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Electrochemical Treatment Of Malachite Green Dye Solution Using Iron Electrode

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Abstract: Present study was performed to investigate the variables that influence the removal efficiency of malachite green (aniline) dye from aqueous solution by an electrochemical (EC) technique. The batch EC studies were performed using iron electrode to evaluate the effect of operating parameters such as pH_o and processes parameters such as current density and initial dye concentration. Parameters pH_o, current density and initial dye concentration were varied in the range of 3.5–8.5, 39.21–117.64 A/m^2 and 100–400 mg/L, respectively, at 60 min of operating time. Optimum value of variable such as pH, current density and initial dye concentration were found to be 8.5, 117.64 A/m^2 and 100 mg/L, respectively. At optimum condition, 99% color and 75% COD efficiencies were obtained. Removal efficiency increased with an increase in the current density due to initially increase the electrode dissolution at optimum pH_o and initial dye concentration.
Keywords: Malachite green; electrochemical (EC) treatment; COD; color removal; iron electrode.

1. Introduction

Organic dyes are widely used in a broad range of industries, especially in textiles[1] .As compared to natural dyes, the synthetic dyes are extensively used in textile dyeing, leather dyeing, paper printing and color photography. Widespread use of synthetic dyes is because of ease of manufacture and cost effective synthesis, high resolution and stability against light, temperature, detergent and microbial attack and availability in large number of colors[2].The discharge of highly colored effluents affects the water characteristics and oxygen solubility in water-bodies such as lakes, ponds and rivers[3]. Many dyes are considered as toxic and carcinogenic owing to their preparation from carcinogens aromatic compounds such as benzidine[4,1].

On the basis of the chemical structure of chromophoric group, the dyes are classified into various classes such as anthraquinone, azo, triarylmethane and phthalocyanine dyes[5] . Most of the colored dyes reduce the reoxygenation capacity of natural waters and penetration of sunlight. These dyes are very difficult to degrade biologically thereby upsetting the ecosystem[6]. Moreover, the colors are potentially toxic and, thus, their removal from effluent stream is ecologically necessary for the maintenance and regulation of a clean environment[7]. In textile industry approximately 12–16% of all dyes are directly lost to wastewater through dyeing and finishing processes[8].

Malachite green, a triphenylmethane dye, is extensively used for dyeing of wool, silk, leather, jute, ceramics, etc. It is also used in cotton industries, food additive, pesticide, and fungicide in food, and fish farming industry throughout the world. This dye is difficult to biodegrade and has toxicological effects on the liver, lungs, and other organs of experimental mammals and other aquatic animals[9] . Due to these characteristics, malachite green has been banned in several countries[10]. However, it is still used in many areas of the world due to its low cost, ready efficaciousness, and lack of suitable alternatives[11]. Therefore, the environmental pollution caused by the long-term and extensive usage of malachite green has become a serious problem. A large number of commonly used methods are applied in treatment of dyes wastewater such as adsorption, electrochemical, nanofiltration, coagulation and precipitation, chemical oxidation, electrochemical oxidation, photo-oxidation, ozonation, supported liquid membrane and liquid–liquid extraction[9,12,13] reviewed in several papers[8,14,15]. Among these mentioned methods, electrochemical (EC) treatment method has great attention for dye bearing wastewater because, it is relatively cheap, efficient, and characterized by its lower equipment costs, sludge volume reduction and easy to operation. EC method employs a metal electrode, which acts as an anode, to produce the coagulant via dissolution of electrodes by electrolytic oxidation. At an appropriate pH level, the coagulant turns into precipitates as metal hydroxides[16].

Present study was performed to investigate the variables that influence the removal efficiency of malachite green dye from aqueous solution by an electrochemical (EC) technique using iron electrode.

2. Experimental setup and Experimental procedure

The thermostatically controlled EC reactor with dimensions 108 mm × 108 mm × 130 mm was made of plexiglass. Two monopolar electrodes (i.e. one anode and one cathode) made of iron plates, with each having total effective electrode area =63.75 cm^2 were used for EC study. The electrodes were connected to a digital dc power supply (0–20 V, 0–5 A) equipped with potentiostatic or galvanostatic operational options. Magnetic stirrer was used to agitate the solution**.**

For each experiment, the initial pH (pH_o) of the dye solution was adjusted to desired level by adding 0.1 N NaOH or 0.1 N H_2SO_4 solutions. 1.5 g of electrolyte (NaCl) was added to the solution in each experiment. In the beginning of experiment, 1 L solution of known initial COD concentration (COD_o=214 mg/L) was fed into the reactor. Time was measured when power supply was switched on. Current density was maintained constant during each experimental run. After the desired treatment time, samples were taken from the reactor and its final COD was measured. The % COD removal efficiency (RE) was calculated from the following relationship:

% COD removal efficiency (RE)
$= 100\ (COD_o - COD_t)/COD_o$ ……….(1)

Where, COD_o and COD_t are the initial and final COD_t (mg/L) at any time t.

The color of the dye samples before and after the EC was measured by a UV–vis spectrophotometer (Model Lambda 35, Perkin Elmer Instruments, Switzerland). Sample was first centrifuged at 2000 rpm for 20 min. The absorbance of the sample was measured at an optimum wavelength of 619 nm. The percentage of color removal was calculated from the difference in absorbance values before and after treatment.

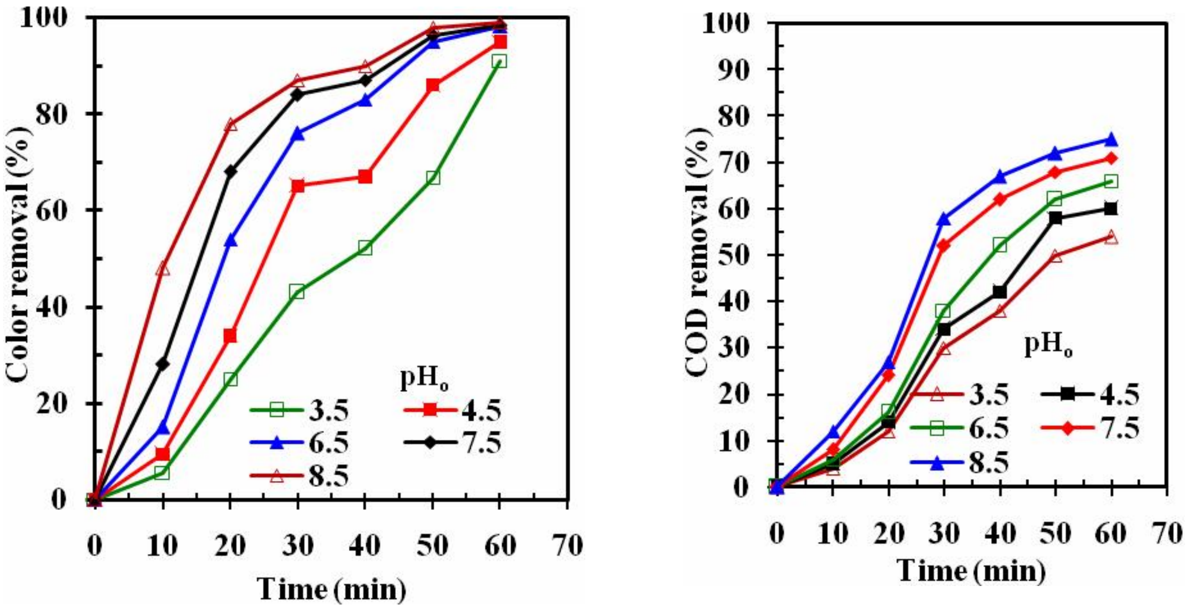
2.1. Analytical method

All the chemicals used in the study were of analytical reagent (AR) grade. COD was measured using digestion unit (DRB 200, HACH, USA) and double beam UV visible spectrophotometer (HACH, DR 5000, USA).

3. Results and discussion

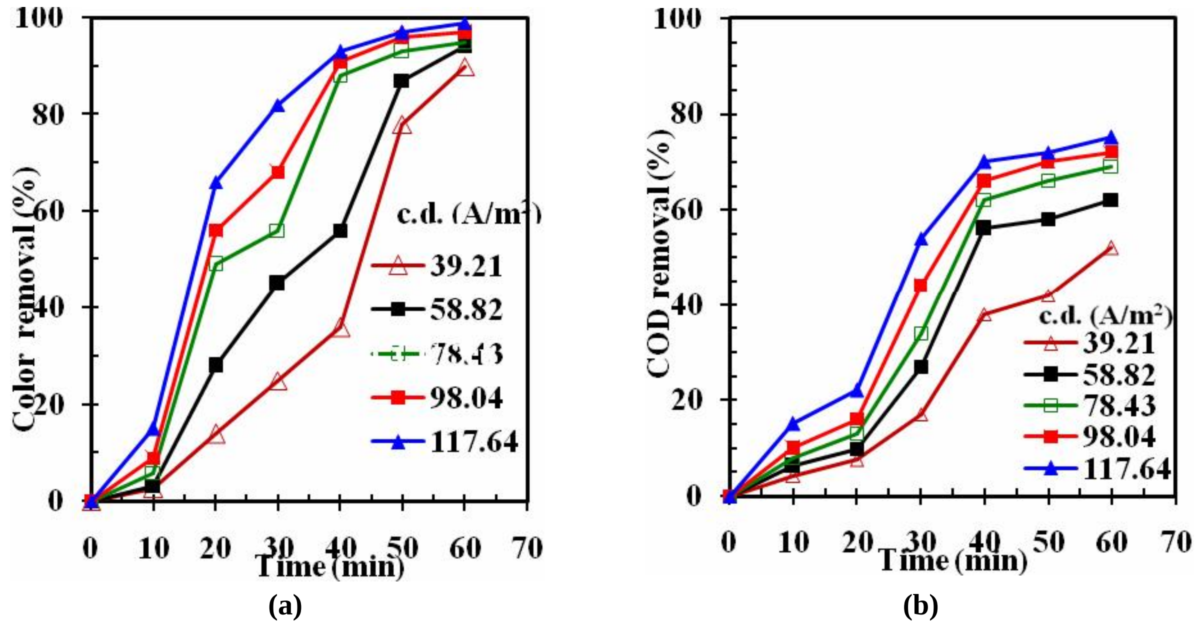
3.1. Effect of pH_o

A series of experiments were conducted by adjusting the pH of the solution to the desired level using sodium hydroxide or hydrochloric acid solutions. Fig. 1a and 1b shows that maximum color and COD removal efficiency is obtained at pH 8.5. At lower acidic pH range, from 3.5 to 6.5, cationic monomeric species such Fe^{+2} and $Fe(OH)^+$ predominant which are not responsible in color removal. When pH increases from acidic to basic (nearly 8.5), the ionic species such as Fe^{+3} and OH^- ions generated from anode and cathode react with monomeric species and transform into insoluble amorphous $Fe(OH)_3(s)$ through complex polymerization/precipitation reactions. These amorphous iron hydroxides consequently adsorb the dye molecules and increase the removal efficiency[17].



(a) (b)

Figure 1. Effect of pH$_o$ on the removal efficiency (conditions: c.d: 117.64 A/m^2; t: 60 min; electrolytic concentration: 1.5g/L; c$_o$: 100 mg/L).



(a) **(b)**

Figure 2. Effect of current density (c.d.) on the removal efficiency (conditions: pH$_o$: 8.5, t: 60 min; electrolytic concentration: 1.5g/L; c$_o$: 100 mg/L).

3. 2. Effect of current density

Current density plays an important role in the removal efficiency of color and COD with time as shown in Fig. 2a and 2b.

As the current density increases, the rate of iron dissolution increases at constant pH (of 8.5). Also amount of H_2 gas formed on cathode increases with an increase in current density as per Faraday's law. At the same time, the amount of iron hydroxide monomers and polymers also increase that are responsible for adsorption and precipitation of dye molecule. The optimum current density of 117.64 A/m^2 was used for the color and COD removal for malachite green dye solution.

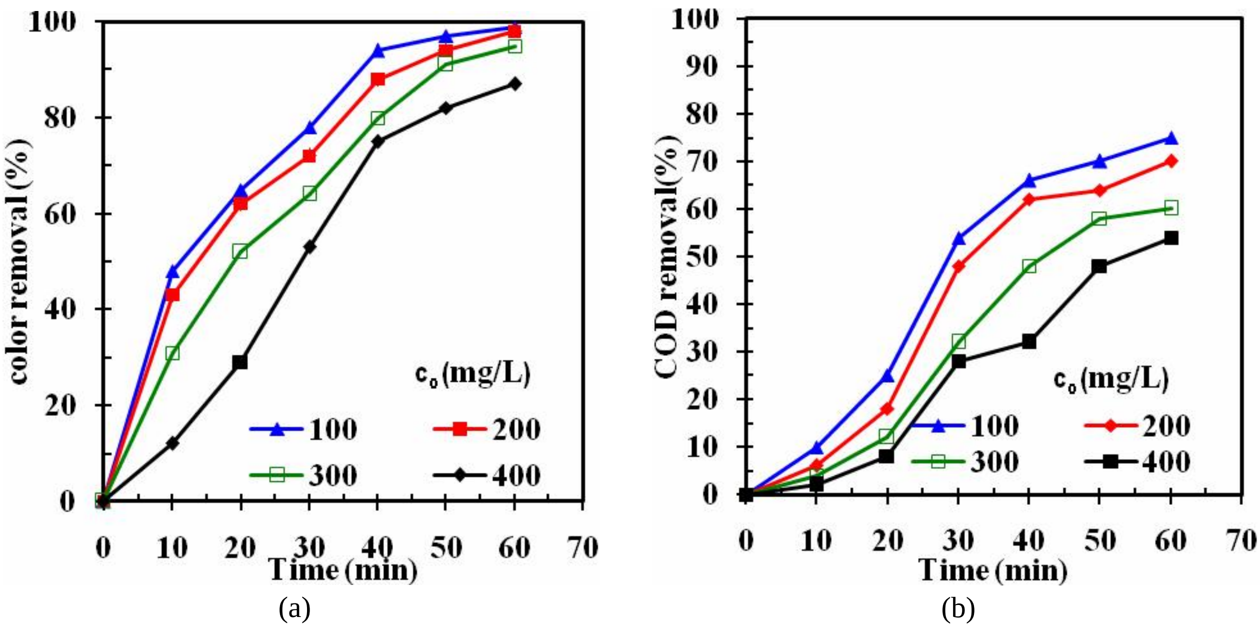


Figure 3. Effect of initial dye concentration (c_o)on the removal efficiency (conditions: pH_o: 8.5, t: 60 min; c.d.: 117.64 A/m^2).

3.3. Effect of initial dye concentration

The effects of initial dye concentration on the removal efficiency of color and COD with time are shown in Fig. 3a and 3b at four 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. 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 and 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. [18]Daneshvar et al. reported similar behaviour for decolorization of basic dye solution through EC treatment method.

4. Conclusion

The present study demonstrated the applicability of electrochemical treatment method for dye removal. Under optimal value of process parameters, 99% color and 75% COD removal was obtained for treatment of malachite green dye solution. The removal efficiency was greatly affected by the current density, initial pH and initial dye concentration.The result show that when the dye concentration increases beyond 100 mg/L, the removal efficiency decrease whereas removal efficiency increases with an increase in the current density.

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