd need steps and procedures of development to meet the standard criteria of a primary treatment since the effluent is discharged to water bodies.
- Using coagulants such as Lime, Alum, Ferric chloride and Lime + 5% sea water would improve COD, BOD5 and SS removal efficiencies.
- The adopted program during this study, including treatment with chemical coagulants, not only helps to reduce cadmium concentration but also helps to reduce other similar elements from the influent wastewater.

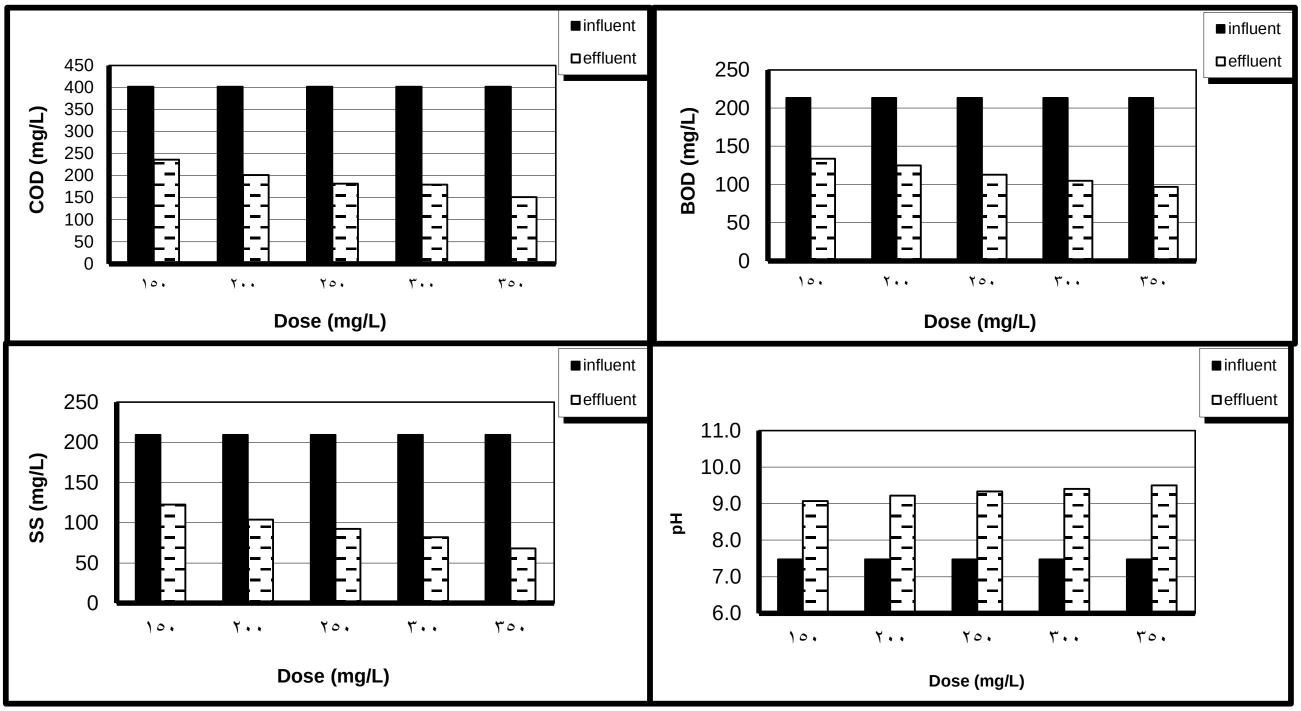

Fig. 4. The relation between Lime + 5% Sea water dose application (mg/l) on the average values of COD, BOD, SS and pH.

- Statistically, the chemicals coagulants dosages showed very highly significant effects on the pH, COD, BOD, SS and Cd parameters.
- Economically, this study has considered that the Lime salt + 5% seawater at dosage of 300 mg/l is the most promising candidate as a chemical precipitant, since lower amount of sludge would be produced than using lime only, and also to its lowest cost as compared with alum and ferric chloride.

5. Recommendations

It is proposed that additional experiments be conducted to gain more complete understanding for the efficiency of sedimentation tanks of the ETP of AGOSD. These further studies may include:

1. Conduct similar jar test runs using a different coagulant(s), possibly calcium carbonate or calcium sulphate (gypsum). This would be useful to improve the wastewater quality for reuse in agriculture and for environmental protection.
2. Conduct similar jar test runs using ferrous sulphate ($FeSO4$) instead of ferric chloride ($FeCl3$) as a coagulant to reduce expenses and to reduce the chloride hazards in agriculture use.
3. Investigate the high contents of the nitrogen in wastewater which might cause eutrophication in receiving water bodies, like Lake Mariut.
4. More experiments are required to study: (i) The effect of using different coagulants in the inlet of the sedimentation tanks on the produced sludge, (ii) sediment-driven density currents in radial sedimentation tanks and (iii) the produced sludge after using the different dosage of the tested coagulants.

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