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Surface Water Pretreatment via Fenton Oxidation with Coagulation

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Abstract

Steam system water inventory is mainly supplied by surface sources, such as lakes or rivers. The incoming surface water is highly contaminated with organic matter and mineral salts. Inadequate treatment of such water sources results in severe and widespread deposits and water-side corrosion. This paper studied the Fenton oxidation with coagulation as pretreatment of the surface water from Nile River (Ismailia Channel) used as makeup boiler water. The incoming water has been analyzed and characterized for one year; the examined characteristics in this work are pH, total dissolved solid (TDS), total hardness (TH), chlorides, total alkalinity (TA), and organic matter (OM). Additionally, the effect of two types of coagulants and Fenton oxidation process on the reduction of the above characteristics has been studied. Moreover, the effect of the combination of Fenton/coagulation process was investigated. The influence of Fe^{2+} concentration and coagulant dosages was studied. The experimental work was carried out by using Jar test. The results proved that coagulation with ferric chloride is more beneficial than alum at similar doses. It is also found that treatment by Fenton oxidation with coagulation is more effective than coagulation or Fenton oxidation, under operating conditions ($[Fe^{2+}]$ = 10 mg/L; Fe^{2+}:H_2O_2 = 1.25:1; initial pH = 2.8; followed by coagulation at initial pH 8 with 5 mg/L ferric chloride).

***Keywords**: Surface water treatment; Coagulation, Alum; Ferric chloride; Fenton oxidation; Makeup boiler water.*

1. Introduction

Surface water, such as lakes or rivers are the main water sources of steam generation plants. Common impurities in water include calcium and magnesium hardness, dissolved oxygen, silica, alkalinity, and iron. [1]. Severe treatment of boiler water is important to protect the boiler as well as the distribution system. Such treatment could be classified as external treatment, internal treatment, and blowdown. External treatment involves the pretreatment of makeup water to eliminate alkalinity, dissolved gases, hardness and other impurities prior to water supply to the boiler. Internal treatment is achieved by supplying special chemicals directly either into the boiler drum itself or the feedwater just before it enters the boiler. The feed water quality is adversely affected by inadequate pretreatment [2]. Inadequate pretreatment could experience deleterious effects, such as severe and widespread deposits and water-side corrosion [1,3]. So, effective pretreatment helps to enhance the boiler efficiency by reducing blowdown requirements in addition to reducing internal treatment costs.

External treatment involves four main processes: settling, aeration, coagulation and filtration. The purpose of aeration is to remove undesirable dissolved gases, while the target of coagulation is to minimize turbidity, coarse suspended solids, color, silt and colloids. Settling and coagulation take place in the clarifier. Filtration, which is the last step in the pretreatment process, is carried out to eliminate any particulate matter or residual floc from the water discharge of the clarifier. In addition, the external water treatment process consists of chemical softening process, demineralization, and condensate polishing. On the other hand, efficiency of organics removal through conventional processes (coagulation, sedimentation, filtration, and disinfection) are limited when treating polluted surface water [4].

Selection of the necessary pretreatment equipment requires careful analysis of the capital, operating and maintenance costs, as well as the operating characteristics of the unit. Then the unit must be considered in the light of its specific pretreatment needs, performance and the wastewater generated. A lot of published papers aimed to introduce the best technique for water pretreatment system. Batisha suggested the use of poly aluminum chloride (PAC) for the purpose of coagulation and flocculation of raw water prior to feeding to reverse osmosis (RO) membrane [5]. Wang *et al.* [6] reported that PAC can efficiently remove algae from water, as it acts as a non-polluting flocculation foam. Sheng *et al.* [7] treated the highly polluted river water by aeration; which is a combination of biological, chemical and engineering processes. This process resulted in a significant removal of COD, BOD (>70%) and odour from the polluted river water [7]. Gozan *et al.* [3] introduced several process stages for raw water pretreatment. The stages include coagulation in rapid mixing, flocculation, sedimentation, disinfectant, and ultra-filtration membrane. They concluded that sand filtration unit should be replaced by ultra-filtration membrane. Wenten suggested the use of ultra-filtration as competitive pretreatment for RO system [8], while Bates discussed the advances in micro-filtration and ultra-filtration technology as pretreatment to reverse osmosis for colloidal fouling reduction [9].

Coagulation processes remain ubiquitous in water treatment. Many studies during the past decades have focused on the floc characteristics evolution during coagulation process in stirred tanks [10-12]. The most common chemicals used for precipitation and coagulation/flocculation process were aluminum sulfate (alum), lime, ferrous sulfate, and ferric chloride. However, the biggest disadvantage of such process is the production of large amount of sludge; thus, it needs high operating costs for final disposal.

Oxidation of organic constituents by a blend of hydrogen peroxide and iron (II) is known as Fenton process. It produces hydroxyl radicals (HO·), which has a high oxidation potential (E_0 = 2.80 V), and iron (III) according to reaction 1 [13].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{=} + OH^{\cdot} \qquad (1)$$

Iron (III) is suitable for subsequent coagulation in the system. Fenton process could be considered as a much interesting and promising process in most water treatment applications; this is due to the powerful oxidation and coagulation which could be carried out in one technological unit at the same time.

The main objectives of this work include characterization of surface water from Nile River (Ismailia Channel) and generated water after screening followed with sedimentation. In addition, a jar test was used to treat this water as a pretreatment unit to enhance the quality of makeup boiler water. The experiments were studied to compare the effectiveness of using coagulation, Fenton oxidation, and combined Fenton/coagulation. Two coagulants were tested in this work: ferric chloride and aluminum sulfate (alum). The effect of different concentrations of Fe^{2+} and coagulants doses was studied.

2. Experimental work

Raw water samples were collected from Nile River (Ismailia Channel). Water went through screen and sedimentation tank. The experimental work was performed in two parts; the first part includes standard characteristics of water. These standards include total dissolved solid (TDS), total hardness (TH), total alkalinity (TA), pH, chlorides, and organic matter (OM). The study was carried out during a year (the period of January through December). Samples, kept at 4°C, were analysed without much delay to avoid any alteration.

The second part includes treatment methods of the surface water to remove the pollutants from the water by coagulation, Fenton oxidation and combination of them. The experiments were carried out by using Jar test apparatus with six vertical agitators, equipped with 6 corresponding beakers. The mixing speed and time during rapid and slow mixing were automatically controlled by a timer installed in the jar test apparatus. The driving motor has a variable speed control in the range (0-200) rpm. In all experiments, water samples were removed from the cold room and were conditioned for about 1 hour under ambient temperature. Sample container was thoroughly shaken for re-suspension of possible settling solids. 500 mL of adjusted pH water was transferred into the cylindrical beakers of 1 L of capacity.

Preliminary batch experiments were conducted to study different concentration of Fenton reagents. All Fenton oxidation experiments were performed for 15 min. It was concluded that, the ratio of H_2O_2/ Fe^{2+} of 1 to 1.25 was chosen so that no residual H_2O_2 was remained after Fenton oxidation [14]. Ferrous sulfate (Fe^{2+}), the iron source was added to the water. After adding iron salt to the water, it was mixed until the salt was completely dissolved, and then 35% hydrogen peroxide solution was added in the determined amount. The concentration of Fe^{2+} was added to be in the range 5 mg/L to 20 mg/L. The pH was kept at 2.8 using H_2SO_4. Mixing was provided at 100 rpm. Samples taken after Fenton oxidation were basified to pH 8 with NaOH to quench any sustaining reactions by OH radical and settled for 60 min.

Fenton/coagulation in this study is defined as the reaction including Fenton oxidation at pH 2.8, followed by coagulation at neutral or elevated pH typically of eight. After the pH adjustment by NaOH, samples were further flocculated for 20 min at 20 rpm, and settled for 60 min.

To study coagulation: Two types of coagulants were used: aluminum sulfate (alum), and ferric chloride (ferric). The coagulant dosages ranged from 2 to 16 mg/L. The coagulant is added to the water, then a high-intensity mixing is initiated at 120 rpm for 3 min followed by slow stirring at 20 rpm for 20 minutes to allow floc growth. The mixing is stopped, and the floc is allowed to settle for 60 min.

All the samples from Fenton oxidation, coagulation, and Fenton/coagulation after settling time were then withdrawn from the level located at 5 cm below the water for analysis. Raw surface water and treated water samples were analyzed for pH, TSD, TH, TA, chlorides, and OM. All the analysis procedures were taken from the standard methods in the examination of water and wastewater manual published in 1994 (ASTM) [15]. A volumetric determination of organic matter (OM) can be measured as oxygen mg/L with potassium permanganate titration method. pH values and TDS of the samples were determined with a digital apparatus (HANNA instruments, made in Portugal, HI 9811).

3. Results and discussion

3.1. Characteristic of surface water

The characteristics of surface water are very important aspects of the quality of water and give the line of the treatment technology of it. The water quality of the Nile River (Ismailia Channel) supply which serves the many plants at different places (such as in Ismailia and Suez in Egypt) was compared with days of sampling and analysis for a year (the period of January through December). It was observed that, the surface water from this supply has low concentration of organic matter (OM) (2.2–2.6 mg/L as oxygen). OM in boiler makeup should be as low as reasonably possible (< 0.2 mg/L) since it may result in serious potential risks to the integrity of steam turbines. Additionally, organic acids species such as acetic and formic acids could be formed within the steam/water circuit of boiler plant as a result of the degradation of these particulates. These organic acids in steam could result in general corrosion in the system.

Figures 1-5 show the relation between the characteristics of pH, TDS, chlorides, TH, and TA. From Figure 1, the maximum and minimum values of total hardness the water were 194-158 mg/L, respectively. It was found that the total hardness concentration increased in January to half February and dropped through the following seven months and again the concentration of TH begun to increase to December. An observed variation of pH, TDS, chlorides, and TA was found from January to December (see Figures 2-5). The rang of surface water of maximum - minimum value of 8.1-7.9, 385-290 mg/L, 102-58 mg/L, and 140-130 mg/L for pH, TDS, chlorides, and TA, respectively. The presence analysis of this water supply indicates that, all these results are outside the allowable range for water used as makeup for the boiler system. Water fed to boiler should be free of mineral. The risk of corrosion, sludge formation or deposition within the boiler could be effectively reduced by taking into consideration the safety related requirements for the boiler feedwater, boiler water or circulating hot water. This implies that there is a need to treat the water to reduce high levels of TDS, hardness and other contaminants. In addition, water undergoes pretreatments and finally goes to demineralisation plant.

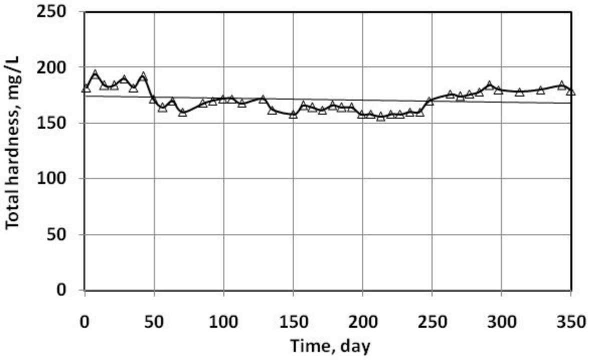

Figure 1. Total hardness concentration of the surface water from Nile River (Ismailia Channel)

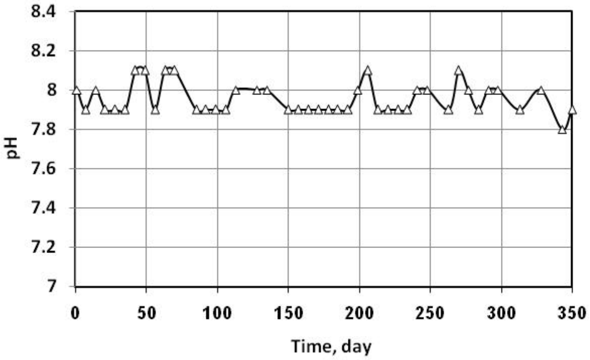

Figure 2. pH value of the surface water from Nile River (Ismailia Channel)

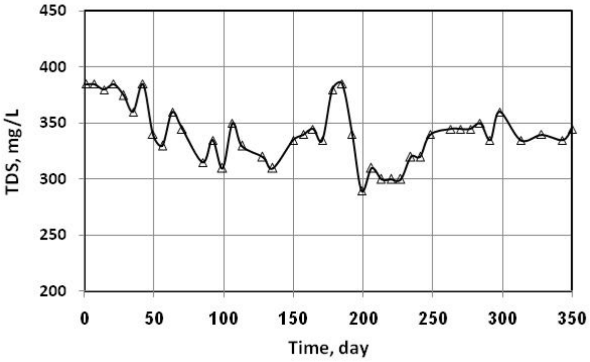

Figure 3. TDS concentration of the surface water from Nile River (Ismailia Channel)

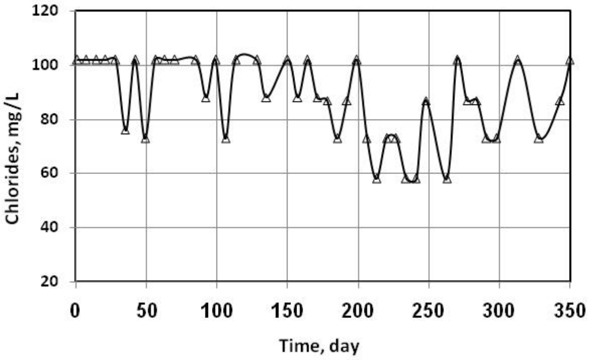

Figure 4. Chlorides concentration of the surface water from Nile River (Ismailia Channel)

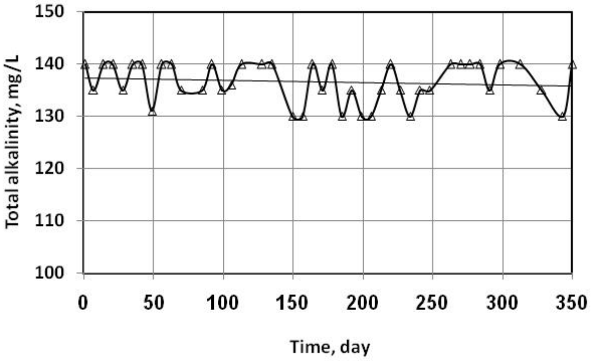

Figure 5. Total alkalinity concentration of the surface water from Nile River (Ismailia Channel)

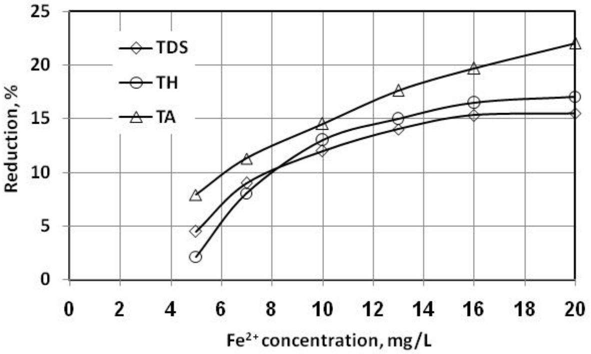

Figure 6. Effect of Fe^{2+} concentration in Fenton oxidation on reduction of TDS, TH and TA, at initial pH=2.8, 100 rpm for 15 min

3.2. Effect of Fenton oxidation

The reduction efficiency with Fenton oxidation was investigated by varying Fe^{2+} concentration from 5 to 20 mg/L at the Fe^{2+} to H_2O_2 ratio was 1.25 to 1 and initial pH 2.8. Figure 6 shows the influence of Fenton oxidation on the reduction of TDS, TH, and TA in the water. It was reported that, the almost removal percentage of the pollution in water by Fenton oxidation was achieved in the first 10 minutes of oxidation reaction [16-17], so the reaction time was adjusted for 15 min. It was observed that, by Fenton oxidation (without a subsequent coagulation), 15.5%, 17%, and 22% of TDS, TH, and TA reduction efficiencies were achieved at 20 mg/L of Fe^{2+} concentration, respectively. The dependence of TDS, TH, and TA reduction on Fe^{2+} concentration was found, for example, variation from 5 to 20 mg/L of Fe^{2+} concentration increased the TH reduction by eight times. These results are explained by reaction (1), which represents the main pathway of OH radical generation by Fenton oxidation. Immediately after their generation, the hydroxyl radicals initiate nonselective oxidation processes on the surrounding organic and inorganic species present in the water. It is worth to mention that Fenton reaction has a short reaction time among all advanced oxidation processes, in addition to other important advantages. The low price of iron and H_2O_2, non-toxicity, unlimited mass transfer due to its homogenous catalytic nature, no energy involved as catalyst and the easily run and control of the process encourage the usage of Fenton in many surface water treatment applications.

3.3. Effect of coagulants type

Both alum and ferric chloride were used as coagulants and the data given in Figures (7 and 8) are representative of the results obtained. Figures (7 and 8) show the effect of coagulant dose on TDS, TH, and TA reduction from surface water. These figures show that the reduction of water pollution was dependent on the coagulant. The reduction efficiency of TDS, TH and TA at 16 mg/L dose of alum is (3%, 4%, and 7.5%), respectively. Whereas the coagulation with ferric chloride proved to be more effective than alum at similar doses in the reduction of TDS, TH and TA (4.5%, 5.8% and 10%) respectively. It was reported that $FeCl_3$ solution is more acidic than alum; and so, more alkalinity is consumed for formation of ferric hydroxides [18]. Consequently, coagulation pH would be less with $FeCl_3$ at similar coagulant doses. The results show that an increase in the coagulant dose is associated with a decrease in the solution pH. The initial pH of the water was 8. After the addition of alum and ferric chloride at the doses in the range of 2-16 mg/L the pH decreased. A reduction occurs in pH when the concentration of coagulant is in the range of 10-16 mg/L, which gives a final pH value of 7.5 (alum) and 7.1 (ferric chloride). The better efficiency of $FeCl_3$ may be also due to that the difference in specific surface area and surface charge between iron hydroxides and aluminum hydroxides. According to literature, the surface of specific area of Fe and Al hydroxides are in different ranges of 160-230 and 200-400 m^2/g, respectively, however, the total available surface for $FeCl_3$ is much more than for alum due to higher active metal concentration in $FeCl_3$ and higher molecular weight of Fe [19]. Moreover, the produced sludge, when using ferric chloride, has much lower volume and weight than in case of alum.

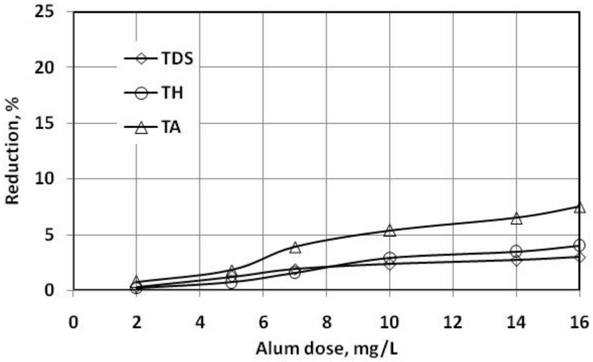

Figure 7. Effect of alum dose on reduction of TDS, TH and TA, at initial pH=8, 120 rpm for 3 min and 20 rpm for 20 min

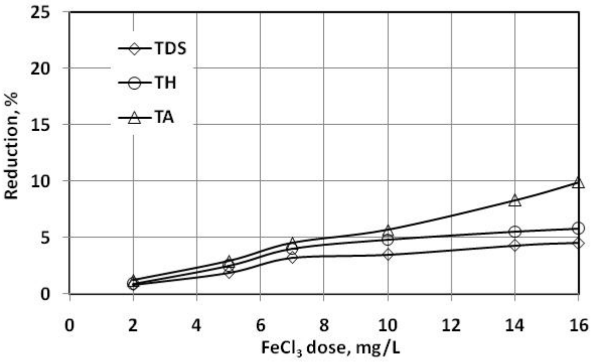

Figure 8. Effect of ferric chloride dose on reduction of TDS, TH and TA, at initial pH=8, 150 rpm for 3 min and 20 rpm for 20 min

In general, the Figures (7 and 8) show that the reduction efficiency is increased as coagulants doses are increased and higher dosages of coagulants than 16 mg/L were required to achieve more reduction of TDS, TH, and TA in the water. The increase dose of coagulants means the more costs of chemicals and to several problems with respect to final sludge disposal.

3.4. Effect of Fenton oxidation combined with coagulation

The ferric ions produced in Fenton reaction (According to reaction 2) could be used for subsequent coagulation purpose, which may further improve the reduction of TDS, TH, and TA, and OM. Therefore, reusing of sludge from Fenton oxidation to coagulation process was attempted to reduce the coagulant dose, sludge production, and improve the reduction of pollution. So, at the end of Fenton oxidation experiments, the Fenton sludge was reusing into coagulation after adjusted the initial pH to 8. The subsequent coagulation was carried out for 20 min at 20 rpm. The results are obtained in Figure 9. From these results, the Fenton/coagulation gives additional efficiency to the pollution reduction. The reduction efficiency of TDS, TH, and TA at the same dose of Fe^{2+} and coagulant (alum and ferric) (16 mg/L) is increased in the following order: Fenton/coagulation > Fenton oxidation > ferric coagulation > alum coagulation. In other words, the efficiency of the treatment by Fenton/coagulation was approximately 18%, 16.5%, and 15.5% more for TDS, TH, and TA, respectively than alum coagulation.

Also Figure 9 shows the results obtained by combination of Fenton oxidation and the addition of coagulants dose. The coagulant (5 mg/L) was added to the water at the end of Fenton oxidation (10 mg/L of Fe^{2+}) and controlled to initial pH 8, then mixed at 100 rpm for 2 min followed by slow mixing at 20 rpm for 20 min. The result of combination of Fenton oxidation and coagulants indicates more efficiency in pollution reduction. The reduction of TDS, TH, and TA was increased about (10%, 8% and 5%) by Fenton oxidation combined with ferric chloride respectively than Fenton oxidation. This level of reduction may be enough for meeting the requirements of the stage of demineralization. The use of excess Fe^{2+} concentration and coagulant dose to reach less TDS, TH, and TA concentrations, the excess production of sludge is experienced. On the other hand, the process (Fenton + coagulant alum or ferric) causes the formation of flocks more quickly and increases the rate of sedimentation.

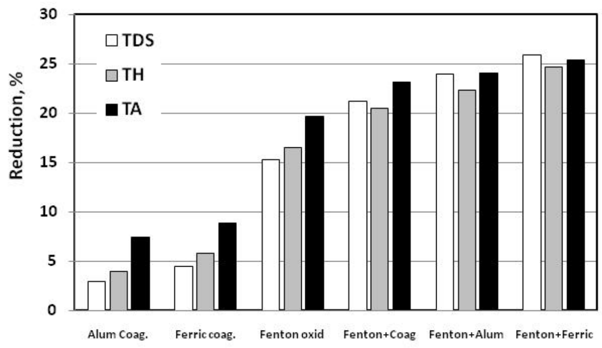

Figure 9. Effect of different processes on reduction of TDS, TH and TA

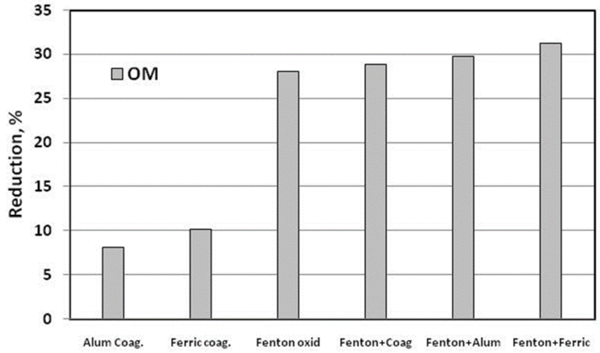

Figure 10. Effect of different processes on reduction of organic matter

In order to determine the most effective process to reduce the organic matter (OM) in raw surface water a comparison was made on basis of the percentage of residual (Figure 10). With some exceptions, the percent reduction of OM increases as the coagulants dose and Fe^{2+} concentration increase. The enhanced reduction of OM was achieved with Fenton oxidation of about 28% than 8% and 10% with alum and ferric coagulation respectively. As it was illustrated in Figure 10, adding coagulant (5 mg/L alum or ferric) at the end of Fenton oxidation (10 mg/L) and subsequent with coagulation was slightly influential in reduction of OM. The enhanced reduction is due to increased organic matter adsorption onto amorphous ferric hydroxide precipitates [20].

Based on the TDS, TA, TH, and OM reduction results described above, it is obvious that Fenton/coagulation with addition coagulants could be used as an alternative coagulation because the combination process could enhance the reduction efficiency and the settling velocity of sludge was also faster, resulting in savings of chemicals and treatment/disposal costs.

4. Conclusions

This investigation has studied the treatment of surface water from Nile River (Ismailia Channel) used as makeup boiler water in two parts, in the first part, characterization of water after screening followed by sedimentation, such as pH, total dissolved solid (TDS), total hardness (TH), chlorides, total alkalinity (TA), and organic matter (OM) have been analysed for one year. In the second part, a jar test was used to treat this water as a pretreatment unit to reduce the above parameters for utility as makeup boiler water with different processes coagulation, Fenton oxidation, and combined Fenton/coagulation. It is concluded that in coagulation, reduction efficiency was found to increase with increasing doses of coagulant and ferric chloride produced better results than alum. Higher dosages of coagulants in coagulation process may increase TDS, TH, and TA reduction but were not economical. For the treatment by Fenton oxidation proved to be more effective than coagulation. The combination Fenton/coagulation process reduced the OM, TDS, TH, and TA by 29%, 21%, 20.5, and 23%, respectively. In addition, the maximum reduction was attained for OM, TDS, TH, and TA at Fenton oxidation combined with ferric coagulation, under operating conditions ($[Fe^{2+}]$ = 10 mg/L; Fe^{2+}**:**H_2O_2 = 1.25:1; initial pH = 2.8; followed by coagulation at initial pH 8 with 5 mg/L ferric chloride).

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