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Organic pollutants removal by flocculation process using ferric chloride/cationic polyelectrolyte for wastewater agricultural reuse

Mohamed Y. Eddeeb[a], Ghada Heikal[b], Abeer El Shahawy[c,*]

[a]*Civil Engineering, Technical Department, Concord for Engineering & Contracting, Cairo, Postal code 11931, Egypt, email: meddeeb@concord-ec.com*
[b]*Environmental Engineering Department, Faculty of Engineering, Zagazig University, Postal code 44519, Egypt, emails: reemhatem2006@hotmail.com, ghhekal@zu.edu.eg (G. Heikal)*
[c]*Department of Civil Engineering, Faculty of Engineering, Suez Canal University, PO Box 41522, Ismailia, Egypt, emails: ahmedabeer12000@yahoo.com, abeer_shahawi@eng.suez.edu.eg (A.EL Shahawy)*

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ABSTRACT

A physicochemical treatment (coagulation–flocculation–sedimentation) was applied for drainage wastewater using ferric chloride ($FeCl_3$) aided by cationic polyacrylamide (SedipurCF304BASF) as flocculant to evaluate the effectiveness of coagulation/flocculation/sedimentation method for removal of total chemical oxygen demand (COD), filtered COD, total suspended solid (TSS), total phosphorus (TP), turbidity and sludge volume production. An Imhoff and jar test has been conducted to locate the optimum settling time and dose of the coagulant and flocculant to be used. The optimum removal efficiency was obtained by adding 50 ppm $FeCl_3$ with 2 ppm cationic polyelectrolyte (CP) dose. The achieved maximum removal efficiencies were 99%, 99.29%, 99.27%, 73.08%, 99.98% of TCOD, FCOD, TSS, TP and turbidity, respectively at pH = 7.7. The dual use of ferric chloride and CP resulted in 6 mL/L sludge volume production with reduction of 60% of the amount produced, during using only $FeCl_3$. It can be concluded from this study that treated wastewater could be safely used for agricultural purposes according to Egyptian law for irrigation. The maximum operating cost was found to be equal to 0.5812 US$/m^3, which corresponds to a coagulant dose of 50 mg/L and flocculent dose of 2 mg/L.

Keywords: Ferric chloride; Polyacrylamide; Flocculation; Drainage; Cost

1. Introduction

Water deficiency is a universal problem arising from the growing demand on water due to urbanization, rapid population growth and climate changes. Thus, to overcome this problem, there is an urgent need to depend on a variety of non-conventional water sources, such as water reuse, rather than the dependence on the limited number of water sources. However, few researchers focused on this topic (new water sources) and consequently there is a lack of information about new water sources and their associated treatment technologies. The reuse of drainage water can provide a fundamental supplement to Egypt's water supply. It can supply a quantity of water which is larger than that falls as rain and pumped from deep aquifers in Egypt. The discharge of such polluted wastewater into the environment is not only aesthetically displeasing but also impedes light penetration, damages the receiving streams wholesome and may be poisonous to remedy techniques, to food chain and to aquatic lifestyles [1–3].

Lake El Temsah is one of the most important lakes in Egypt. The lake is located almost at the mid-point on Suez Canal. It commonly receives excessive salinity waters from the Great Bitter Lake in the south. These waters are over lined with the aid of: (i) a layer of sparkling and brackish water coming into the lake from the outflow of Ismailia freshwater

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* Corresponding author.

canal. (ii) sparkling water from four drains: El-Mahsama, EI-Bahtini, Abu-Gamous and El-Forsan. El-Mahsama drainage is the largest one; its discharge reaches 1,984,608 m^3/d [4]. All waste discharges of El-Mahsama drainage come from the growing human activities, raw liquid and waste municipal sewage, agriculture run off and industrial wastewater. In addition to hydrocarbons, several other potential chemical contaminants originate from various pollutant sources. All the previous contaminated discharge along the shoreline of the drainage have had a quite horrible effect on it, caused the demolition of fisheries, and stopped the flow of water from the lake to lagoons on the eastern bank of the lake. These lagoons were then used as sedimentation basins for the dredged ruin, which boost the water salinity and therefore lead to the killing of numerous species of fish [4].

Coagulation–flocculation has continually attracted widespread attention for yielding high elimination performance in wastewater treatment; this method may be immediately applied to wastewaters to do away with organics collectively with suspended solids, without being affected by the toxicity inside the wastewater.

Also Coagulation will play a crucial role, at once or indirectly, within the control of particulates, microorganisms, natural and artificial organic depend, precursors of disinfection via (DBPs) and some organic ions and metals in water and wastewater treatment.

Coagulant materials may be classified into inorganic coagulants (e.g., aluminum and ferric salts), synthetic organic polymer, or coagulants from natural sources [5].

Aluminum and iron coagulants are commonly used in most industries. However, when aluminum is used as a coagulant in wastewater treatment, it can cause several harmful effects on human health such as constipation, loss of memory, convulsions, abdominal colic's, loss of energy and learning difficulties. With the wide application of Al-based coagulants, high contents of residual Al in treated water has become a major concern because of its neurotoxicity and consequent potential for skeletal and hematopoietic toxicity. Ferric salts have been found to be economically preferable in wastewater treatment since they are highly abundant and non-toxic. Also they are preferred due to the low solubility of the resulting ferric hydroxide in wastewater, over a wide range of pH [6].

One of the principle drawbacks of using traditional Al and Fe coagulants is the formation of massive quantities of sludge that need disposal.

On the other hand, the use of Fe-based coagulants has inherent merit over the use of Al ones. For example, ferric chloride was considered as one of the most effective chemicals to remove anionic surfactants and COD compared with aluminum-based coagulants. This was attributed to the fact that ferric chloride can generate thicker and heavier flocs than aluminum salts. The sludge post-treatment is considered as one of the big challenges in all water treatment works due to the high treatment cost and environmental concerns [6]. To overcome these barriers, many studies have proven that twin-coagulants (clearly going on flocculant used as coagulant resource with inorganic coagulants) are used as a cost reduction technique. It reduces the dose of certainly taking place flocculants collectively with the enhancement of the flocculation interest leading to better treatment efficiency as they help in agglomeration of slow-settling micro-flocs into large denser flocs [7]. Many researches have revealed that cationic coagulants coagulation/flocculation procedure may be used as a pretreatment prior to biological remedy, which will enhance biodegradability of the wastewater all through the organic treatment [6,8]. Polymer flocculant is a water-soluble material which has adsorbable sites onto suspended particles. Polyelectrolytes are advantageous over chemical coagulants because they are safer to handle and are easily biodegraded. Generally, organic polymers generate less sludge than inorganic salts since they do not add weight or chemically combine with other ions in the water to form precipitate. Flocculation occurs by a process of adsorption of polymers on the particles, followed by a process of bridging of polymer chains between particles and/or charge neutralization of the particles. Polymer adsorption onto suspended particles is affected by many factors such as molecular weight of the polymer, its constituent monomer species and their combination, its concentration in a target colloidal system, the affinity between polymer and colloidal particles, solution environment (pH, ionic strength, etc.), particle concentration, and mixing intensity. Polyelectrolyte has huge molecules with a high molecular weight which has a high ionization power. It produces a large amount of ions in water and shows the properties of both polymers and electrolytes. Polyelectrolyte includes anionic and cationic types. The most practical benefit of poly electrolytes is the formation of massive flocs. These massive flocs speed up the flocs settling velocity, reduce the expenses of decolonization and also decrease settled sludge volume.

$FeCl_3$ with polymer can be used to enhance the biodegradability of wastewater during the biological treatment. Several of the problems with chemical precipitation are that the volume of sludge is increased and the resulting sludge may have poor settling and dewatering characteristics. In addition, metal salts used as coagulation aids consume alkalinity and can depress the pH of the effluent water. However, the coagulation process is not always perfect as it may result in small flocs when coagulation takes place at a very low temperature or fragile flocs which break up when subjected to physical forces. It is necessary not only to overcome these problems but also to improve the coagulation and flocculation processes to obtain a good-quality effluent and rapid sedimentation of the flocs formed. For this, several products, denominated coagulant aids, can be used to bring together and agglutinate the flocs formed by the coagulant in order to increase floc density and, hence, to improve sedimentation. Polymeric additives can act either by polymer bridging or charge neutralization. Thus, the sludge produced by the use of ferric chloride in combination with polyelectrolyte was compact and reduced in volume.

Tertiary treatments are applied in conventional wastewater treatment plants (WWTPs) after the secondary treatment to reuse reclaimed wastewater in agricultural use. Tertiary treatment further improves quality by nitrification–denitrification (to reduce the nitrogen level) and soil and aquifer treatments. In recent years, modern WWTPs have been constructed and operated with tertiary (or advanced) treatment. Processes studied in the bibliography for tertiary treatment includes coagulation–flocculation, sedimentation, filtration, disinfection and ultrafiltration. Coagulation, flocculation and sedimentation systems are intended to reduce total suspended solid (TSS), biodegradable organics and nutrients (nitrogen and phosphorus compounds) in the feed [8].

The objectives of this study were to investigate the feasibility of simulating coagulation/flocculation/sedimentation process efficiency as a pretreatment for agricultural reuse of drainage wastewater with respect to removal of total COD, filtered COD, turbidity, TSS, total nitrogen (TKN, nitrate), total phosphorus and sludge volume using ferric chloride either alone or with CP and also to investigate optimum mixture of coagulant/flocculant dosages with minimum sludge production.

2. Materials and methods

2.1. Materials

All the chemicals and reagents were of analytical grade. Sulfuric acid (98% m/m), $FeCl_3$ (96% m/m), NaOH, and CP (Sedipur CF304 BASF) polyacrylamide polymer were purchased from Chemproha Chemiepartner B.V. Coagulation process was performed on EL-Mahsama in the south of Ismailia, Egypt. The characteristics of the source water are shown in Table 1.

2.2. Sample analysis

Turbidity and pH were measured using (HI98703-01 Turbidity Portable Meter) and (AD1000, HANNA instruments, Egypt), respectively. Coagulation was carried out using a six-paddle stirrer using jar test (IMASS) apparatus.

2.3. Study area

The study area occupies the eastern side of Suez Canal navigation route, between the Red Sea to the south and the Mediterranean Sea to the north. It lies between latitudes 32°16′–32°18′ E, and longitudes 30°33′–30°35′ N. El-Mahsama drainage is considered one of the largest drains that pours into Lake Al-Temsah and its discharge reaches an amount of 22.97 m^3/s. The lake is small water body (~15 km^2), lies on the Suez Canal at midway between Port Said and Suez with a depth ranging between 6 and 10 m, and containing about 34 million cubic meters of water. Ibtehal [4] reported that the lake can be distinctly divided into three basins; El Temsah Lake, the western lagoon (Al Sayadin Lagoon) and the Suez Canal pathway (Fig. 1). It was reported that the pollution levels of El Temsah Lake were relatively high in general when compared with the other lagoons on the Nile coast. The following map shows the approximate location of El Mahsama drainage which discharge directly in El Temsah Lake.

Table 1
Characteristics of the source water

Parameter	Unit	Raw water
pH	–	7.00
Temperature	°C	28.00
Alkalinity	$mgCaCO_3/L$	166.00
Conductivity	mS/cm	2,270.00
Chlorides	mg/L	517.00
Total dissolved solids (TDS)	mg/L	1,306.00
Total suspended solid (TSS)	mg/L	137.50
Turbidity	NTU	142.00
Oil and grease	mg/L	4.60
Total COD	mgO_2/L	150.00
Filtered COD	mgO_2/L	140.00
Total BOD_5	mgO_2/L	88.00
Filtered BOD_5	mgO_2/L	85.00
Total nitrogen	mg/L	4.55
N-TKN (Kjeldahl)	mg/L	3.36
N-nitrate	mg/L	0.41
Total phosphorus	mg/L	0.78
Sulfates	mg/L	234.00

2.4. Experimental work

2.4.1. Imhoff cone measurements (decanting test without chemical products)

Measurements of settled solids in Imhoff cones [9] were taken after allowing the samples to settle in intervals within 2 h. The aim of this procedure was to determine the minimum time required for the best settling and the volume of settlable matter at different time. Obtained average values in mL units for each waiting time are determined.

2.4.2. Decanting test with coagulant/flocculant (jar test procedures)

Coagulation experiments were conducted in 1.0 L beakers using a conventional jar test apparatus with six paddles. The drainage wastewaters from EL Mahsama were dosed with different doses of $FeCl_3$ (1, 2, 5, 15 and 50). First, wastewater during coagulant addition was agitated rapidly at 200 rpm for 2 min. Then, the mixing rate was reduced down to 20 rpm for 5 min to allow the growth of flocs. The agitation was stopped and the flocs settled for 30–60 min. Second, a CP (Sedipur CF304 BASF) with molecular weight 8×10^6–12×10^6 as a flocculant was added with 0.5:2 mg/L for each jar at the stage of slowing down the speed of stirring. After that, the stirring rate was slowed down to 20 rpm for 5 min to allow the growth of flocs. Finally, the stirring was stopped and the flocs settled for 30–60 min. After sedimentation, a supernatant sample was extracted for further analysis. Wastewater sample was adjusted to pH 7.7 by using 1.0 M H_2SO_4 or 1.0 M NaOH.

2.5. Analytical methods

COD, filtered COD, total nitrogen (refer to supplementary S), TKN, nitrate, total phosphorus (refer to supplementary S) and the concentration of TSS were analyzed by standard method for examination of water and wastewater [9]. Once the experiment has been performed in the jar test, the volume of decanted sludge is estimated by the volumetric method. The sludge production is determined by direct reading as mL of sludge/L of settled wastewater using the Imhoff cones. Different pH conditions including 4:10 were adopted in this study. The main focus, however, was to evaluate the effect of

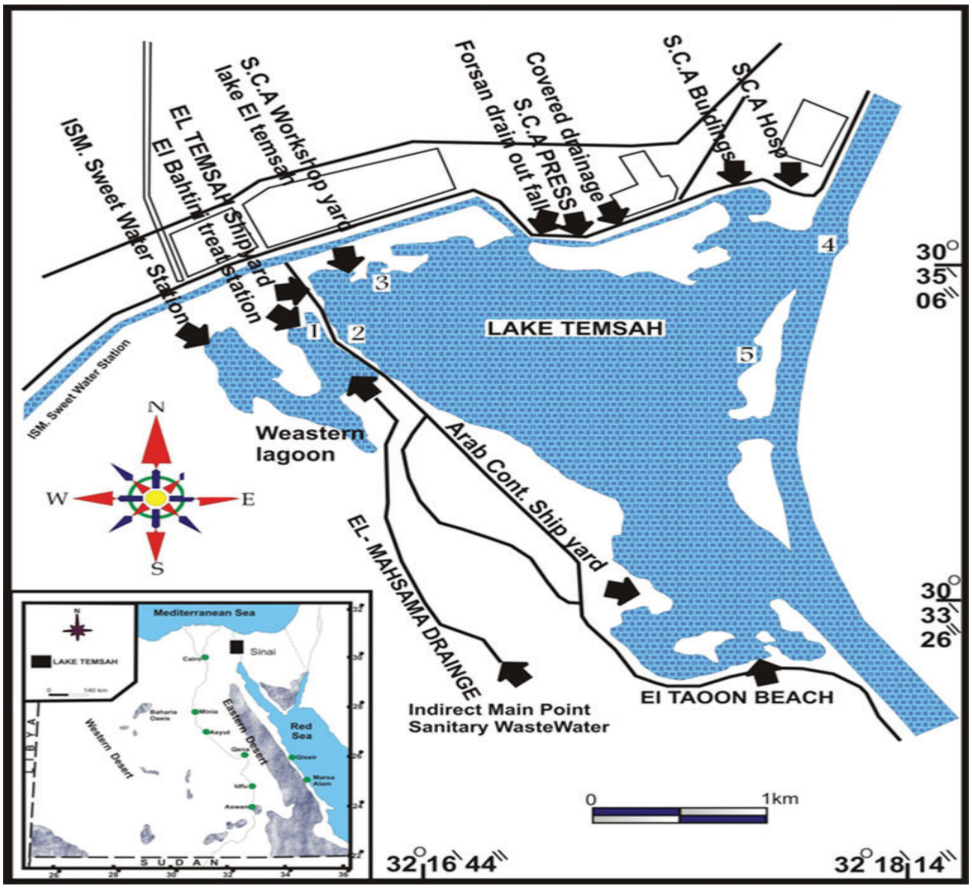

Fig. 1. Geographic map for the study area showing El Mahsama drainage as the largest source of wastewater disposal.

pH on the removal of COD and turbidity to determine the optimum pH value for the coagulation–flocculation process. All the pH values were adjusted to the nearest accuracy of ±0.1 pH units at 25°C unless specified otherwise. All experiments were carried out in triplicates and the average values were recorded.

2.6. Operating cost calculation

Chemical reagents consumption is a very important economic and financial tool when calculating operating costs for the coagulation/flocculation process. Other costs such as labor, maintenance and other provisions are assumed to be fixed and are not included in the calculations. Energy cost can be considered as fixed because all the experiments have been done by jar test IMASS with 0.15 kW, 230 V, 0.68 A and 50 Hz at the same time. The price of electricity obtained from the Egyptian market in April 2018 is 0.08 US$/kWh. Operating cost (OC) can be calculated by the following equation:

$$\mathrm{OC} = Y \cdot C_C + Z \cdot C_F \qquad (1)$$

where C_C is amount of chemical coagulant consumption and C_F is amount of CP flocculent consumption for pollution removal. Y and Z are the prices of chemical coagulant and CP flocculant, respectively. The prices obtained from the Egyptian market in April 2018 are as follows: $Y = 0.0095$ US$/g for chemical coagulant and $Z = 0.0531$ US$/g for CP flocculent. Chemical reagents consumption (C_C, C_F) was calculated from the optimum amount of coagulant and flocculent doses which achieved the highest removal efficiencies for the treated pollutants.

2.7. Statistical analysis

The MINITAB 18.0 software was used for all statistical analysis. All statistical significance was considered when $p < 0.05$. Analysis of variance (ANOVA), with Tukey's test was carried out to verify the significance of differences among the means (Null hypothesis all means are equal, alternative hypothesis not all means are equal, significance level $\alpha = 0.05$). Five water samples were taken along El Mahsama drain which its length is 38.8 km [11].

3. Results and discussion

3.1. Imhoff cone measurements

Measurements of settled solids in Imhoff cones were taken after allowing the samples to settle for 15, 30, 45, 60, 75, 90, 105 and 120 min. The aim of this procedure was to establish the minimum time needed for the most excellent settling and the settleable matter (sludge volume); obtained average values in mL units for each waiting time are given in Fig. 2. Imhoff results are connected with the total amount of solids or suspended solids removed, not just the precipitated portion. The solids in the water sample were first allowed to settle by gravity settling and only this pre-settled material was introduced into the settling cone. Therefore, the settling curve that was measured only reveals these settleable solids.

Analysis of the suspended solids remaining in the supernatant from the initial settling (prior to the Imhoff cone), and the suspended solids remaining in the column after 120 min was functioned to estimate the non-settleable fraction. There was strong positive correlation between settling time and sludge volume with (*r* +0.895, *p* 0.001). This study revealed that 46.55% of the solids in water were found to be non-settleable, the remainder of the settling curve would be based on the 53.45% of the solids that settled during the test, as shown in Fig. 2. The volume of the sludge that settled in 120 min varied from 0 to 0.6 mL/L of the effluent treated. The effect of settling time on the settleable matter volume in Imhoff cone without chemical product was studied. It is considered as plain sedimentation without any coagulants or any flocculants, gravity settling (a standard laboratory method where the entire suspension after coagulation/flocculation was allowed to settle for 30 min in a 1-L graduated measuring cylinder and the volume occupied by settled sludge in mL/L). In general, the larger volume of sludge was recorded at 105 min. As shown in Fig. 3, turbidity residual decreased gradually with increasing settling time with (*r* –0.969, *p* 0.00), maximum turbidity removal ratio was 50.35% at 120 min. Also, TCOD, COD, TSS recorded maximum removal ratio (28, 27.86, 53.45) with (*r* –0.994, *p* 0.00), (*r* –0.991, *p* 0.00) and (*r* –0.983, *p* 0.00) at 120 min, respectively. No removal in total phosphorus (TP) and TN was distinguished in Imhoff cone.

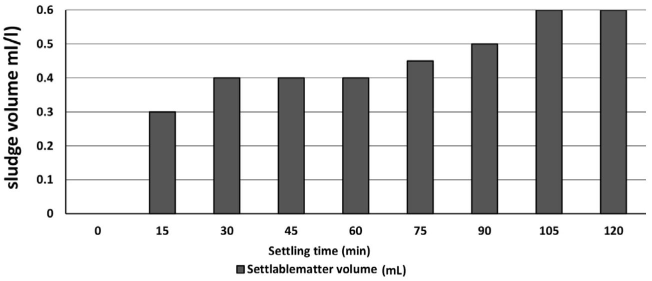

Fig. 2. Effect of settling time on the settleable matter volume in Imhoff cone without chemical product.

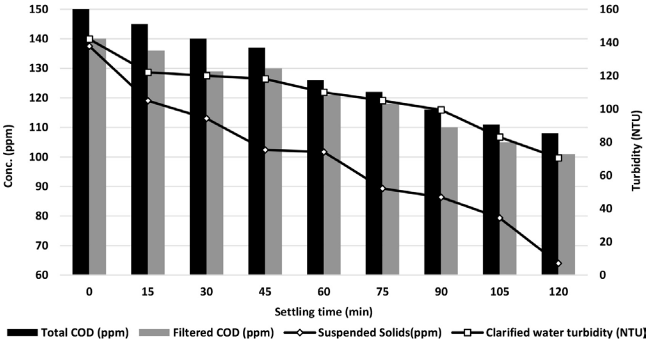

Fig. 3. Effect of settling time on the characteristics of the clarified water through the Imhoff cone without chemical product.

Pavanelli and Bigi [12] stated that Imhoff cone measurements are not significantly affected by differences in particle size distribution among different samples.

3.2. Decanting test with chemical products (jar test)

3.2.1. Effect of pH on $FeCl_3$ performance

pH is a fundamental environmental parameter during coagulation [13]. Consequently, the investigation of the pH effect on the flocculation process was a very crucial parameter. Since the pH values of drainage wastewater were different as a product of various discharges to drain, several different pH values representing acidic, neutral and alkaline conditions were selected for examination. The wastewater initial pH has an excessive impact on the coagulation–flocculation process, the surface charge of the colloid, etc. In this experiment, the effect of wastewater initial pH on turbidity and COD removal efficiency was examined at the coagulant dosage of 1 mg/L, with a rapid stirring speed of 200 rpm and rapid mixing time of 5 min. The wastewater initial pH was adjusted in the range 4–10 using 1.0 mol/L H_2SO_4 and NaOH solutions. Fig. 4 demonstrates the effect of the wastewater initial pH on the turbidity and COD removal efficiency.

The experimental result displayed that when the wastewater initial pH elevated to more than 4, there was an increase in the level of turbidity and COD removal efficiency with (*r* +0.992, *p* 0.001) and (*r* +0.919, *p* 0.028), respectively. Duan and Gregory [14] interpreted this; around neutral pH, Fe(III) has limited solubility, because of the precipitation of an amorphous hydroxide that can perform a very important role in practical coagulation and flocculation processes. Positively charged precipitate particles may deposit on pollutant particles (heterocoagulation), again giving the possibility of charge neutralization.

A further possibility is that surface precipitation of hydroxide could arise, with similar consequences. More importantly in practice, hydroxide precipitation leads to the possibility of sweep flocculation, in which pollutant particles get enmeshed in the growing precipitate and thus are effectively removed. While increased further than 8, there was a distinctly decrease in the level of turbidity and COD removal with (*r* –0.957, *p* 0.188) and (*r* –0.885, *p* 0.308), respectively. Earlier research exhibited that the ability of Fe(III) coagulants to neutralize the negative charge and to sweep the pollutants is optimal in the middle pH range [15]. Therefore, the main cause for the decrease could be the hydrolysis effect. $FeCl_3$ carries a high cationic charge, and the cationic functional groups could strongly interact with suspended, negatively charged particles.

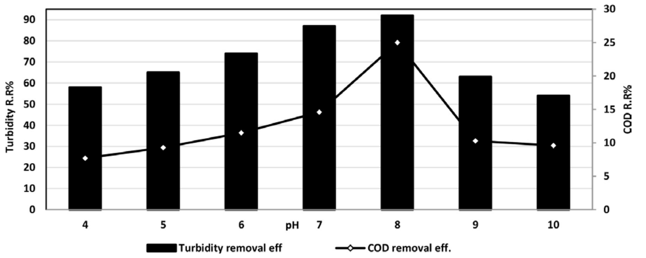

Fig. 4. Effect of different pH on the removal of COD and turbidity from drainage wastewater.

However, at higher pH, iron and aluminum hydrolysis augmented, resulting in the lack of the iron or aluminum species [16]. The coagulation performance worsened as the pH value increased. This phenomenon may be due to the reduction of the charge attraction, caused by both decreasing the positive surface charges of the flocculants and growing the negative surface charges of focus contaminants under higher pH levels. Another significant reason may be that reducing the surface charges of polymeric flocculants caused in weakening the intramolecular repulsion, and thereby the conformation of macromolecules turned compacted [17]. The maximum removal efficiency was achieved at the wastewater initial pH of 8, at which the turbidity and COD removal efficiencies were 92% and 25%, respectively. In addition, at the wastewater initial pH of range 7.7–8 nearly equals 8 by approximation, higher turbidity and COD removal efficiencies of 92% and 25% were also attained, respectively. Because the original wastewater pH was 7.7, and therefore, the wastewater initial pH of 7.7 was adopted as the optimum condition in this study. Employing higher dose of coagulant may attitude health hazard as a result of residual quantities of excess chemical additives [16]. The excess residual coagulant, when discharged into surface water, interferes with fish survival and growth [9].

3.2.2. Ferric chloride and cationic polyelectrolyte performance on physical properties (turbidity), organics (total and filtered chemical oxygen demand) and nutrients (total phosphorus + nitrates)

With gradually increasing ferric chloride alone from 1 to 50 ppm, the quality of wastewater improved as followed; physical properties such as turbidity removal ratio increased from 86.9% to 97.22%, organics content such as total and filtered chemical oxygen demand (TCOD, FCOD) removal ratio raised linearly from 14.67%, 13.57% to 20.67%, 20.71%, for COD and TCOD, respectively. In accordance with ferric chloride dose increase, nutrients such as TP removal ratio increased from 32.05% to 55.13%. Also, solids such as suspended solids removal ratio raised from 84.49% to 99.27%. A study by Belbahloul et al. [18] used extraction from the clados of *Opuntia ficus-Indica*, which achieved residual turbidities at 35 min to be 3 NTU with percentage removal of 98.5%, and at 40 min to be 2 NTU with percentage removal of 98.8% for the high turbid water.

Several studies used grouping of polyelectrolyte (as a coagulant aid) and chemical coagulant in the treatment of wastewater [19]. The dose of polyelectrolyte (cationic polyacrylamide) was varied from 0.5 to 2 mg/L and the ferric chloride dose varied at 1, 2, 5, 15, 50 mg/L. In order to ascertain the optimal dose of the polyelectrolyte with ferric chloride, the removal ratio of TCOD, FCOD, turbidity, suspended solids and TP was considered (Figs. 5–9). From Figs. 5 and 6, it can be perceived that removal of TCOD and FCOD reached 99% and 99.29% during the usage of 50 mg/L ferric chloride and 2 mg/L CP.

The highest removal ratio was attained with the adding of polyelectrolyte and it was realized that the ferric chloride dual coagulant/flocculant aids, at certain pH and agitation speed, provided higher removal efficiencies than using ferric chloride alone. TCOD and FCOD percentage with (*r* +0.779, *p* 0.000) and (*r* +0.743, *p* 0.00), respectively, decreased to 22.67% and 25% when the dose of the polyelectrolyte was reduced to 0.5 mg/L with 1 mg/L ferric chloride. As shown in Fig. 9, maximum TP removal reached 73.08% with the use of 50 mg/L ferric chloride and 2 mg/L dose of CP.

The mode of action of ferric salts is generally explained in terms of two distinct mechanisms: charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate. The relative importance of these mechanisms depends on factors such as pH and coagulant dosage. Coagulation is the process of decreasing or neutralizing the electric charge on suspended particles or zeta potential. Similar electric charges on small particles in water cause the particles to naturally repel each other and hold the small, colloidal particles apart and keep them in suspension. The coagulation/flocculation process neutralizes or reduces the negative charge on the particles. This allows the van der Waals force of attraction to encourage initial aggregation of colloidal and fine suspended materials to form microfloc. Flocculation is the process of bringing together the microfloc particles to form large agglomerations by physically mixing or through the binding action of flocculants, such as long chain polymers. Iron salts can also be used for the chemical precipitation of phosphorus. The basic reactions involved are as follows:

$$2FeCl_3\,6H_2O + 3Ca(HCO_3) \rightarrow 3CaCl_2 + 2Fe(OH)_3 + 6CO_2 + 12H_2O \quad (2)$$

$$Fe^{+3} + PO_4^{-3} \leftrightarrow FePO_4 \quad (3)$$

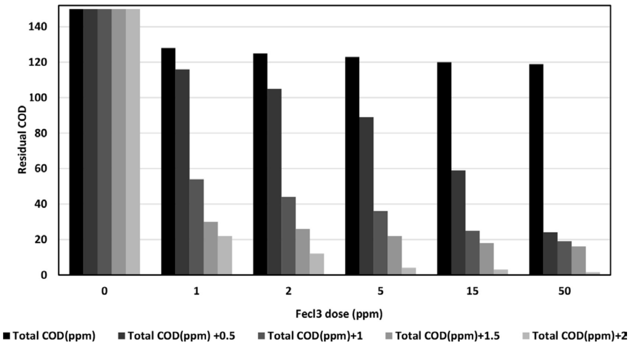

Fig. 5. Effect of different coagulant dose with different cationic polyelectrolyte (0.5–2.00) ppm on the COD concentrations.

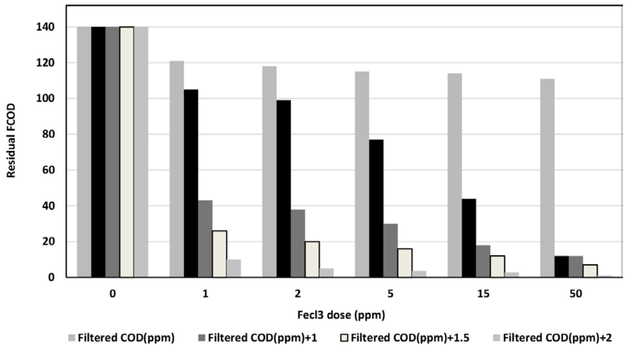

Fig. 6. Effect of different coagulant dose with different cationic polyelectrolyte (0.5–2.00) ppm on the filtered COD concentrations.

Very low removal ratio in total nitrogen may be due to adsorption, which means that total nitrogen exists in soluble matter than suspended.

A study by Abu Bakar and Abdul Halim [21] approached to the operating conditions of this study such as dose concentration and pH with $FeCl_3$; at well-defined optimum experiment condition (coagulant dose: 70 mg/L, coagulant aid dose: 2 mg/L and pH 7), PAC exhibited 70% elimination for COD and 98% of TSS. For $FeCl_3$ and alum, the maximum removal for COD were 64% and 54%, meanwhile TSS removal were 91% and 94%. Another study by Mahmoud [22] presented that the removal of 64% turbidity and 69% of COD was 300 ppm of alum after pH adjustment at pH = 7.2. An experiment detected that the more addition of 300 mg L^{-1} of alum and 1 mg L^{-1} of polymer could supply a reduction of turbidity, COD and phosphorus higher than 75%, 76% and 90%, respectively. In the present study, using 0.5 mg/L CP and 1 mg/L $FeCl_3$, resulted in removal ratio of TP (r +0.676, p 0.001) 42.31%.

As shown in Fig. 8, For the elimination of TSS with (r +0.393, p 0.087), maximum removal of 99.27% was accomplished with usage of 0.5, 1, 1.5, 2 mg/L CP and 50 mg/L ferric chloride, while minimum TSS removal ratio was recorded 90.31% at 0.5 mg/L CP and 1 mg/L ferric chloride. Additional adding of polyelectrolyte above 0.5 mg/L did not affect in the removal of TSS. There was improvement in the elimination of turbidity with the use of 50 mg/L ferric chloride and 2 mg/L CP, maximum turbidity removal ratio was 99.98%.

Zhu et al. [23] showed that COD and turbidity removal efficiency of 82.8% and 98.2%, respectively, was attained at coagulant dosage of 45 mg/L, wastewater initial pH of 8.5, and flash mixing speed of 250 rpm. The results of the present study coincided with the results of the study by Zhang et al. [24] that achieved turbidity removal ratio of PAFC increased with the rise of Al + Fe dosage at the start and accomplished more than 99% for turbidity removal at dosage of 5 mg/L Al + Fe.

The present study, as displayed in Fig. 7, minimum turbidity removal with (r +0.665, p 0.001) ratio was 88.17% at 0.5 mg/L CP with 1 mg/L ferric chloride. Because of the formation of a greater number of flocs, also, increasing the dose of the coagulant increased the super-saturation of the $Fe(OH)_3$ which increased the nucleation rate and hence the floc growth rate. When coagulant dose increases, suspension of greater number of flocs was enhanced, and subsequently removal of larger amount of organic matter was attained, because of the availability of larger surface area on which adsorption of the organic matter took place. Contrariwise, low doses of coagulant led to the formation of larger but fewer flocs as a consequence of faster growth rate relative to nucleation rate that caused in a smaller surface area on which adsorption of organic matter took place. The optimum dose of a coagulant or flocculant is the value over which there is no valuable difference in the rise in removal ratio with more additional coagulant or flocculant [19]. In judgment with the study by Dos Santos et al. [25], which studied using natural coagulant (Acquapol S5T and Tanfloc SL), this concentration was confirmed from statistical analysis (ANOVA, p-value < 0.05; Tukey's test, p-value > 0.05) as 320 mg L^{-1}, capable of removing turbidity (≥88.5%) parameters for treatment of the studied effluent.

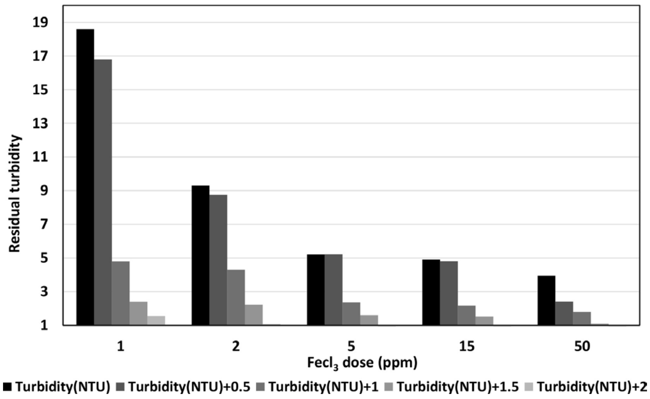

Fig. 7. Effect of different coagulant dose with different cationic polyelectrolyte (0.5–2.00) ppm on the turbidity.

Amuda and Amoo [19] reported 73%, 95% and 97% removal efficiency for COD, TP and TSS, correspondingly. These values were obtained by adding 300 mg/L $FeCl_3·6H_2O$. Additionally, they reported 91%, 99% and 97% removal of COD, TP and TSS, correspondingly with the addition of 25 mg/L polyelectrolyte to 100 mg/L ferric chloride. Produced sludge volume, when ferric chloride was used solely, was higher compared with the use of combination of polyelectrolyte and $FeCl_3·6H_2O$. The dual use of coagulant and polyelectrolyte caused decreasing sludge volume with 60% of the amount formed in case of ferric chloride only.

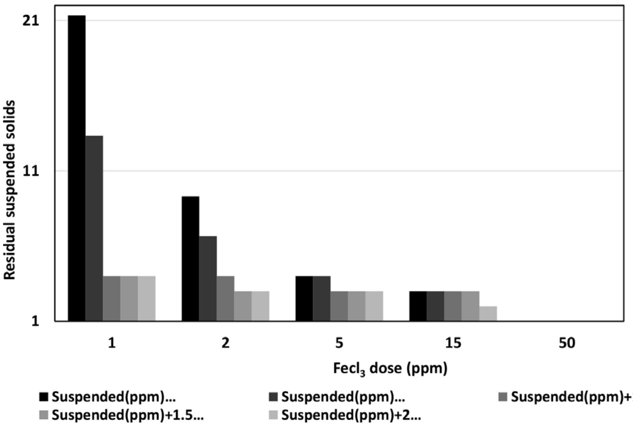

Fig. 8. Effect of coagulant dose with different cationic polyelectrolyte (0.5–2.00) ppm on the concentration of total suspended solids.

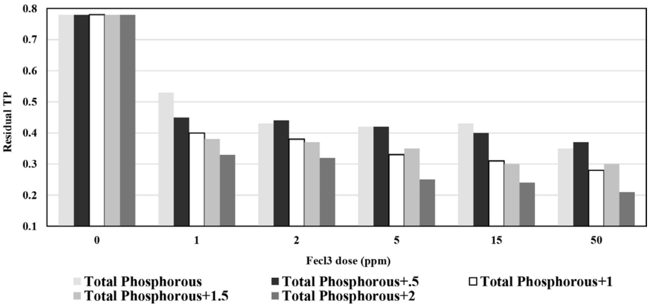

Fig. 9. Effect of different coagulant dose with different cationic polyelectrolyte (0.5–2.00) ppm on total phosphorus concentrations.

Thus, the optimum doses of ferric chloride and CP that improved COD removal were 50 and 2 mg/L, respectively. The use of 50 mg/L dose of ferric chloride at different dose of polyelectrolyte raised the elimination of COD at all the doses of CP; hence, this would be a suitable decisive system for determining optimum dose. 50 mg/L dose of ferric chloride and different doses of polyelectrolyte achieved between 52.56 and 73.08% removal of TP. However, to select proper coagulant and flocculent dose, we mainly focus and arrange the removal priority on COD, TSS and turbidity removal ratio. Certainly, nutrients (P, N) are important. TP did not look to be first parameter for determining the optimum dose, due to its elimination from the wastewater elevated with rise in the polyelectrolyte dose up to the maximum concentration (0.78 mg/L) employed. A synergistic effect of ferric chloride–CP combination achieved higher removal efficiency of the contaminants as illustrated in Table 2. The optimum doses of ferric chloride and polyelectrolyte that improved higher TSS and turbidity removal were 99.27%, 99.98%, respectively. As shown in Fig. 10, low removal ratio (4.88%) was recorded for nitrates.

3.2.3. Ferric chloride and cationic polyelectrolyte performance on solid production

In general, the amount and the characteristics of the sludge produced during the clari-flocculation process are extremely reliant on the specific coagulant used and on the operating conditions [19]. The wet sludge volume at the bottom of the jar test beakers after sedimentation step was used to measure sludge volume. The volume (mL/L) of the settled sludge is shown as functions of coagulant type and dose (mg/L) in Fig. 11. As exhibited in Fig. 11, increase in ferric chloride dose increased sludge production (10.20 ± 2.67) from 6 to 19 mL/L, when ferric dose increased from 1 to 50 ppm. The increase in sludge production resulted in the increase of suspended solids removal ratio (94.38 ± 2.67) from 85.0 to 99.27. Running Tukey test for different ferric chloride doses 1, 2, 5, 15, 50 ppm, the results are displayed in Table 3. There was a weighty difference between 1 and 50 ppm for both sludge volume and TSSs removal ratio as illustrated in Tables 4 and 5, respectively.

The increased volume of sludge produced in chemical sedimentation has mostly obstructed the implementation of the process as a wastewater treatment strategy. A comparison of (*r*, *p*) for sludge production at the different operating conditions are displayed in Table 6. Available data demonstrated that using ferric chloride with 1.5 ppm CP at pH 7.7 in the coagulation process provided the most significant strong correlation, provided sludge volume index (SVI) with high solids content as shown in Fig. 12. At 1, 2, 5, 15, 50 ppm $FeCl_3$ + 1.5 ppm CP, corresponding SVI and sludge concentration was 25.45 ± 7.36 and 134.42 ± 0.479 mL/g, respectively. The SVI (mL/g) (which is settled sludge volume/sample volume [mL/L] * 1,000 [mg/g]/suspended solid concentration [mg/L]) depends

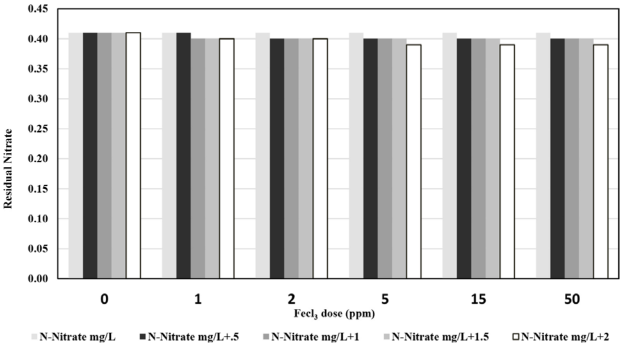

Fig. 10. Effect of different coagulant dose with different cationic polyelectrolyte (0.5–2.00) ppm on N-Nitrate.

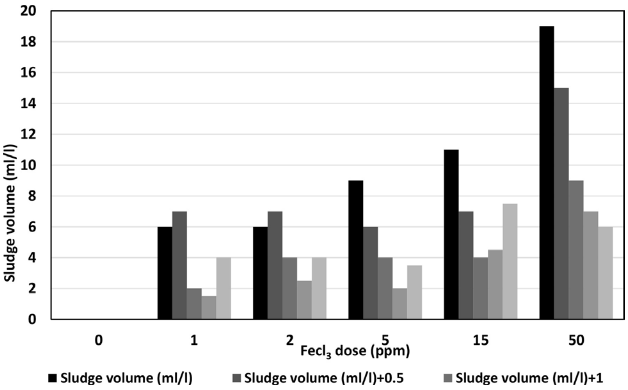

Fig. 11. Effect of different coagulant dose with different cationic polyelectrolyte (0.5–2.00) ppm on the sludge volume.

Table 3
Grouping information using the Tukey method and 95% confidence

CP dose	N	Mean	Grouping	
0.0	5	10.20	A	
0.5	5	8.40	A	B
2.0	5	5.00	A	B
1.0	5	4.60	A	B
1.5	5	3.50		B

Means that do not participate a letter are significantly different.

Table 2
Maximum efficiency for turbidity, TSS, TCOD, FCOD, TP, sludge volume and SVI at (0.5:2) mg/L CP + 50 ppm $FeCl_3$

CP+$FeCl_3$	Turbidity%	TSS%	TCOD%	FCOD%	TP%	Sludge volume (mL/L)	MLSS (ppm)	SVI (mL/g)
2.0+50	99.98	99.27	99	99.29	73.08	6		43.64
1.5+50	99.23		89.33	95	67.95	7	137.5	50.91
1.0+50	98.73		87.33	91.43	64.10	9		65.45
0.5+50	98.3		84		52.56	15		109.091
1.5+15	98.93	97.81	88	91.43	62.82	4.5		32.73

Table 4
Grouping information using the Tukey method and 95% confidence. For sludge volume vs. $FeCl_3$ dose method

Difference of levels	Difference of means	SE of difference	95% CI	T-value	Adjusted *p*-value
2 – 1	0.75	1.78	(–3.05, 4.55)	0.42	0.680
5 – 1	0.25	1.78	(–3.55, 4.05)	0.14	0.890
15 – 1	2.13	1.78	(–1.68, 5.93)	1.19	0.252
50 – 1	5.63	1.78	(1.82, 9.43)	3.15	**0.007**
5 – 2	–0.50	1.78	(–4.30, 3.30)	–0.28	0.783
15 – 2	1.37	1.78	(–2.43, 5.18)	0.77	0.453
50 – 2	4.88	1.78	(1.07, 8.68)	2.73	**0.015**
15 – 5	1.87	1.78	(–1.93, 5.68)	1.05	0.310
50 – 5	5.38	1.78	(1.57, 9.18)	3.01	**0.009**
50 – 15	3.50	1.78	(–0.30, 7.30)	1.96	0.069

Note: Bold values indicate *p*-values ≤ 0.05.

Table 5
Grouping information using the Tukey method and 95% confidence. For TSS RR vs. $FeCl_3$ dose method

Difference of levels	Difference of means	SE of difference	95% CI	T-value	Adjusted *p*-value
2 – 1	1.57	1.16	(–0.89, 4.04)	1.36	0.193
5 – 1	2.24	1.16	(–0.22, 4.71)	1.94	0.072
15 – 1	2.61	1.16	(0.14, 5.07)	2.25	**0.040**
50 – 1	3.88	1.16	(1.41, 6.34)	3.35	**0.004**
5 – 2	0.67	1.16	(–1.80, 3.13)	0.58	0.572
15 – 2	1.03	1.16	(–1.43, 3.49)	0.89	0.387
50 – 2	2.30	1.16	(–0.16, 4.77)	1.99	0.065
15 – 5	0.36	1.16	(–2.10, 2.83)	0.31	0.757
50 – 5	1.64	1.16	(–0.83, 4.10)	1.42	0.177
50 – 15	1.27	1.16	(–1.19, 3.74)	1.10	0.288

Note: Bold values indicate *p*-values ≤ 0.05.

Table 6
Pearson correlation and *p*-value for sludge volume with different treatment cases

Treatment case	(*r*, *p*)
Plain sedimentation	(+0.895, 0.001)
$FeCl_3$	(+0.909, 0.012)
$FeCl_{3+0.5\text{ cationic polyelectrolyte}}$	(+0.308, 0.552)
$FeCl_{3+1\text{ cationic polyelectrolyte}}$	(+0.899, 0.015)
$FeCl_{3+1.5\text{ cationic polyelectrolyte}}$	(+0.923, 0.009)
$FeCl_{3+2\text{ cationic polyelectrolyte}}$	(+0.561, 0.247)

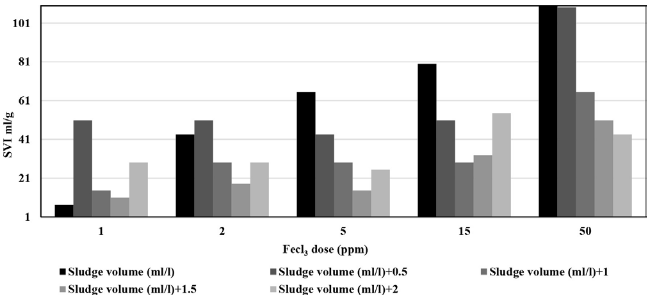

Fig. 12. Effect of different coagulant dose with different cationic polyelectrolyte (0.5–2.00) ppm on the sludge volume index.

on the concentration of total suspended solids, the depth of settling tank, the sludge volume, the stirring velocity, the effect of temperature and the floc structure and dimension is a usual parameter to estimate the activated sludge settling capacity. Because of the rise in oxidation rate resulted in high primary nucleation rates and dampened growth of the particles, the number of particles formed also increased significantly at pH 8 [26].

From Fig. 11, it can be seen that the volume of formed sludge, diminished significantly with rising dose of polyelectrolyte in the coagulation process. This may be attributed to re-suspension of particles at higher doses of the polyelectrolyte and cationic nature of the polyelectrolyte employed in this study, which has high molecular weight, thus, offering long bridges between small flocs to enhance particle growth. It also has the ability to appeal and attract colloidal particles at polar sites on the molecule. Generally, organic polymers produce less sludge than inorganic salts since they do not add weight or chemically combine with other ions in the water to form precipitate. Thus, the sludge formed by the use of ferric chloride with CP was dense and shrunken in volume. These findings are in accordance with our aforementioned studies and those of others [27].

In addition to pollutants removal, sludge production is considered in this work, as it may affect the economic feasibility of the proposed method. In the solid–liquid separation, sludge dewatering has been considered as one of the most expensive processes. As demonstrated in Table 7 for Tukey 95% confidence interval plot and simultaneous tests for differences of means between all studied treatment cases, there was a significant difference between using $FeCl_3$ alone and $FeCl_3$ with 1.5 ppm CP. In the numerical output, 95% family-wise confidence interval goes from –13.10 to –0.3 mm (lower and upper in the numerical output provide the CI endpoints). This interval does not contain 0 since its upper end point is –0.3 mm, this estimate of the difference used to determine whether the difference is practically significant. The confidence intervals for the remaining pairs of means all include zero, which indicates that the differences are not significant. So we can now say that there is evidence that $FeCl_3$ alone and $FeCl_3$ with 1.5 ppm CP have different true mean growth rates.

The *p*-values can be used to establish the significance of different studied cases. Ferric chloride without any coagulant aids stands alone and ferric chloride with 1.5 ppm CP are then indistinguishable from each other.

No significant difference between the performance of ferric chloride at 15 ppm and 50 ppm with 1.5 ppm CP. So, from the opinion of healthy and economic view, this study recommended using 15 + 1.5 ppm of ferric chloride and CP, respectively, that produced the lowest sludge volume 4.5 mL/L. The addition of coagulant aids crops a minor volume of decanted sludge compared with the result obtained when the coagulant is used alone. The amount of the produced sludge was 11 mL L^{-1} when 15 ppm of ferric chloride was added, diminished up to 4.5 mL L^{-1} when this coagulant acted together with 1.5 ppm of CP. In the case of coagulation–flocculation, the combinations used lead to appreciably nearly equal removal percentages 98.93%, 97.96% for turbidity, suspended solids and 88%, 91.43% for COD, FCOD, respectively. The use of ferric chloride and CP flocculants has a higher dewaterability of sludges than ferric chloride alone. This indicates that (cationic flocculant) is beneficial on the dewaterability of settled sludges. Bohm and Kulicke [28] have observed a better dewaterability of sludge when using dual cationic and anionic polyelectrolytes concurrently. To compare the results attained with $FeCl_3$ and each of the combination of coagulant and flocculants, we consider the ratios between the volume of sludge produced and the percent of COD, TSS, turbidity and TP removals with balance in organic removal efficiency and solids matters. The handling treatment and removal of the sludge generated in chemical sedimentation process are central features to judge choosing coagulant and coagulant aid products [27]. Considering the results attained if a small amount of sludge is to be treated, the most appropriate combination for the treatment of drainage wastewater would be coagulant ($FeCl_3$) and CP.

This study displayed the worst case in low particle concentration and low turbidity water, resulting in the formation of small, and loose flocs when a lower dosage of coagulant aid is used. Further, these flocs may be suspended in water due to low collision rate, resulting in a higher level of residual. At low colloidal concentrations, the removal mechanism of coagulation is controlled by precipitate formation. On the other hand, at high colloidal concentrations a double layer mechanism is almost certainly governing, such as that described by the Gouy–Chapman model. The first effect must be compression of the diffuse part of the double layer, rather than extensive adsorption which takes place with its eventual related charge reversal. For a physical double layer mechanism, colloid concentration has no effect on the coagulant dosage for destabilization. It should be noted, however, that if the coagulant dosage is very high, then metal–hydroxide precipitates will form, but there would appear to be little advantage from the point of view of destabilization efficiency [29].

3.3. Operating cost

Variations of the operating costs for the treatment of drainage wastewater are shown in Fig. 13. It was noticed that the total cost was calculated to be equal to 0.811 US$/m^3, which corresponds to a coagulant dose of 50 mg/L and flocculent dose of 2 mg/L, because of increasing in coagulant and CP flocculent doses (refer to excel sheet). The minimum operating cost was observed at coagulant dose of 1 mg/L and zero CP flocculent dose, which was equal to 0.0095 US$/m^3. This corresponds to low dosage of chemical reagents. According

Table 7
Tukey simultaneous tests for differences of means and 95% confidence for sludge volume vs. cationic polyelectrolyte dose method

Difference of levels	Difference of means	SE of difference	95% CI	T-value	Adjusted *p*-value
0.5 – 0.0	–1.80	2.14	(–8.20, 4.60)	–0.84	0.915
1.0 – 0.0	–5.60	2.14	(–12.00, 0.80)	–2.62	0.105
1.5 – 0.0	–6.70	2.14	(–13.10, -0.30)	–3.13	**0.038**
2.0 – 0.0	–5.20	2.14	(–11.60, 1.20)	–2.43	0.148
1.0 – 0.5	–3.80	2.14	(–10.20, 2.60)	–1.77	0.414
1.5 – 0.5	–4.90	2.14	(–11.30, 1.50)	–2.29	0.190
2.0 – 0.5	–3.40	2.14	(–9.80, 3.00)	–1.59	0.521
1.5 – 1.0	–1.10	2.14	(–7.50, 5.30)	–0.51	0.985
2.0 – 1.0	0.40	2.14	(–6.00, 6.80)	0.19	1.000
2.0 – 1.5	1.50	2.14	(–4.90, 7.90)	0.70	0.954

Individual confidence level = 99.28%.
Note: Bold values indicate *p*-values ≤ 0.05.

to these results, there is a direct association between amount of coagulant dose, polyelectrolyte flocculent dose and operating cost. This cost increases with increasing amount of coagulant dose, polyelectrolyte flocculent dose and vice versa.

Under optimal conditions the general cost was found to be 0.5812 US$/m^3. This result showed that the coagulation/flocculation process for the treatment of drainage wastewater effluent under optimum conditions is quite economical. This result is in agreement with those observed in the study by Said and Mostefa [30].

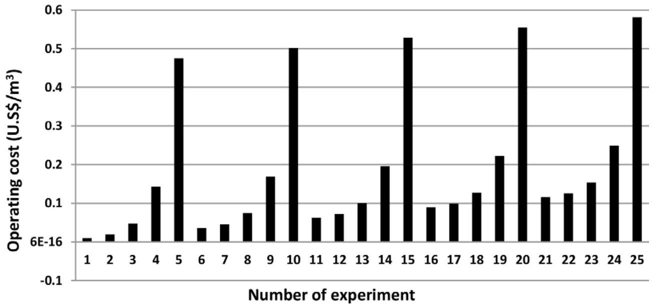

Fig. 13. Evolution of operating cost in the experiments of coagulation/flocculation treatment.

4. Conclusion

Coagulation of drainage wastewater may be achieved with any of the conventional water coagulants including ferric chloride and CP. The preference is established on appropriateness for a particular waste, availability and cost. Ferric chloride generally offers good clarification, rapid settling sludge and warrants using simple method of recovery that also guarantees destruction of most sewage solids in the resulting sludge, the whole experimental work is shown in Fig. 14. The removal of TCOD, FCOD, TSS, TP and turbidity removals ranged from 22.67% to 84%, 25% to 91.43%, 90.31% to 99.27%, 42.31% to 52.56% and 88.17% to 90.31%, respectively, when ferric chloride was used alone in the range of 1:50 mg/L, at pH =7.7. When CP was used instead, the TCOD, FCOD, TSS, TP and turbidity removals ranged between 22.67% and 99%, 25% and 99.29%, 90.31% and 99.27%, 42.31% and 73.08%, 88.17% and 99.98%, respectively. Sludge volume was 19 mL/L (SVI = 138.18 mL/g) with 50 ppm ferric chloride only, which reduced to 6 mL/L after addition of 2 ppm CP to 50 ppm $FeCl_3$ (about 68.42% sludge volume reduction with SVI=43.64 mL/g). As displayed in Table 8, effluent discharge standards in assigns to COD, BOD, TDS, TP, nitrate-nitrogen and TSS removals (according to Egyptian law 48/1982 for irrigation) could be safely obtained at 1.5–2 mg/L dose of CP with addition of 15–50 mg/L ferric chloride with pH = 7.7. Ferric chloride with CP produced a more compacted sludge as compared with ferric chloride only.

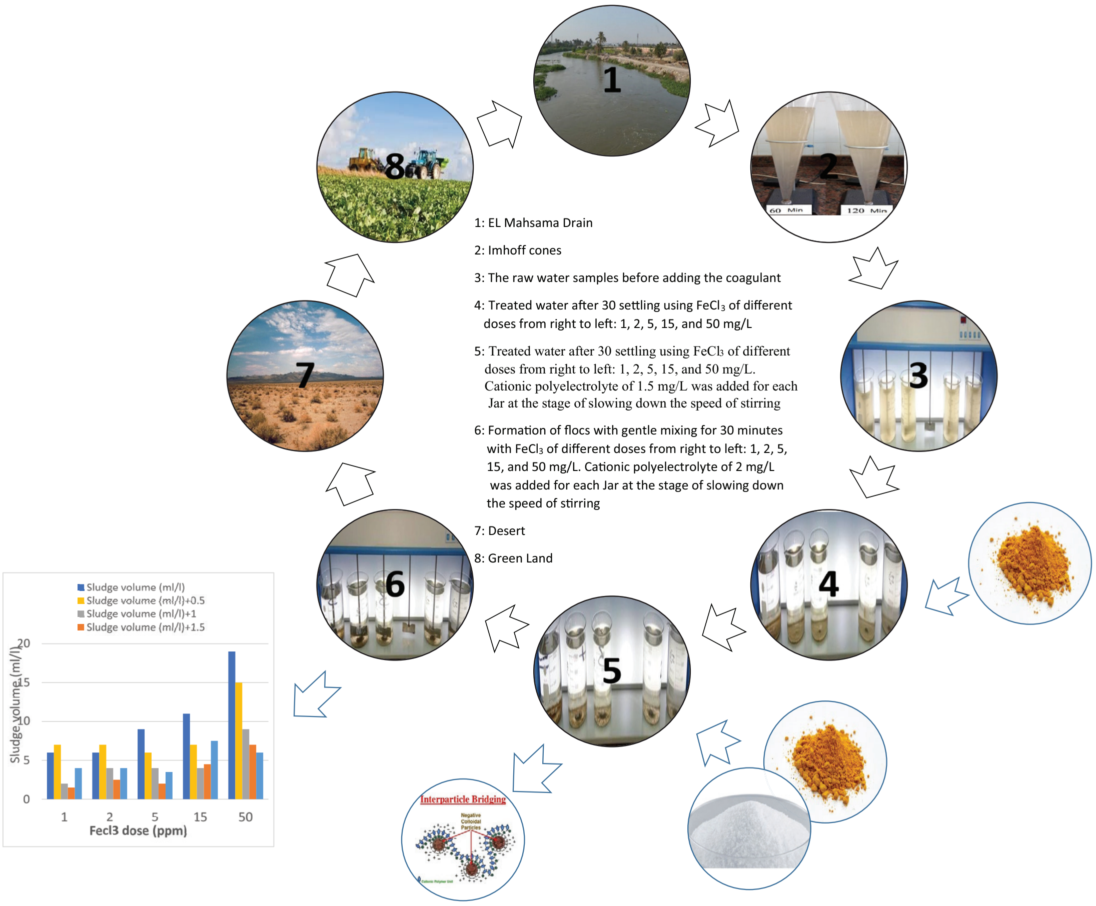

Fig. 14. A flow line for the whole experimental work.

Table 8
Guidelines of water quality for irrigation water according to Egyptian law

Parameter ppm (mg/L)	Unit	Effluent after C/F/S[a] in this study	Law 48/1982 for irrigation water[b]
BOD		0.76	40
COD		1.3	80
TDS		1306	2000
Nitrate-nitrogen		0.39	50
TP (total phosphorus)		0.21	3
TSS		50	50

[a] Coagulation/flocculation/sedimentation.
[b] Egyptian code of Environmental Regulations (1982): (4/1994) Appendix no. 1.

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References

[1] J. Barnes, Mixing waters: The reuse of agricultural drainage water in Egypt, Geoforum, 317 (2012) 625–633.

[2] H. Park, S. Lim, H. Lee, D. Woo, Water blending effects on coagulation-flocculation using aluminum sulfate (alum), polyaluminum chloride (PAC), and ferric chloride ($FeCl_3$) using multiple water sources, Desal. Wat. Treat., 57 (2016) 7511–7521.

[3] G.E. Üstün, S.K. Solmaz, F. Çiner, H.S. Başkaya, Tertiary treatment of a secondary effluent by the coupling of coagulation–flocculation–disinfection for irrigation reuse, Desalination, 277 (2011) 207–212.

[4] F.M. Ibtehal, Environmental geochemistry of El Temsah Lake sediments, Suez Canal district, Egypt, Arab. J. Geosci., 6 (2013) 4145–4153.

[5] A. Hatamie, H. Parham, B. Zargar, Z. Heidari, Evaluating magnetic nano-ferrofluid as a novel coagulant for surface water treatment, J. Mol. Liq., 219 (2016) 694–702.

[6] Y.X. Zhao, B.Y. Gao, G.Z. Zhang, S. Phuntsho, H.K. Shon, Coagulation by titanium tetrachloride for fulvic acid removal: factors influencing coagulation efficiency and floc characteristics, Desalination, 335 (2014) 70–77.

[7] M. Verma, R.N. Kumar, Can coagulation—flocculation be an effective pre-treatment option for landfill leachate and municipal wastewater co-treatment?, Perspect. Sci., 8 (2016) 492–494.

[8] L.F. Da Silva, A.D. Barbosa, H.M. De Paula, L.L. Romualdo, L.S. Andrade, Treatment of paint manufacturing wastewater by coagulation/electrochemical methods: proposals for disposal and/or reuse of treated water, Water Res., 101 (2016) 467–475.

[9] APHA-AWWA, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, D.C., 2005.

[10] P. Rowe, Essential Statistics for the Pharmaceutical Sciences, John Wiley & Sons, Ltd., 2016.

[11] G.W. Snedecor, W.G. Cochran, Statistical Methods, Iowa State University Press, Ames, 1989.

[12] D. Pavanelli, A. Bigi, A new indirect method to estimate suspended sediment concentration in a river monitoring programme, Biosyst. Eng., 92 (2005) 513–520.

[13] A. Sworska, J.S. Laskowski, G. Cymerman, Flocculation of the Syncrudefine tailings: part I. Effect of pH, polymer dosage and Mg^{2+} and Ca^{2+} cations, Int. J. Miner, Process, 60 (2000) 143–152.

[14] J. Duan, J. Gregory, Coagulation by hydrolyzing metal salts, Adv. Colloid Interface Sci., 100 (2003) 475–502.

[15] T.B. Chen, B. Gao, Q. Yue, Effect of dosing method and pH on color removal performance and floc aggregation of polyferric chloride–polyamine dual-coagulant in synthetic dyeing wastewater treatment, Colloid Surf., A, 355 (2010) 121–129.

[16] H. Zhao, H. Liu, J. Qu, Aluminum speciation of coagulants with low concentration: analysis by electrospray ionization mass spectrometry, Colloid Surf. A, 379 (2010) 43–50.

[17] P.J. Flory, Principles of Polymer Chemistry. Cornell University Press, New York, 1953.

[18] M. Belbahloul, A. Zouhri, A. Anouar, Bioflocculants extraction from Cactaceae and their application in treatment of water and wastewater, J. Water Process Eng., 7 (2015) 306–313.

[19] O.S. Amuda, I.A. Amoo, Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment, J. Hazard. Mater., 141 (2007) 778–783.

[20] A. Aygun, T. Yilmaz, Improvement of coagulation-flocculation process for treatment of detergent wastewaters using coagulant aids, Int. J. Chem. Environ. Eng., 1 (2010) 97–101.

[21] A.F. Abu Bakar, A. Abdul Halim, Treatment of Automotive Wastewater by Coagulation/Flocculation Using Poly-aluminum Chloride (PAC), Ferric Chloride ($FeCl_3$) and Aluminum Sulfate (alum), AIP Conference Proceedings, Vol. 1571, 2013.

[22] E.K. Mahmoud, Chemically enhanced primary treatment of textile industrial effluents, Polish J. Environ. Stud., 18 (2009) 651–655.

[23] G. Zhu, H. Zheng, W. Chen, W. Fan, P. Zhang, T. Tshukudu, Preparation of a composite coagulant: Polymeric aluminum ferric sulfate (PAFS) for wastewater treatment, Desalination, 285 (2012) 315–323.

[24] Y. Zhang, S. Li, X. Wang, X. Li, Coagulation performance and mechanism of polyaluminum ferric chloride (PAFC) coagulant synthesized using blast furnace dust, Sep. Purif. Technol., 154 (2015) 345–350.

[25] J.D. Dos Santos, M.T. Veit, P.T. Juchen, G.C. Gonçalves, S.M. Palácio, M. Fagundes-Klen, Use of different coagulants for cassava processing wastewater treatment, J. Environ. Chem. Eng., 6 (2018) 1821–1827.

[26] M.A. Aboulhassan, S. Souabi, A. Yaacoubi, M. Baudu, Improvement of paint effluents coagulation using natural and synthetic coagulant aids, J. Hazard. Mater., 138 (2006) 40–45.

[27] F. El-Gohary, A. Tawfik, U. Mahmoud, Comparative study between chemical coagulation/precipitation (C/P) versus coagulation/dissolved air flotation (C/DAF) for pre-treatment of personal care products (PCPs) wastewater, Desalination, 252 (2010) 106–112.

[28] N. Bohm, W.M. Kulicke, Optimization of the use of polyelectrolytes for dewatering industrial sludge of various origins, Colloid Polym. Sci., 275 (1997) 73–81.

[29] B. John, Coagulation and Flocculation in Water and Wastewater Treatment, 3rd ed., IWA Publishing, 2016.

[30] H.K. Said, N.M. Mostefa, Optimization of turbidity and COD removal from pharmaceutical wastewater by electrocoagulation: isotherm modeling and cost analysis, Pol. J. Environ. Stud., 24 (2015) 1049–1061.

[31] F. Koroleff, Determination of total nitrogen in natural waters by means of persulfate oxidation [in Swedish], Int. Counc. Explor. Sea (ICES). Pap. C. M. 1969/C: 8; revised, 1970.

[32] J.D. Strickland, T.R. Parsons, A Practical Handbook of Seawater Analysis, Bulletin – Fisheries Research Board of Canada, 1972, p. 167.

[33] P.J. Williams, LEB. 1969, The wet oxidation of organic matter in seawater, Limnol. Oceanogr., 14 (1969) 292–297.

[34] M.I. Liddicoat, S. Tibbitts, E.I. Butler, The determination of ammonia in seawater, Limnol. Oceanogr., 20 (1975) 131–132.

[35] L. Solorzano, Determination of ammonia in natural waters by the phenolhypochlorite method, Limnol. Oceanogr., 14 (1969) 799–801.

[36] N. Gravitz, L. Gleye, A photo- chemical side reaction that interferes with the phenolhypochlorite assay for ammonia, Limnol. Oceanogr., 20 (1975) 1015–1017.

[37] K.H. Nicholls, A single digestion pro- cedure for rapid manual determinations of Kjeldahl nitrogen and total phosphorus in natural waters, Anal. Chim. Acta, 76 (1975) 208–212.

Supplementary material

1. Method for measuring total nitrogen

A persulfate oxidation technique for TN determination has also been developed [31].

All reagents should be of analytical reagent grade. Nitrogen-free distilled water (NFDW) is prepared by UV oxidation and deionization or by double distillation from acid persulfate and alkaline permanganate. Glassware is pre-rinsed in dilute HCI and NFDW. TPN reagents and procedure.

1. Oxidizing reagent: 3.0 g of NaOH and 6.7 g of low N (<0.001%) potassium persulfate (peroxydisulfate), $K_2S_2O_8$, are dissolved in 1 L of NFDW just before use.
2. 0.3 N HCl: stable for months.
3. Buffer solution: 30.9 g of H_3BO_3 are dissolved in deionized water, 101 mL of 1 M NaOH are added, and the solution made to 1 L; stable for months.
4. NO_3^- reduction columns and NO_{2-} reagents are as given by Strickland and Parsons [32].

Fifteen milliliters of oxidizing reagent are added to 10.0 mL of sample in 25 × 150-mm (50-mL capacity) borosilicate screw cap culture tubes. A $Mg(OH)_2$ precipitate forms in seawater samples. Blanks for undiluted samples consist of 15.0 mL of oxidizing reagent only. The tubes are capped immediately with size 24 polypropylene screw closures (e.g., Nalgene 2150-0240). Samples are autoclaved at 100°C–110°C [33] for at least a half hour and slowly brought back to atmospheric pressure. The tubes can then be removed and cooled to room temperature. To each sample are added 1.5 mL of 0.3 N HCI. The samples are mixed with a Vortex mixer until the precipitate dissolves, 2.0 mL of buffer solution is added, and then de-ionized water to a mark on the tube indicating 50 mL (alternatively, 23.5 mL of a stock solution of 2 parts buffer solution to 21.5 parts of deionized water can be added). Twenty milliliters of each sample are washed through the nitrate reduction column in small aliquots and are discarded. The final 30 mL is passed through the column and analyzed for NO_2^- (Strickland and Parsons 1972). As the borate buffer does not appear to complex Cd^{2+} well, the columns will tend to clog unless rinsed every few samples with about 10 mL of dilute NH_4Cl solution (Strickland and Parsons 1972).

TKN reagents and procedure:

1. Digestion mixture: 50 parts of concentrated H_2SO_4 to 50 parts of NFDW to 5 parts of 5% $CuSO_4$.
2. Ammonium reagents: phenol and alkaline solutions as given by Solórzano [35]; sodium nitroprusside solution 0.25% of sodium nitroprusside; oxidizing solution 0.2 g of sodium dichloroisocyanurate [34] per 100 mL of alkaline solution.

Two milliliters of digestion mixture and two glass beads are added to 25.0 mL of sample in a Kjeldahl flask. The flask is heated to volatilize the water and digested until the remaining solution turns clear. After rinsing with a minimum amount of NFDW, the solution is transferred to a beaker, cooled on ice, and the pH is adjusted to 5.0–5.2 with NaOH. An aliquot of the solution is poured into a 50-mL volumetric flask and diluted to volume. Samples can be stored overnight at this point. The reagents for NH_4^+ determination are added as prescribed by Solórzano [35], and the color developed in the dark [36] for a consistent period (not less than 90 min) at room temperature. The factor (*F*) relating absorbance to NH_4^+ concentration should be determined by difference in absorbance from NH_4Cl spiked and unspiked seawater. TKN blanks are obtained using NFDW. Absorbances are recorded at 640 nm in a 1-cm cuvette. We have found that although the $CuSO_4$ catalyst in the digestion mixture gives a slight blue color after addition of the NH_4^+ reagents [37], it does not interfere with indophenol blue color formation. We have chosen to retain the catalyst for samples only in the higher TKN ranges [37]. The present procedure affords a range of detection from about 2 to 50 µg-atoms N liter^{-1}. During the past year, we have randomly used NH_4^+, NO_3^-, glycine, EDTA and urea as standards to obtain the factor (*F*) relating 1-cm cuvette absorbance to TPN concentration. Except for NH_4^+ ($0.05 < p < 0.1$; t-test), we have found no significant difference (i.e., $p < 0.1$) in N recovery between NO_3^-, which we considered 100% recoverable, and the other standards. Presumably, the significant difference in NH_4^+-N recovery was due to its dissociation and partial volatilization upon addition of alkaline persulfate reagent as this raises the pH to about 10.8. However, recovery of NH_4^+-N was excellent (96%) and losses should be inconsequential except in samples containing mostly NH_4^+-N.

2. Method for measuring phosphorus concentration

Reagents

- phenolphthalein indicator (aqueous solution)
- 6 M HCl, hydrochloric acid
- activated carbon
- vanadate-molybdate reagent
- standard phosphate solution: dissolve in distilled water 0.2195 g anhydrous KH_2PO_4 and dilute to 500 mL; this gives a 100 ppm of P as PO_4 solution

Preparing phosphate standards and determining concentration

1. Prepare 100 mL of a 1-ppm standard by pipetting 1.00 mL of the 100-ppm P standard into a 100-mL flask. Dilute to 100 mL with distilled water. Repeat this procedure to prepare 3-, 5- and 7-ppm standards.
2. To establish the calibration curve, treat each standard as follows:
   a. Pipette 10 mL of the 1-ppm standard into a 25.0-mL volumetric flask.
   b. Pipette 4.0 mL of the vanadate-molybdate reagent into this flask and dilute to 25 mL with distilled water. Mix thoroughly.
   c. Repeat with 3-, 5- and 7-ppm standards.
   d. Prepare a blank by pipetting 4.0 mL of the vanadate-molybdate reagent into a 25.0-mL volumetric flask and bring to volume with distilled water.
   e. After 10 min but no more than 30 min, measure the percent transmittance at 400 nm.

3. Prepare a calibration curve by plotting absorbance as a function of ppm phosphate-phosphorus.

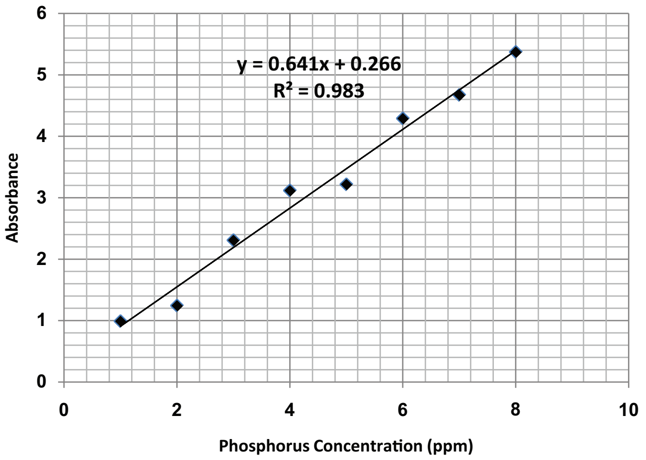

Fig. S1. Calibration curve of phosphorus concentrations.