Indirect electrochemical degradation of methyl orange dye on graphite bifunctional electrode

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ABSTRACT

The aim of this study was to show the efficiency of graphite as bifunctionalelectrode material on the electrochemical degradation of the synthetic solutions of methyl orange (MO) dye. Graphite material was obtained from recycled spent lithium ion batteries. The electrode material was successively treated and characterized. Afterwards, they were used as anode and cathode in electrochemical device for discoloration and degradation studies. The dye discoloration was monitored spectrophotochemically by measuring the absorbance of the remaining dye at the maximum absorption wavelength λmax=465nm (methyl orange). To measure methyl orange degradation, chemical oxygen demand (COD) removal also was evaluated. The influence of operating parameters, including sodium chloride (NaCl) dosage, current density, initial dye concentration, time of electrolysisand pH, on the removal of MO was studied. It was found that maximum dye discoloration was 99.5% (current density 10mA/cm^2, electrolysis time 30 min, NaCl concentration 2.5 g/L, and initial dye concentration 8mg/L).Maximum COD removal was recorded 48.61% at current density 72 mA/cm^2, electrolysis time 240 minutes, NaCl concentration 10 g/L, and initial dye concentration 75mg/L. The energy consumption per unit COD mass (EC$_{COD}$) of the indirect anodic oxidation of MO synthetic solution was 1.14kWh (g COD)$^{-1}$ after 240min of treatment. The instantaneous current efficiency was 8.69% also after 240 minutes of electrolysis. Electrochemical degradation of MO was achieved over graphite as a bifunctional electrode. The results also showed that graphite electrode from spent lithium ion batteriesin presence of chloride ion, has a good efficiency for electrogeneration active chlorine species played an important role inelectrochemical degradation of refractory dyes in aqueous solution and the method could beused for this purpose but it is suitable and environment-friendly.It was concluded that current density and supporting electrolyte concentration are the most effective factors for electrochemical discoloration of pollutant.

INTRODUCTION

Nowadays, some types of natural and synthetic dyes are widely used in many fields involving paper production, food processing, agricultural research, leather tanning industry and textile industry (Djonga et al., 2019). In developing countries, textile effluents are discharged onto rivers and affect the ecosystem in many ways. Example, color reduces penetration of light into water bodies thus affecting the photosynthetic activity of aquatic plants resulting in reduction of dissolved oxygen, thereby having undesirable impact on their growth (Jamal et al., 2014; Regina et al., 2009). In textile industry, azo dyes are the most employed. Methyl orange was chosen as the model compound of azo dyes because they are used in textile dyeing since early antiquity such as cotton and are toxic and mutagenic (Tiar et al., 2018; Tsafam et al., 2017).Characteristics of MO molecule are shown in table1. The removal of dyes like MO is a necessary environmental process. Furthermore, some of these compounds mainly aromatic azo dyes comprise about two-thirds of the total. Because of their undesirable color, high toxicity and refractory, dye wastewater has received particular environmental concern (Tiar et al., 2018; Javaid et al., 2019).
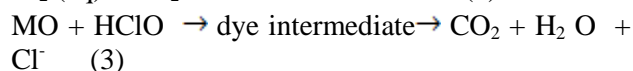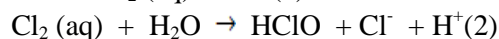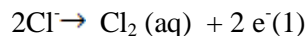
Some treatment methods such as biological treatments and physicochemical process including adsorption, filtration, coagulation/ flocculation, photocatalysis, electroflotation, precipitation and electrocoagulation have been developed to remove synthetic dyes from water (Chen et al., 2016; Sala et al., 2016; Baddouh et al., 2018; Djonga et al., 2019;Javaid et al., 2019; Mosbah and Hadda, 2019) Thus, it is important to note that some ofthese methods have some limitations (removal efficiencies unsatisfactory, cost of chemicals used for example). As an example, chemical coagulation requires some reagents (iron and aluminum hydrolysable salts), a permanent pH adjustment and this leads in general to secondary pollution. Based on their characteristics, textile wastewaters are not good treated by the conventional methods, because these techniques do not allow a complete elimination of organic pollutants (Singh et al., 2017). On the other hand, the characteristics of textile effluent are not same in all countries depending to the textile production or treatments and several factors such as scarcity of space, land cost, complexity of handling, availability of chemicals, etc.

Nowadays, the most method employed in the field of degradation of textile wastewater is electrochemical incineration of dyes developed in mid 90s. Electrochemical technique is commonly based on the elimination of pollutants directly on the anode surface, via production of OH· Radical (direct oxidation) (Li et al., 2012; Chen et al., 2016; Baddouh et al., 2018) or/and other oxidant species such as persulfate, chlorine, hydrogen peroxide, and others (indirect oxidation) (El Hajj Hassan and Jamal, 2013; Massoudinejad, 2015; Körbahti and Turan, 2016, Bahadir and Sezgintürk, 2016).The indirect anodic oxidation (IAO) is more efficiency and extensively utilized to decontamination. According to Comninellis, the IAO could be summarized as two approaches: electrochemical conversion and combustion (Comninellis et al., 1994). Indirect oxidation process can be performed to treat industrial wastewater because of its simplicity, versatility and environmental compatibility. IAO has some advantages, such as simple equipment, minimization of chemicals, fast degradation of organic pollutants and also their mineralization. In this process, anode material plays an essential role in the electrogeneration oxidizing species and electrodegradation of organic pollutants.

Various materials have been tested and assessed for dye removal from effluents. One of the most employed is the dimensionally stable anode (DSA) whom is made of titanium base metal covered with a thin conducting of some metal oxides (Stupar et al., 2017). Another material is boron doped diamond (BDD) (Peralta-Hernández et al., 2012). Both of them materials have a high chemical and electrochemical stability even at high current densities, good operating lifetime and good efficiency for mineralization of pollutants (Maamar et al., 2017). On the other hand, they are not available in developing countries and their high costlimit their utilization. In other to fight against their scarcity and high cost, graphite material has been chosen in this study.

Graphite material have been collected from spent lithium ion batteries and used as anode and cathode in the electrochemical device. The choice of graphite can be justified by its available at no cost, good efficiency for chlorine evolution reaction and widely used as anode material in some electrochemical processes. The electrogeneration of chlorine as indirect oxidant have been noted to be effective in several king of dyes, acid dyes, azo dye and disperse dyes. Active chlorine including free hypochlorous acid (HClO), hypochlorite ions (ClO⁻)

and free chlorine gaseous depending on the pH, which oxidize the organic matter present in the effluents, according to the following reactions (1) – (4) (Do Vale-Júnior et al., 2016; Ghimire et al., 2019):

$$2Cl^- \rightarrow Cl_2 \text{ (aq)} + 2\,e^- \quad (1)$$
$$Cl_2 \text{ (aq)} + H_2O \rightarrow HClO + Cl^- + H^+ \quad (2)$$
$$MO + HClO \rightarrow \text{dye intermediate} \rightarrow CO_2 + H_2O + Cl^- \quad (3)$$
$$HClO \leftrightarrow ClO^- + H^+ \quad (4)$$

From a kinetic point of view, the indirect oxidation is more effective in comparison to the direct oxidation. The basic indirect oxidation agent used in wastewater degradation treatment is active chlorine, which can be easily obtained by the electrolysis of chloride containing solutions (Stupar et al., 2017).

This work was structured in two parts. In the first one, the method for obtainment graphite electrode was described and the sample was characterized. The second part of this paper is based on the application of the indirect electrochemical oxidation of MO dye. Some operating parameters such as current density, time of electrolysis, pH medium, NaCl concentration and initial dye concentration were studied in the discoloration and degradation studies.

According to our knowledge, no work in the literature has not already study the electrochemical oxidation of dye on graphite from spent lithium ion batteries. Thus, the main goal of this work is to study the discoloration and the degradation of synthetic solution of methyl orange on graphite material from spent lithium ion batteries by electrogeneration of active chlorine species.

MATERIAL AND METHODS

Chemicals and material

MO was obtained from Merck specialties Pvt. Ltd., the solution of MO dye was prepared by dissolving 1g of dye in 1L distilled water from required dilutions were prepared. sulfuric acid and sodium hydroxide were purchased from Sigma-Aldrich and were used to adjust pH of solution. Sodium chloride, were used as supporting electrolyte and was obtained from Merck. All chemicals were of analytical reagent grade and were used without any purification.

Table 1: Characteristics of MO

Characteristics	Data
Molecular formula	C14H34N3NaO3S
Molecular weight (g mol-1)	327.33
Solubility in water (g L-1)	5.20
Wave length (nm)	465, 497 and 508
Type	Azo dye
Chemical structure	

Electrode treatment

In this study, the main material used is graphite. The samples of graphite tube were obtained from the recycling of used batteries. Indeed, alkaline batteries contain manganese dioxide, graphite, steel and zinc. Thus, the used batteries Tiger Head brand (type R20 UM-1) were collected and shredded to obtain the samples of graphite. These samples having apparent density of 1.63 g cm^{-2} and an effective area 12.058 cm^2. After collect and shredded, the substrates were deprived of grease and stripe from the following steps. Firstly, graphite samples were washed using acetone. Secondly graphite was sandblasting in alumina during five minutes and thirdly, the supports were treated by the chemical treatment in oxalic solution 10% during 45minutes and dried at 105°C for 10 min.

Electrode characterization

Raman spectra was collected using a Laser Raman microscope (LabRam HR, Horiba) with 633 nm wavelength Renishaw. X-ray diffraction (XRD) patterns in 2θ scan mode were obtained using Bruker D8 Advance X-ray Diffractometer with Cu Kα (λ=1.5405 Å) radiation in the 2θ range from 15 to 60°. Fourier Transform infrared (FT-IR), Bruker spectrometer (Model no TENSOR 27) was used to determine the functional groups located in graphite. Potassium bromide (KBr) was mixed with sample to make the pellet and the spectra were recorded from 400 to 4000 cm^{-1}.

The electrochemical process

Synthetic solution of methyl orange was prepared by dissolving its powder in distilled water at a concentration of 2, 4, 6, 8 and 10 mg/L for discoloration study and 25, 75 and 125mg/L for degradation study. The electrochemical oxidation of dye was performed in a bath reactor (200 ml) equipped with two graphite electrodes as anode and cathode in conjunction with an adjustable power supply unit LW LONGWEI LK-K30100 (Figure 1). The inter electrode spacing was fixed at 10mm. The duration of all the electrolysis experiments was varying. The reactor was placed on magnetic stirrer (MIVAR MAGNETIC STIRRER) for mixing its content during the electrolysis in order to maximize mass transport.
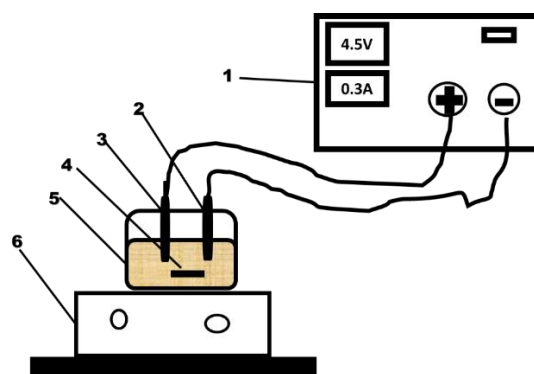

Figure 1: The schematic diagram of experimental sep-up. 1: Power supply; 2: cathode (graphite); 3: anode (graphite); 4: magnetic bar; 5: electrolytic cell; 6: magnetic stirrer.

Analytical methods

The performance of the electrochemical device on the degradation of MO was evaluated on the basis of four main factors such as removal of color, COD removal, instantaneous current efficiency and energy consumption per COD unit. The dye decolorization was monitored spectrophotometrically by measuring the absorbance of the remaining dye at the maximum absorption wavelength of 465 nm on an ultraviolet-visible spectrophotometer GENESIS-10S-UV-Vis. The amount of MO removal was calculated using the following formula:

$$MO\ removal\ (\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (5)$$

Where, A_0 and A_t are the absorbance before and after the electrolysis, respectively.

The degradation efficiency of synthetic solution containing MO was monitored by measuring its COD evolution. COD_0 was determined by the dichromate method based on the oxidation of organic matter by excess of potassium dichromate in concentrated sulfuric acid medium in the presence

of silver sulfate (Ag_2SO_4) and mercuric sulfate ($HgSO_4$). The solution obtained is heated for 2 h at 150°C. The excess of dichromate is titrated from iron sulfate (Jean et al., 2009). The COD removal was calculated using Eq. (6):

$$COD \ removal \ (\%) = \frac{(COD \ 0 - COD \ t)}{COD \ 0} \times 100 \ (6)$$

Where COD_0 and COD_t are the solution COD values at initial and t time of the electrolysis, respectively.

The instantaneous current efficiency (ICE) for the anodic oxidation of the methylene blue was calculated from the values of the COD using the relationship:

$$ICE \ (\%) = \frac{[(COD)t - (COD)t + \Delta t] \times F \times V \times 100}{8I\Delta t} (7)$$

Where $(COD)_t$, $(COD)_{t+\Delta t}$, are the COD at time t and $t + \Delta t$ [g O_2 L^{-1}] respectively, I is the current (A), F is Faraday's constant [96487 C mol^{-1}], Δt is the time (S) and V is the volume of treated wastewater in L. The equivalent mass of oxygen is 8(Indu et al., 2014; Comninellis and Pulgarin, 1993).

The specific energy consumption, expressed in kWh gCOD^{-1}, is the energy used to remove a unit mass of COD from wastewater and can be calculated using the following relationship:

$$Ec = \frac{I \times U \times t}{[(COD)t - (COD)t + \Delta t] \times V} (8)$$

Where EC is the energy consumption in KWh per g COD reduced, U is the cell voltage (V), I is the applied current (A), t is the electrolysis time in hours, $(COD)_t$, $(COD)_{t+\Delta t}$, are the COD at time t and $t + \Delta t$ [g O_2 L^{-1}] respectively and V is the volume of treated wastewater in L (Panizza et al., 2007; Anthuvan Babu et al., 2012; Indu et al., 2014).

RESULTS AND DISCUSSION

Electrode characterization

The characterizations were carried out on the graphite samples in order to confirm its ability to be used in electrochemical process for oxidation organic pollutants.

Raman analysis

Raman spectroscopy is widely used for the characterization carbon structural properties Gambou-bosca and Daniel, 2015). The Raman spectra of graphite and is shown in figure 2a. The Raman spectra of graphite presents three peaks which denominated D (1348 cm^{-1}), G (1575 cm^{-1}) and 2D (2668 cm^{-1}) bands. The G band is the main fundamental peak which arises from the crystalline structure of graphitic samples and is associated to the symmetric E_{2g} vibrational mode observed for graphitic materials. This peak is related to the sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice. Another dominant peak is the D band is related to the defects and disorder in the hexagonal graphitic layer (Jiang et al., 2014). The latter peak is 2D band is also attributed to the sp^2-bonded carbon atoms in a two-dimensional lattice. The intensity ratio (I_D/I_G) of the D to the G bands of the graphite is about 0.98.

FTIR analysis

The FTIR spectra of graphite in the range of 4000-400 cm^{-1} are shown in Figure 2b. The graph presents in the region from 2700-3000 cm^{-1}, the bands at 2744 cm^{-1} and 2916 cm^{-1} are attributed to C-H interaction in the graphite. The graph also shows an intense peak at 1490 cm^{-1} corresponding to the C= C band and skeletal vibration of graphitic structure. Another peak can be seen from graph at 3317 cm^{-1} which could be attributed to the O-H absorption which is related to water molecules.

XRD analysis

For studying the crystallinity and crystal, phases of the graphite material, X-Ray diffraction is used. Figure 3 shows the experimental XRD patterns of the graphite. All diffraction patterns show the well-known carbon (002) and (004) diffraction peaks typical of a highly graphitic ordered and crystalline structure in graphite (Rashed and El-moneim, 2017). The interlayer spacing determined from Bragg's law ($2d\sin\theta = n\lambda$) for the (002) peak is 0.335nm.
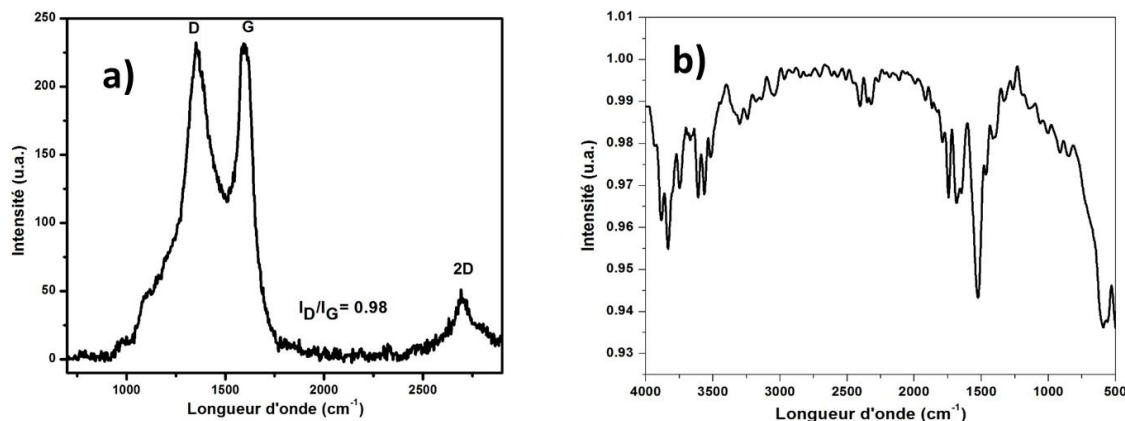
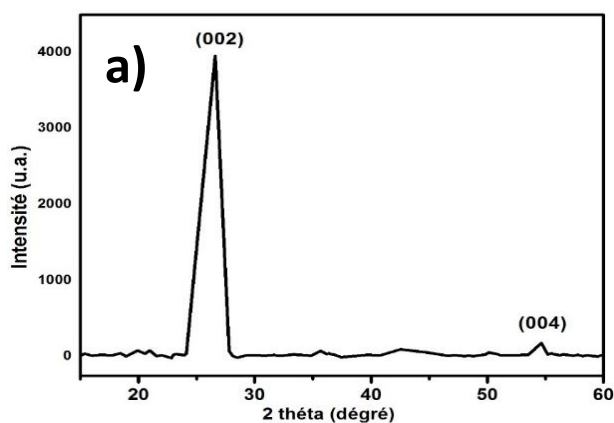**Figure 2:** a) Raman spectra of graphite and b) FTIR spectra of graphite.

Figure 3: a) Typical XRD patterns of graphite

Discoloration study of MO

Effect of current density

In this part, experiments were conducted in order to investigate the effect of current density on dye removal through electrochemical oxidation. Figure 4a represents the results of the effect of current density on color removal efficiency. Three current densities were applied in this work. A slight increase in dye removal was noticed with an increase of current density up to a value of 30 mA cm^{-2}. It has been noticed that the discoloration rate or the oxidation rate of Methyl orange increase linearly with increase in current density, due to the fact that by increasing the current density, it means a large amount of charge entering the electrochemical cell and electro-generating more of active chlorine species from electrolysis of chloride ion at anode surface according to the equation 3. At 50mA cm^{-2} the efficiency of dye removal was diminished. This observation can be justified by the high current density values may lead towards the formation of by-products by diminishing the actual dye removal however; during the electrolysis some species can be produced trough not having the same efficiency of chlorine species like hypochlorous acid, hypochlorite ion and chlorine gaseous. This is because beyond the limiting current density the increasing current was not used for oxidation of dyes but for producing oxygen which leads to a decrease in current efficiency. Mass transfer during anodic oxidation could explain the limitation of increase in current density to oxidize dyes beyond a certain limiting current density.

Effect of time of electrolysis

In order to study the effect of electrochemical treatment time on MO removal, experiments were conducted for which a current density of 10 mA/cm^2, a concentration of 8 mg/L, the initial pH of dye solution was 3, the inter electrode spacing was 10 mm and the supporting electrolyte concentration of was 1.5 mg l^{-1} was maintained and kept constant for all experiments. Figure 4a presents the results. It is clear in figure 5a that dye removal is in direct proportion to the treatment time. The effect of treatment time was studied up to a maximum of 30 min. Thus, the maximum dye removal was found at 30min of electrolysis and could be optimized for getting maximum dye removal through electrochemical oxidation.
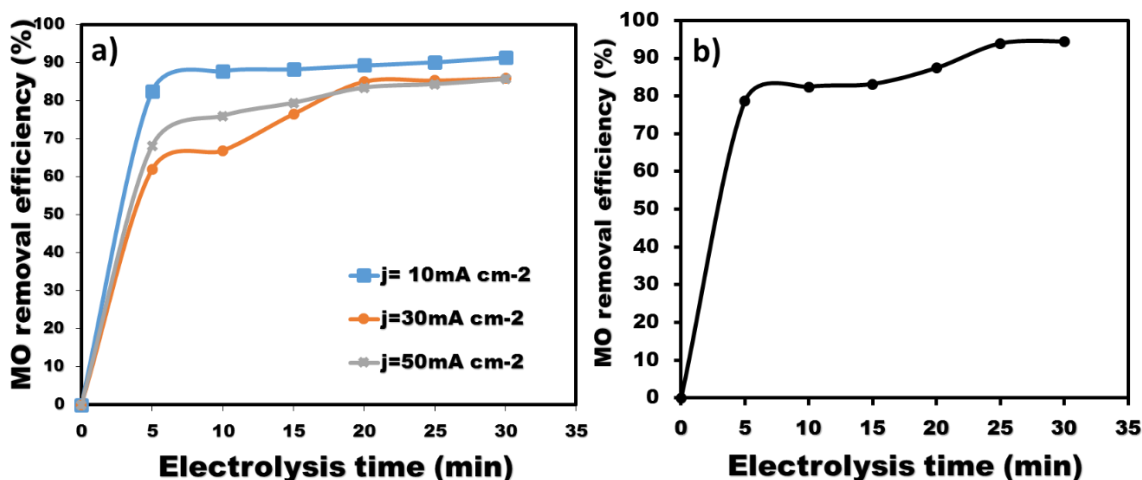
Figure 4: a. Effect of current density on MO removal efficiency and b. Effect of electrolysis time on MO removal

Effect of supporting electrolyte concentration

Some studies were found NaCl is the best supporting electrolyte for the reaction (Indu et al., 2011; Zhang et al., 2014; Baddouh et al., 2018). Figure 5a presents the results of the effect of different concentration of NaCl on colour removal. Experiment shows that the electrolysis of MO with NaCl, results in an indirect electrochemical oxidation effect with the generation of chlorine/hypochlorite which is the main pathway for removal of pollutants. Therefore, results indicate that the MO removal increases with increase in the chloride concentrations. These results were also found by panizza et al., (Panizza et al., 2007) and Indu et al. (Indu et al., 2011). Chloride ion contributes to the improvement the electrochemical degradation through increasing the chlorine species generation and the cell conductivity. Their formation enhances the destruction of organic matter present in the wastewater. The increase chlorine species up to 1.5mg L^{-1} favored the reaction

but with further increase in dose of chloride ion the current density increased leading to scavenging of hydroxyl radical and formation of chlorine, which explains the reduction in efficiency of dye removal at higher chloride concentration.

Effect of initial dye concentration

The influence of initial dye concentration on MO color removal was carried out in a range from 2 to 10 mg L^{-1}. Experiments were conducted at a chloride concentration of 2.5 g L^{-1} and a current density of 10 mA cm^{-2} and the results are shown in figure 5b. Aliquots were taken at an interval of 5 min. From this fig, it is clear that the efficiency of electrochemical oxidation increases with the initial dye concentration up to 8 mg L^{-1}. When the dye concentration is up to 8 mg L^{-1}, the efficiency of color removal decreases. At 20 min of electrolysis, maximum color removal was achieved with an initial concentration of 8 mg L^{-1}.
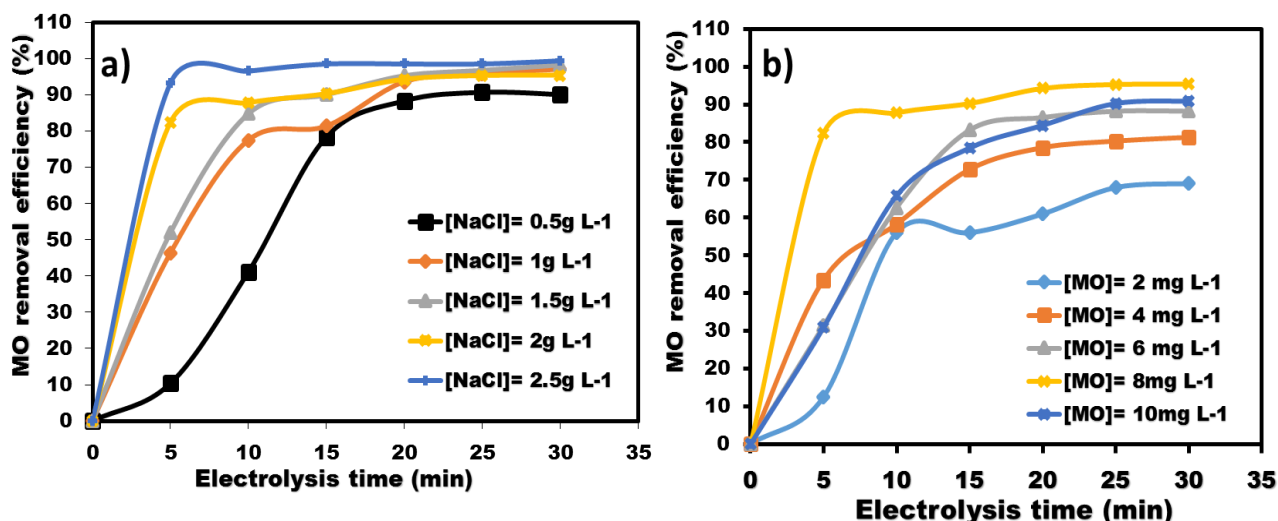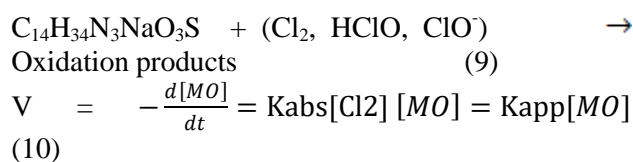
Figure5: a. Effect of supporting electrolyte concentration on MO removal and **b.** Effect of initial dye concentration on MO removal

Effect of pH

pH is one of the important factors that affect the performance of the electrochemical process. There are several reports on the effect of pH, nevertheless the results are dissimilar and even opposing due to different organic molecules and electrode materials (Baddouh et al., 2018). The pH where the high MO removal with graphite electrode was found at 3. Which is probably due to the effect of pH on the existing from active chlorine in the solution. Thus, in presence of chloride ion the major oxidant produced are hypochlorite, hypochlorous and chlorine. There is an ionization equilibrium existing between them (equations 2 and 4). When pH was higher than the pKa, hypochlorite ($E^0 = 0.89$ V vs. SHE), whose oxidative ability was weaker than that of hypochlorous acid (Zhang et al., 2014), accounted for higher proportion in all the active substance. Thus, acidic media is more favorable to the oxidation of organic compounds, because lower pH values restrict the chlorine evolution reaction and favor organic pollutant oxidation. The same results have been found by El Hajj Hassan (2013) during their study related on the kinetic study of the electrochemical oxidation of methylene blue with Pt electrode. It is also seen from this figure that at pH 12 the efficiency of MO removal was lower than at acidic medium. Additionally, the MO appeared negative electrical property in alkaline solution. In this work, pH 3may be considered as optimum to the electrochemical degradation of MO. The low efficiency noted to pH 2 may be attribute to the stronger inhibition for the hydrolysis of Cl_2 (eq. 2) in highly acidic environment should be the main reason for this decrease on reaction rate.

Kinetic study of the decolorization of MO on graphite electrode

The kinetics of MO synthetic solution discoloration was followed during 30 minutes of electrolysis by indirect anodic oxidation on graphite electrode. In order to determine the reaction order, some calculations were carried out. Table 3summarizes the main results (R^2 and K_{app}) related to each electrolyte supporting concentration. It can be seen from this table that, the experimental kinetic can be satisfactorily described by a pseudo-first order reaction kinetic (Table 2and Figure 6.b), assuming the quasi stationary state for chlorine concentration:

$$C_{14}H_{34}N_3NaO_3S + (Cl_2, HClO, ClO^-) \rightarrow \text{Oxidation products} \quad (9)$$

$$V = -\frac{d[MO]}{dt} = Kabs[Cl2][MO] = Kapp[MO] \quad (10)$$

Where MO is methyl orange, K_{abs} the absolute rate constant and K_{app} the apparent rate constant ($K_{app} = K_{ads}[Cl_2]$).

The apparent kinetic rate constant value K_{app} for the oxidation of MO corresponds of the slope of the linear fit of $\ln([MO]_0/[MO])$ versus time. The found K_{app} (0.012 min^{-1}) was calculated from linear regression of the pseudo-first order kinetic model with related coefficient R^2 equal to 0.99 (Table 2). These values are in good agreement with other apparent rate constant for chlorine reactions of aromatic compounds with chlorine species. Furthermore, Louafi and Brahmia have studied the electrochemical oxidation process to degradation of

aqueous solution dyes. They have found that the apparent rate constant values of different dyes (Methyl orange (MO), Congo red (CR) and Methyl green (MG)) treated by indirect anodic oxidation using a platinum anode and Cobalt ion as mediator were 0.0119 min^{-1}, 0.003 min^{-1} and 0.01 min^{-1}, respectively (Louafi and Brahmia, 2016). The determination of the reaction order was also conducted by Pang et al, (Pang et al., 2013) for MO synthetic solution discoloration by cooperative

electrochemical oxidation in anodic-cathodic compartment. The same ascertainment was performed. Indeed, MO synthetic solution discoloration by this process followed a pseudo-first order kinetic model. The apparent rate constants obtained were equal to 0.1156 min^{-1} and 0.0610 min^{-1} in the anodic and cathodic compartment respectively. These results are in good agreement with findings by Noor and Sarmad (Jawad and Najim, 2018).
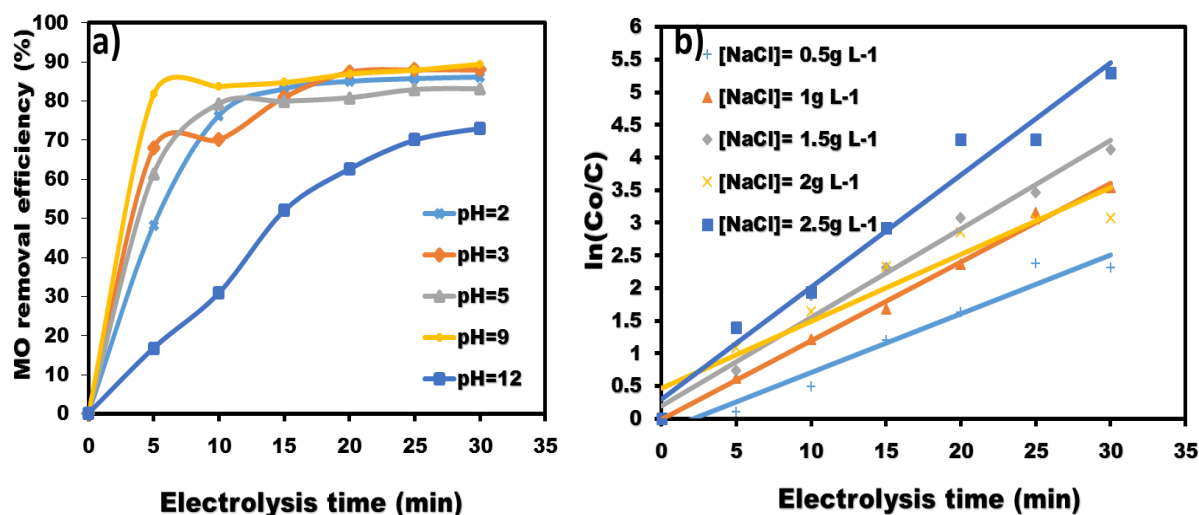

Figure 6: a. Effect of pH on MO removal b. the kinetic fitting curve of M.O. indirect removal.

Table 2: The first order reactions kinetic parameters of different supporting electrolyte concentrations

NaCl Concentration	K_{app}	R^2
0.5 g L^{-1}	0.0901	0.9583
1 g L^{-1}	0.1204	0.9957
1.5g L^{-1}	0.1357	0.9816
2 g L^{-1}	0.1025	0.9137
2.5g L^{-1}	0.1714	0.9727

Degradation of MO synthetic solution by indirect anodic oxidation on graphite electrodes:

Evolution of COD removal

Although the main requirement established by law in many countries in the world is only related with the industrial effluents coloration, the reduction of the organic load is also of environmental interest. In electrochemical conversion the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing. In electrochemical combustion, the organics are completely oxidized to CO_2 and H_2O. The progress of the destruction of the organic

pollutant has been monitored by COD estimation. The potentials required for oxidation of organic pollutants are generally high and the production of oxygen from the electrolysis of water molecules may determine the reaction yield. In order to know the graphite anodes performance on degradation and its electrochemical efficiency, the COD removal was followed under the different conditions of experiments.

Effect of current density on COD removal

The effect of current density on the evolution of COD removal percentage during the electrochemical degradation of MO synthetic

solutions is shown in figure 7a as function of treatment time. Experiments were conducted at 6 different current densities from 18 to 108 mA cm^{-2}. Results showed that COD removal efficiency increases with increase in current density up to 72mA cm^{-2}. When the current density was increased, the rate of generation of chlorine species increased. The increase in chlorine species in the media approaches equilibrium with degradation of organics. Results also showed that after 300minutes of electrolysis the DCO removal efficiency decreases this is almost at current densities. This result was not in agreement with the findings of some authors (Babu et al., 2009).Electrochemical process may be described by two processes such as the direct anodic electro-oxidation and/or indirect anodic electro-oxidation. In direct electrochemical conversion, organics can be oxidized directly at the anode surfaces through physically adsorbed hydroxyl radicals, which produce carbon dioxide as a final product. Indirect anodic electro-oxidation, anodically generates chlorine and hypochlorite which are used as the oxidizing agents for the decomposition of organics in the presence of chloride ions. An increase current density leads to the increase charge loading, which in turn increases the pollutant removal.

Effect of time

Figure 7b present the DCO removal efficiency as function of time. An abatement of 45.66% was achieved after first 60 minutes. It then Increase to 48.61%, when treatment time was reached to 240 min. After 240 min, abatements were kept constant. It can be noted that the COD removal efficiency increases with the increase of electrolysis time, indicating that they could be further removed if given much more time. Usually, a long reaction time in hours is required to attain a significantly increased COD and color removal. This result exposes not only time influence on the DCO abatement, but also the fact that this effluent is rich of recalcitrant organic compounds. During electrolysis process, high current densities carried out oxidation of graphite material. This is can be due to the high potential of corrosion of chlorine species which are not only used to oxidation compound but also to oxidation of graphite electrode.
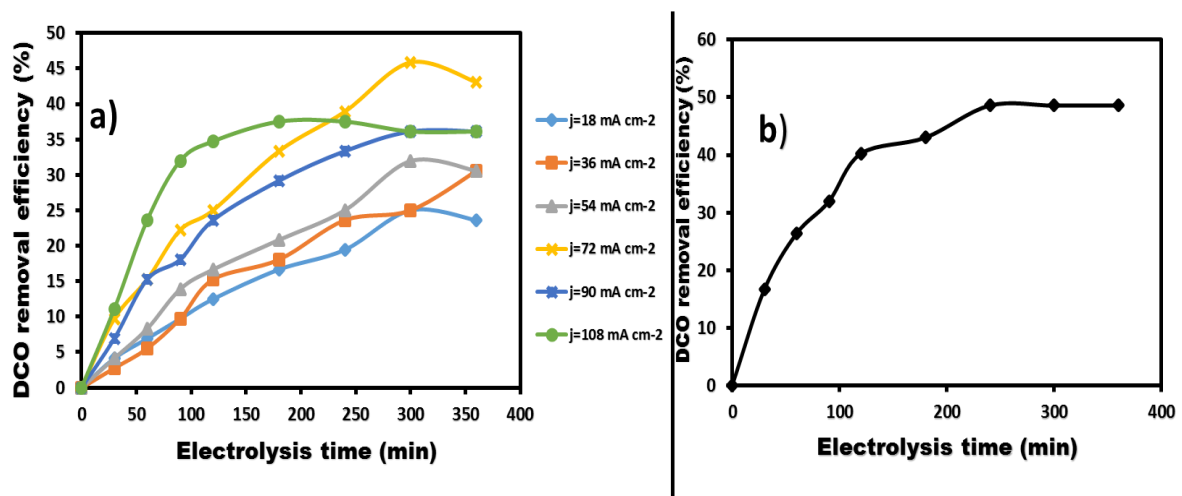

Figure 7: a. Effect of the current density on COD removal with electrolysis time, b. effect of the electrolysis time on COD removal.

Effect of supporting electrolyte concentration

In this study, the effect of different concentration of NaCl for initial dye concentration of 75 mg/L on COD reduction was studied. Chloride plays a very important role in the indirect electrochemical oxidation of organic compounds. The chloride ions in the solution were oxidized to chlorine at the anode and hydrolyzed to form hypochlorous acid (HOCl) (Eq. 2), which was subsequently changed to hypochlorite ions (OCl$^-$) and hypochlorous acid, depending on the pH of the wastewater (Domga Richard and Tchatchueng, 2017).Figure 8a shows the results. Maximum COD reduction was obtained at 10g/L of NaCl and further studies were conducted with this value. The increase of NaCl concentration favors the electrogeneration of chlorine species. Thus, the rate of degradation increased with supporting electrolyte concentration. At lower chloride concentration, the pollutant degradation is

small compared to higher chloride concentration. This is can be due to the fact that graphite electrodes have low over potential for chlorine evolution reaction. On the other hand, notice that beyond the electrolyte concentration higher than 10g/L, the efficiency of COD removal decreases, this is can be due to the secondary reaction is favored in comparison with organic oxidation. The reason for the decline in Cl^- ions could have been due to the escaping chlorine gas (Cl_2) from solution or the electrochemical formation of chlorates and perchlorates (Ghimire et al., 2019).After the NaCl concentration reached 10 g/L, the COD removal was not obviously improved with further increase of NaCl. Therefore, the optimal concentration of NaCl is 10 g/L.

Effect of initial dye concentration

The evolution of COD removal percentage during the degradation of MO in aqueous synthetic solution is shown in figure 9b as function of treatment time by IAO on graphite electrode. COD results provided us with information about the MO oxidation

efficiency of the IAO during 360 minutes. The influence of initial dye concentration on DCO removal efficiency was investigated in the range of 25 to 125 g/L. Tests were conducted at a chloride concentration of 10 g/L. An intensity current 72 mA cm^{-2} was used. COD reduction was independent of initial concentration in the range tested. The initial dye concentration plays an important role in practical applications. In general, a lower initial concentration is favored to attain the efficient and complete decomposition of the dyes (Javaid and Qazi, 2019). As the effluent released from industries contains a very high concentration of the dye contents, dilution is required before proceeding for catalytic treatment regardless of the type of oxidant used. At higher dye concentrations, the generation of chlorine species from the electrode material was suggested to be reduced since the active sites of the catalyst might be occupied by the dye molecules. An increased number of dye molecules and insufficient concentration of the active chlorine species decreased the efficiency of the decomposition process.
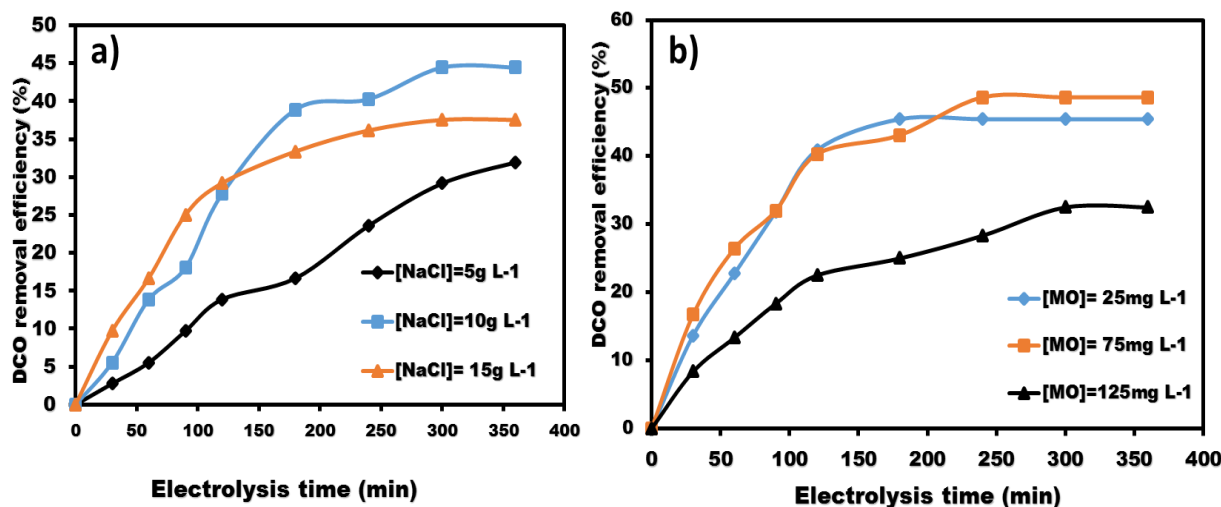

Figure 8: a. effect of the supporting electrolyte concentration on COD removal with electrolysis time, b. effect of the dye initial concentration on COD removal with electrolysis time.

Kinetic study of COD removal

In this study, the dye degradation reactions follow pseudo first order kinetics. The rate constants were obtained for pseudo first order reaction as 1.1 x 10^{-3}min^{-1}, 1.8 x10^{-3}min^{-1} and 1.8 x10^{-3}min^{-1} for 5 g L^{-1}, 10 g L^{-1} and 15 g L^{-1} NaCl concentration, respectively. Reaction rate constants increase with the increase in NaCl concentration. It can be due to the generation of chlorine species when the NaCl

concentration increase. The rate of degradation relates to the probability of chlorine species formation in electrochemical cell.

Instantaneous current efficiency study

In the present study the instantaneous current efficiency (ICE) was calculated for all the experiments. Figure 9b shows the variation of ICE with reaction time. It can be observed that the ICE increases with time, the increase can be attributed to

the complexity of the intermediates formed, especially some hard-to-treatment products. After 120 minutes of electrolysis, it decreases. Thus 120 min of electrolysis can be the time that the oxidation was important to degrade some by-products. The

maximum COD removal was 48.61%, thus during the process MO was not all degrade, it can be due to the low chlorine evolution reaction on graphite electrodes and the use of chloride ion produced some refractory by-products during the electrolysis.
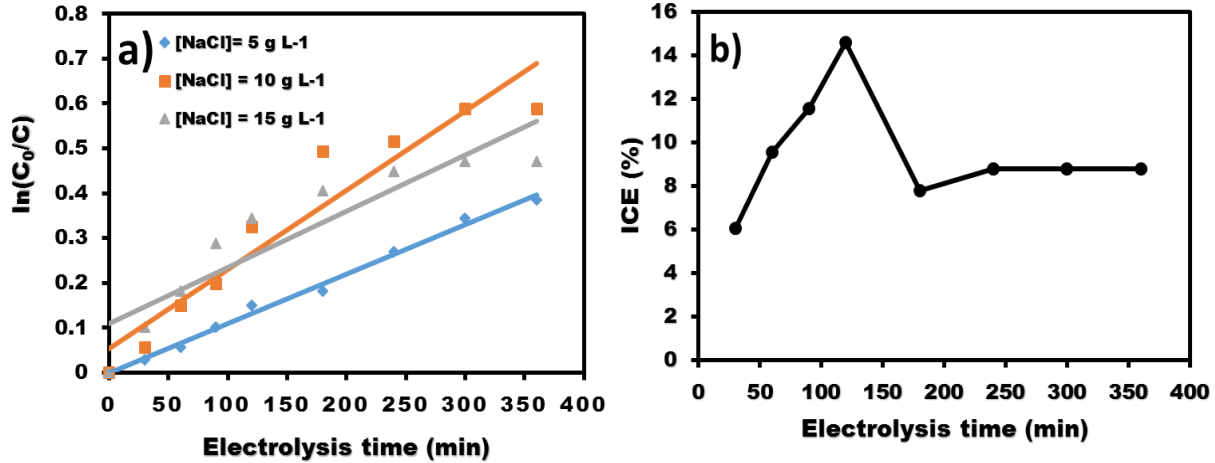

Figure 9: a. kinetic fitting curve of M.O. degradation b. Variation of ICE with electrolysis time

Table3: The first order reactions kinetic parameters as function of NaCl concentration

NaCl Concentration	K_{app}	R^2
5 g L^{-1}	0.0011	0.9932
10 g L^{-1}	0.0018	0.9165
15 g L^{-1}	0.0018	0.8291

Table 4: Energy consumption of MO oxidation versus electrolysis time

Treatment time (minutes)	EC_{COD} (kWh (g COD)$^{-1}$)
30	0.16
60	0.28
120	0.51
240	1.14

Energy consumption

It is very important to estimate the treatment costs in large industrial application. In this study, after investigation of COD removal of MO synthetic degradation, the energetic cost of the process was investigated (Table 4). From the Eq. 7, the energetic cost of MO degradation by IAO on graphite electrode was equal to 0.16 kWh (g COD)$^{-1}$ within 60 minutes and it increase to reach 1.14kWh (g COD)$^{-1}$ after 240 minutes.

In this study, the energy consumption was estimated in the order of 1.14 kWh/g COD. Bahadir et al, (2016) reported that the energy consumption was about 0.3179 kWh/g COD removal (lower than the

present study) during treatment of acid violet textile dye using Pt/Ir electrodes. The low results may be attributed to the distinct electrode characteristics. It is a matter of fact that the electrochemical treatment of wastewater is an energy intensive process. However, it has robust performance and capability to adjust to variations in the influent composition and flow rate. It is particularly well suited for decentralized water treatment because the mechanism trough which electrochemical processes are controlled, the electrode potential and cell current, are easier to control remotely than conventional and biological processes.

CONCLUSION

The elevated cost of anodic materials used in the anodic oxidation for water treatment of effluents undermines the real application of these technologies. The study of novel alternative materials more affordable is required. In this work, we report the application of graphite material from spent lithium ion batteries alloys as cheap anodic material to decolorize and degrade azo dye Methyl orange synthetic solutions. This study demonstrated that graphite electrodes have good properties to its use in the electrochemical oxidation of azo dye pollutant. The experimental results of the discoloration and degradation studies indicated that the electrochemical device was very effective for treating dye wastewater. Under the most favorable treatment conditions, discoloration removal was 97% at 10 mA/cm^2, 2.5g NaCl, 20min and 8mg/L of MO concentration. The COD reduction is significantly affected by the initial pollutant concentration, supporting electrolyte concentration and current density. Thus maximum COD removal was 48.61% at 72mA/cm^2, 10g/L NaCl, 75mg/L of MO concentration. The results also showed that, during indirect oxidation of the AB111 dye, it was found out that the pseudo first reaction rate constant increases with the increase of the supporting electrolyte concentration in discoloration and degradation studies. Although the reaction proceeds faster with the higher NaCl concentration, it is more economical to use lower concentration. The results of this study are unique and could provide important information for practical applications. This method can be utilized for the treatment of other organic pollutants and help to meet the requirements for treatment of wastewater discharged to environment.

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