

A Designed Electro-flotation Cell for Dye Removal from Wastewater

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P A P E R I N F O	A B S T R A C T
<p>Chronicle: Received: Revised: Accepted: Available :</p>	<p>An Electro-flotation cell was designed for industrial wastewater treatment. The affecting parameters of the Electro-flotation process such as, pH, initial dye concentration, temperature, current density, current type, ionic strength, stirring speed and number, connection and inter-distance of electrodes were investigated using a synthetic Acid Red 1 (anionic), Basic Violet 3 (cationic) and Disperse Blue 14 (nonionic) dyes. Two textile wastewater samples were employed for performance evaluation. The maximum removal for all dyes is achieved at pH 7. The AC current and the bipolar electrodes were preferred. The maximum removal was achieved with AC current density of 80 A/m² at 5 Volts through a bipolar connection of 8 electrode with 2 cm inter-distance. The designed Electro-flotation cell could remove 91.7 – 98.9 % of constituents of textile wastewater samples. The energy consumption was 1.39 Kwh/m³ of the treated wastewater.</p>
<p>Keywords : <i>Electro-flotation Dye removal. Wastewater. Textile effluents. Cell design.</i></p>	

1. Introduction

With an ever increasing world population, textile production remains one of the prominent industries that require large amount of water and produce highly polluted wastewater [1] which may cause severe environmental pollution if they are released to the environment without any proper treatment [2]. The dye stuff poses a major problem to industrial wastewater effluents [3]. The textile industry produces 5000 tons of dyeing materials that are discharged into the environment every year [4]. The treatment of this colored wastewater is of great concern nowadays, because many dyes and their degradation products are toxic and carcinogenic [5]. Generally, the treatment of the dyestuff effluents can be classified into biological, chemical and physical treatments. Such techniques are generally multistep, time consuming and require extensive equipment, chemicals and handling. To date, various methods have been used for the removal of textile dye such as activated sludge process, flotation, coagulation/flocculation, filtration, ozonation, photocatalysis, electrolysis and adsorption on activated

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carbon. Among all these processes, electro-coagulation has been found to be an attractive alternative for the treatment of textile dyes [6-8].

Electro-flotation is a technology that combines the functions and advantages of conventional coagulation, flotation and electrochemistry in wastewater treatment. Compared with conventional flotation, electro-flotation has many advantages, firstly its fine bubbles which are uniformly dispersed thus increasing the contact area between the flocks and bubble, making the clarification efficient and fast. Secondly, it generates less sludge. Thirdly, it offers the possibility of automation and easy operation by adjusting the electrical current. Electro-flotation units are small, compact and fast. It requires lower maintenance and running costs. The main advantage of this method is not to use any chemicals for treatment as conventional coagulation. It is not time consuming and sheep require extensive equipment and handling [9-10]. The Electro-flotation process operates on the base of the principle that the cations produced electrically from iron or aluminum anodes are responsible for the coagulation of contaminants from an aqueous medium [11]. The flocculated particles attract by small bubbles of oxygen and hydrogen generated from electrolysis of water, thus the flocculated particles float towards the surface [12]. The most important parameters that can affect the electrochemical process is the current density. The current not only determines the coagulant dosage rate but also the bubble production rate [13]. Anions such as sulfate and carbonate are passivating agents, reduce the production of metal cations and increase electrical consumption. Chloride ions induce breakdown of the passive layer and pitting corrosion [14]. The stirring speed, temperature, and electrode's number and inter-distance and connection mode are important parameters that can affect the electrochemical process and energy consumption [15].

Madani et al. [16] studied the principal parameters (feed tension U , distance between electrodes D , period of treatment t , pH and conductivity κ) affecting the electro-flotation process using a simulated model of wastewater. The application of the optimized parameters ($U = 20$ V, $D = 1$ cm, $t = 20$ min) on an industrial wastewater derived from an Algerian velvet manufacture showed a high removal of biological oxygen demand after 5 days ($BOD_5 = 93.5\%$), chemical oxygen demand ($COD = 90.3\%$), turbidity (78.7%), suspended solids ($SS = 93.3\%$) and color ($> 93\%$).

Electro-flotation of Acid Red1 (anionic), Basic Violet 3 (cationic) and Disperse Blue14 (nonionic) dyes from aqueous solutions showed that, the maximum dye removal was achieved at pH 7. The order of the dye removals are nonionic > cationic > anionic. The removal process follows pseudo first-order kinetics. Freundlich and Langmuir isotherm models indicate that the adsorption is characterized by physical and chemical adsorptions. The dimensionless equilibrium parameter, R_L values were between 0 and 1, indicates favorable adsorption. The ΔH° and ΔG° values indicated that the process becomes less favorable at high temperatures [17].

This study aims to determine the performance of designed Electro-flotation cell for treatment of textile wastewater. The pH, initial dye concentration and temperature were investigated. The crystal violet dye was selected to optimize the affecting parameters of Electro-flotation cell. The current density and type, ionic strength, stirring speed and electrode number, connection and inter-distance were investigated. Also, investigate the treatment performance for two textile wastewater samples.

2. Materials and Methods

2.1. Chemicals

Acid Red 1 (anionic), Basic Violet 3 (cationic) and Disperse Blue 14 (nonionic) dyes of analytical grade; 99.9% purity (Sigma-Aldrich and Merck) were used for preparation of synthetic dye solution. The pH was adjusted by 0.01 M solutions of HCl and NaOH as required. The studied wastewater samples were collected from a local textile dyeing factory. The textile effluents were employed to evaluate the designed cell for treating industrial effluents containing dyes.

2.2. Procedure

A laboratory DC power supply apparatus (Farnell Instruments LTD) was used to maintain a constant current. The voltage and current were measured by a multimeter (PHYWE). The pH and the temperature were measured using a Hanna (HI-8314) pH meter connected to a combined electrode and comprising a temperature sensor (HI-1217D).

An electrolytic cell with an anode and a cathode is basically what an Electro-flotation reactor consists of. The conductive metal plates are commonly known as sacrificial electrodes. The designed reactor composed of a plastic box of length 19.2 cm, width 5.2 cm and height 6.5 cm which is placed in a bigger one of dimension 22 cm × 8 cm × 7 cm to collect floated flocks, **Fig 1. A 600 ml of examined dye solution was placed and stirred with a magnetic bar. A pair or more (up to four pairs) of commercially obtained aluminum plates of size 6 cm × 5 cm × 0.15 cm immersed to a 6 cm depth with an effective area of 62.5 cm² each was used as electrodes. The inter-electrode distance can be changed up to 6 cm. Sodium chloride salt was added for preventing passivation on the aluminum electrode surface and to reduce the resistance of the solution. The residual dye concentrations were determined by UV/Vis spectrophotometer (LLG-UniSPEC 2).**

The removal percent and the amount of adsorbed dye were calculated by Eqs. (1) and (2), respectively [18, 19]:

$$Removal (\%) = \frac{C_0 - C_t}{C_0} \times 100. \quad (1)$$

Where, C_0 and C_t are the concentrations of dye solution (mg/L) at time of zero and t , respectively.

$$q_e = \frac{(C_0 - C_t)V}{M}. \quad (2)$$

Where, q_e is the sorption capacity of Al(OH)₃ in (g/g), V is the volume of the dye solution in liter and M is the mass of Al(OH)₃ in (g) which calculated by Eq. 3 [20]:

$$m \text{ Al(OH)}_3 = \frac{I \cdot t \cdot M}{z \cdot F} \quad (3)$$

Where, I = current intensity (A), t = time (s), M = Molecular weight of aluminum hydroxide (g/mol), z = number of electrons transferred in the reaction $\text{Al} \rightarrow \text{Al}^{3+} + 3e$, F = Faraday's constant (96500 Cb/mol).

Characterization of the dye wastewater before and after treatment was evaluated using, COD (Chemical Oxygen Demand), BOD (Biochemical Oxygen Demand), TS (Total Solid), TSS (Total Suspended Solid), TOC (Total Organic Carbon) and heavy metal ions measurements according to Standard Methods [21]. Turbidity was recorded on a 2100N IS Turbidity meter (Hatch). Color is determined by visual comparison of the sample with known dilutions of a colored Platinum-Cobalt stock solution [22].

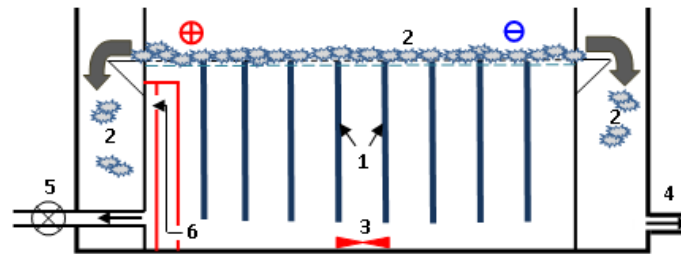


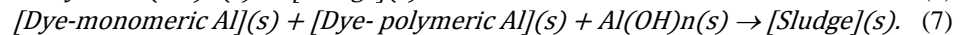
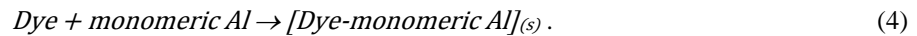
Fig 1. Designed electro-flotation reactor

(1-Aluminum electrodes, 2-Flocks, 3-Magnetic bar, 4-Flocks outlet, 5-Treated water outlet & 6-Flocks Trap)

3. Results and Discussions

3.1. Effect of pH

The maximum removal for all dyes is achieved at pH 7, Fig 2. In neutral pH, $Al(OH)_3$ is stable and insoluble in water and thus can absorb dyes from water. The order of the dye removal was nonionic > cationic > anionic. The lower adsorption of anionic and cationic dyes as charged dyes may be due to that the physical adsorption was predominating [23-24]. There is another mechanism may be occurred in addition to simple adsorption mechanisms. The concentration of the aqueous complexes (polymeric aluminum species: $Al_3(OH)_4^{5+}$, $Al_2(OH)_2^{4+}$, $Al(OH)_2^+$, $AlOH^{2+}$) of the dissolved aluminum becomes maximized between pH 5-7. The aluminum ions of these species act as electron acceptor for electron pair donated by different dyes [25]. These polymeric species can form instantaneous agglomerates with dyes as follows:



Increasing of initial dye concentration increases its adsorbed amount, Fig 3. The higher concentration overcomes the resistance to mass transfer of dye between the aqueous phase and the adsorbent [26]. By applying Freundlich model, it describes reversible adsorption (physical adsorption) and is not restricted to the formation of the monolayer [27]:

$$\ln q_e = \ln k_f + \frac{1}{n} (\ln C_e). \quad (8)$$

Where, q_e is the amount of the dye adsorbed at the equilibrium time, C_e is the equilibrium concentration of the dye in solution. The K_f is the Freundlich isotherm constant and $1/n$ is the heterogeneity factor which indicates the capacity and the intensity of the dye adsorption, respectively. The values of "n" are greater than unity which indicates the favorable nature of adsorption, Table 1.

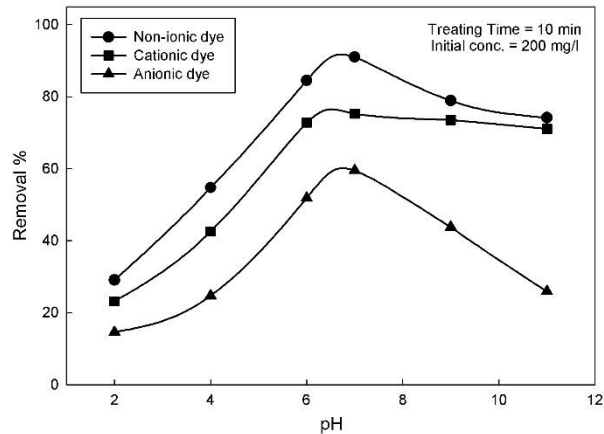


Fig 2. Effect of initial pH on removal efficiency different dyes

3.2. Effect of Initial dye concentration

By applying Langmuir model it describes also that the adsorption occurs uniformly on the adsorbent (chemical adsorption) [28]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \cdot q_{max}} \quad (9)$$

Where, C_e is the dye concentration at equilibrium (mg/L), q_e is the amount adsorbed of dye at equilibrium in unit mass of adsorbent; q_{max} and b are the Langmuir coefficient.

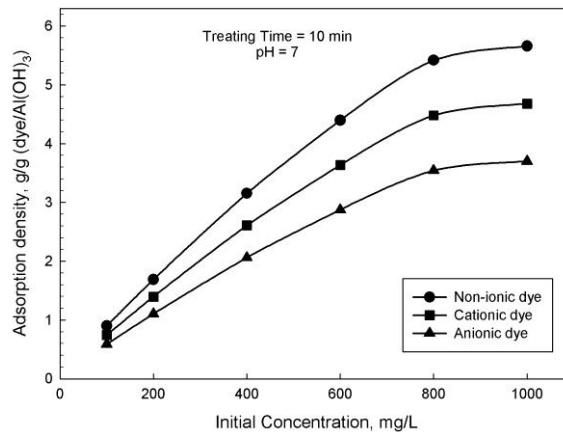


Fig 3. Effect of initial dye concentration on the adsorption by $Al(OH)_3$

Table 1. Calculated constants for freundlich and langmuir isotherms

Dye	Freundlich isotherm			Langmuir isotherm			
	R ²	n	K _f	R ²	Q _{max} Cal.	Q _{max} Exp.	b
Non-ionic	0.986	2.469	57.18×10 ⁻²	0.989	6.25	5.66	23.79×10 ⁻³
Cationic	0.978	1.667	13.44×10 ⁻²	0.991	6.33	4.68	6.29×10 ⁻³
Anionic	0.981	1.455	5.35×10 ⁻²	0.981	5.99	3.70	2.99×10 ⁻³

3.3. Effect of temperature and thermodynamic study

Fig 4 shows that with increasing the temperature decreases the removal efficiency. This behavior indicates that this process is an exothermic process [29]. The thermodynamic parameters; Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°); for the sorption of dyes were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. The change in enthalpy (ΔH°) and entropy (ΔS°) were calculated using the van't Hoff equation [30].

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

Where, $k_c = F_e/(1 - F_e)$, and $F_e = (C_o - C_e)/C_o$, T is the temperature in degree K, and R is the gas constant [8.314 J/mol K]. The values of ΔH° and ΔS° have been computed from the slope and the intercept of the plot of $\ln k_c$ versus $1/T$, Fig 5, which gives a straight line with an acceptable coefficient of determination ($R^2 \geq 0.97$).

From the plot of $1/T$ against $\ln k_c$, Slope = $-\Delta H^\circ/R$ and Intercept = $\Delta S^\circ/R$. The values of ΔH° are -41.9, -43.3 and -48.9 kJ/mol for Nonionic, Cationic and Anionic dyes, respectively. The negative values of enthalpy changes (ΔH°) suggest that the reactions are exothermic and their higher values than 40 kJ/mol, confirming extent of some chemical actions with Al (OH)₃ flocks [31]. The negative values of ΔS° (-121, -134 and -159) showed that the decreasing in randomness at the solid/liquid interface during the adsorption, indicated the adsorption was not favorable at higher temperatures. The values of the standard Gibbs free energy change (ΔG°) were estimated using equation 11. The values of ΔG° at all tested temperatures are negative which indicate that this adsorption process is spontaneous in nature whereby no energy input from outside of the system is required. The increase in the ΔG° with increasing temperature indicates that the process becomes less favorable at high temperatures [32].

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

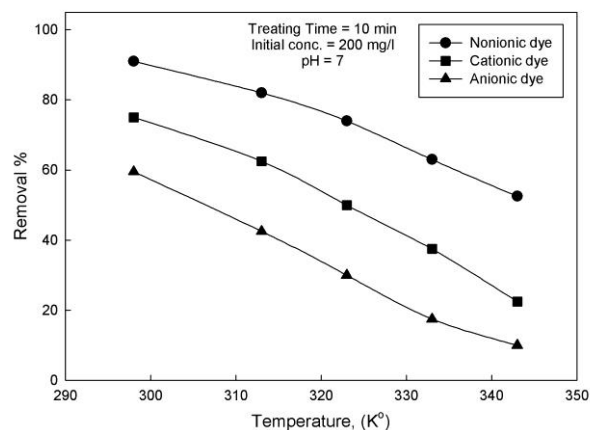


Fig 4. Effect of temperature on the removal efficiency of different dyes

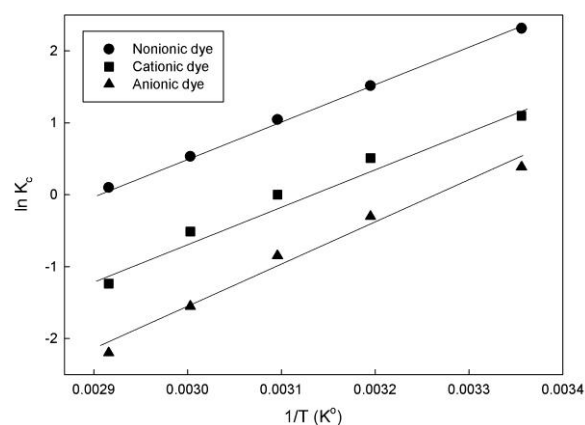


Fig 5. Effect of temperature on the removal kinetic of different dyes

3.4. Effect of current density

Fig 6 shows that increasing the current density up to 80 A/m^2 increased the removal efficiency and reduced the treatment time from 60 to 5 min. Current density probably has some influence on the chemical dissolution of aluminum cathode, as it affects the rate of hydroxyl ions production at the cathode [33]. The increase in the removal efficiency could be explained by greater percentage of destabilized dye molecules, as a result of charge neutralization with more aluminum species released from the electrodes with increasing current density with more aluminum species released from the electrodes with increasing current density. In addition, at higher current density more aluminum hydroxide form low density flocks. The current not only determines the coagulant dosage rate, but also the bubble production rate [13]. Researchers stated that the bubble size distribution is a function of the current density for a given electrode [34]. More studies showed that with an increase in the current density, the bubble diameter decreases [35]. Small bubbles have a higher probability of providing a smaller contact angle, which produces more stable aggregates [36]. Furthermore, the detention time of small bubbles in the flotation unit is longer than that of larger bubbles as they have a lower rising velocity. This promotes the probability of collision between gas bubbles and flocks [37].

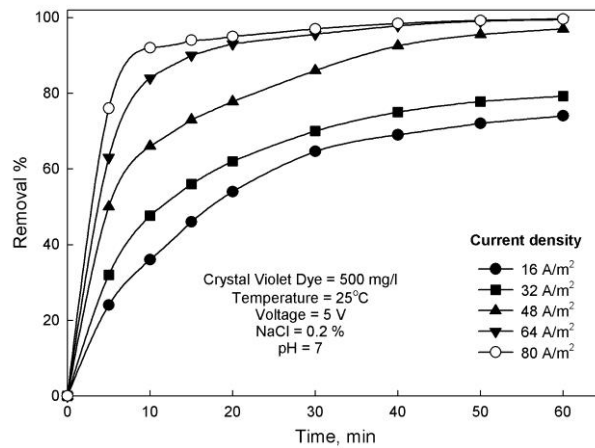


Fig 6. Effect of current density on dye removal as a function of treatment time

3.5. Effect of ionic strength

Greater ionic strength increases the conductivity and thus increases the current density for the same cell voltage. Fig 7 shows that the increase in sodium chloride concentration added (ionic strength) increased the removal efficiency [38]. An increase in conductivity decreased the resistance between electrodes and therefore more aluminum ions could be produced at the same energy input. As increasing in conductivity, the energy requirement increased at the same voltage.

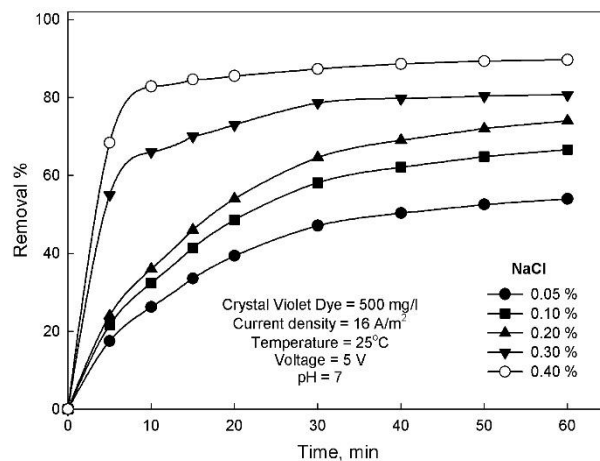


Fig 7. Effect of ionic strength on dye removal as a function of treatment time

3.6. Effect of stirring speed

Fig 8 shows that the increase in the stirring speed from 0 to 100 rpm increased the removal efficiency from 11.4% to 36.2% at 10 min and from 47% to 69.2% at 40 min. The increasing of stirring speed provides a significant gain on the kinetics of electro-coagulation and thus the distribution of coagulants becomes larger. Thus, the flocks were formed and attached together and flotation took place easier. With further increase in the stirring speed up to 500 rpm, the flocks were degraded, desorption started and removal efficiency decreased. By doing this experiment, the optimum stirring speed was found to be 100 rpm.

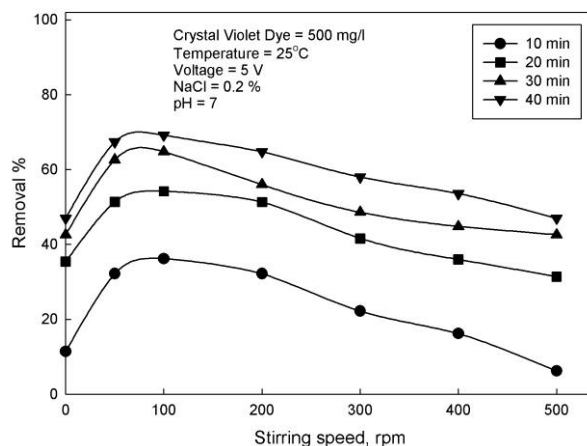


Fig 8. Effect of treatment time on dye removal as a function of stirring speed

3.7. Effect of electrodes inter-distance

The electrolysis voltage required in an Electro-flotation process is mainly from the resistance drop of the aqueous phase, particularly when the conductivity is low and the current density is high. Therefore, it is important to reduce the inter-electrode distance for reducing the electrolysis energy consumption [15]. Fig 9 shows that the decreasing of space between electrodes increased the removal efficiency. This can be explained by noting that the decreasing of the space between electrodes reduces the resistance through the solution which increased the rate of aluminum dissolution and consequently leads to more pollutant removal from the solution [15]. In addition, decreasing of the space could enhance the flotation process by limiting the generated bubbles in a narrow space which results in higher removal efficiencies. This effect is inverted with a very narrow inter-distance. The removal efficiency was decreased at gap of 1 cm.

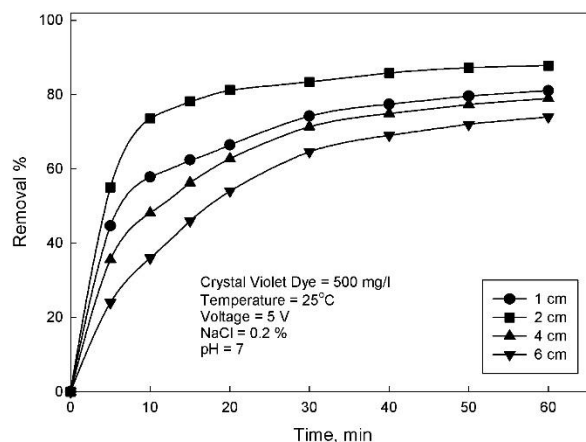


Fig 9. Effect of inter-electrode distance on dye removal as a function of treatment time

3.8. Effect of current type

Fig 10 shows that the DC and AC current can remove dye with similar efficiencies. There is significant difference with long treatment time. In addition, the difference was significant at low current

density. The lower rate of dye removal with DC current may be due to passivation of the anode. On the other hand, the energy consumption is slightly lower with AC.

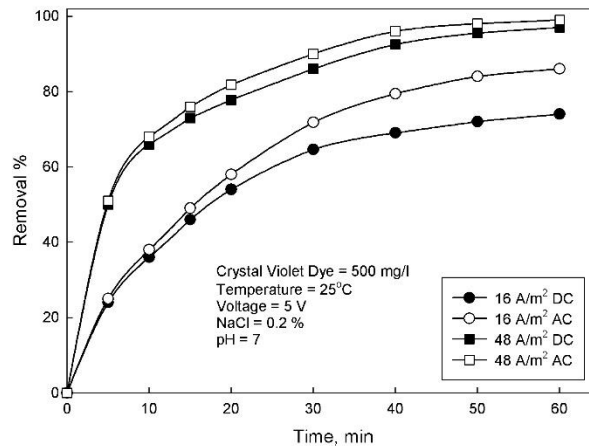


Fig 10. Effect of current type on dye removal as a function of treatment time

3.9. Effect of numbers of electrodes

Fig 11 shows that the removal efficiency increased with increasing number of electrodes up to 8 (4 pairs). A 91.1% removal was obtained with 8 electrodes after 5 min while it was 55 % only with 2 electrodes. The highest removal efficiency of 97.6 % was obtained with 8 electrodes after 60 min. On the other hand, the maximum removal efficiency with 2 electrodes after 60 min was 87.8 %.

The addition of new electrodes provides a significant gain on the kinetics of electro-coagulation. The use of eight electrodes reduces the time of Electro-flotation from 60 to 5 min. This can be explained by the increase of the electrode area exposed to the solution. In addition, the use of higher number of electrodes reduces solution resistance, increases aluminum dissolution rate and generates more gas bubbles in a narrow space. Therefore, the distribution of coagulants becomes larger. This reaction occurs without additional power consumption and less energy consumed [19].

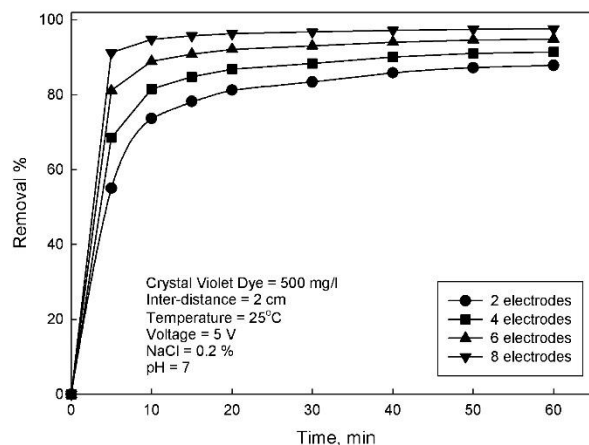


Fig 11. Effect of number of electrodes on dye removal as a function of treatment time

3.10. Effect of electrodes' connection

An arrangement and connection of the Electro-flotation reactor with monopolar electrodes or bipolar electrodes is shown in Fig 12 [33]. In bipolar, the neutral sides of the connected plate will be transformed to charged sides, which have opposite charged compared to the parallel side beside it. The sacrificial electrodes are referred to as bipolar electrodes [35]. Fig 13 shows that the dye removal in the bipolar connection was higher than that of the monopolar connection at 5 min with 10 %. The highest removal efficiency of 99.2 % was obtained with the bipolar connection of 6 electrodes after 60 min. On the other hand, the maximum removal efficiency with the monopolar connection was 94.8 %. This can be explained by the decreasing passivation of electrodes as a result of polarity reversal [36].

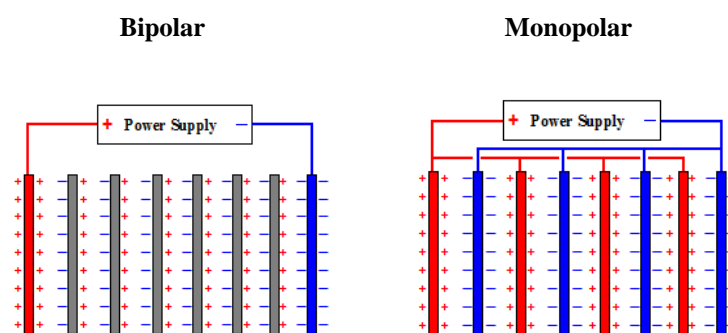


Fig 12. Connection and electrode's polarity in: (a) bipolar & (b) monopolar systems

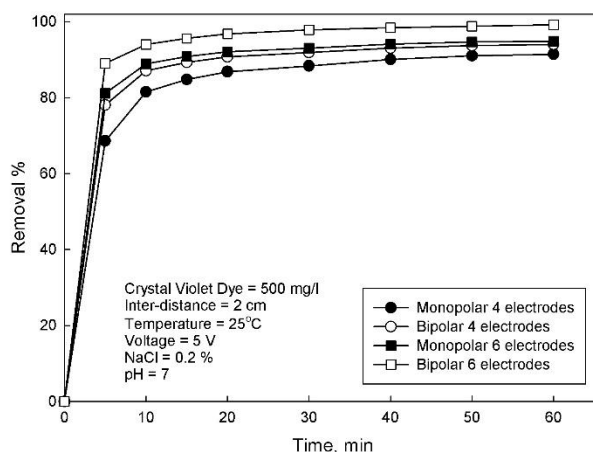


Fig 13. Effect of electrodes' connection on dye removal as a function of treatment time

3.11. Kinetic investigations

The results of color removal at the optimum conditions as a function of Electro-flotation time were used to investigate the kinetics of the process. The results of the residual color of dye could be fitted to second order kinetic equation with correlation coefficients of 0.9836, Fig 14.

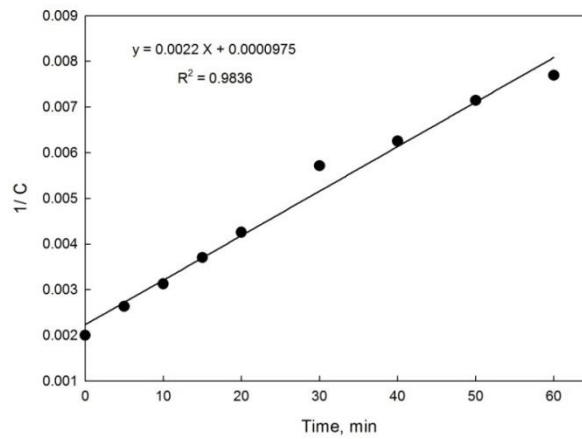


Fig 14. Second order kinetic analysis for electro-flotation unit based on color removal

3.12. Application on textile effluents

The designed Electro-flotation reactor, Fig 1, was employed to treat two wastewater samples which were collected from a local textile dyeing factory. These effluents contained different types of dyes and chemical depending on the dyeing processes at the factory. The treatment process was carried out as a batch process for 10 min at 25°C, 5 Volts, stirring speed 100 rpm and 80 A/m² of AC-current through a bipolar connection. The inter-electrodes distances were 2 cm. Table 2 showed that the removal efficiency of all constituents was in range from 91.7 – 98.9 % for both industrial effluents.

The electrical energy consumption E is calculated using equation 2 [37]:

$$E = \frac{U \cdot I \cdot t}{V} \times 10^{-3} . \quad (12)$$

Where, U is the operating voltage (volt), I is the operating current (amperes), t is the time of treatment (hours), and V is the volume of wastewater (m³).

The electrical energy consumption for treatment of the studied industrial effluents at latter conditions was 1.39 kWh/m³. It is acceptable with those calculated by other scientists. The energy consumption for treatment of washing soil contaminated by heavy metals was 14 kWh/m³ [38], while for removal of arsenic and organic matter it was 1.7 kWh/m³ [19].

Table 2. Evaluation of designed electro-flotation reactor for textile effluent treatment

Constituent	Wastewater 1			Wastewater 2		
	Untreated	Treated	Removal %	Untreated	Treated	Removal %
pH	8.3	8.6	--	7.9	8.4	--
TS, mg/l	4592	243	94.7	2645	61	97.7
TSS, mg/l	286	3.12	98.9	192	2.3	98.8

TOC	197	16	91.9	413	28	93.2
COD	963	75	92.2	591	37	93.7
BOD	132	11	91.7	217	16	92.6
Color (<i>Hazen</i>)	164	6.3	96.1	428	25.3	94.0
Fe	3.1	0.20	93.6	1.8	0.10	94.4
Zn	1.2	0.08	93.3	2.8	0.21	92.5
Turbidity (NTU)	279	2.9	98.9	168	1.8	98.9

4. Conclusions

The affecting parameters of Electro-flotation process for the designed cell showed that, the maximum removal for all dyes is achieved at pH 7. The order of the dye removal was nonionic > cationic > anionic. Increasing of current density and ionic strength increased the removal efficiency while increasing the temperature and space between electrodes decreased the efficiency. The negative values of (ΔH°) suggest that the reactions are exothermic and their higher values than 40 kJ/mol, confirming extent of some chemical actions with Al (OH)₃ flocks. The negative values of ΔS° indicating that the decreasing in randomness at the solid/liquid interface during the adsorption. The values of ΔG° were negative which indicate that this adsorption process is spontaneous in nature whereby no energy input from outside of the system is required. Increasing the ΔG° with temperature indicates that the process becomes less favorable at high temperatures.

Increasing of initial dye concentration increases its adsorbed amount. Increasing the current density up to 80 A/m² increased the removal efficiency due to decreasing the bubble diameter which produces more stable aggregates and promotes the probability of collision between gas bubbles and flocks. The stirring provides a significant gain on the kinetics of Electro-flotation and thus the flocks were formed and attached together and flotation took place easier. Decreasing space between electrodes reduced the resistance and enhanced the flotation process by limiting the generated bubbles in a narrow space. The DC current causes passivation of the anode, thus AC current is preferred. The use of eight electrodes reduced the time of Electro-flotation from 60 to 5 min. The bipolar electrodes increase the removal efficiency than that of monopolar electrodes connection.

The designed Electro-flotation cell could treat dyeing effluents. The removal efficiency of 91.7 – 98.9 % for all constituents was achieved at 25°C, 5 Volts, stirring speed 100 rpm, 10 min and 80 A/m² of AC-current through a bipolar connection with inter-electrodes distances of 2 cm. The electrical energy consumption was 1.39 kWh/m³.

References

- [1] Berrios, M., Martín, M. Á., & Martín, A. (2012). Treatment of pollutants in wastewater: adsorption of methylene blue onto olive-based activated carbon. *Journal of Industrial and Engineering Chemistry*, 18(2), 780-784.

- [2] Dutta, A., Diao, Y., Jain, R., Rene, E. R., & Dutta, S. (2015). Adsorption of cadmium from aqueous solutions onto coffee grounds and wheat straw: equilibrium and kinetic study. *Journal of Environmental Engineering*, 142(9), C4015014.
- [3] Shah, V., & Madamwar, D. (2013). Community genomics: Isolation, characterization and expression of gene coding for azoreductase. *International Biodeterioration & Biodegradation*, 79, 1-8.
- [4] Pirkarami, A., Olya, M. E., & Limaee, N. Y. (2013). Decolorization of azo dyes by photo electro adsorption process using polyaniline coated electrode. *Progress in Organic Coatings*, 76(4), 682-688.
- [5] Upendar, G., Dutta, S., Bhattacharya, P., & Dutta, A. (2017). Bioremediation of methylene blue dye using *Bacillus subtilis* MTCC 441. *Water Science and Technology*, 75(7), 1572-1583.
- [6] Abdel-Khalek, M. A., Rahman, M. A., & Francis, A. A. (2017). Exploring the adsorption behavior of cationic and anionic dyes on industrial waste shells of egg. *Journal of Environmental Chemical Engineering*, 5(1), 319-327.
- [7] Lemlikchi, W., Khaldi, S., Mecherri, M. O., Lounici, H., & Drouiche, N. (2012). Degradation of disperse red 167 azo dye by bipolar electrocoagulation. *Separation Science and Technology*, 47(11), 1682-1688.
- [8] Abdel Khalek, M. A., El Hosiny, F.I., Selim, K. A. & Osama, I. (2016). Electro-kinetic Study of Heavy Metal Ions Removal from Wastewater Effluent via Electro-flotation. *J. Ore Dressing*, 18, 36, 1302-6798.
- [9] Petsriprasit, C., Namboonmee, J., & Hunsom, M. (2010). Application of the electrocoagulation technique for treating heavy metals containing wastewater from the pickling process of a billet plant. *Korean Journal of Chemical Engineering*, 27(3), 854-861.
- [10] Nandi, B. K., & Patel, S. (2017). Effects of operational parameters on the removal of brilliant green dye from aqueous solutions by electrocoagulation. *Arabian Journal of Chemistry*, 10, S2961-S2968.
- [11] Chaturvedi, S. I. (2013). Electro-coagulation: a novel wastewater treatment method. *International Journal of Modern Engineering Research*, 3(1), 93-100.
- [12] Sahu, O., Mazumdar, B., & Chaudhari, P. K. (2014). Treatment of wastewater by electrocoagulation: a review. *Environmental science and pollution research*, 21(4), 2397-2413.
- [13] Marmanis, D., Dermentzis, K., Christoforidis, A., Ouzounis, K., & Moutzakis, A. (2015). Electrochemical treatment of actual dye house effluents using electrocoagulation process directly powered by photovoltaic energy. *Desalination and Water Treatment*, 56(11), 2988-2993.
- [14] Al-abdalaali, A. A. (2010). *Removal of boron from simulated iraqi surface water by electrocoagulation method* (Doctoral dissertation, MS thesis, Dept. Env. Eng, Baghdad Univ).
- [15] Chen, X., & Chen, G. (2010). *Electroflotation*. In: Comninellis C, Chen G, editors, *Electrochemistry for the Environment*, Springer Science and Business Media, LLC, P. 263-77.
- [16] Belkacem, M., Khodir, M., & Abdelkrim, S. (2008). Treatment characteristics of textile wastewater and removal of heavy metals using the electroflotation technique. *Desalination*, 228(1-3), 245-254.
- [17] El-Hosiny, F. I., Abdel Khalek, M. A., Selim, K. A. & Osama, I. (2017). Physicochemical Study of Dye Removal Using Electro-Coagulation-Flotation Process. *Physicochemical Problems of Mineral Processing, Print online*, DOI: <https://doi.org/10.5277/ppmp1825>.
- [18] Hunsom, M., Pruksathorn, K., Damronglerd, S., Vergnes, H., & Duverneuil, P. (2005). Electrochemical treatment of heavy metals (Cu 2+, Cr 6+, Ni 2+) from industrial effluent and modeling of copper reduction. *Water Research*, 39(4), 610-616.
- [19] Mohora, E., Rončević, S., Dalmacija, B., Agbaba, J., Watson, M., Karlović, E., & Dalmacija, M. (2012). Removal of natural organic matter and arsenic from water by electrocoagulation/flotation continuous flow reactor. *Journal of hazardous materials*, 235, 257-264.
- [20] Dermentzis, K., Christoforidis, A., & Valsamidou, E. (2011). Removal of nickel, copper, zinc and chromium from synthetic and industrial wastewater by electrocoagulation. *International Journal of Environmental Sciences*, 1(5), 697.
- [21] Standard, A. P. H. A. (1998). *Methods for the Examination of Water and Wastewater*. American Public Health Association.
- [22] Eaton, A. D., Clesceri, L. S., Rice, E. W., Greenberg, A. E., & Franson, M. A. H. (2005). APHA: standard methods for the examination of water and wastewater. *Centennial Edition., APHA, AWWA, WEF, Washington, DC*.
- [23] Parsa, J. B., Vahidian, H. R., Soleymani, A. R., & Abbasi, M. (2011). Removal of Acid Brown 14 in aqueous media by electrocoagulation: Optimization parameters and minimizing of energy consumption. *Desalination*, 278(1), 295-302.
- [24] Adhoum, N., & Monser, L. (2004). Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation. *Chemical Engineering and Processing: Process Intensification*, 43(10), 1281-1287.

- [25] Pirkarami, A., & Olya, M. E. (2017). Removal of dye from industrial wastewater with an emphasis on improving economic efficiency and degradation mechanism. *Journal of Saudi Chemical Society*, 21, S179-S186.
- [26] Hamed, O., & Chmielewski, H. (2003). *U.S. Patent Application No. 10/683,164*.
- [27] Krishna, G. & Susmita, S. (2006). Adsorption of Fe^{3+} from water by natural and acid activated clays: Studies on equilibrium isotherm. *kinetics and thermodynamics of interactions*, 12, 185-204.
- [28] Demiral, H., Demiral, I., Tümsek, F., & Karabacakoğlu, B. (2008). Adsorption of chromium (VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models. *Chemical Engineering Journal*, 144(2), 188-196.
- [29] El-Hamshary, H., El-Sigeny, S., Taleb, M. F. A., & El-Kelesh, N. A. (2007). Removal of phenolic compounds using (2-hydroxyethyl methacrylate/acrylamidopyridine) hydrogel prepared by gamma radiation. *Separation and Purification Technology*, 57(2), 329-337.
- [30] Alkan, M., Demirbaş, Ö., Celikcapa, S., & Doğan, M. (2004). Sorption of acid red 57 from aqueous solution onto sepiolite. *Journal of Hazardous Materials*, 116(1), 135-145.
- [31] Murray, J. W., & Dillard, J. G. (1979). The oxidation of cobalt (II) adsorbed on manganese dioxide. *Geochimica et Cosmochimica Acta*, 43(5), 781-787.
- [32] Aksu, Z., & Kabasakal, E. (2004). Batch adsorption of 2, 4-dichlorophenoxy-acetic acid (2, 4-D) from aqueous solution by granular activated carbon. *Separation and Purification Technology*, 35(3), 223-240.
- [33] Lin, S. H., & Peng, C. F. (1994). Treatment of textile wastewater by electrochemical method. *Water research*, 28(2), 277-282.
- [34] Cheballah, K., Sahmoune, A., Messaoudi, K., Drouiche, N., & Lounici, H. (2015). Simultaneous removal of hexavalent chromium and COD from industrial wastewater by bipolar electrocoagulation. *Chemical Engineering and Processing: Process Intensification*, 96, 94-99.
- [35] Mollah, M. Y. A., Schennach, R., Parga, J. R., & Cocke, D. L. (2001). Electrocoagulation (EC)—science and applications. *Journal of hazardous materials*, 84(1), 29-41.
- [36] Wang, L. K., Hung, Y. T., & Shammas, N. K. (Eds.). (2007). *Advanced physicochemical treatment technologies*. Humana Press.
- [37] Patil, B. N., Naik, D. B., & Shrivastava, V. S. (2011). Photocatalytic degradation of hazardous Ponceau-S dye from industrial wastewater using nanosized niobium pentoxide with carbon. *Desalination*, 269(1), 276-283.
- [38] da Mota, I. D. O., de Castro, J. A., de Góes Casqueira, R., & de Oliveira Junior, A. G. (2015). Study of electroflotation method for treatment of wastewater from washing soil contaminated by heavy metals. *Journal of Materials Research and Technology*, 4(2), 109-113.