Electrochemical Oxidation of Methylene Blue in Aqueous Solution

H. M. A. Asghar, T. Ahmad, S. N. Hussain, and H. Sattar

***Abstract*—An electrochemical oxidation technique was used for mineralizing the methylene blue dye dissolved in water. For this purpose, an electrochemical cell was used consisting of electrodes made from stainless steel and graphite. The effect of various factors on dye removal was studied such as current density, treatment time and initial concentration of dye solution. A substantial increase in dye removal was found to be in direct proportion with initial dye concentration. However, the dye removal was found to be increased with an increase of treatment time up to 30-40 min and current density up to 0.06 A cm^{-2}.**

***Index Terms*—Electrochemical oxidation, methylene blue & current density.**

I. Introduction

Water is a fundamental requirement for all living bodies. It has a vital role for industrial operations. In near future, the availability of drinking water will be a challenge in all over the world. The term waste water treatment refers to the treatment of dissolved impurities collected and transported from industrial discharge effluents. Waste water can generally be classified into domestic and industrial. The waste water from each source may contain both dissolved and suspended impurities. The suspended particles can be removed by filtration where as dissolved contaminants required further treatment. The type of contaminant may vary with each type of discharge from industrial sector. These industries may include food processing units, dairy operations, meat packing, poultry, oil & gas, paper, fertilizer, petrochemical etc. In addition to organic waste materials, inorganic pollutants may also present in water. The inorganic wastes may originate from metal plating, battery shops, furniture manufacturing, dry cleaning units etc. Waste water treatment can be classified into primary, secondary and tertiary treatments. It is desirable to remove suspended particles prior to treatment processes which may otherwise cause serious operational and mechanical problems. Pre-treatment is followed by primary treatment comprising of gravity settlers for the removal of total dissolved solids. Secondary and tertiary treatments are then followed. The environmental agencies have made strict rules and regulations for industries in order to treat their waste water to ppb and ppt levels. The colored organic compounds present in water may resist oxygen diffusion in to the aqueous phase. The presence of these contaminations stops the aerobic action in water as well. Even organic contaminations in small amount destroy the aquatic life. Some of the contaminants are still non-biodegradable which remain present in water for long time. The Royal Commission has set a standard of maximum value of BOD (Biological Oxygen Demand) in industrial effluents in order to remove all contaminations from water which shows the biodegradability of organic compounds while COD (Chemical Oxygen Demand) shows a precise measurement of presence of organic compounds in water [1]. A number of methods have been devised to remove contaminants from water such as adsorption, bacterial action, absorption, membrane, direct oxidation, reverse osmosis etc. In general these methods can be classified into three groups naming physical, chemical and biological. However, ultimate selection has always been challenging in the perspective of economical and process related constraints. Biological way of removing organic contaminants has always been popular due to cheaper in cost. However, with the development of biologically non-degradable organics complex derivatives, other treatment methods have emerged equally competitive.

A study on the fermentation of waste water of cassava was conducted. This method should be utilized on industrial scale for source of amylase. Treated waste water can be reused for different applications. Israel is using 70% of treated waste water for agriculture purpose. Treated waste water can also be used for drinking purposes as well, however many illness causing pathogens still exist in waste water. The 150 pathogens have been reported which may present in waste water however, with the passage of time more are being discovered [2]. There are biological, physical and chemical methods to treat waste water. Different systems can be designed like primary, secondary and tertiary treatment by combining any of these methods. Traditional water treatment processes are somehow restricted to destroy toxic and biologically non-degradable organic pollutants such as berbicides, pesticides and endocrine disrupting compounds which are found with relatively high concentrations in the aquatic environment. In addition to synthetically manufactured organic derivatives, these are released by various sources such as cow manure, sewage and solvents used in dry cleaning chemicals and detergents.

The study of electrochemical oxidation was started in 19th century when the dissociation of cyanide into its ions was studied. In the last twenty years, the research has been focused to enhance the power of oxidants used for different industrial effluents on different operating conditions to improve the efficiency of the process. The anodic oxidation is an important method of electrochemical oxidation. High voltage is used with anode made of different materials like Pt. and BDD (boron doped diamond) etc. to generate hydroxyl radicals. The hydroxyl radical is an important oxidizing agent that reacts with organic compounds to produce carbon

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dioxide, water and inorganic ions. In this process, organic compounds in aqueous solutions are degraded by anodic process. Therefore, an electrochemical oxidation technique is widely being used for multiple industrial effluents. The efficiency of this process depends on various factors. For direct oxidation process, temperature does not have a significant impact on process output however, for meditate processes; temperature has its importance. The contributing factors are pH of the solution, time of oxidation, concentration of electrolyte, and concentration of required contaminants to be extracted. The material of which electrode is made is very important. The material should have following properties:

1) It should be highly electrically conductive.
2) It should have less cost to life ratio.

It should be physically and chemically stable with strong resistance to corrosion and erosion. The electrochemical oxidation has many benefits over other wastewater treatment technologies. Multiple industrial effluents can be treated using this method. The temperature and pressure conditions required for this method were reported to be comparatively low [3]. It is being practiced in a range of industrial effluents such as pulp and paper, petrochemical, pharmaceutical, textile and tanneries. It is also being used for Food industry as well like olive oil and dairy manure. [4]. Because of presence of sodium chloride in textile dyes the process of electrochemical oxidation is very easy to use without any addition of chemicals. The mechanism of electrochemical reactions involved is considered to be complex [5]. Although bye the use of biological treatment, the maximum amount of colored contaminations from waste water can be extracted but certainly there are also some drawbacks. These biological treatments are very friendly and cheap. Anaerobic decolourisation of azo dyes generates amines which have dangerous effects on living organisms in water [6]. Electrolyte solution is prepared by adding $NaSO_4$ or H_2SO_4 OR NaCl. In order to avoid possibility of formation of toxic intermediates, NaCl is preferred. However, few drops of HCl may be added in order to control the solution pH. It was suggested that electrode material should have high electrochemical activity [7]. The function of electrode is to produce large amount of free radicals as a result of electrolysis and permits mineralization of the organic compound.

The objective of this study was to investigate the effect of current density, electrochemical treatment time and initial dye concentration on electrochemical degradation (removal) of methyl blue from its aqueous solution through electrochemical potential.

II. Materials and Methods

Stock solution of methylene blue (with purity 99%) was prepared in distilled water. The brine solution (1% w/w) was prepared in distilled water and acidified at pH 2 by adding few drops of HCl. The acidified brine solution was used as catholyte. The aqueous solutions of methylene blue were analyzed using UV/Vis spectrophotometer (Perkin Elmer Lambda 25). The photometric analysis was conducted at a lambda max of 660 nm. [6]

The electrochemical oxidation of methylene blue was conducted in an electrochemical cell as shown in Fig. 1. The cell comprised of two compartments naming anodic and cathodic as show in Fig. 1-Fig. 4 below. The anode was made of graphite and the cathode was made from a perforated sheet of stainless steel. Both the compartments were separated by placing a poly-ethylene based membrane (DARAMIC 350). The cathodic and anodic compartments were filled with catholyte and methylene blue solution respectively. The methylene blue solution was filled with a known concentration and after the treatment the remaining concentration was determined using spectrophotometer. After filling the said solutions in both the compartments, the electrodes were connected to a DC power supply. The effect of initial concentration, current density and treatment was studied with reference to the percent removal of methylene blue from its aqueous solution.

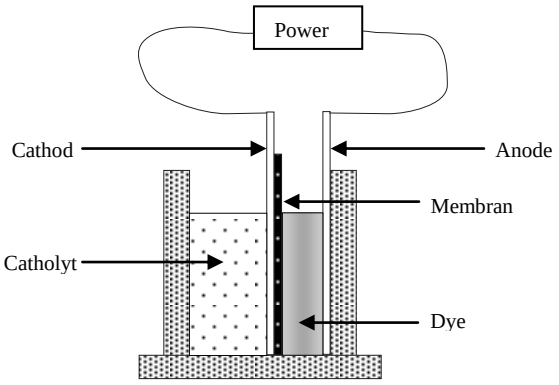

Fig. 1. Electrochemical cell used for electrochemical oxidation of methylene blue dissolved in water.

III. Results and Discussions

In order to study the effect of electrochemical treatment time on dye removal, series of experiments were conducted for which a current density of 0.002 A/cm^2 and a concentration of 100 mg/L was maintained and kept constant for all experiments. The initial pH of dye solution was found to be at around 2. The result is shown in the Fig. 2 below. It is evident in Fig. 2 that dye removal is in direct proportion to the treatment time. The effect of treatment time was studied up to a maximum of 60 min. Although, a treatment time of 40 min was found to be optimized for getting maximum dye removal through electrochemical oxidation. However, a treatment time of 30 min was selected as there was not a significant difference in dye against a treatment time of 40 min [8].

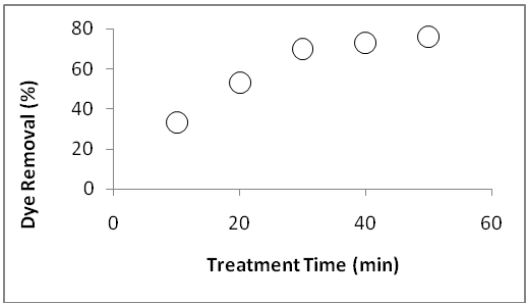

Fig. 2. Effect of treatment time on dye removal (%).

Based on these results, a treatment time of 30 min was selected for remaining experiments. It is notable that a sharp increase in dye removal was obtained in between the treatment time of 10-30 min and beyond this range there was a gradual increase in dye removal as a function of treatment time. It may be speculated due to some unwanted or side reactions which may proceed at longer treatment times. However, in order to validate this hypothesis, further research work is required [8]. These results were found consistent when compared with results as reported in past [9]-[14].

Fig. 3 shows the effect of initial dye concentration on its %-removal through electrochemical oxidation. A current density of 0.002 A/cm^2 was maintained for a treatment time of 30 min. The initial pH of dye solution was found to be 2. An increase in dye removal was found with an increase of initial dye concentration. The effect of initial concentration was studied up to a range of 140 mg/L of dye solution. Lower dye concentrations might cause total dye removal and therefore, slightly higher range of dye solution was selected in order to carry out these experiments. A maximum of 78% dye removal was found against initial dye concentration of 140 mg/L and a minimum of 68% dye removal was observed at an initial concentration of 100 mg/L [8].

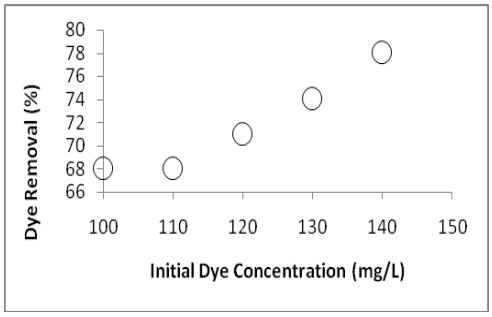

Fig. 3. Effect of initial dye concentration on dye removal through electrochemical oxidation [7].

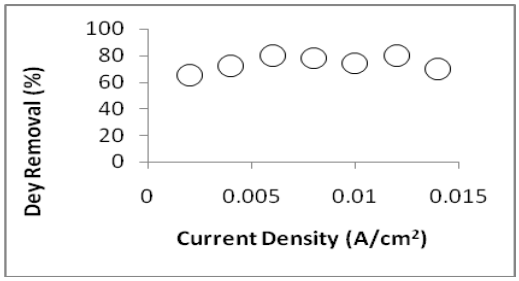

Fig. 4. Effect of current density on dye removal through electrochemical oxidation.

Experiments were conducted in order to investigate the effect of current density on dye removal through electrochemical oxidation. Fig. 4 presents the data points obtained through experiments. A slight increase in dye removal was noticed with an increase of current density up to a value of 0.008 A/cm^2 and beyond this range no significant change was noticed. High current density values may lead towards the formation of by-products by diminishing the actual dye removal however; it is speculation which may not be true. In order to validate the actual reason that why there was no further increase in dye removal beyond current density value of 0.008 A/cm^2. Further research work is recommended in order to investigate the hypothesis [8]. The effect of current density on the dye removal was found to be consistent with compared with the cased reported for the removal of acid violet 17 using modified graphite based adsorbent material [9]-[14].

Significant results on electrochemical regeneration have recently been reported which explained the exploitation of electrochemical oxidation of contaminating organic species adsorbed on the surface of graphite based adsorbents. The investigations revealed that breakdown products might formed during the electrochemical regeneration process of dissolved organic species. These breakdown products may include in liquid or gaseous form. The previous work was reported for the adsorption of various organic pollutants on the surface of solid graphite flake material followed by electrochemical regeneration. During electrochemical regeneration, electrochemical oxidation was supposed to be carried out in order to mineralize the adsorbed organic molecules on the surface of graphite intercalation based adsorbent material. However, further investigations are still in progress and authors assume this work to be of worth publishing once investigations have been accomplished. Similarly, during the electrochemical oxidation of methylene blue as investigated in an electrochemical cell as described in previous section might lead the formation of breakdown products. However, the formation of breakdown products which assumed to be formed have not been investigated as not being the scope of this work and will be reported in later stage (15-18). However, no formal study has yet been reported for the investigation of breakdown products generated during direct electrochemical oxidation of organic pollutants dissolved in water. It requires further investigations and therefore, will be addressed in separated project as not being under the scope of this research work.

IV. Conclusions

The study comprised of methylene blue (dye) removal from its aqueous solution using electrochemical oxidation method. An electrochemical cell consisting of two compartments was used for this purpose. The results revealed that % removal of the methylene blue from aqueous solution was in direct proportion with its initial concentration. A treatment time of 40 min and current density of 0.06 A/cm^2 showed a maximum dye removal of up to 80% and no significant change in dye removal was observed beyond these limits.

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