

Evaluation of Low Cost Electrodes for Electrochemical Degradation of Pharmaceuticals: A Case Study on Methylene Blue

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Abstract

The possibility of water contamination by pharmaceuticals has greatly increased due to the increased and widespread manufacture together with extensive use of these compounds. Humans and ecosystems undergo significant risk upon chronic exposure to these pharmaceuticals and cumulative build-up of these contaminants in the various environmental compartments. Moreover, conventional water treatment methods often cannot degrade these pharmaceuticals. Among different alternative treatment methods, electrochemical degradation (ED), which depends on the generated ions in aquatic medium, has already proved to be a promising and interesting technique for effective oxidation of various organic pollutants. However, choice of electrode material largely contributes to the effectiveness of ED. Consequently costly electrodes had been chosen in most studies significantly decreasing the affordability of the ED process for waste water treatment application. Accordingly the objective of the present work is to evaluate low cost material as electrodes in ED process for degrading pharmaceutical compounds. Iron, aluminum and conductive carbon are the low cost electrode materials examined in the study. Methylene blue (MB) is chosen as a model pharmaceutical. The effect of electrode materials with varying pollutant concentration, current density and concentration of conductivity modifier are thoroughly examined using common salt and alum as conductivity modifier to find out the optimum condition for decolorization of MB. The results showed that 95 percent decolorization of 100 mg/l MB can be achieved at 10 minutes in ED process with conductive carbon electrode using 5g/l common salt as conductivity modifier. The electrodes are characterized by gravimetric and microscopic analysis. Negligible loss of electrodes mass but change in surface composition of electrodes has been observed for ED process associated with significant mineralization of pharmaceuticals. The novelty is that the present work demonstrates an alternative decolorization (and mineralization) option using low cost electrode materials which can significantly enhance the affordability and acceptability of the ED process for degrading pharmaceutical pollutants.

Index Terms— degradation, electrochemical, electrodes, low cost materials, methylene blue, pharmaceutical, pollutants, water.

1 INTRODUCTION

THE contamination of water by pharmaceuticals has greatly increased due to widespread manufacture and extensive use of pharmaceutical compounds. In addition, conventional water treatment methods often cannot degrade the pharmaceutical compounds. The importunate exposure to the pharmaceuticals and growing accumulation in the various environmental compartments pose momentous threat to humans and ecosystems [1-7]. Different treatment techniques, such as flocculation combined with flotation, ion exchange, membrane filtration, adsorption and coagulation have been evaluated in earlier studies for degradation of pharmaceuticals [8-10]. However, these treatment techniques either have operational problem or are expensive [11-14]. Among alternative treatment options, electrochemical degradation (ED), holds great potential for degradation of various organic pollutants, including pharmaceuticals [15-17]. But, the choice of electrode material has significant influence on the effectiveness of ED.

The costly electrode materials had been largely investigated in various studies for ED of organic pollutants which significantly decrease the affordability of the ED process for waste water treatment application [18-27]. Accordingly the objective of the

present work is to evaluate low cost material as electrodes in ED process for degrading pharmaceutical compounds. Iron, aluminum and conductive carbon are the low cost electrode materials examined in the study. Methylene blue (MB), 3,7-bis(Dimethylamino)-phenazathionium chloride trihydrate, is chosen as a model pharmaceutical and the effect of electrode materials with varying pollutant concentration, current density and concentration of conductivity modifier are thoroughly investigated using common salt as electrolyte (conductivity modifier) to find out the optimum condition for decolorization of MB.

2 MATERIALS AND METHODS

The electrode materials, iron (sheet with 0.5 mm thickness) and aluminum (sheet with 0.25 mm thickness) are procured from local market (commercial grade). A carbon prepared in house with low resistivity (of 2.5 ± 0.35 ohms/cm) is evaluated as electrode materials. Electrodes are fabricated in-house (institute workshop). The ED experimental setup consists of a regulated DC Power supply (A) connected with the electrodes (B) with an insulating copper wire (C). The electrodes (B) were then dipped into one electrolytic cell (D), filled by the experimental liquid (E). The experimental solution was continuously stirred with the help of a magnetic stirring bar (F) and a magnetic stirrer (G). A regulated DC Power supply (LQ6324, Aplab, Thane, India) capable of varying the current from 0-2 ampere (A) was used for applying potential across electrodes. A 200 ml open cylindrical vessel with electrodes with effective cross sectional area of 4000 mm^2 (0.004 m^2) is chosen for the experiment, such that the current density was kept at 250, 375 and 500 A/m^2 . The separation distance between electrodes was maintained at 20 mm. The electrolyte or conductivity modifier, namely common salt, was examined at

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molar concentration of 2.5 g/l, 5 g/l, 7.5 g/l. The concentration of MB (pollutant) was varied from 100 mg/l to 500 mg/l. All experiments are conducted under ambient condition under stirring at rate 200 rpm using magnetic stirrer (5MLH, Remi, Mumbai, India). The experimental parameters were examined in one factor at a time approach. The iron, aluminum and carbon electrodes before and after ED was characterized using a field emission scanning electron microscope (SEM) (Quanta 200, FEI Company, Hillsboro, OR) and energy dispersive spectroscopy (EDS) with GENESIS material characterization software (EDAX Inc., Mahwah, NJ) to analyze the stoichiometric composition of the electrodes. The decolorization of MB was monitored at 664 nm (λ_{max}) in UV/Vis Spectrophotometer (Lamda35, Perkin Elmer, India) with Winlab software (Perkin Elmer, India) and mineralization is studied using total organic carbon (TOC) analyzer (TOC-LPH, Shimadzu Asia Pacific, Singapore). The concentrations were computed through in-house calibration from respective instrumental measurements. The computed decolorization kinetics was used to compute the apparent rate constants for oxidation of MB are monitored. All chemicals used in the study are of research grade and obtained from Merck, India. The water used in the study is of ultra-pure grade (>18Mohm resistivity) generated in house (Option Q, Elga, India).

3 RESULTS AND DISCUSSION

3.1 Kinetic study

The decolorization profile of MB for a pollutant concentration is presented in Figure 1a. A constant decrease of absorbance at λ_{max} was observed in electrochemical degradation (ED) of MB. The decolorization data of MB well fitted the first order kinetics (Fig. 1b). The ED of MB at different concentration level followed the same rate order. Mineralization study was conducted to confirm the degradation of MB associated with the decolorization. The mineralization study confirmed the degradation of MB during decolorization. The extent of mineralization well correlated with decolorization level observed at different parameter settings. Highest mineralization was recorded for 200 mg/l MB in 10 min time at 500 A/m² current density with carbon electrodes.

3.2 Effect of current density

The current density for ED was varied by changing the applied current across electrode. The effect of current density for ED was studied for 100 mg/l MB with 5 g/l common salt using carbon electrode. The current density was varied from 250 A/m² to 500 A/m². Increase in current density increases the availability of electron at the electrode surface. The electrons mediate the decolorization of MB. Accordingly, the decolorization of MB was observed to increase linearly with the increase of current density (Figure 2a).

3.3 Effect of MB concentration

The effect of MB concentration on ED was studied at 500 A/m² current density with 5 g/l common salt for MB concentration varying from 100 mg/l to 500 mg/l. The decolorization of MB increases with increase in MB concentration from 100 mg/l to 200 mg/l, however on further increase in MB concentration decolorization decreases (Figure 2b). Increase in MB concentration initially increases the utilization of electrons but at higher concentrations available electrons at a specific current density limit the decolorization of the MB.

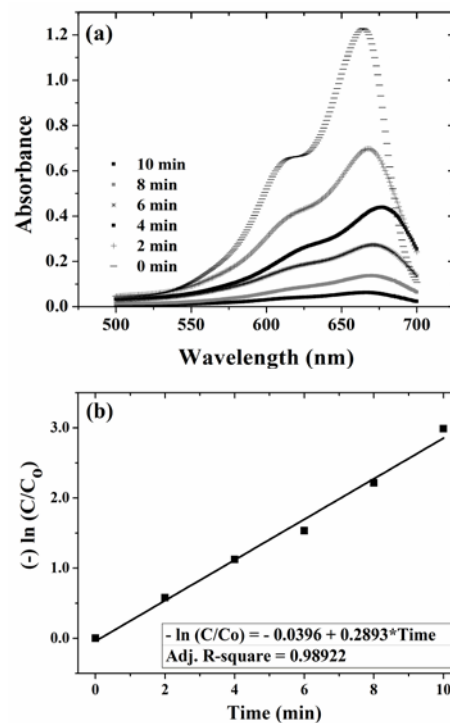


Figure 1. (a) Decolorization profile of MB and (b) rate kinetics of decolorization of MB using carbon electrodes with 5 g/l common salt at 500 A/m² current density for 100mg/l MB concentration.

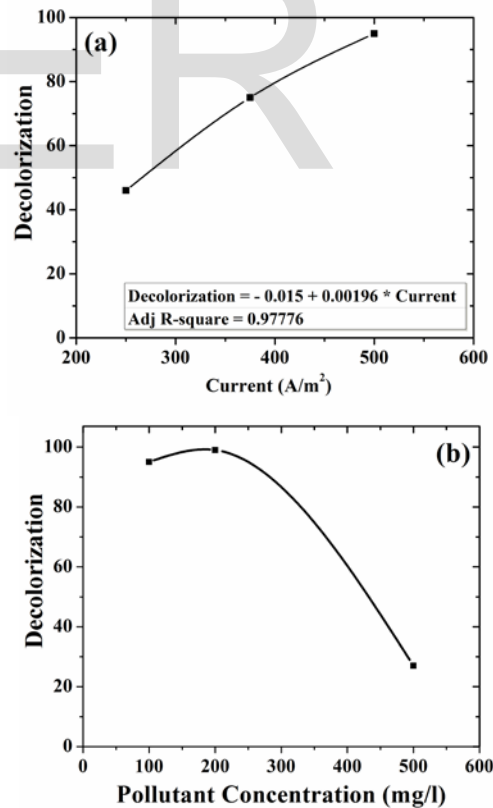


Figure 2. The effect of - (a) current density at 100 mg/l MB and (b) MB concentration at 500 A/m² on decolorization percent with 5 g/l common salt using carbon electrode.

3.4 Effect of electrolyte concentration

The decolorization of 100 mg/l MB was studied at 500A/m² current density with common salt as electrolyte at three different concentrations varying from 2.5g/l to 5g/l to investigate the effect of electrolyte concentration on decolorization and apparent rate. The optimum electrolyte level for ED was identified at 5 g/l concentration (Figure 3a). Increase in electrolyte concentration beyond 5 g/l hinder the decolorization of MB. At higher concentration of common salt (electrolyte), the abundant chloride ions compete with MB for electrons at electrode which impede the decolorization of MB.

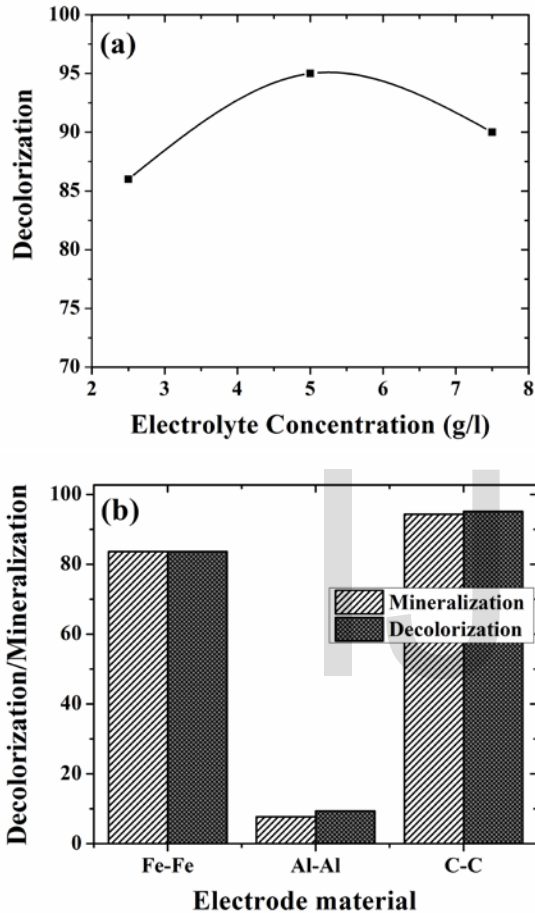


Figure 3. The effect of - (a) electrolyte concentration and (b) electrode material on decolorization of 100 mg/l MB at 500 A/m² current density.

3.5 Comparison of electrodes

The ED studies were performed with electrodes constructed of different electrode materials at 500A/m² current density with 100 mg/l MB using 5 g/l common salt as electrolyte. Among the three electrode materials, namely, iron, aluminum and carbon, that were evaluated, carbon recorded a maximum of 95% decolorization within 10 minutes time, followed by iron and later by aluminum (Figure 3b). The mass loss of carbon and aluminum electrodes was comparatively lower than iron and a maximum of 2% mass loss was recorded for iron electrode (Table 1). Blank experiment (without current) were conducted to determine the absorption based loss of MB. For all the three electrodes the absorption based loss of MB was negligible, maximum being around 4% for carbon.

3.6 Characterization of electrodes

The electrodes (iron, aluminum and carbon) before and after electrochemical degradation was characterized by EDS to determine the stoichiometric composition. The EDS spectrum showed that before electrochemical treatment the electrodes were primarily constituted of the respective element, namely, iron, aluminum and carbon. However stoichiometric fraction of oxygen at the electrode surface increased after treatment (Table 1). The increment in weight percent of oxygen at electrode surface is about 20% for iron, 8% for aluminum, and 14% for carbon. The presence of oxygen as constituent at electrode surface confirmed the formation of metal oxo-ions for iron and aluminum and oxidative degradation mechanism of MB in the ED process [28 -30]. The decrease in weight percent of constituent element was lowest for aluminum (7%) and highest for iron (18%). The weight proportion of constituent element (carbon) was reduced around 15% for carbon electrode after ED process.

TABLE 1: The effect of electrochemical degradation on electrode for different electrode material

Electrode materials	ED parameter	Anode Mass loss after treatment	Anode composition	
			Before treatment	After treatment
Iron (Fe)	500 A/m ² , 60 min	2 %	Fe 78.6% O 15.2%	Fe 60.1% O 34.7%
Aluminum (Al)	500 A/m ² , 60 min	< 1%	Al 75.5% O 19.4%	Al 67.8% O 27.1%
Carbon (C)	500 A/m ² , 60 min	< 1%	C 86.1% O 8.0%	C 71.3% O 21.6%

TABLE 2: Comparative study of electrochemical degradation with the literature.

Electrode materials	Parameter	Decolorization	Reference
Platinum on activated carbon	0.1A, 20 min, 0.1 mM NaCl, pH 3-5	97.6%	Li et al, 2013
Platinum	0.6V, 90 min, 0.5M KCl, pH 2	72%	Hasnat et al, 2014
Zinc, Copper, Platinum	40 mA/cm ² , 0.2M NaCl,	Zinc 56% Copper 43% Platinum 50%	Rao and Venkatarangaiah, 2014
Iron	500 A/m ² , 10 min, 5 g/L NaCl	92.5%	Present study
Carbon	500 A/m ² , 10 min, 5 g/L NaCl	95%	Present study

3 CONCLUSIONS

The effects of different operating variables, namely, current density, electrolyte concentration and pollutant concentration on decolorization of a model pharmaceutical compound, MB, were evaluated in the study in one-factor-at-a-time approach. The decolorization of MB was correlated with mineralization to confirm the degradation of the model pollutant at each factor level setting. Increased current density linearly effected increased the decolorization of MB. The maximum decolorization of MB was recorded at optimum level of electrolyte (common salt) concentration of 5 g/l and pollutant (MB) concentration of 200 mg/l. Among three low cost electrode materials evaluated in this study, carbon was observed to have highest decolorization and mineralization percent. 99% decolorization was recorded in the ED process for 200 mg/l MB concentration at 500A/m² current density with 5 g/l common salt electrolyte in 10 minutes using carbon electrode. The extent decolorization of MB reported in this study is well comparable with that reported in the literature for expensive platinum electrode. Thus the present study demonstrated an alternative treatment option for recalcitrant and hazardous pollutants, such as, for pharmaceuticals contaminants, using low cost electrode materials in ED process. The application of low cost materials as electrode can significantly enhance the affordability and acceptability of the ED process as alternative treatment for various contaminants including pharmaceuticals.

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REFERENCES

- [1] Panizza, M., et al. *Sep. Purif. Technol.*, 2007. 54(3): p. 382-387.
- [2] Heberer, T. *Toxicol. Lett.* 2002. 131(1-2): p. 5-17.
- [3] Jones, O.A., et al. *Trends Biotechnol.*, 2005. 23(4): p. 163-167.
- [4] Stackelberg, P.E., et al. *Sci. Total Environ.*, 2004. 329(1-3): p. 99-113.
- [5] Fent, K., et al. *Aquatic Toxicol.* 2006. 76(2): p. 122-159.
- [6] Mei Fun Choong, A., et al. *J. Toxicol. Environ. Health, Part A*, 2006. 69(21): p. 1959-1970.
- [7] Bendz, D., et al. *J. Hazard. Mater.*, 2005. 122(3): p. 195-204.
- [8] Ong, S.-T., et al. *Water*, 2011. 3(1): p. 157-176.
- [9] Robinson, T., et al. *Biores. Technol.*, 2001. 77(3): p. 247-255.
- [10] Hassan, M., El Jamal, M. *Portugaliae Electrochimica Acta*, 2012. 30(5): p. 351-359.
- [11] Aleboye, A., et al. *Sep. Purif. Technol.*, 2005. 43(2): p. 143-148.
- [12] Bali, U., et al. *J. Hazard. Mater.*, 2004. 114(1-3): p. 159-166.
- [13] Dutta, K., et al. *J. Hazard. Mater.*, 2001. 84(1): p. 57-71.
- [14] Muthukumar, M., et al. *Dyes Pigments*, 2004. 63(2): p. 127-134.
- [15] Chen, G. *Sep. Purif. Technol.*, 2004. 38(1): p. 11-41.
- [16] Fernandes, A., et al. *Dyes Pigments*, 2004. 61(3): p. 287-296.
- [17] Sanromán, M.Á., et al. *J. Chem. Technol. Biotechnol.*, 2004. 79(12): p. 1349-1353.
- [18] Cañizares, P., et al. *Ind. Eng. Chemistry Res.*, 2002. 41(17): p. 4187-4194.
- [19] Comninellis, C., Pulgarin, C. *J. Appl. Electrochemistry*, 1993. 23(2): p. 108-112.

- [20] Feng, J., et al. *J. Electrochem. Soc.*, 1995. 142(11): p. 3626-3632.
- [21] Gandini, D., et al. *J. Appl. Electrochemistry*, 2000. 30(12): p. 1345-1350.
- [22] Gherardini, L., et al. *J. Electrochem. Soc.*, 2001. 148(6): p. D78-D82.
- [23] Panizza, M., Cerisola, G. *Electrochimica Acta*, 2005. 51(2): p. 191-199.
- [24] Polcaro, A., et al. *J. Appl. Electrochemistry*, 1999. 29(2): p. 147-151.
- [25] Polcaro, A.M., et al. *Electrochimica Acta*, 2004. 49(4): p. 649-656.
- [26] Stucki, S., et al. *J. Appl. Electrochemistry*, 1991. 21(2): p. 99-104.
- [27] Tahar, N.B., Savall, A. *J. Appl. Electrochemistry*, 1999. 29(3): p. 277-283.
- [28] Daneshvar, N., et al. *J. Hazard. Mater.*, 2006. 129(1-3): p. 116-122.
- [29] Kobya, M., et al. *J. Hazard. Mater.*, 2003. 100(1-3): p. 163-178.
- [30] Mahesh, S., et al., *Ind. Eng. Chemistry Res.*, 2006. 45(8): p. 2830-2839.