

De-Colorization of Methylene Blue Dye Bearing Waste by Electrocoagulation Technique

Mohammad Abid Muslim Altufaily and Zahraa Ahmed Abedalaama
University of Babylon, Hillah, Iraq

Abstract: This study aims to investigate removal of methylene blue dye from synthetic wastewater using electrocoagulation method. Two electrocoagulation reactors with a new configuration were used in this study. One of them with aluminum electrodes and the other with iron electrodes. The effects of several parameters such as initial pH, detention time initial concentration, current density, electrode surface area and conductivity on the removal efficiency were studied. Experimental results revealed that the removal efficiency using aluminum and iron electrodes increased with the increase of every parameter stated except for the initial concentration. It was found that the optimum conditions for aluminum and iron electrodes were: initial concentration of 10 mg/L, current density of 4 A/m², electrode surface area of 1.3 m², conductivity of 2200 μS/cm and initial pH of 7 and 11 for aluminum and iron electrodes, respectively. The results showed that within 70 min of detention time and at the optimum conditions, the maximum removal efficiency of dye was 93.62 and 97% for aluminum and iron electrodes, respectively. At the optimum conditions, it was found that the energy consumption for dye removal using aluminum and iron electrodes was 0.634 and 0.375 kW.h/m³, respectively.

Key words: Electrocoagulation, iron electrode, aluminum electrode, methylene blue, synthetic wastewater, parameter

INTRODUCTION

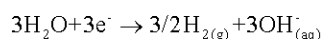
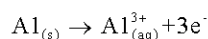
The effluents of many industries (textile, leather, pulp and paper, printing, photographs, cosmetics, pharmaceutical, food) contain dyes which represent an important environmental problem. Textile industry uses large amount of produced dyes in world. Textile industries produce wastewaters that are the source of important pollution problems in environment that need solution. It is estimated that up to 15% of the dyes are released in wastewater due to their limited fixation efficiency. Unused dyes from textile industries must be removed as they represent an undesirable color to water and in some cases they are harmful compounds and can develop dangerous by-products through oxidation, hydrolysis and or other chemical reactions taking place in the waste solution (Alizadeh *et al.*, 2015). Methylene Blue (MB) is an important basic dye and widely used in many industries. MB can cause eye burns and if swallowed it causes irritation with symptoms of nausea, vomiting and diarrhea (Taha *et al.*, 2014). Conventional methods for removal of dyes from wastewaters consist of various combinations of biological, physical and chemical methods. Physical methods such as adsorption and precipitation processes are relatively time-consuming and costly with low efficiency while most chemical methods

such as additions of aluminum sulfate and chlorine can generate secondary pollutants. Although, biodegradation process is cheaper than other methods it is less effective because of the toxicity of the dyes that induces an inhibiting effect on bacterial development (Daneshvar *et al.*, 2003).

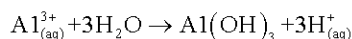
During recent decades, research on electricity applied directly in water treatment has progressed well, making it an attractive method for coagulation or clarification of water, usually known as the electrocoagulation/electrochemical method (Kobya *et al.*, 2003). Electrocoagulation is a complex process involving chemical and physical mechanisms operating simultaneously to remove pollutants from wastewaters. When sacrificial electrodes are used, metal ions are produced (in situ) resulting in the removal of pollutants. The process takes place in three successive stages: formation of coagulants by the oxidation of the sacrificial anode, destabilization of the pollutants, particulate suspension and emulsion breaking, aggregation of the destabilized phases and formation of flocs (Mollah *et al.*, 2004). These flocs can be easily separated either by gravity settling or by electroflotation where the evolved hydrogen gas bubbles at the cathode would enhance flocs growth and their separation by flotation (Elsayed *et al.*, 2013). Aluminum or iron is usually used as

electrodes and their cations are generated by the dissolution of sacrificial anodes upon the application of direct current. The metal ions generated are hydrolyzed to produce metal hydroxide ions (Bensadok *et al.*, 2008).

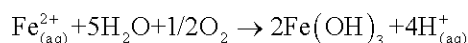
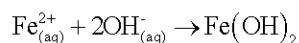
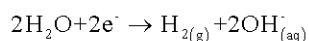
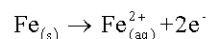
When a DC electric field is applied, the following electrolysis reactions are expected in the vicinity of the aluminum electrodes (Ghosh *et al.*, 2008):



Then, Al^{3+} ion and OH^{-} ions react to generate $\text{Al}(\text{OH})_3$



A similar mechanism has been proposed for the case of iron electrodes (Zaroual *et al.*, 2006):



The formation of gelatinous compounds, $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ is responsible for removal of pollutants by adsorption/complexation process.

Many researchers have been focused on performance of electrocoagulation process in water and wastewater treatment. Phalakornkule *et al.* (2009) conducted a study to investigate the removal of direct dye (Direct Red 23) using electrocoagulation process. Kumar and Sahu (2013) studied the removal of reactive scarlet dye using electrocoagulation process with iron electrodes. Pirkarami and Olya (2017) studied the effects of several factors that affect the removal efficiency of Reactive Red 120. A comparison between aluminum and iron electrodes used in electrocoagulation process for the removal of methylene blue was carried out by Alizadeh *et al.* (2015). The removal of COD, lignin and color from pulp and paper wastewaters was investigated by Aghdam *et al.* (2016).

The objective of the present research is to investigate the performance of continuous electrocoagulation process using two electrocoagulation reactors with a new configuration (large electrode surface area) to remove methylene blue dye. One of the reactors with aluminum

electrodes and the other with iron electrodes. Several parameters such as initial pH, detention time (t) initial concentration (C_0), Current Density (CD), electrode surface Area (As) and conductivity (k) were investigated in term of MB removal.

MATERIALS AND METHODS

Experimental setup: Figure 1 shows a schematic diagram of the pilot plant used in this study. It consists mainly of a rectangular electrocoagulation reactor made of glass and a power supply. The dimensions of the reactor are 65 cm height, 30 cm length, 30 cm width and 5 mm wall thickness. Two electrocoagulation reactors with a new configuration were used in the present study. One of them with aluminum electrodes with 99.43% purity and other with iron electrodes with 99.573% purity. Six vertical and concentric cylinders with diameters of 21.5, 18.5, 15.5, 12.5, 9.5, 6.5 cm are connected together to act as a single cathode. The anode also consists of six vertical and concentric cylinders with diameters of 20, 17, 14, 11, 8, 5 cm also connected together. All the cylinders are perforated, the diameter of each hole is 5 mm and the distance between the holes is 4 cm. The height of all cylinders is 30 cm, the concentric gap between electrodes is 0.75 cm and the thickness of all cylinders is 1 mm (Fig. 2). The effective surface area is 1.3 m² and the anode surface area to effective reactor volume ratio (As/V) is (27.7 m²/m³). Before each run, the cathode is placed in the electrocoagulation reactor, then, the anode cylinders are inserted between the cathode cylinders. The anode and cathode are attached to a power source by using a copper wire. The electrical current was supplied by a power supply (type DAZHENG with range of 0-5 A and 0-30 V). During the experiments, the wastewater flows through the perforated electrodes this leads to wastewater turbulence inside the reactor which leads to better mixing and increasing mass transfer, thus, leading to increased removal of contaminants.

Chemicals: Methylene Blue (MB) with formula ($\text{C}_{16}\text{H}_{18}\text{ClN}_3 \cdot \text{XH}_2\text{O}$ [X = 2, 3]) and molecular weight (319.86 mole) was used in this study to produce synthetic wastewater. Solutions of dye were prepared before each experimental run by dissolving appropriate amounts of MB in a known volume of tap water. The initial pH of the wastewater was adjusted to the required value using HCl or NaOH solutions. For conductivity adjustment, NaCl salt was added to the wastewater (Fig. 2).

Procedures and analysis: Prior to starting each run, the electrodes were washed carefully with diluted HCl to remove the oxide layer from the surface and then rinsed

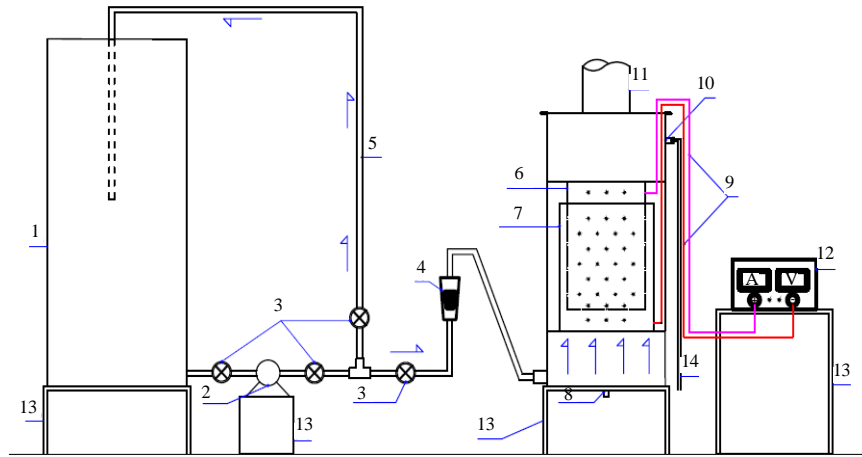


Fig. 1: The pilot plant used in the study: 1) Storage tank; 2) Pump; 3) Gate valve; 4) Rotameter; 5) The return pipe; 6) Anode electrode; 7) Cathode electrode; 8) Drain valve; 9) Wires; 10) Effluent valve (sampling port); 11) Pipe for gaseous by-product vent; 12) Power supply; 13) Stand and (14) Tube to drainage hole

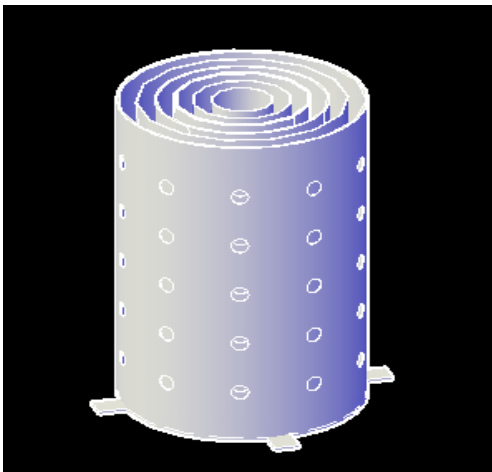


Fig. 2: Schematic diagram of the electrodes used in the study

with water before dipping in the electrocoagulation reactor to remove any solids accumulated on the surfaces. The experiments were carried out by introducing the wastewater into the storage tank. The wastewater was pumped by centrifugal pump from the storage tank to the electrocoagulation reactor and the desired flow rate was achieved by adjusting the valve in the feed pipe. The DC power supply was switched on as soon as the wastewater fills the electrocoagulation reactor. The desired current was achieved easily by manipulating the dial for control of current in the power supply. To monitor the progress of MB removal process, samples were collected from the reactor at 10 min intervals and allowed to be settle for 30 min and then analyzed by using (UV-Visible

spectrophotometer). The concentration of dye was determined using the initial calibration curve which was recorded after spectrophotometric measurement of the solution absorbance for dye standard concentration at the specific wavelength corresponding to the maximum absorption of dye $\lambda_{max} = 663.5$ nm. The removal efficiency (R%) was determined using the following equation:

$$R (\%) = \left[\frac{(C_0 - C)}{C_0} \right] \times 100 (\%)$$

where, C_0 and C are the initial and final concentration, respectively. The energy consumption (E) was calculated as follows (Ghosh *et al.*, 2011):

=

Where:

- E = The energy consumption (kWh/m³)
- I = The current (A)
- V = The Voltage (V)
- t = The detention time (h)
- Vol. = The volume of solution (m³)

RESULTS AND DISCUSSION

Effect of initial pH and detention time: This parameter (pH) significantly influences the performance of electrocoagulation process as it governs the speciation of metal hydroxides. To investigate the effect of initial pH on MB removal, a series of experiments were conducted

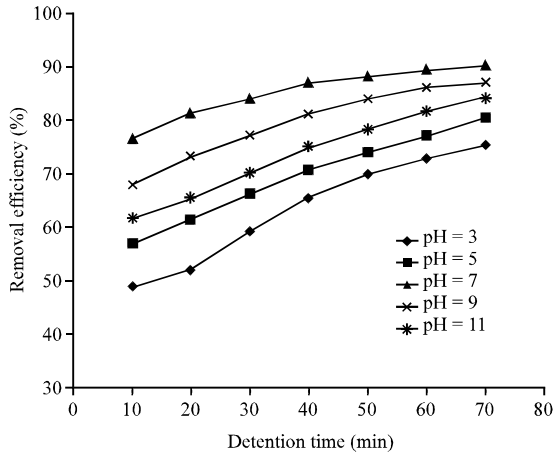


Fig. 3: Effect of initial pH on dye removal efficiency using aluminum electrodes ($C_0 = 10 \text{ mg/L}$, $CD = 4 \text{ A/m}^2$, $Q = 40 \text{ L/h}$, $As = 1.3 \text{ m}^2$, $k = 1100 \text{ }\mu\text{S/cm}$)

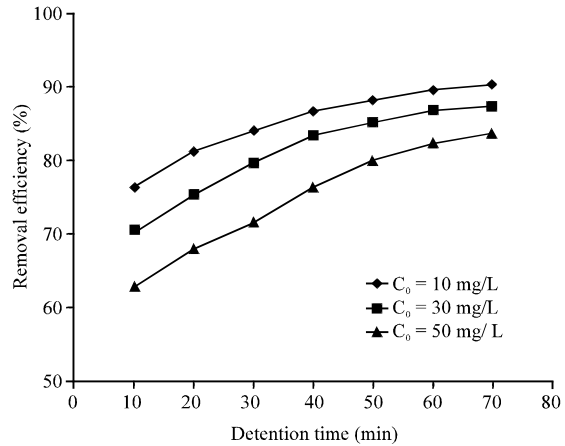


Fig. 5: Effect of initial dye concentration on dye removal efficiency using aluminum electrodes ($\text{pH} = 7$, $CD = 4 \text{ A/m}^2$, $Q = 40 \text{ L/h}$, $As = 1.3 \text{ m}^2$, $k = 1100 \text{ }\mu\text{S/cm}$)

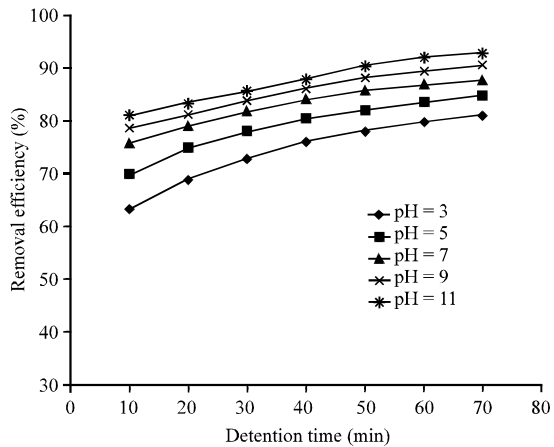


Fig. 4: Effect of initial pH on dye removal efficiency using iron electrodes ($C_0 = 10 \text{ mg/L}$, $CD = 4 \text{ A/m}^2$, $Q = 40 \text{ L/h}$, $As = 1.3 \text{ m}^2$, $\kappa = 1100 \text{ }\mu\text{S/cm}$)

using synthetic wastewaters with different initial pH values 3, 5, 7, 9 and 11. While, the other parameters were kept constant.

Figure 3 shows that, dye removal efficiency using (Al) electrodes increased as the initial pH increased from 3-5 to reach its maximum value at pH 7 and then declined with further increase of pH. This change of dye removal with the initial pH is mainly attributed to the predominant species of aluminum where in $\text{pH} = 7$, the majority of aluminum coagulants were formed, especially $\text{Al}(\text{OH})_3$ which has a minimum solubility at this pH (Fagnekar and Mane, 2015).

Figure 4 shows that, dye removal efficiency using (Fe) electrodes increased as the initial pH increased to

reach its maximum value at pH 11. This result is discussed as follows, iron dissolves as Fe^{+2} which is a poor coagulant compared to Fe^{+3} , due to higher solubility of its hydroxides. If the pH is alkaline and there are oxidants such as oxygen, present in sufficient concentration, Fe^{+2} is oxidized in bulk solution to Fe^{+3} which is a good coagulant, hence, increase the removal efficiency (Vepsalainen, 2012).

Figure 3 and 4 also show that the removal efficiency for both electrodes increased as the detention time increased. A fast increase in the removal efficiency was occurred in the first 10 min. After 10 min, the removal efficiency increased gradually with increasing detention time. The removal efficiency depends directly on the concentration of metal ions (Al^{+3} and Fe^{+3}) produced on the electrodes. Based on Faraday's law increasing the detention time leads to an increase in both the concentration of metal ions and the accumulation of hydroxide flocs. After 70 min detention time, the maximum removal efficiency using (Al) electrodes was found to be 90.1% at pH 7 while the maximum removal efficiency using (Fe) electrodes was found to be 92.5% at pH 11.

Effect of initial concentration: The influence of initial concentration on the removal efficiency was examined using synthetic wastewaters with initial concentration of 10, 30 and 50 mg/L. The other operating parameters were kept constant. Figure 5 and 6 shows that the removal efficiency of dye for both aluminum and iron electrodes decreased with increasing initial concentration from 10-50 mg/L. This result is explained as follows, constant amounts of aluminum or iron ions are dissolved from the anode at the same detention time and current density

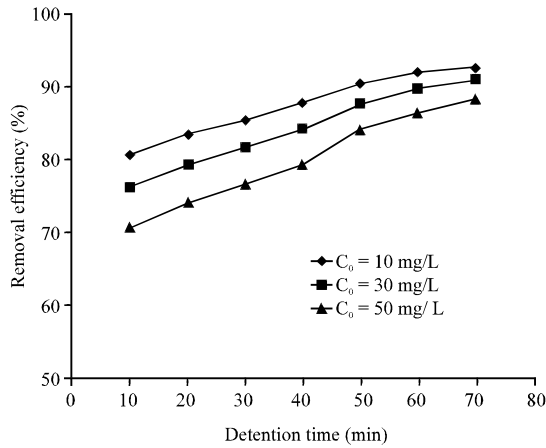


Fig. 6: Effect of initial dye concentration on dye removal efficiency using iron electrodes (pH = 11, CD = 4 A/m², Q = 40 L/h, As = 1.3 m², k = 1100 μS/cm)

(according to Faraday’s law) this means constant amounts of coagulants are produced in the electrocoagulation reactor for all initial dye concentrations and the active surface area for these coagulants becomes totally saturated with molecules of dye with no more active surface left to capture further molecules at high initial concentrations (Hashim *et al.*, 2017). After 70 min and at initial concentration of 10 mg/L, the maximum removal efficiency was found to be 90.1 and 92.5% using aluminum and iron electrodes, respectively.

Effect of current density: Current density is one of the main important parameters which influences electrocoagulation process. According to Faraday’s law, CD highly influences the dosage of coagulants and hence the removal efficiency. Current density also influences the generation rate of bubbles:

$$X = \frac{ItM}{ZF}$$

Where:

- X = The released coagulants from the anode (g)
- I = The applied current (A)
- t = Detention time (sec)
- M = The molecular weight of electrode metal (g/mol)
- Z = The number of electrons
- F = Faraday’s constant (96487 C/mol)

The effects of different current densities 0.77, 1.54, 2.31, 3.1 and 4 A/m² on the removal efficiency were studied. The other parameters were kept constant.

The variation of dye removal efficiency with the studied current densities is shown in Fig. 7 and 8. It is well noted that dye removal efficiency increased noticeably

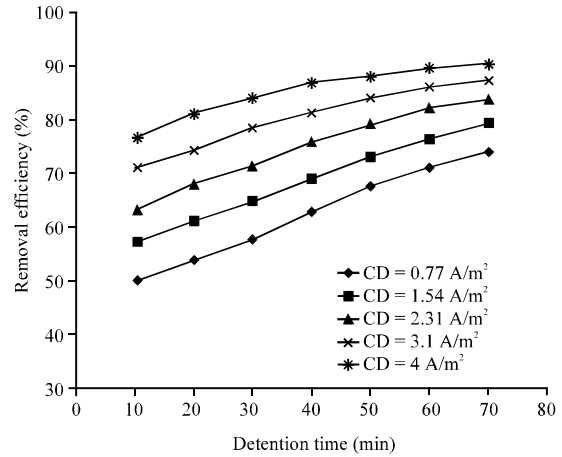


Fig. 7: Effect of current density on dye removal efficiency using aluminum electrodes (pH = 7, C₀ = 10 mg/L, Q = 40 L/h, As = 1.3 m², k = 1100 μS/cm)

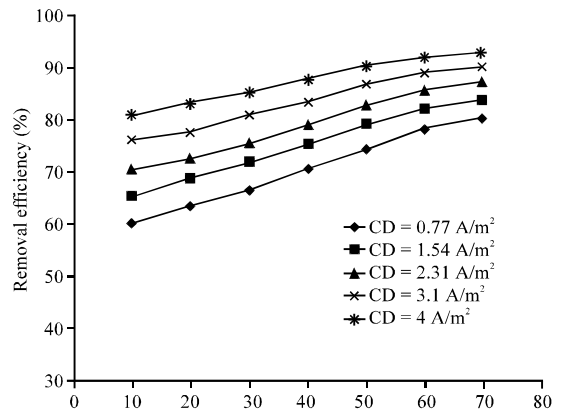


Fig. 8: Effect of current density on dye removal efficiency using iron electrodes (pH = 11, C₀ = 10 mg/L, Q = 40 L/h, As = 1.3 m², k = 1100 μS/cm)

when the current density increased from 0.77-4 A/m². The increase in the removal efficiency with increasing current density is attributed to the increase of the electrophoretic motion under the applied electrical field; beside to the increase of the dissolved coagulants (according to Faraday’s law). The increase of both electrophoretic motion and the dissolved coagulants will enhance charge neutralization of pollutant particles which improve their removal. In addition, as current density increases hydrogen bubble generation rate increases and bubble size decreases. The generated bubbles improve the mixing of Al³⁺ and Fe³⁺ hydroxides with pollutant molecules which could improve floc formation and their subsequent flotation (Merzouk *et al.*, 2009). It was found that after 70 min of detention time and at

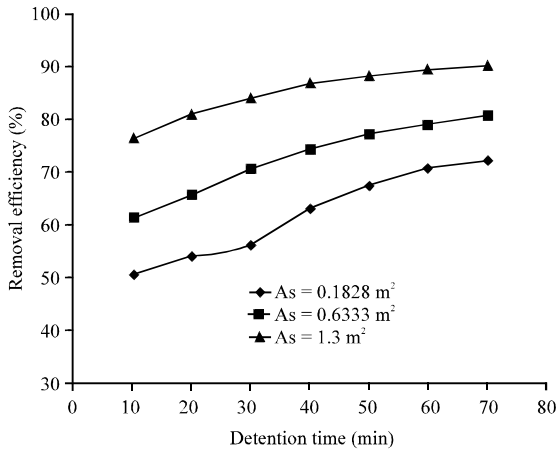


Fig. 9: Effect of electrode surface area on dye removal efficiency using aluminum electrodes (pH = 7, C_o = 10 mg/L, CD = 4 A/m², Q = 40 L/h, k = 1100 μS/cm)

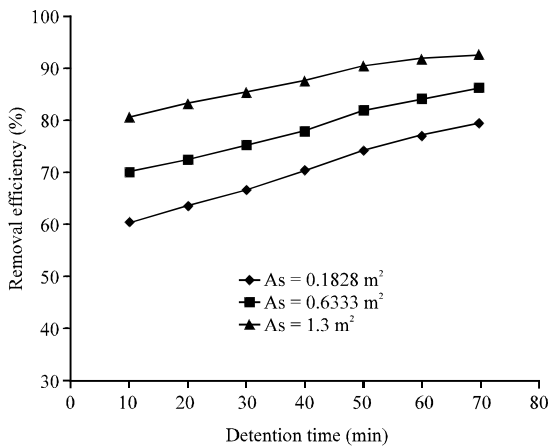


Fig. 10: Effect of electrode surface area on dye removal efficiency using iron electrodes (pH = 11, C_o = 10 mg/L, CD = 4 A/m², Q = 40 L/h, k = 1100 μS/cm)

4 A/m², the maximum removal efficiency was 90.1 and 92.5% for (Al) and (Fe) electrodes, respectively.

Effect of electrode surface area: Electrodes with three different surface areas 1.3, 0.6333 and 0.1828 m² were used to investigate the influence of electrode surface area. The surface area of 0.6333 m² was obtained by removing the two outer cylinders from the electrode while the surface area of 0.1828 m² was obtained by removing the four outer cylinders from the electrode. The other operating parameters were kept constant.

As shown in Fig. 9 and 10, the removal efficiency of dye increased as the electrode surface area increased from 0.1828-1.3 m². This result is due to the fact that greater

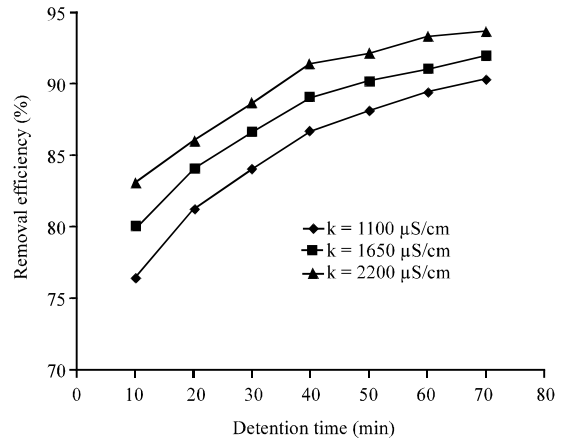


Fig. 11: Effect of conductivity on dye removal efficiency using aluminum electrodes (pH = 7, C_o = 10 mg/L, CD = 4 A/m², Q = 40 L/h, As = 1.3 m²)

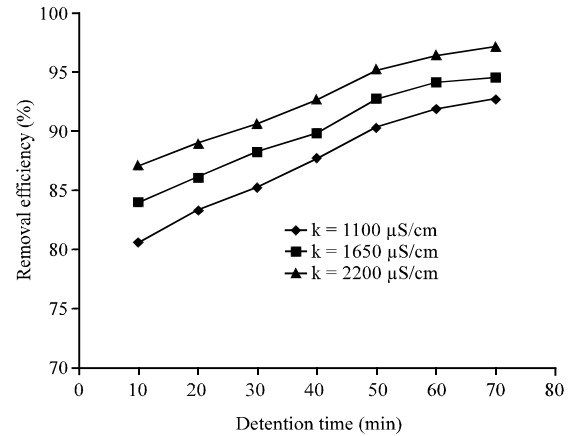


Fig. 12: Effect of conductivity on dye removal efficiency using iron electrodes (pH = 11, C_o = 10 mg/L, CD = 4 A/m², Q = 40 L/h, As = 1.3 m²)

electrode surface area produces larger quantities of cations and anions from the anode and cathode which means greater quantities of aluminum or iron ions and greater number of (OH⁻). The greater electrode surface area increases the rate of floc's formation which in turn increases the removal efficiency. Also, the increase in electrode surface area enhances the distribution of the coagulant in the reactor which enhances the removal efficiency (Chopra and Sharma, 2013).

After 70 min and at 1.3 m², the maximum removal efficiency was found to be 90.1 and 92.5% for aluminum and iron electrodes, respectively.

Effect of conductivity: To have a better understanding of the effect of conductivity on the removal efficiency, solutions with three different values of conductivity 1100, 1650 and 2200 μS/cm were used. Figure 11 and 12 shows

that the removal efficiency of dye using both Al and Fe electrodes increased with increasing conductivity. For instance, after 70 min of detention time, the removal efficiency of dye using Al and Fe electrodes increased from 90.1-93.62% and from 92.5-97%, respectively when the conductivity increased from 1100-2200 $\mu\text{S}/\text{cm}$. These results are explained as follows; increasing conductivity using NaCl, means increasing NaCl concentration which enhances the removal efficiency because the antipassive Cl^- ions can destroy the passive oxide layer that formed on the surface of the anode and hence, increase the anodic dissolution rate of metal. Also, chloride anions could significantly reduce the adverse effects of other anions such as HCO_3^- and SO_4^{2-} . Indeed, the existence of carbonate anion would lead to the precipitation of Ca^{2+} ion. These can form an insulating layer on the surface of the cathode which could increase the ohmic resistance of the electrochemical cell (El-Ashtouky *et al.*, 2016).

In addition, increasing conductivity by addition of NaCl reduces the voltage at constant current due to the decrease of the ohmic resistance of the solution and hence, energy consumption will be decreased. It is noted that after 70 min, the energy consumption decreased from 1.049-0.634 $\text{kW}\cdot\text{h}/\text{m}^3$ and from 0.712-0.375 $\text{kW}\cdot\text{h}/\text{m}^3$ for (Al) and (Fe) electrodes, respectively when the conductivity increased from 1100-2200 $\mu\text{S}/\text{cm}$.

CONCLUSION

The present research has investigated the removal of methylene blue dye from synthetic wastewater in a continuous electrocoagulation system. Two electrocoagulation reactors with a new configuration were used in the study. One of the reactors with aluminum electrodes and the other with iron electrodes. The new electrocoagulation reactor was proven to be efficient and economic as it reduced the energy consumption and enhanced mixing and mass transfer inside the reactor which reduced the need for external stirring device which requires extra power to work. The obtained results showed that the removal efficiency using Al and Fe electrodes is directly proportional to CD as conductivity and detention time. Contrarily, removal efficiency is reversely proportional to the initial concentration. From the experimental results, it was found that iron electrode is superior to aluminum in removal of dye with maximum efficiency of 93.62 and 97% for (Al) and (Fe) electrodes, respectively at the optimum conditions. The results also showed that most concentration of dye was removed in

the first 10 min. Energy consumption is a very important economical parameter. The results showed that as the conductivity increased, energy consumption decreased. It was found that iron electrodes consumed less energy than aluminum electrodes with energy consumption of 0.634 and 0.375 $\text{kW}\cdot\text{h}/\text{m}^3$ for aluminum and iron electrodes, respectively.

REFERENCES

- Aghdam, M.A., H.R. Kariminia and S. Safari, 2016. Removal of lignin, COD and color from pulp and paper wastewater using electrocoagulation. *Desalin. Water Treat.*, 57: 9698-9704.
- Alizadeh, M., E. Ghahramani, M. Zarrabi and S. Hashemi, 2015. Efficient De-colorization of Methylene blue by electro-coagulation method: Comparison of iron and Aluminum electrode. *Iran. J. Chem. Chem. Eng.*, 34: 39-47.
- Bensadok, K.S., S. Benammar, F. Lapique and G. Nezzal, 2008. Electrocoagulation of cutting oil emulsions using Aluminium plate electrodes. *J. Hazard. Mater.*, 152: 423-430.
- Chopra, A.K. and A.K. Sharma, 2013. Removal of turbidity, COD and BOD from secondarily treated sewage water by electrolytic treatment. *Appl. Water Sci.*, 3: 125-132.
- Daneshvar, N., D. Salari and A.R. Khataee, 2003. Photocatalytic degradation of azo dye acid red 14 in water: Investigation of the effect of operational parameters. *J. Photochem. Photobiol. A*, 157: 111-116.
- El-Ashtouky, E.S., A.A. Mobarak and Y.O. Fouad, 2016. Decolourization of reactive blue 19 dye effluents by electrocoagulation in a batch recycle new electrochemical reactor. *Intl. J. Electrochem. Sci.*, 11: 1883-1897.
- Elsayed, E.M., T.M. Zewail and A.A. Zaatout, 2013. Particulate solids removal from synthetic and real turbid water and wastewater by electro coagulation using vertical expanded al anode. *J. Chem. Eng. Process Technol.*, 4: 177-183.
- Fagnekar, N.A. and S. Mane, 2015. Removal of turbidity using electrocoagulation. *Intl J. Res. Eng. Technol.*, 1: 537-543.
- Ghosh, D., C.R. Medhi and M.K. Purkait, 2008. Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections. *Chemosphere*, 73: 1393-1400.

- Ghosh, D., C.R. Medhi and M.K. Purkait, 2011. Techno-economic analysis for the electrocoagulation of fluoride-contaminated drinking water. *Toxicol. Environ. Chem.*, 93: 424-437.
- Hashim, K.S., A. Shaw, R. Al-Khaddar, M.O. Pedrola and D. Phipps, 2017. Iron removal, energy consumption and operating cost of electrocoagulation of drinking water using a new flow column reactor. *J. Environ. Manage.*, 189: 98-108.
- Kobya, M., O.T. Can and M. Bayramoglu, 2003. Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *J. Hazard. Mater.*, 100: 163-178.
- Kumar, K. and O.P. Sahu, 2013. Removal of dye by electrocoagulation method. *Hydrol.*, 1: 8-11.
- Merzouk, B., B. Gourich, A. Sekki, K. Madani and M. Chibane, 2009. Removal turbidity and separation of heavy metals using electrocoagulation-electroflotation technique: A case study. *J. Hazard. Mater.*, 164: 215-222.
- Mollah, M.Y.A., P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga and D.L. Cocke, 2004. Fundamentals, present and future perspectives of electrocoagulation. *J. Hazard. Mater.*, 114: 199-210.
- Phalakornkule, C., S. Polgumhang and W. Tongdaung, 2009. Performance of an electrocoagulation process in treating direct dye: Batch and continuous upflow processes. *World Acad. Sci. Eng. Technol.*, 57: 277-282.
- Pirkarami, A. and M.E. Olya, 2017. Removal of dye from industrial wastewater with an emphasis on improving economic efficiency and degradation mechanism. *J. Saudi Chem. Soc.*, 21: S179-S186.
- Taha, D.N., I.S. Samaka, L.A. Mohammed and A. Saib, 2014. Adsorption studies of direct red 28 dye onto activated Carbon prepared from low cost material. *Civ. Environ. Res.*, 6: 149-160.
- Vepsalainen, M., 2012. *Electrocoagulation in the Treatment of Industrial Waters and Wastewaters*. VTT Technical Research Centre of Finland, Espoo, Finland, ISBN:9789513879402.
- Zaroual, Z., M. Azzi, N. Saib and E. Chainet, 2006. Contribution to the study of electrocoagulation mechanism in basic textile effluent. *J. Hazard. Mater.*, 131: 73-78.