Treatment of orange II azo-dye by electrocoagulation (EC) technique in a continuous flow cell using sacrificial iron electrodes

Mohammad Y.A. Mollah[1], Saurabh R. Pathak, Prashanth K. Patil, Madhavi Vayuvegula, Tejas S. Agrawal, Jewel A.G. Gomes, Mehmet Kesmez, David L. Cocke*

Gill Chair of Chemistry and Chemical Engineering, Lamar University, PO Box 10022, Beaumont, TX 77710, USA

Abstract

This paper describes the EC treatment of orange II dye solution in a flow cell using sodium chloride as an internal electrolyte. In this technique dye solutions were passed through a flow-through EC apparatus consisting of a flow-through cell, the electrode assembly, the feed pump and the DC power supply unit. The cell contained five parallel iron electrodes, which form four parallel cells. Experiments were run at 25 °C under various electrolyte concentrations, dye concentrations, current density, flow rate of the solution, and pH at dc current range of 2–5 A. Various number of recycles of the treated dye solution were also performed at the same dc current range. Optimum conditions to get high removal efficiency were experimentally determined. It was found that 98.5% of the dye was removed from the solution under the optimum conditions. The residue from a blank run (pH = 7.3) and a dye added run (pH = 8.5) were collected by vacuum filtration and analyzed by XRD after drying in a vacuum desiccator. The XRD data indicated the presence of mainly maghemite (γ-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) in the residue. However, there is not much difference between the X-ray diffractograms of the blank sample and the dye-containing residue to warrant any conclusions therefrom with regard to the interactions between the oxides and the dye molecules.
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Keywords: Electrocoagulation; Iron electrodes; Orange II dye; Sodium chloride

1. Introduction

Dyeing and finishing are the two most important processes usually applied in almost all textile-manufacturing industries. These two processes generate considerable amount of wastewater, which may contain strong color, suspended particles, high pH and high chemical oxygen demand (COD) concentration. In the developed countries these wastewaters are normally treated by traditional methods like, biological, physical and chemical, which are rather inadequate. In the Third World countries these wastewaters are directly discharged into river or any other natural water streams causing serious pollution problems as well as endangering the lives of many aquatic wild lives. The biological methods are cheap and simple to apply, but cannot be applied to most textile wastewaters because most commercial dyes are toxic to the organisms used in the process [1] and result in sludge bulking [2–5]. The electrocoagulation (EC) technique is considered to be potentially an effective tool for treatment of textile wastewaters with high removal efficiency. A number of authors have reported the treatments of textile dye wastewater by EC technique [6–10]. In addition specific applications of EC include, defluorination of drinking water [11], industrial wastewater containing heavy metals [12–14], oil-containing wastewater [15], foodstuff containing wastewater [16,17], organic matter from landfill leachate [18], wastewater containing suspended particles [19–22], chemical and mechanical polishing waste [23], separation of aqueous suspensions of ultrafine particles [24], removal of nitrate from wastewater [25], recovery of phenolic compounds [26], arsenic removal [27], refractory organic pollutants including lignin, EDTA [28], and polyaromatic organic pollutants [29].

Orange II dye belongs to a class of organic compounds known as azo-dyes, which are abundantly used in textile industries for dyeing. Orange II dye is resistant to the degradation by light, and action to oxygen. It is also resistant

to common acids and bases. It has also been reported that orange II dye does not undergo biological degradation in wastewater treatment plants [30]. Augugliaro et al. [31] have reported the photo-degradation of orange II dye mediated by TiO$_2$. Advanced oxidation technologies mediated degradation of the orange II azo-dye has been the subject of several recent studies by Kamat and co-workers [32,33] and Kiwi and co-workers [34–38]. Xiong et al. [39] have reported the treatment of simulated wastewater containing orange II dye using a stirred batch EC cell with three-phase three-dimensional electrodes. The authors used granular activated carbon as particle electrodes. However, in the present article we are presenting the results of a study involving EC of orange dye II in a flow-through EC apparatus using iron electrodes and the analyses of the flocs formed as well as the aqueous phase.

2. Experimental

A flow-through EC apparatus (FTEA) was supplied by Kaselco EC Treatment System, Texas, USA. The FTEA essentially consists of a flow-through cell, the electrode assembly, the feed pump and the DC power supply unit. A schematic diagram of the FTEA is shown in Fig. 1.

The cell contained five parallel carbon steel (recycled steel, hot rolled, not pickled) electrode plates (11.0 cm × 11.4 cm) placed 6.0 mm apart, which forms a four parallel cells. Before use, the plates were cleaned manually by abrading with sand papers. The internal volume of the cell is approximately 450 mL. A variable transformer was used to control the current and the applied potential.

The orange dye II was purchased from ProSciTech, Australia and used without any further treatment. Standard solution of simulated dye wastewater containing orange II was prepared by using deionized water with conductivity of

2.80 μS/cm and the conductivity of the solution was raised by adding 2.0 g NaCl (Fisher Scientific, 99.80%) in 1.0 L solution (0.034 M) used as an internal electrolyte. The conductivity and pH of the solutions were measured before and after each experiments. The pH was adjusted using either 0.15 M NaOH or 0.1 M HCl as necessary.

In a typical EC experiment the dye solution was pumped through the FTEA at a predetermined flow rate (usually 525 mL/min) and after 3.00 L of the dye solution were treated, the EC run was stopped. The absorbance of the dye solution in the treated sample was recorded at 485 nm (λ_{max}) by a UV-Vis spectrophotometer and the concentration was determined from the previously constructed calibration chart using Beer–Lambert's law ($A = \varepsilon bc$, where A is absorbance ($A = \log_{10} I_i/I_0$), ε is the molar extinction coefficient with units of L/mol cm, b is the path length of the sample in cm, c is the concentration of the compound in solution, expressed in mol/L). A good linear relationship (A versus c) was obtained. The flocs were separated by vacuum filtration and dried in vacuum desiccators at room temperature for XRD analyses.

The color removal efficiency (%RE) was calculated from

$$\%RE = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

where C_0 is the concentration of the dye before the experiment, and C_f the concentration of the dye after the experiment.

2.1. X-ray diffraction

The XRD analyses of the residues were carried out with a Bruker AXS D4 Endeavor diffractometer operating with Cu Kα radiation source filtered with a graphitic monochromator ($\lambda = 1.5406$). The samples were crushed to a fine powder and pressed into a sample holder. The XRD scans were recorded from $2\theta = 10°$ to $110°$ using a step size of $0.02°$ and a count time of 6 s.

3. Results and discussion

The effects of electrolyte concentration, dye concentration, current density, flow rate, number of cycles of the flow of the dye solution and pH of the dye solution on electrochemical oxidation of orange II dye solution were investigated in order to determine the optimum operating conditions for maximum removal efficiency of the dye. The results of the effects of these operating parameters on electrochemical oxidation of orange dye II are now presented.

3.1. Effect of electrolyte concentration

As can be seen in Fig. 2 the percent color removal efficiency (%RE) increased from 93.0 to 98.0% when the electrolyte concentration was increased from 0.034 to 0.102 M.
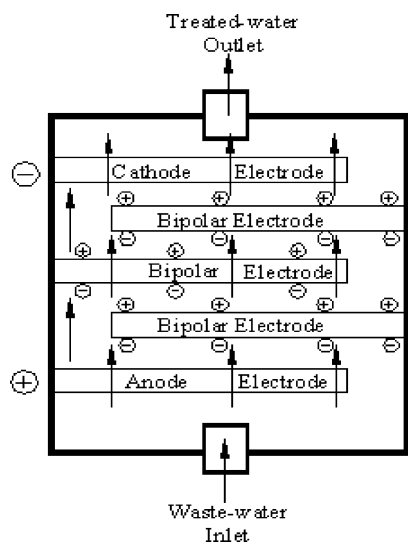

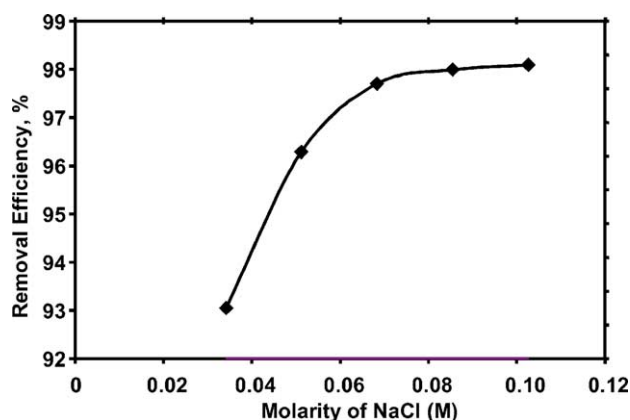Fig. 1. Schematic diagram of a flow-through EC apparatus.

Fig. 2. Effect of electrolyte concentration on the removal efficiency of orange II dye (C_{dye} = 30 ppm, initial pH = 8.2, no. of cycle = 1, temperature = 25 °C).

Fig. 3. Effect of dye concentration on the removal efficiency of the dye (C_{NaCl} = 0.034 M, current strength = 159.5 A/m^2, initial pH = 8.2, temperature = 25 °C).

Similar kinds of effect of increase in removal efficiency with increase in conductivity was also reported by Lin and Peng [5] and Kobya et al. [40]. The conductivity of the solution was also increased linearly from 3.76 to 10.53 mS/cm with electrolyte concentration.

The effect of the increase in conductivity of the dye solution on the color removal efficiency exhibited similar behavior as in the case of increasing electrolyte concentration. The current density (current in A/area of cross-section of the electrode) increased correspondingly from 119.62 to 398.72 A/m^2. However, although the maximum removal efficiency was obtained at higher NaCl concentration (0.102 M), subsequent experiments were carried out with 0.034 M NaCl solution in order to minimize the addition of excess Cl$^-$ ions in solution as well as to lower the current density.

3.2. Effect of dye concentration

Five experiments with 10, 25, 30, 40 and 50 ppm of dye solutions were carried out at constant voltage of 40 V and a current strength of 159.5 A/m^2 to examine the effect of dye concentration on the removal efficiency. The initial conductances of the solutions were approximately 3.76 mS/cm and the final conductances after the experiments were approximately 3.60 mS/cm. The results are shown in Fig. 3.

It can be seen that the removal efficiency decreased from 90.4 to 55.0% almost linearly with increase in concentration of the dye. This is possibly due to the formation of insufficient number of iron hydroxide complexes produced by the electrode for a given conductivity and applied cell voltage to coagulate the excessive number of orange dye molecules at higher concentrations. It is, therefore, quite clear that under the present experimental conditions the lower is the dye concentration, the better is the removal efficiency. But at higher concentration the removal efficiency may be enhanced by recycling the treated solution as described below.
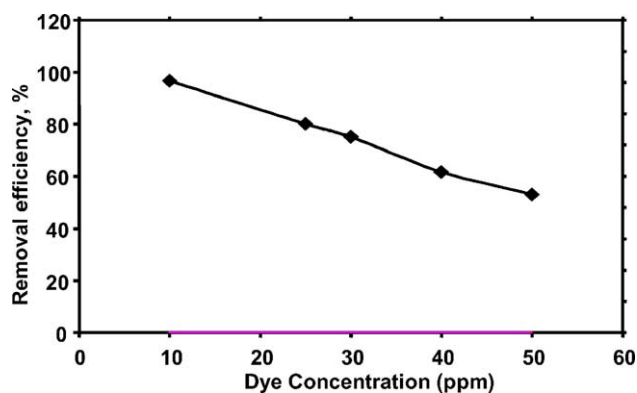
3.3. Effect of current density

The rate of removal of orange II dye is mainly dependent on the current at a fixed potential, therefore, the voltage applied to the electrodes was kept at a constant value of 40 V. It is also observed that the rate of removal of orange II dye is proportional to the dye concentration in the bulk solution by taking into account of faradaic currents. The rate of release of iron ions into the solution from the iron anode follows Faradays law and it is expressed as

$$C = \frac{ItM}{ZFW} \tag{2}$$

where C is the iron concentration in the electrolytic cell, I the current, t the time, M the molecular weight of anode (iron), Z the chemical equivalence, F the Faraday's constant and W the volume of the electrolytic cell [41]. From the above equation it is clear that, higher currents will generate significant amount of iron ions, which in turn will trap the dye molecules and enhance the removal efficiency.

The effect of current density on the removal efficiency of orange II dye is shown in Fig. 4. The color removal efficiency was increased to 98% at 398.7 A/m^2 from 92% at 159.5 A/m^2 and the maximum efficiency was observed at ca. 200 A/m^2. As the applied current density was increased from 200 to 400 A/m^2 the color removal efficiency did not change significantly. However, it is advisable to limit the current density in order to avoid excessive oxygen evolution as well as to eliminate other adverse effect, like heat generation [31].

3.4. Effect of flow rate

In order to find out the optimum flow rate of the simulated wastewater dye solution that yields maximum removal efficiency the experiments were carried out at 350, 440, 525 and 600 mL/min with 30 ppm dye solution. The conductivity of the solution was increased with 0.034 M NaCl and a constant current strength of 159.5 A/m^2 was applied in each case. The removal efficiency as function of flow rate is shown in Fig. 5. It can be seen that the removal efficiency
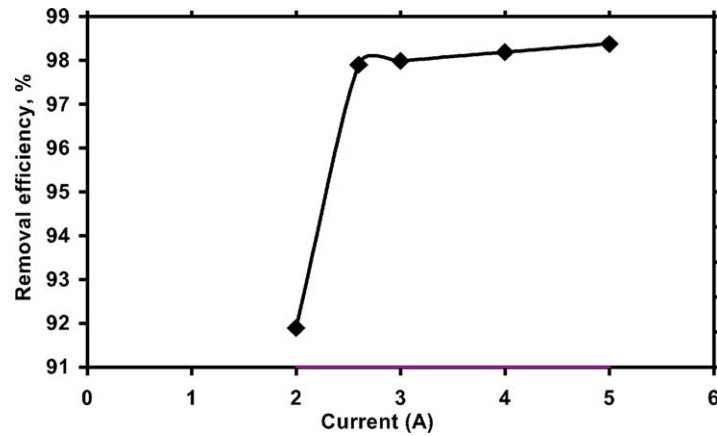
Fig. 4. Effect of current strength on the removal efficiency of orange II dye (dye concentration: 25 ppm, initial pH = 8.0, C_{NaCl} = 0.17 M, temperature = 25 °C, no. of cycle = 1).

decreased from 98% at 350 mL/min to 86% at 600 mL/min. The decrease in removal efficiency with increasing flow rate is rather expected, since slower is the flow rate higher is the residence time. Higher residence time means the untreated dye solution remains in the electrocoagulation cell for more time, which in turn provides more time for the reaction. The slower flow rate allows the coagulant generated by electrochemical oxidation of the anode material and the dye molecules to mix properly and thereby enhance the rate of coagulation. Otherwise at higher flow rate the residence time is lowered in a flow reactor, which, in effect, lowers the rate of coagulation.

3.5. Effect of recycling the treated solution

An experiment was carried out with 50 ppm of dye solution and 0.034 M NaCl and the treated solution was recycled six times. The current strength was maintained at 128–135 A/m^2 at the same voltage (40 V). The results are shown in Fig. 6.

It can be seen that 97% color was removed in the first cycle, while in the sixth cycle the removal efficiency was 98% indicating that from practical point of view one cycle is good enough to remove the maximum amount of dye from the simulated wastewater.

3.6. Effect of pH of the solution

The EC process is highly dependent on the pH of the solution [16]. The experiments were carried out at pH 4.7, 6.0, 8.5, 10.0 and 11.0 with 30 ppm solution and 0.034 M electrolyte. The current density was maintained at 159.5 A/m^2. The removal efficiency as a function of pH is shown in Fig. 7.

It can be seen that the initial pH had no significant effect on the removal efficiency of the dye. Close examination of the %RE versus pH clearly indicates that the removal efficiency increases slowly with pH and it remains unchanged between pH 6.0–8.0 and then on further increase of pH, the %RE decreases. There is maximum removal efficiency at the pH of 6.9, which is almost neutral. Therefore, it can be
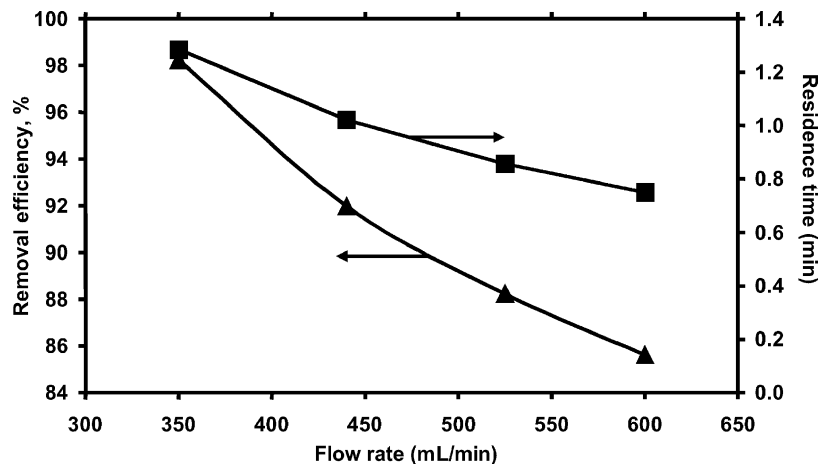

Fig. 5. Effect of flow rate on the removal efficiency of orange II dye (dye concentration = 30 ppm, current strength = 159.5 A/m^2, initial pH = 8.5, C_{NaCl} = 0.034 M, temperature = 25 °C).
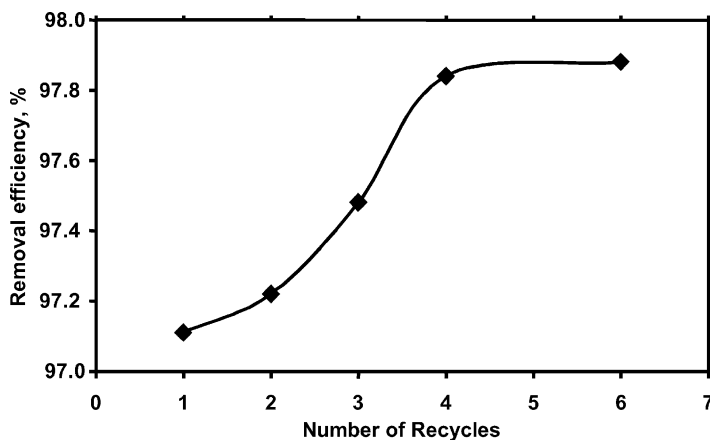
Fig. 6. Effect of the number of recycles on the removal efficiency of orange II dye (dye concentration $= 50$ ppm, $C_{NaCl} = 0.034$ M, initial pH $= 8.2$, current strength $= 128–135$ A/m^2).

concluded that at this pH, the majority of iron complexes (coagulants) are formed and it is the optimum pH for carrying out the electrocoagulation. From the Pourbaix diagram [44], it can be deduced that the major complexes formed at this pH are $Fe(OH)_2^+$ and $Fe(OH)^{2+}$. However, it has been reported that majority of textile wastewater collected from equalization tanks have pH in the range of 5.0–10.0 [5] which is within the optimum operating range in the present experiment.

3.7. XRD analyses of the residue collected after EC experiments

Residues from a blank sample (pH $= 7.3$) and a dye-loaded sample (pH $= 8.5$) were collected by vacuum filtration and dried at room temperature in a vacuum desiccator. The XRD data were compared with standard data reported in the literature [42] as shown in Table 1.

It can be observed that maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) are the two main components present in the residue. A close examination of the diffractograms did not reveal any discernible change.

3.8. Optimum run

An experiment was carried by applying the optimum conditions with regard to different variables derived from the preliminary experiments as described above. The optimum conditions are: current $= 4.0$ A (42 V); initial pH $= 7.3$; conductance $= 3.81$ mS/cm; flow rate $= 350$ mL/min; dye concentration $= 10$ ppm; $C_{Nacl} = 4.0$ g/L of dye solution. The experimental temperature was $25\,^\circ$C. The removal efficiency was 98.50%. From the comparison of the color of the 10 ppm solution and the dye solution after EC under the optimum conditions, it was clearly evident that the color of the dye solution had almost completely disappeared, thus exemplifying the effectiveness of the EC process.

3.9. Formation of iron oxides and their role in electrocoagulation

Two mechanisms have been proposed to describe the formation of $H_{2(g)}$ and $OH_{(aq)}^{1-}$ (cathode) and Fe^{2+}/Fe^{3+} ions and $H_{(aq)}^+$ (anode) in an EC process involving iron
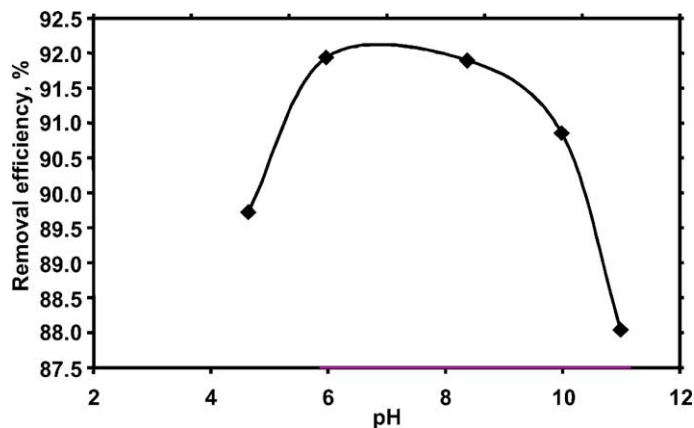

Fig. 7. Effect of pH on the removal efficiency of orange II dye (dye concentration $= 30$ ppm, $C_{NaCl} = 0.034$ M, current density $= 159.5$ A/m^2, temperature $= 25\,^\circ$C).
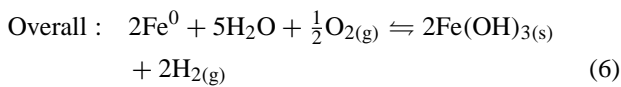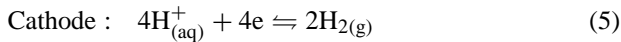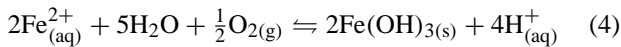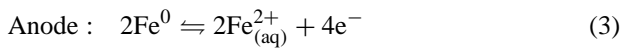
Table 1
XRD data of the residue collected from blank and orange II added EC experiments

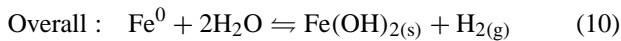| Oxy hydroxide compounds	d-Spacing (nm)[a]	d-Spacing (nm) (blank)	d-Spacing (nm) (dye added)
Goethite (α-FeOOH)	4.180, 2.693, 2.453	–	–
Akaganeite (β-FeOOH)	7.400, 3.310, 1.640	–	–
Lepidocrocite (γ-FeOOH)	6.260, 3.299, 2.478	–	–
Hematite (α-Fe$_2$O$_3$)	2.690, 1.696, 2.478	–	–
Maghemite (γ-Fe$_2$O$_3$)	2.520, 2.950, 1.610	2.516, 2.938, 1.608	2.517, 2.943, 1.608
Magnetite (Fe$_3$O$_4$)	2.530, 1.608, 1.480	2.516, 1.608, 1.477	2.517, 1.608, 1.474
Barnalite Fe (OH)$_3$	–	–	–
Feroxyhite (δ-FeOOH)	–	–	–

[a] Ref. [42].

electrodes [8]:

- Mechanism I

Anode : $\quad 2Fe^0 \leftrightharpoons 2Fe^{2+}_{(aq)} + 4e^-$ $\qquad$ (3)

$$2Fe^{2+}_{(aq)} + 5H_2O + \tfrac{1}{2}O_{2(g)} \leftrightharpoons 2Fe(OH)_{3(s)} + 4H^+_{(aq)} \quad (4)$$

Cathode : $\quad 4H^+_{(aq)} + 4e \leftrightharpoons 2H_{2(g)}$ $\qquad$ (5)

Overall : $\quad 2Fe^0 + 5H_2O + \tfrac{1}{2}O_{2(g)} \leftrightharpoons 2Fe(OH)_{3(s)}$
$$+ 2H_{2(g)} \qquad (6)$$

- Mechanism II

Anode : $\quad Fe^0 \leftrightharpoons Fe^{2+}_{(aq)} + 2e^-$ $\qquad$ (7)

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \leftrightharpoons Fe(OH)_{2(s)} \qquad (8)$$

Cathode : $\quad 2H_2O + 2e^- \leftrightharpoons H_{2(g)} + 2OH^-_{(aq)}$ $\qquad$ (9)

Overall : $\quad Fe^0 + 2H_2O \leftrightharpoons Fe(OH)_{2(s)} + H_{2(g)}$ $\qquad$ (10)
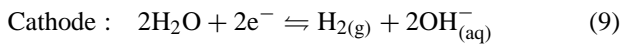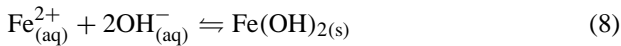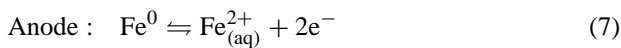
The gelatinous suspension of Fe(OH)$_{n(s)}$ formed as a result of this electrochemical process can remove the pollutants from wastewaters, either by complexation or by electrostatic attraction followed by coagulation and flotation [43]. However, examination of the Pourbaix diagram (Eh-pH diagram) [44] reveals that Fe^{3+} ion is stable only in a very oxidizing acidic medium, whereas the Fe^{2+} ion is stable over relatively a large Eh-pH range. The highly insoluble compound Fe(OH)$_3$ is the predominant iron species over a very wide Eh-pH range. It is, however, generally accepted that iron hydroxyl complexes are formed after initial oxidation of Fe^0 at the anode according to the reactions shown below:
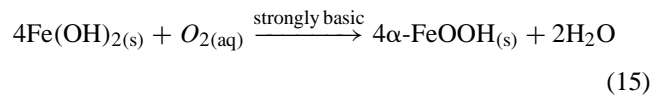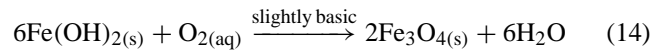
$$Fe^0 \leftrightharpoons Fe^{2+} + 2e^- \qquad (11)$$

In an anaerobic environment and at sufficiently high pH ferrous hydroxide will be precipitated:

$$Fe^{2+} + 2OH^- \leftrightharpoons Fe(OH)_{2(s)} \qquad (12)$$
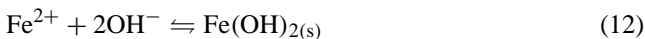
However, in oxygenated water and at lower pH, Fe^{2+} is converted to Fe^{3+}:

$$4Fe^{2+} + 4H^+ + O_{2(aq)} \leftrightharpoons 4Fe^{3+} + 2H_2O \qquad (13)$$
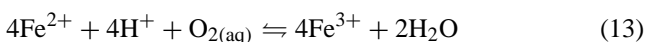
Thermodynamic considerations will, however, determine the final products in an EC process. In a discussion of the mechanism of atmospheric corrosion, Misawa et al. [45] reported that either goethite (α-FeOOH) or magnetite (Fe$_3$O$_4$) is produced depending upon the pH of the environment:

$$6Fe(OH)_{2(s)} + O_{2(aq)} \xrightarrow{\text{slightly basic}} 2Fe_3O_{4(s)} + 6H_2O \qquad (14)$$

$$4Fe(OH)_{2(s)} + O_{2(aq)} \xrightarrow{\text{strongly basic}} 4\alpha\text{-FeOOH}_{(s)} + 2H_2O \qquad (15)$$

If the sludge is in contact with oxygen, it is possible that the Fe(OH)$_2$ is converted to Fe(OH)$_3$ or other intermediate Fe^{2+}/Fe^{3+} hydroxysalts (green rusts). Other parameters, such as temperature and moisture content may also influence the final products.

The experimental evidence from this study is consistent with the results found by Misawa et al. [45]. At lower pH values, magnetite was generated as a result of the EC process. At higher pH maghemite (γ-Fe$_2$O$_3$) was formed, which may also be formed from magnetite and the transformation of goethite (α-FeOOH) to maghemite has been observed previously [46]. The higher treatment efficiency obtained in the present experiment is considered to be due to chemical coagulation involving maghemite (γ-Fe$_2$O$_3$) and/or magnetite (Fe$_3$O$_4$) produced in the system as well as electrooxidation. However, the present experimental data is not sufficient to propose a mechanism of interaction between these iron oxides and the dye molecules. Further work in this regard is in progress.

4. Conclusions

The treatment of orange II dye in a flow-through EC cell described in the present experiment can effectively remove ca. 99% of the dye from the waste stream under the optimum conditions. The removal efficiency was found to be dependent on the initial pH, the electrolyte concentration, the dye concentration, the applied current density, the flow rate and the recycling of the dye solution. The higher treatment efficiency is considered to be due to chemical coagulation

involving maghemite (γ-Fe_2O_3) and/or magnetite (Fe_3O_4) produced in the system as well as electrooxidation. The presence of mainly magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) were characterized by XRD analyses of the residue. Since the EC apparatus described in this experiment is simple in design and operation, it can be used as a potentially viable and inexpensive tool for electrocoagulation of textile dyes.

Acknowledgements

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