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Simultaneous Removal of Iron and Manganese from Ground Water by Combined Photo-Electrochemical Method

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Abstract: Ground water is highly important source of drinking water in Egypt. Some provinces suffer from high content of iron and manganese in ground water which threat human health. Different processes, such as electrochemical (EC), photo (UV), and combined photo-electrochemical (CPE) methods were used to attain both metals content to the level in accordance to reports of World Health Organization (WHO). A cell containing aluminum electrode as anode, graphite electrode as cathode and UV lamp were used and filled with waste water enriched with iron and manganese as an electrolytic solution. A limited quantity of sodium chloride salt was added to enhance the electric conductivity through the solution. A comparison between different methods was undertaken to evaluate the applied conditions and the efficiency of Fe and Mn removal at different times and initial concentrations. The results revealed that CPE method was the best choice for the simultaneous removal of both iron and manganese in a short time < 10 min.

Keywords: Ground water; Egypt; electrochemical (EC); photo (UV); combined photo-electrochemical (CPE); World Health Organization (WHO).

1. Introduction:

Some regions in Egypt suffer from the contamination of ground water with high concentration of iron and manganese, which threat human health and leading to chronic diseases. Groundwater pollution can occur in various ways, in addition to natural or geochemical contamination, by leaks in pipelines, from landfill leachates, etc. It can be divided into three main contamination categories, by organic compounds, by microorganisms, and inorganic pollutants. The contamination of groundwater with metals of inorganic pollution comprises a danger environmental problem due to the fact that metals are not biodegradable and can cause severe adverse effects on human health [1].The presence of iron and manganese compounds in groundwater, and eventually in drinking water, is a serious environmental problem. When iron and manganese compounds are present in both surface and groundwater, even at low concentrations, they can be linked to various water quality problems and their removal is essential. The Safe Drinking Water Act (SDWA) secondary standards for iron in drinking water is 0.3 parts per million (ppm) and for manganese it is 0.05 ppm. Iron and manganese are both known to stain the water supply. They can make water appearance red or yellow, create brown or black stains, and give off an easily detectable metallic taste. Several years ago, it was believed that incumbent soil layers, acting as natural filters and protected ground waters, but actually it was found that soil ores of iron and manganese can be easily dissolved into ground water particularly at highly acidic medium [2].

Iron in water supplies causes aesthetic and operational problems, such as bad taste and color, staining and deposition in the water distribution system leading to high turbidity. Manganese is a very common compound that can be found everywhere on earth and it is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and cycles through its various oxidation states. Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body [3]. Manganese is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states. Manganese occurs principally as pyrolusite (MnO_2), and to a lesser extent as rhodochrosite ($MnCO_3$). Manganese, in the form of potassium permanganate, may be used in drinking water treatment to oxidize and remove iron, manganese, and other contaminants [4-6].Manganese in ground water is difficult to remove by using normal methods, where it required a high potential to overcome its high activation energy required for manganese oxide formation, where MnO_2 is formed by highly oxidizing and high pH conditions [7, 8].

In recent years, various treatment technologies have been employed to enhance water quality by removing inorganic and organic contaminants. Both photo and electro-chemical oxidation technologies recently have become more popular for water treatment. Doan and Saidi [9] used combined electrochemical and photochemical oxidation for the removal of inorganic contaminants like Zn and Ni, and organic contaminants like alkylbenzene sulfonate. They found that the results of combined system are at comparable levels to those obtained in the sole electrochemical system. Peralta-Hernández et al [10] designed an annular tube reactor of combined photo- electrochemical system for the generation of H_2O_2 and Fenton reagent in situ, the rate of oxidation was increases substantially when the semiconductor anode was illuminated as compared to the same processes carried out in the dark. These processes are considered as attractive options in solving the issues concerning iron and manganese removal from water particularly, if other compounds such as ammonia, total dissolved solids or natural organic matter (NOM) are found [11]. To solve this problem, Fe^{+2} or Fe^{+3} can be introduced into the system, constructing an electro-Fenton's reagent as one of a special class of oxidation techniques defined as advanced oxidation processes (AOPs) [12]. These processes are characterized by the capability of exploiting the high reactivity of free hydroxyl radicals. Free hydroxyl radical ($OH^{\bullet}$) is a non selective and very powerful oxidant agent able to oxidize organic and inorganic pollutants in water and is generated from chemical, electro and photochemical (by using light irradiation) processes. Electro-Fenton process can be enhanced in presence of UV radiation [13]. Stephen and Charlotte were used electrolytic cell containing aluminum and iron electrodes of high surface area relative to the volume of electrolyte for the generation of fine flocs of Al(OH)3 acting as colloids and adsorption centers for contaminants dispersed in waste water [14].

In the present study an approach was studied and evaluated for the removal of heavy metals like, iron and manganese to avoid their harm to human health. Combined photo electrochemical oxidation technique was investigated for the removal of iron and manganese from water, since a little information is available on this approach. The removal of iron and manganese from synthetic solution using bench-scale CPE oxidation system was evaluated using different concentrations levels of both iron and manganese at different conditions.

2 - Materials and Experimental:

2.1. Materials

Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) were used as a source of iron in form of Fe (II) was supplied by S.D. Fine Chem. Ltd. Manganese sulfate mono-hydrate ($MnSO_4.H_2O$) was used as sources of manganese in form of Mn (II) was supplied by S.D. Fine Chem. Ltd. Pure sodium chloride (NaCl) was used as electrolyte, purchased from Merck. Distilled water was used throughout. Analar Sulfuric acid 98 % purchased from ADWIC.

2.2. Experimental Set-up

A laborator combined photo electrochemical unit was used for the batch experiments. The schematic diagram of the experimental set-up used is shown in Fig.1. It consists of a cylindrical quartz photo reactor (1.2 L), with a coaxial and immersed medium pressure UV mercury lamp used as the UV emitter and light source (Heraeus TQ150, input energy of 150 W) emitting a polychromatic radiation in the range from 100 to 280 nm wavelength. The UV lamp was equipped with a cooling water jacket to maintain the temperature of the reaction of wastewater treatment at room temperature. The reaction vessel was filled with authentic solution containing both iron and manganese. The electrochemical characterization of the solution was carried out by using DC power supply GW 3030 an two electrodes, graphite cathode and aluminium anode. The measurements were performed at room temperature and the mixing was accomplished by using continuous magnetic stirrer.

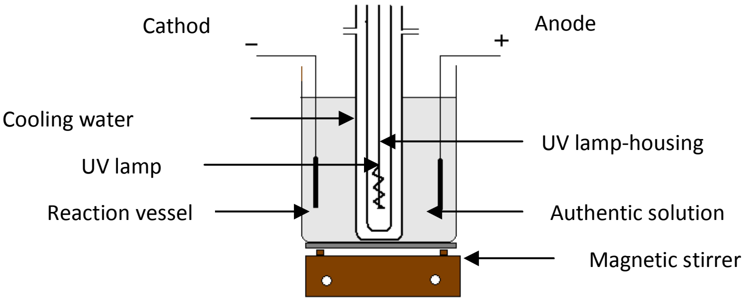

Figure (1): The schematic diagram of the experimental set-up

2.3. Procedures and Analysis

Workers have developed an approach for the removal of heavy metals like, iron and manganese. Three techniques were examined for the removal of iron and manganese namely, Electrochemical (EC), photochemical (UV), and combined photo- electrochemical (CPE) methods, where the study comprised a comparison between all techniques to track the most efficient one by determination of removal efficiency. Authentic solutions of different iron and manganese concentrations are prepared as model of ground water by dissolving definite concentrations of both a mixture $FeSO_4.7H_2O/MnSO_4.H_2O$ in distilled water.

Definite amounts of NaCl were added to improve the conductivity and ionic mobility through the electrolyte. The solution was acidified by drops added of prepared dilute sulfuric acid 15 % to pH 3. The efficiency of the process was evaluated by measuring the metal removal from samples at the end of each experiment. Samples are filtered before the measurement of metals by using atomic adsorption (Percken Elmar 1100B, Germany) [15].

3. Results and Discussion:

3.1. Comparative removal behaviour of different methods

Before iron and manganese can be filtered, they need to be oxidized to a state in which they can form insoluble complexes. Oxidation involves the transfer of electrons from the iron and manganese to the oxidizing agent. Oxidation methods using additives like chlorine, ozone, air; or those using an oxidizing filter media fall to oxidize iron and manganese. UV oxidation, electrochemical oxidation (EC) and combined photo-electrochemical (CPE) methods were used for removal of both dissolved iron and manganese from authentic solution. Fig.2 represents a comparison between the removal efficiency of dissolved iron and dissolved manganese by using combined CPE method from a mixture solution of concentration 5 ppm $FeSO_4.7H_2O$ and 5 ppm $MnSO_4.H_2O$. A highly removal efficiency was achieved after a short time, where the concentration of Fe was decreased from 5 ppm to less than 0.1 ppm after 5 min (R=98%), while the removal of Mn was decreased from 5 ppm to 1.7 ppm after 5 min. (R= 66 %), and it was highly decreased to 0.2 ppm after 20 min (R= 96%). It is obviously shown that the removal efficiency of Mn was less than Fe after the same time, where the removal of Mn required an oxidation potential higher than iron, so the removal efficiency of Mn can be improved by using high potential and adequate time.

This indicates that the electrochemical potential supported by UV irradiation (CPE) enhanced the oxidation of both soluble Fe^{2+} and Mn^{2+} to insoluble Fe^{3+} and Mn^{4+} ions in a short time, which can be adsorbed on the surface of formed $Al(OH)_3$ floc. The lowest concentration obtained of Mn after CPE treatment was 0.2 ppm (R = 96 %), but it still higher than the recommended standard values according to the reports of WHO. So, the second treatment may be required for the removal of residue of Mn to attain the standard concentration 0.05 ppm (R = 99.6 %), Another method was carried out by using electrochemical oxidation, where the solution was totally exposed to electric field between anode and cathode. Some reactions were taken place at the surface of electrodes and in the bulk of electrolytic solution, where Al^{3+} ions were generated by anodic oxidation, reduction of hydrogen ions at the surface of cathode and water molecules were electrolyzed to OH^- and H^+.

$$Al \rightarrow Al^{3+} + 3e^- \qquad (1)$$

$$H_2O \rightarrow OH^- + H^+ \qquad (2)$$

$$Al^{3+} + OH^- \rightarrow Al(OH)_3 \qquad (3)$$

The concentration of dissolved iron was decreased sharply from 5 to 0.1 ppm within 10 min of oxidation time as shown in Fig.3 (R= 98 %). The concentration of Mn was decreased slowly from 5 to 2.2 ppm after 5 min (R = 56%) and by elongation of time, the removal efficiency was improved to (R= 76%), where the concentration of manganese was decreased from 5 to 1.2 ppm after 20 min. In the electrochemical method, the formed $Al(OH)_3$ floc gave a high important role as a suspended colloids having an electrostatic adsorption capability of agglomeration of dissolved Fe^{2+} and Mn^{2+} ions. On the other hand, one can observe the comparative removal of iron and manganese of different methods. As shown in Fig.4, a quite slow removal of 5 ppm of Fe by using UV light after 20 min was occurred to attain the lowest concentration 0.5 ppm after 20 min (R=90%), while the lowest concentration residue of Mn was 3.5 ppm (R= 30 %) was obtained after 20 min. This indicates the low energy produced and consequently low effect of UV irradiation, where the generation of a very small concentration of the main oxidant $OH^{\bullet}$ radical from the decomposition of water.

Also, it was obviously observed that the removal efficiency values of (EC) method was approximately similar to (CPE) method; i.e. the oxidation activation energy of (EC) method >> the oxidation activation energy of (UV) irradiation method. This indicates the low effect of UV irradiation for metal oxidation process by CPE method. On the other hand, the removal efficiency of iron by all methods was generally higher than the removal efficiency of manganese; this behavior can be attributed to the higher oxidation potential required for oxidation of Mn, where the insoluble form MnO_2 is formed by high potential (1.05 V) and high pH value 9. While a high removal efficiency of iron was achieved due its lower oxidation potential (0.77 V) required for the formation of $Fe(OH)_3$. UV irradiation participates marginally in the oxidation of Fe and Mn, while the participation of electrochemical oxidation was proved in Fig.2. The role of photo oxidation can be outlined in the following points: (i) It accelerates the oxidation of Fe and Mn to the insoluble high oxidation state, (ii) In the presence of photo oxidation $^{\bullet}OH$ free radical can be formed by the photolysis of H_2O and (iii) it can be excellently used for the disinfection of municipal water.

In the electrochemical oxidation, hydroxyl radicals may be produced over the surface at high-oxygen over voltage anode from water oxidation and electro generation of hydrogen peroxide (H_2O_2) formed from the two-electron reduction of O_2 at a graphite cathode [16]. The oxidizing H_2O_2 can be enhanced in the presence of catalytic Fe^{2+}, due to the formation of hydroxyl radicals from the classical Fenton's reaction between both species.

$$H_2O \rightarrow OH^{\bullet} + H^+ + e^- \qquad (4)$$

$$O_{2\,(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (5)$$

It can be seen from Fig.2, the quicker iron removal found by combined photo electrochemical oxidation where 96.8 % iron removal was obained within 10 minutes reaction time due to the generation of more hydroxyl radicals with the enhancement of electrochemical oxidation in the presence of UV light (CPE). Moreover, in both EC oxidation and CPE oxidation processes, by using aluminum as anode in the electrolytic cell, aluminum ions (Al^{3+}) are formed which reacts with hydroxyl ions (OH^-) and forms aluminum hydroxide as flocs which adsorb Fe^{2+} and Mn^{2+} ions and co-precipitate together.

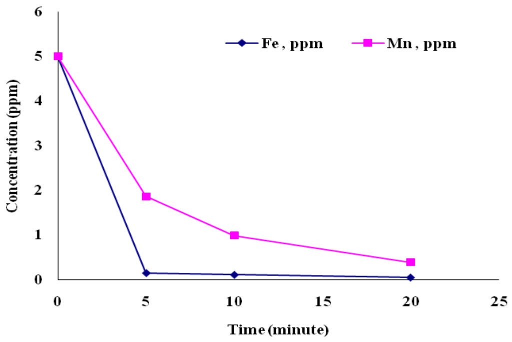

Fig. 2: Removal efficiency of Fe and Mn by (CPE) oxidation method from a mixture authentic solution of (Fe&Mn) [Initial concentration 5 ppm, 150W, 0.25 A]

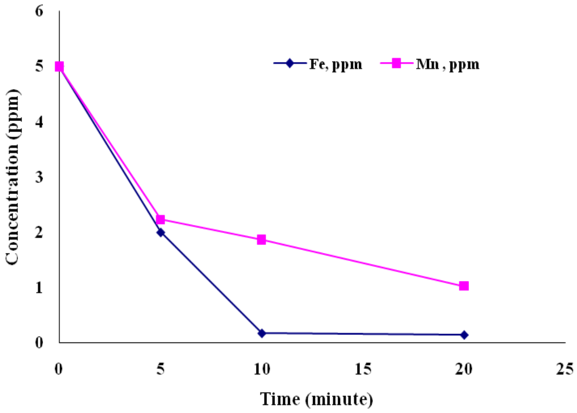

Fig.-3 : Removal efficiency of Fe and Mn by (E) oxidation method from a mixture authentic solution of (Fe&Mn) [Initial concentration 5 ppm, 0.25 A]

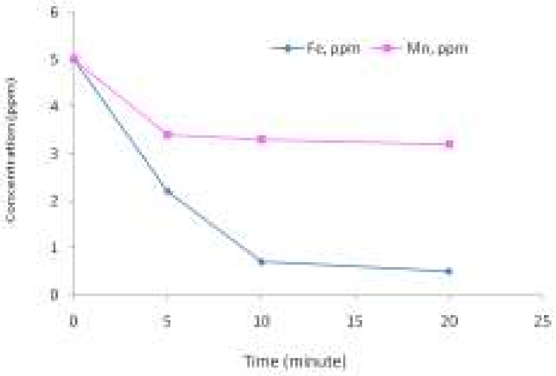

Fig.-4 : Removal efficiency of Fe and Mn by (UV) oxidation process from a mixture authentic solution of (Fe&Mn) [Initial concentration 5 ppm, 150W].

3.2. Effect of initial concentration on the removal of Fe and Mn by CPE

The presence of high concentration of dissolved metals into ground water gives an advantage for the treatment by electrochemical or combined CPE method, where the dissolved salts increase the electric conductivity and the ionic mobility of ions through the solution toward or backward both electrodes.

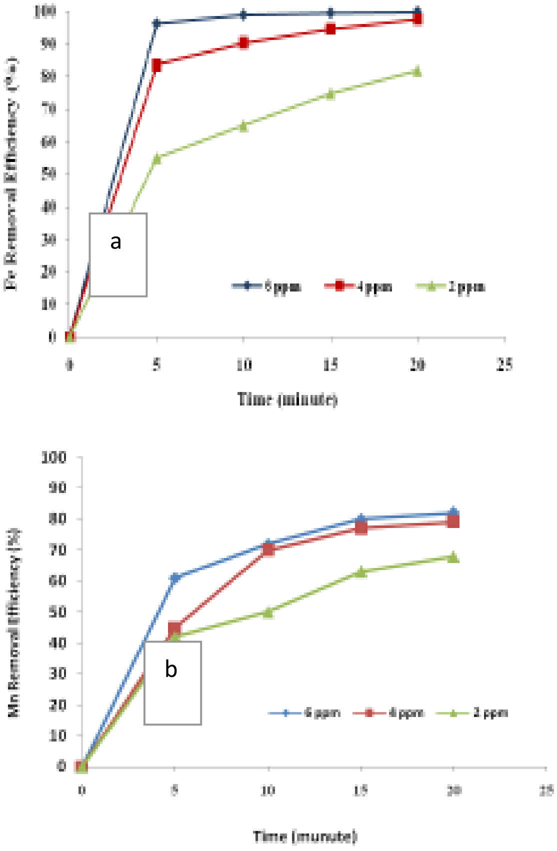

Fig. 5: Removal Efficiency of (a) Fe and (b) Mn from mixture solutions of different concentrations 2, 4, and 6 ppm by (CPE) method.

As shown in Fig. 5, the removal efficiency was highly affected by the initial concentrations of mixture solution Fe/Mn. Fig.3a showed the rapid and high removal efficiency of iron (R= 96 %) from high concentration 6 ppm of mixture Fe/Mn solution after 5 min, while after the same time, the treatment of less concentrations 2 and 4 ppm by CPE method showed a lower removal efficiencies 54 and 82 % respectively. Generally, the removal efficiency was enhanced with time in low concentration. Removal efficiency of manganese in a mixture solution Fe/Mn as shown in Fig. 5b revealed lower removal efficiencies than Fe, this is attributed to the high activation energy required for oxidation of Mn more than Fe, so removal of Mn needs a long time and high potential more than Fe, where R of Mn of concentration 6 ppm was 63 % and 89 % after 5 min and 20 min, respectively. While at low concentration 2 ppm 54% was achieved after 20 min.

It can be observed that the removal efficiency of high concentrations 6 ppm of dissolved Fe and Mn revealed better values more than less concentrations 2 ppm, where the high concentrations strengthen the electrochemical reactions and overcome the resistance of ionic mobility through the solution.

3.2. Effect of current on the removal of Fe and Mn by CPE

The applied electric current played a big role in the removal efficiency enhancement, where at high electric current there is a better condition for the electrolysis of water molecules to produce OH^- and anodic oxidation of aluminum to produce Al^{3+}. Finally, a high content of $Al(OH)_3$ flocs were formed which are a strong adsorbed electrostatic particles.

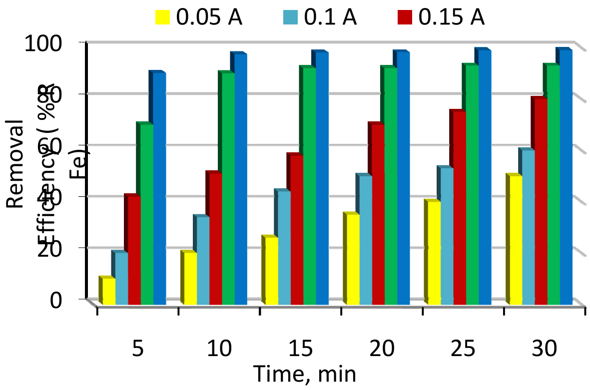

Fig.6 : Effect of current density on the removal efficiency of iron by CPE method at different time

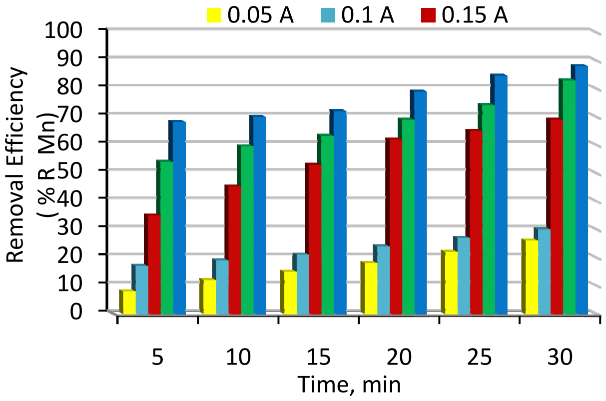

Fig.7 : Effect of current density on the removal efficiency of manganese by CPE method at different time

As shown in Fig.6, according to the applied electric current, the removal efficiency was varied , where at low applied electric current, a low values of % R was obtained, but by elongation of time, the removal efficiency was improved. At low time 5 min, the removal efficiency was less than 10% at low current 0.05 A, and it did not exceed 68 % by increasing current to 0.25 A. Removal efficiency was increased with time from 5 to 30 min, where at low electric current 0.05A the removal efficiency was 10 % after 5 min and 49 % after 30 min, while at high electric current 0.25 A, the removal efficiency was 89 % and 97% after 5 min and and 30 min, respectively. The study of removal of dissolved Mn by CPE method showed that the removal efficiency was less than Fe at the same concentration, pH, temperature in spite of increasing of electric current or time. As shown in Fig.7, the removal efficiency of Mn at low current 0.05 A was less than 6 % and 24 % after 5 min and 30 min , respectively. While at higher current 0.25 A, the removal efficiency was 68 % and 87 % after 5 min and 30 min , respectively. Thus, it was ascertained that the removal efficiency of iron was higher than manganese at the same conditions, this phenomenon is attributed to the high oxidation potential of Mn (1.05 V) more than iron (0.44 V). Moreover, because the oxidation of iron at low potential takes place before Mn, the major $Al(OH)_3$ flocs were consumed in the adsorption of Fe^{2+} ions before the adsorption of Mn^{2+}.

3.2. Effect of NaCl dose added on the removal of Fe and Mn by CPE

In both CPE and EC methods, the addition of salt to the solution such as sodium chloride has an important role to reduce the resistivity and improve the ionic mobility through the solution and hence electrochemical reactions are going forward. Sodium chloride was added according to the limits of standard WHO values, where the concentration added was not exceed 45 ppm. Without addition of salts, the final pH was not varied where pH was 3 in the beginning of treatment. An additional advantage of using NaCl is the bacteriacidal effect by the chlorination, where Iron and manganese bacteria are destroyed. Moreover, Hypochlorite and chlorate anions can be formed by oxidation of chloride ions, forming strong oxidizing agents in the solution as the following:

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \longrightarrow HOCl + Cl^- + H^+$$

$$HOCl \longrightarrow OCl^- + H$$

$$2HClO + OCl^- \longrightarrow ClO_3^- + 2\ HCl$$

Fig. 8 shows the effect of NaCl added where, as the dose of NaCl increased from 15 to 45 ppm, pH was varied from 5.5 to 7.2 and also current intensity was increased from 120 to 260 mA.

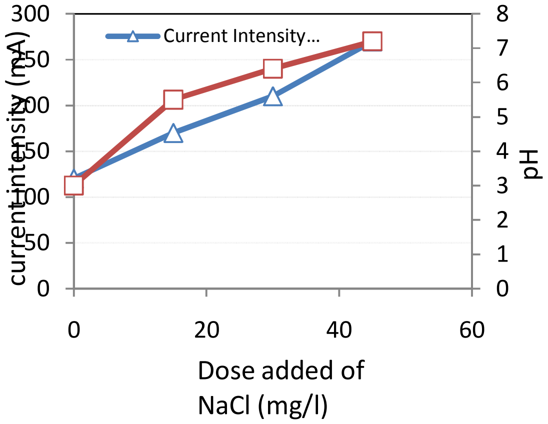

Fig.8: Effect of addition of NaCl on both current intensity and final pH

Furthermore, without addition of NaCl, the removal efficiency was very low (R=60%), while it was increased from 77 to 92 as the dose of NaCl added from 15 to 45 ppm. The removal efficiency was increased as the dose added of NaCl increased, this indicate the importance of salt addition to the solution when the conductivity is not adequate for the ionic transfer between the bulk solution and the surface of electrodes. The presence of manganese into the solution of iron may behave as a catalyst for the oxidation of Fe^{2+} to Fe^{3+} and Mn^{2+} is oxidized to Mn^{4+} and co-precipitated together. So, it can be considered that the presence of two or several types of dissolved metals is more applicable in the electrochemical or CPE methods, where the dissolved salts enhance the conductivity and hence, reduce the potential required. They behave as a catalyst and mediators for oxidation according to their redox potential.

4. Conclusion:

A combined photo electrochemical method was used for oxidation of soluble forms Fe^{2+} and Mn^{2+} to the insoluble forms Fe^{3+} Mn^{4+}. The combined method (CPE) revealed more efficiency than a sole EC and UV methods. The presence of both dissolved iron and manganese has the advantage of less resistivity of the solution of waste water. Low concentration of NaCl (15-45 ppm) was added to increase the conductivity and electric current beside its bactericide effect after electrolysis to chlorine. The effect of Fe^{2+} and Mn^{2+} concentrations revealed that the higher concentration of dissolved iron and manganese ions, the higher removal efficiency obtained. The study showed the rapid oxidation of Fe^{2+} more than Mn^{2+} due to the lower oxidation potential of iron than manganese and the catalytic oxidation behaviour of manganese may accelerate the oxidation of iron.

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