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Effective Decolorization of Eriochrome Black T, Furschin Basic and Malachite Green dyes from Synthetic Wastewater by Electrocoag-nanofiltration

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ABSTRACT

This study examines the use of electrocoagulation treatment process followed by nanofiltration process in removing color from synthetic wastewater. Three representative dye molecules were selected for the synthetic dye wastewater: Azo dye (Eriochrome Black T), Furschin Basic and Malachite Green dyes. Iron electrode was use as a sacrificial anode in the study. The influence of electrolysis time, operating current density, initial pH, initial dye concentration and temperature on process performances was investigated. Experiments were conducted to find the desired conditions for removal of particular concentration of the dyes. The results showed that 91% of Eriochrome Black T, 92% of Furschin Basic and 80% Malachite dye was decolorized for initial dye concentration of 100 mg/l with the current density of 1559 A/m^2, electrolysis time of 25 minute and initial pH of 10. The electrochemical technique showed satisfactory color removal efficiency and reliable performance in treating the dye types. Electrode mass loss and energy consumed were also calculated.

Keywords: nanofiltration; electrocoagulation; dye; synthetic waste water; removal efficiency; optimization.

1.0 Introduction

Nanofiltration is a relatively recent membrane filtration process used most often with low total dissolved solids water such as surface water and fresh groundwater, with the purpose of softening (polyvalent cation removal) and removal of disinfection by-product precursors such as natural organic matter and synthetic organic matter. Nanofiltration is also becoming more widely used in food processing applications such as dairy, for simultaneous concentration and partial (monovalent ion) demineralisation

Electrocoagulation is an alternative technology for wastewater treatment and recovery of valuable chemicals from wastewater. It is an electrochemical technique whereby anodes (aluminum or iron) corrode to release active coagulants into solution. The generated metallic ions, i.e. $Al^{3+}(aq)$ and $Fe^{3+}(aq)$, will undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxide [1]. These hydroxide/ polyhydroxide/polydroxymetallic compounds have a strong affinity with dispersed/ dissolved molecules to cause coagulation/adsorption [1, 2].

The technology for colour removal can be divided into three categories: biological, chemical and physical [3]. All of them have advantages and drawbacks. The main advantages of electrocoagulation over other conventional techniques such as chemical coagulation and adsorption are in situ delivery of reactive agents, no generation of secondary pollution, and compact equipment. Many studies have reported the potentials of electrocoagulation in treating a variety of wastewater, including removing suspended solids [4, 5], removing dyes [6, 7], breaking oil emulsions in water [2].

The textile industry consumes considerable amounts of water during dyeing and finishing operations. Dye-containing effluent is toxic to the environment since dyes are stable compounds, with low biodegradability and can be carcinogenic. Dyes are normally very large aromatic molecules consisting of many linked rings. Three common dyes, classified according to the fibers to which they can be applied and their chemical nature are: (1) acid dyes; (2) reactive dyes; (3) disperse dyes [6]. Acid dyes are water-soluble anionic compounds, applied from an acidic solution to nylon, wool, silk, and some modified acrylic textiles in an acidic medium. Acid dyes attach to fibers via hydrogen bonding, van der Waals forces and ionic bonding. Reactive dyes are water-soluble anionic compounds, mainly applied to cotton and rayon. Reactive dyes form covalent bonds with fibers. Disperse dyes are mostly used for oleophylic fibers and polyesters, and applied as a dispersion of finely ground powders. Typical textile effluent contains various types of dye molecules and might have fluctuating properties due to varying dyeing activities. Excellent colour fastness and UV stability is displayed and so these expensive dyes are often used for fabrics that must withstand frequent, harsh washing such as military uniforms and hospital textiles or those continuously exposed to daylight such as furnishings. However, dyeing activities of a factory can vary according to its customer's orders, resulting in different levels of dye types in wastewater. Therefore, the study of decolourization of mixed dyes is a necessary step toward the development of more effective treatments of textile wastewater and synthetic wastewater.

In this study, operational parameters were investigated that are suitable for treating synthetic wastewater containing an azo dye alone, a vat dye alone and synthetic dyes. These parameters included electrode type, electrode distance, current density, and electrocoagulation time. The effects of environmental factors, i.e. pH and temperature, on the process efficiency of the synthetic wastewater were also investigated.

1.1 Theory of Electrocoagulation

In electrocoagulation process, the coagulants produced in situ have been discussed by a number of researchers as involving three stages:

1. Formation of coagulants by electrolytic oxidation of the sacrificial anodes.
2. Destabilization of the contaminants, particulate, suspension and breaking of emulsions.
3. Aggregation of destabilized phases to form flocs.

When potential is applied to the metal anodes, it causes two spate reactions:

1. Fe/Al is dissolved from the anode generating corresponding metal ions which is almost immediately hydrolysed to polymeric iron or aluminium hydroxide. The polymeric hydroxide formed is an excellent coagulating agent. The consumable metal amides are used to continuously produce polymeric hydroxide in the vicinity of the anode. When these metal cations combine with the negative particles carried towards the anodes by electropheric motion, coagulation occurs.
2. Water is also electrolyzed in a parallel reaction producing bubbles of oxygen at the anode and hydrogen at the cathode. The bubbles attract the flocculated particles and through natural buoyancy floats to the surface. Destabilization mechanism of the contaminant, particulate suspension and breaking of emulsion from the other hand, has been described in broad steps and summarized as follows;
   a. Compression of the diffused double layer around the charged species by the interaction of ions generated by oxidation of the sacrificial anodes.
   b. Charge neutralization of ionic species present in wastewater by counter-ions produced by the electrochemical dissolution of the sacrificial anodes. These counter-ions reduce the electrostatic antiparticle repulsion to the extent that the Van der Waals' attraction predominates, thus, causing coagulation. A zero-net charge results in the process.
   c. Flocs formation as a result of coagulation. This creates a sludge blanket which entraps and bridges the colloidal particles still remaining in the aqueous medium. The solid oxides, hydroxides and oxy-hydroxides provide active surfaces for the adsorption of the polluting species.

1.1.2 Reactions at the electrode

For a given electrochemical cell, set up is made up of metallic electrode as illustrated in figure 1, a potential difference is applied from an external DC power source, the anode undergoes oxidation by loss of electrons while the cathode, by reduction or deposition of elemental metal. The electrocoagulation reaction between metal "M" is summarized below.

At the anode:

$M_{(s)} + ne^- \longrightarrow M^{n+}{}_{(aq)}$

$2H_2O_{(l)} + 4e- \longrightarrow 4H^+{}_{(aq)} + O_{2(g)}$

$Al_{(s)} \longrightarrow Al^{3+}{}_{(aq)} + 3e^-$ (for aluminium electrode)

$Fe_{(s)} \longrightarrow Fe^{2+}{}_{(aq)} + 2e^-$ (for iron electrode)

At the cathode:

$M^{n+}{}_{(aq)} + ne^- \longrightarrow M(s)$

$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-$

Depending on the pH of the aqueous medium, the Al^{3+} ions or Fe^{2+} ions generated undergoes hydrolysis producing complexes. These hydroxides, polyhydroxides, polyhydroxymetallic compounds have strong affinities for dispersed particles as well as counter ions to cause coagulation.

These gases evolved at the electrode (bubbles of hydrogen and oxygen at the cathode and anode respectively) impinge on and causes flotation of the coagulated materials.

The different electrode materials had an effect on the effectiveness of water treatment because of its mechanisms.

Aluminium:

Aluminium upon oxidation in an electrolytic system produces aluminium hydroxide, $Al(OH)n$, where n=2 or 3

Anode:

$2Al(s) \longrightarrow 2Al^{3+}(aq) + 6e-$

$2Al^{3+}(aq) + 6H_2O(l) \longrightarrow 2Al(OH)_3(s) + 6H^+(aq)$

Cathode:

$6H^+(aq) + 6e^- \longrightarrow 3H_2(g)$

Overall reaction:

$2Al + 6H_2O(l) \longrightarrow 2Al(OH)_3(s) + 3H_2(g)$

Iron:

Iron upon oxidation in an electrolytic system produces iron hydroxide, $Fe(OH)n$ where n=2 or 3.

Two mechanism has been proposed for the production of $Fe(OH)n$.

Mechanism 1: (Anodic medium)

Anode:

$4Fe(s) \longrightarrow 4Fe^{2+}(aq) + 8e-$

$4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \longrightarrow 4Fe(OH)_3(s) + 8H^+(aq)$

Cathode:

$8H^+(aq) + 8e^- \longrightarrow 4H_2(g)$

Overall:

$4Fe(s) + 10H_2O(l) + O_2(g) \longrightarrow 4Fe(OH)_3(s) + 4H_2(g)$

Mechanism 2:

Anode:

$Fe(s) \longrightarrow Fe^{2+}(aq) + 8e^-$

$Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$

Cathode:

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

Overall:

$Fe(s) + 2H_2O(l) \longrightarrow 4Fe(OH)_3(s) + 4H_2(g)$

2.0 Materials and Methods

The Electrocoagulation unit consists of a cylindrical glass cell as shown in figure 2, in which the anode and cathode electrode made of Iron were fixed at a distance of 5.7cm from each other, a direct current power supply, a magnetic stirrer, and a synthetic wastewater. A Laboratory model DC power supply apparatus (HUPE Model LN003C) was used to maintain constant DC current. A multimeter (ALDA DT-830D) was used to measure current and voltage. UV spectrophotometer was use to check the concentration of the dyes. The synthetic wastewater stock solution was prepared by dissolving 0.5g of each dyes (Orange-G, Vat yellow and Erythrosine) in $1dm^3$ of distilled water, of which the working solution was taking from it at different concentrations (500mg/l, 300mg/l, 200mg/l, 100mg/l and 50mg/l). HCl and NaOH (Merck), NaCl (Aldrich) were used.

The electrocoagulation cell had a working volume of 250ml, considering the dimensions of the electrodes as well as their submergence depth; this provides an electrode area to volume ratio of $5.1x10^{-6}$ m^2/m^3 in the reactor. The direct current was supplied by a laboratory model power supply instrument in which the current density could be regulated at a given level. Appropriate dosage of current was added to 250ml of synthetic dyes. The suspension, charged with NaCl solution by adding 5ml drops, the pH is tuned to range 3-10 by adding HCl/NaOH. All runs were performed at 150rpm, followed by 15minutes of settling. Nano-Max50 (a heavy duty, two axis nanoposition-ing stage designed to carry heavy experimental assemblies) was used as nanofilter. The nanofiltrate samples were measured using the visible spectrometer. A calibration curve for various dyes and corresponding concentration were made to enable determination of final conc. Ce, prior to starting.

R_E = ((Co – Ce) / (Co)) X 100

Co = Initial concentration before coagulation.

Ce = Final concentration after coagulation.

R_E = Percentage removal efficiency.

Before each run, electrodes were washed with acetone to remove surface grease, and then washed thoroughly with distilled water to remove any solid residues on the surfaces, dried. Typical runs were conducted at 303K, but some runs were conducted at 308K, 313K, 318K and 323K in order to study the effect of temperature.

3.0 Result and discussion

The electrocoagulation **is** usually affected by different parameters. They include; concentration, electrocoagulation time, pH, current density, temperature, electrode distance.

3.1 Effect of pH

pH is a major effective parameter in the performance of the Electrocoagulation process. The kinetics of Fe2+ conversion to Fe3+ is strongly affected by the pH; the surface charge of the coagulating particle also varies with pH. [6]. To examine its effect, in each experiment, the sample was adjusted to a distinct pH using sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4). In EC, where Fe electrode is used, it has been observed that Fe (OH) 3 precipitation occurs and the sweep-flock mechanism dominates. [6]

It has been recognized that pH has a considerable effect on the efficiency of electrocoagulation process. Also as observed by other investigators, the pH of the medium was changed during the process. This change depends on the electrode type, initial pH and the alkalinity. In addition, pH measurements were found to be very important in showing the type of dominant reactions at the anode and cathode electrodes. Experimental findings related to removal efficiency of the metal ions as a function of initial pH have accounted for decrease in removal efficiency observed at extreme pH vales. This decreased was attributed to the formation of soluble A13+ |Cations at strong acidic pH and the formation of monomeric anions $Al(OH)^-_4$ at strong alkaline pH, therefore , the formation of these species are not constructive for water treatment processes. The pH increases at a low initial pH of less than 7 owing to the evolution of hydrogen and generation of OH^- ions at the cathodes. But at pH greater than 7, the final pH does not change significantly because the generated OH^- ions at the cathode are consumed by the generated Fe^{2+} ions at the anode forming the needed Fe (OH) flocs.

In this work, experiments were conducted using solutions of dyes i.e. malachite green, fuchsine basic and enchrome black T dyes of 250mg/l each in the initial pH range of 3-10 from Fig. 3, the removal efficiency of all the studied dyes after 25 mins of electrocoagulation at constant voltage of 1.5V reached very high values >90% for eriochrome black t dye,>80% for fuchsine basic dye and >60% for malachite green dye. However, at pH 10 the removal efficiency increases above 90% for fuchsine basic dye and 80% for malachite green dye but decreases below 40% for eriochrome black t dye.

There was a decrease in removal efficiency at strong acid and a slight increase in alkaline solution of malachite green and fuchsine basic dye but the reverse is the case for eriochrome basic dye whose optimum pH is at 3

3.2 Effect of Current Density

Current density plays an important part in the removal efficiency of colour with time as shown in Fig. 4 . As the current density increases, the rate of iron dissolution increases at constant pH. Also, the amount of H_2 gas on the cathode increases with an increase in current density as per faraday's law. At the same time, the amount of hydroxide monomer and polymers also increase thus responsible for adsorption and precipitation of dye molecule. The optimum current density of 2Amp was used for the tested dyes. In any electrocoagulation process current density (A/m^2) and time of electrolysis were important operational parameters setting the ultimate removal efficiency for the process. Some investigators have reported that in electrocoagulation, current density can influence the treatment efficiency [8], while others have reported that current density has no significant role on pollutant removal [9]. Therefore, it remains unclear that whether the current density affects the treatment efficiency or not. It was observed from the figure 4 that colour removal decline gradually at the beginning and becomes nearly constant between currents 1.5 to 2 volts respectively of operation for the tested dyes. Therefore, 25 minutes was adopted as a constant operation time to optimize the energy consumption for further observations.

3.3 Effect of Concentration

The effects of initial dye concentration on the removal efficiency of color with time are shown in Fig. 5 at five different initial dye concentrations. It can be seen that the rate of removal decreases substantially when the initial concentration of the dye is greater than 100 mg/L.

Initial dye concentrations of 50mg/L and 100mg/L gave high removal percentages of greater than 80% for eriochrome and malachite green dyes respectively and above 90% for fuchsine basic dyes.

At the time of electrolysis, cathodic reaction occurs on the negative electrode while the positive electrodes proposed anodic reaction. The released opposite charge ions neutralize the particle charges and thereby initiate electrocoagulation. The removal efficiency directly depends directly on the concentration of ions generated during anodic dissolution of anode on EC processes. When the electrolysis period increases, its increases the concentration of ions their hydroxide flocs occur through the interaction of hydroxide ions. However when initial dye concentration is greater than 100 mg/L, the site of adsorption capacity of flocs gets exhausted and the % of removal efficiency decreases. Still, with an increase in the concentration of the dye, the rate of removal decreases considerably. Daneshwar et al [1] reported similar behavior for decolorization of basic dye solution through EC treatment method.

The optimum concentration was gotten at 50mg/L which gave a percentage removal of 82.04% for malachite green dye, 87.04% for eriochrome black T and 96.05% for fuchsine basic dye. However, effective concentration was adopted at 100mg/L for effective calculation of removal efficiencies.

3.4 Effect of Electrocoagulation Time

The percentage removal efficiency depends directly on the concentration of ions produced by the electrodes. The concentration of ions and their hydroxide flocs increases with an increase in electrolysis time. During electrolysis, the positive electrode undergoes anodic reactions while cathodic reactions occur on the negative electrode. The released ions neutralize the particle charges and thereby initiate coagulation. Accordingly, with an increase in the electrolysis time there is an increase in the removal of dye efficiency [10]. Figure 6 shows that the rate of dye removal is very fast when time is increased from time 5 to 10 mins. This can be because of the formation of OH- ions on the cathode. Electrocoagulation time was varied for the studied dyes. As shown in this figure, when time increased from 5 to 10mins, dye removal percentage increased from 35.6 to 68.75% for fuchsine basic dye, 34.72% to 75.71% for EBT dye and 32.4% to 65.48% for malachite green. Thus, with increasing time of reaction from 1 to 25 mins at constant voltage, dye removal gradually increased. The results show at first 5 min of reaction, dye removal efficiency is low but with increasing reaction time, efficiency increased. Voltage and time of reaction are two major operation parameters that determine the coagulant dosage rate during electrocoagulation. The highest removal rate was observed at 25 mins.

3.5 Effect of Temperature

The effect of temperature can be deduced from Fig. 7. It was discovered that temperature had very little or no effect on the electrocoagulation process. At increasing temperatures, the percentage removal increased at very little quantities. From Fig. 7 it was also observed that furschin basic dye had a higher percentage removal ranging between 99.83 to 99.99. Eriochrome black T dye recorded percentage removal values of 95.47 to 96. While malachite green dye recorded removal values of 87.12 to 88.77. Temperature values tested were 303K, 308K, 313K, 318K and 323K.

4.0 Conclusion

The electrocoagulation and nanofiltration process are successfully applied to remove the synthetic dye from aqueous solution. The colour removal efficiency was found to be dependent on some tested parameters like concentration, electrocoagulation time, initial pH and current density. The eriochrome dye solution decolorized more efficiently at initial pH of 3 i.e. in acidic medium while both malachite green and fuchsine basic dyes decolourizes more efficiently at pH of 10 (basic medium). It was found that for an initial concentration of 100 mg/l, the percent removal was about 90% with electrocoagulation time of 15 min beyond which the color removal efficiency was found to be negligible. Ten iron electrodes with an effective area of were $5.1x10^{-6}$ m^2/m^3 in the reactor optimized at a voltage of 2.0 V with an operating current density of 1562.5 A/mm^2. It was seen that with an increase in initial concentration of 50-500 mg/l color removal efficiency decreased remarkably. Therefore, initial concentration greatly affects the color removal efficiency. Effect of temperature was termed to negligible. The electrocoagulation setup described in this study is simple in design and operation and can be used as a convenient tool in the removal of dyes from synthetic waste water.

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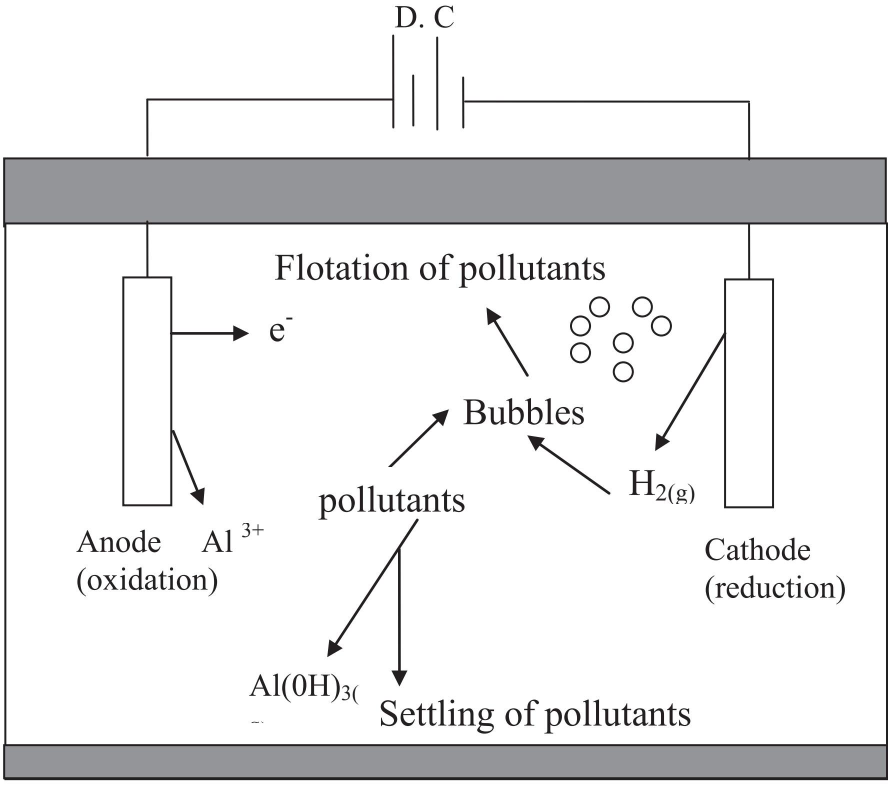

Fig. 1 Schematic Diagram of Two-Electro EC Cell.

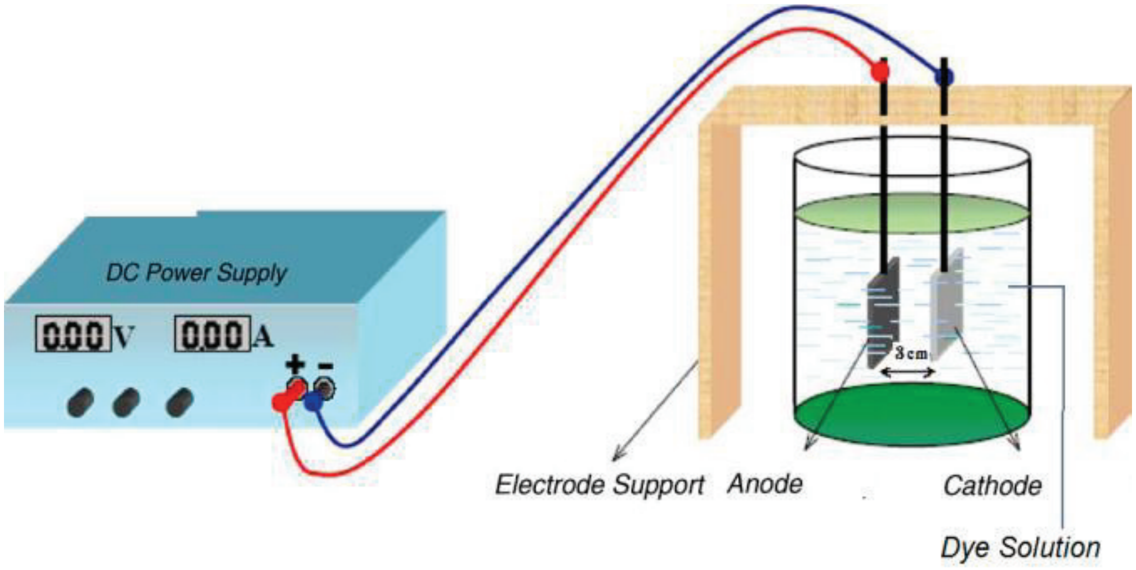

Fig 2 Experimental set-up.

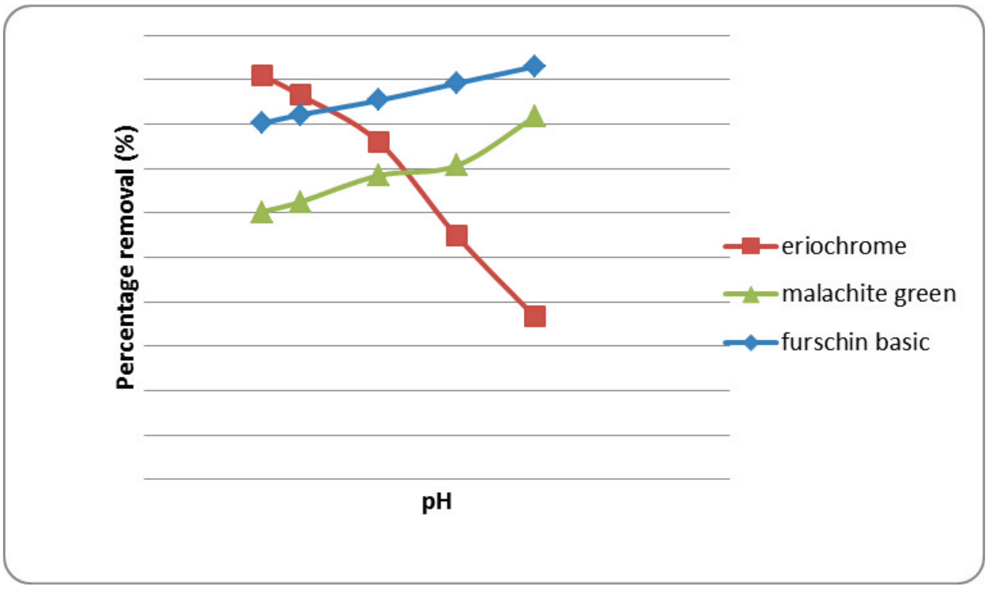

Fig. 3 Effect of pH on the percentage removal of studied dyes. (Duration of electrocoagulation: t = 25 min; Concentration: 100 mg/ L; Temperature = 303 K; Stirring speed =100 rpm Current= 1.5 V)

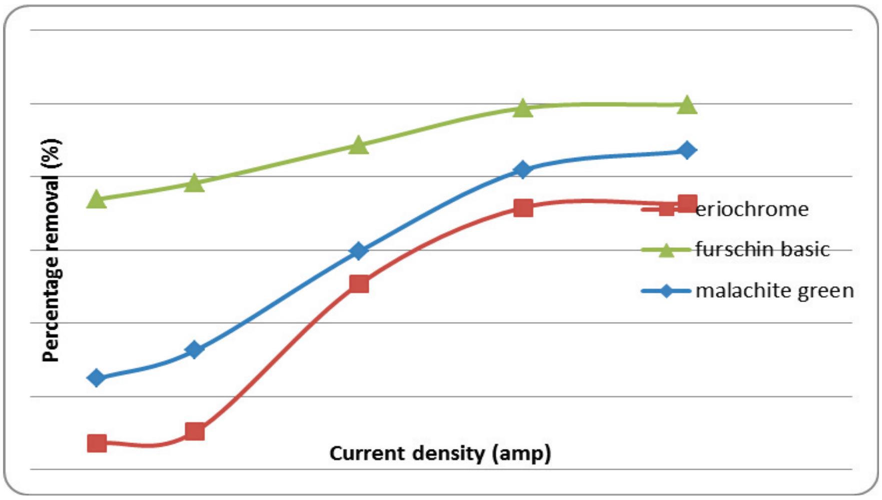

Fig. 4 Effect of current density on the percentage removal of studied dyes. (Duration of electrocoagulation: t = 25 min; Concentration: 100 mg/ L; Temperature = 303 K; Stirring speed =100 rpm; pH= 10 for malachite green and fuchsine basic dyes, pH= 3 for Eriochrome black T dye)

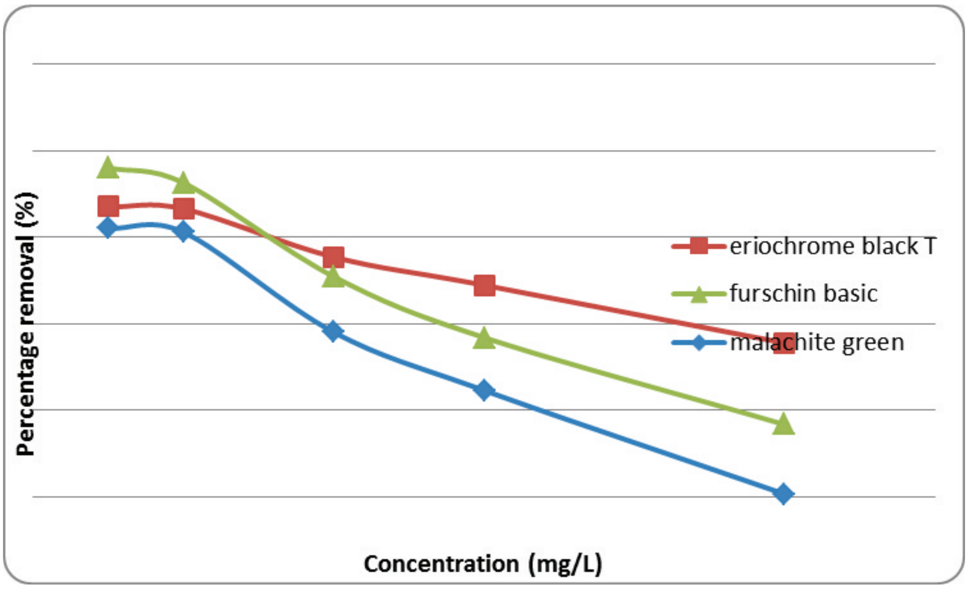

Fig. 5 Effect of initial dye concentration on the percentage removal of studied dyes. (Duration of electrocoagulation: t = 15 mins; Stirring speed =100 rpm Current= 1.5A, Temperature =303K)

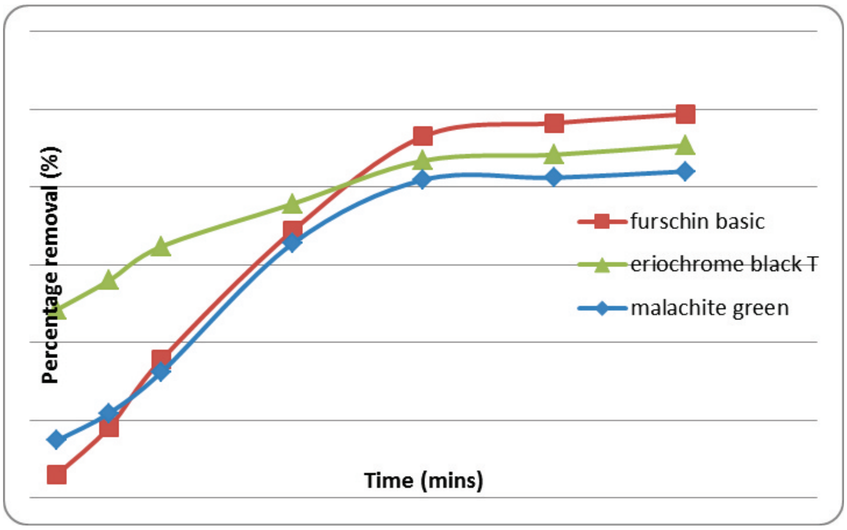

Fig. 6 Effect of Time on the percentage removal of studied dyes. (Concentration = 100 mg/ L; Temperature = 298 K; Stirring speed =100 rpm; Current= 1.5 V)

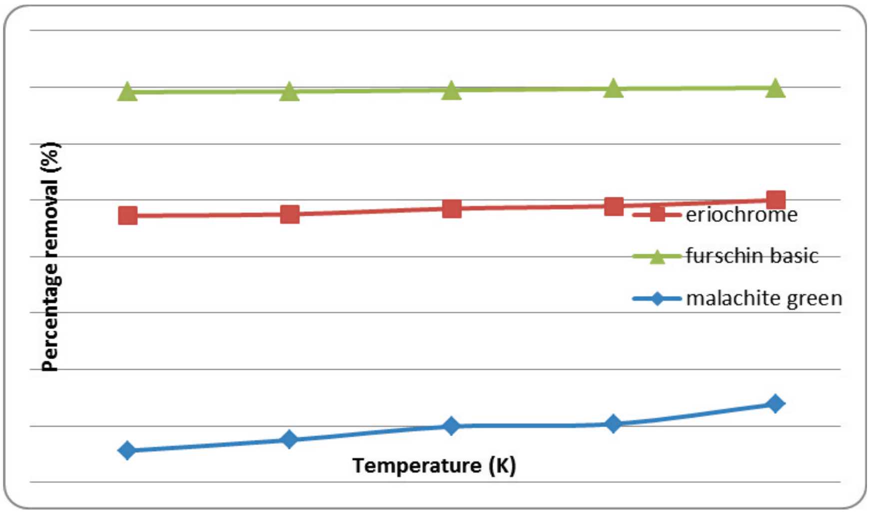

Fig. 7 Effect of temperature on the percentage removal of studied dyes. (Duration of electrocoagulation: t = 25 min; Concentration: 100 mg/ L; Temperature = 298 K; Stirring speed =100 rpm Current= 1.5 V pH= 10 for malachite green and fuchsine basic dyes and 3 for Eriochrome black T dye)

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