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Removal of textile dye Lanaset Red G from waters by electrochemical degradation and spectrophotometric determination

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ABSTRACT

The removal of Lanaset Red G, a kind of azo dye, has been studied with graphite electrodes in aqueous solution by electrochemical method. Graphite electrodes were used as anode and cathode in the decolourization process. Concentration of dye molecules in aqueous solution was determined by the ultraviolet-visible spectrophotometric technique. The operational parameters including initial pH, effect on the conductivity and time of electrolysis were optimized. The surface morphology of electrodes was also investigated and found that the surface of anode was affected by electrolysis. The results indicated that for a solution of $50\,\mathrm{mg\,L^{-1}}$ dye, almost 94% of dye was removed under optimum conditions. The optimized conditions were successfully applied to remove dye molecules present in real textile effluent and lake waters.

Keywords: Azo dyes; Electrochemical degradation; Graphite electrode; UV–vis spectrophotometry

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1. Introduction

The textile industry is one of the most polluting sectors when wastewater discharge amounts and effluent composition are considered [1]. Water is of prime importance in textile dyeing processes and the main waste which has to be treated to reduce environmental contamination [2]. Synthetic dye pollutants are the main part of these wastes in the textile industry. The treatment of wastewater has long been a concern of textile industry. The release of coloured wastewater into the ecosystem causes a dramatic natural pollution and defects in an aquatic life [3]. Dye-contaminated wastewater is known to contain strong colour and many of the commercially used dyes are resistant to biodegradation, and less than $1\,\mathrm{mg\,L^{-1}}$ of dye concentration causes an obvious water colourization [4]. Dyes are usually stable under sunlight and resistant to microbial attack and temperature. The most of these molecules are not degradable in wastewater treatment plants [5]. The removal of dyes in waters is an important process in textile industry and wastewater treatment.

There are several treatment methods that were processed to treat textile wastewaters, such as Fenton's reaction [6], biological treatment [7], chemical

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precipitation [8], adsorption [9], ozonation [10] and electrochemical methods [11].

The electrochemical technologies have been largely developed as an alternative wastewater remediation. It introduces promising approaches for the decolourization of dye molecules [12]. Electrochemical degradation methods of dye molecules have been in great interest in recent years [13]. This technique can be considered as an option to conventional chemical dye treatment methods. It may be more environmentally friendly in comparison with other water treatment methods [5,14]. The electric current causes redox reactions which involve the destruction of organic molecules and completes the reaction to CO_2 and H_2O in some cases.

According to Rivera et al., the electrochemical processes mainly follow two possible paths; first one is an anodic oxidation in which an electron transfer reaction takes place at the metal/solution interface between the anode dye molecules and the second is the cathodic reduction where the reductive breaking of the bonds of azo groups leads to a decrease in the absorbance values of dye molecules [15]. As a result, electrochemical treatment of wastewaters has several advantages. These processes are generally carried out at room temperature and pressure and the consumption of the chemicals in this technique is less than the other methods [16].

The objective of the present work is to investigate the performance of electrochemical decolourization of a synthetic dye Lanaset Red G (LRG) (Fig. 1) [17] by using carbon electrodes. LRG is a commonly used dyestuff in cotton dyeing, and possibly being introduced to the environment due to the discharge of factory wastewaters.

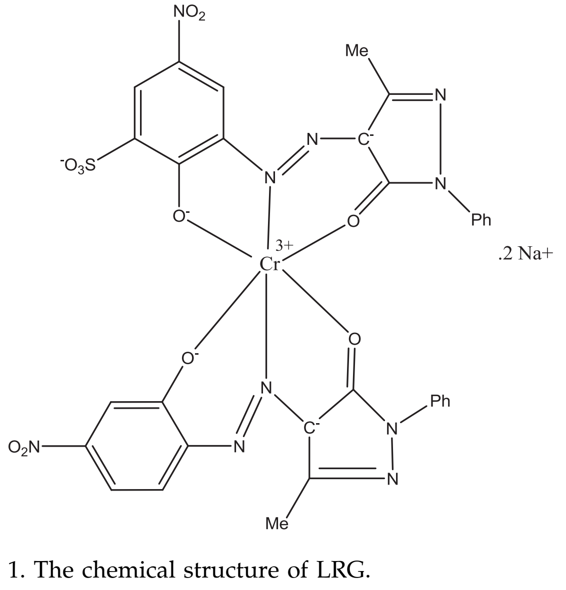

Fig. 1. The chemical structure of LRG.

2. Experimental

2.1. Reagents and apparatus

All reagents used were of analytical grade, purchased from Aldrich, Steinheim, Germany and Merck, Darmstadt, Germany, and used without further purification. The experiments were carried out with a conventional three-electrode cell. The working and the counter electrodes (cylindrical graphite rods) were embedded in polyester and about 1.57 cm^2 surface area (for each graphite electrode) was in contact with aqueous medium. The carbon electrodes were chosen as anode and cathode instead of metal electrodes, because they have relatively higher specific surface areas than metallic ones, which make them an ideal electrode for the removal of pollutants, especially organic molecules [5]. Another reason for the choice of carbon electrode is the electrochemical activation of metal electrodes which may decrease after a long time of electrolysis [1]. Electrical conductivity of electrodes was provided by a copper wire. Throughout all of the experiments, the electrode surface was cleaned in water and degreased in acetone, washed with distilled water and finally dried. The Ag/AgCl (3 M KCl) electrode supplied from Crison Instruments (Barcelona, Spain) was used as reference.

The conductivity of solutions was raised up and adjusted to the desired values by adding Na_2SO_4. These values were recorded by using WTW LF-330 model conductivity metre. The solutions were stirred by a magnetic bar at 200 rpm in all the experiments. A potentiostat/galvanostat (EG&G Instruments, Princeton Applied Research, Model 362) was used to control the applied potential during electrolysis. Degradation of the azo dye was analysed and monitored by using Shimadzu UV-160 A model spectrophotometer. Surface micrographs of electrodes were analysed with an Olympus SZ X16 Microscope and same brand C 5060 model 5.1 mega pixels camera.

2.2. Electrochemical treatment

In order to achieve the degradation of LRG dye by electrochemical treatment, a 1,000 ppm of dye solution was prepared at first and 50 ppm of stock solution was prepared by dilution. The treatment was carried out in a 100 mL Pyrex glass beaker containing 50 mL of dye solution in which the three electrodes were immersed. Mixing in the cell was done by a Teflon-covered stirring magnetic bar installed at the bottom of the cell. The anode and cathode electrodes were connected to the positive and negative outlets of the potentiostat, and reference electrode was immersed and connected. Potentials up to 2.5 V (vs. Ag/AgCl, 3 M KCl) were applied to the system during the treatments at room temperature. The schematic diagram is shown in Fig. 2.

2.3. Analytical methods

The concentration of the untreated and treated LRG solutions was measured spectrophotometrically. The UV–vis measurements were carried out before and after electrolysis by using a 5 mL aliquot of dye solution which contains Na_2SO_4. Then, the solution was added to the treatment cell back after measurement. Samples were also taken during electrolysis at convenient times and measured. The decomposition, given in terms of colour-removal percentage (CR%), was calculated according to Eq. (1) given below by using the diminution of the dye concentration during the electrochemical treatment at 492 nm.

$$\mathrm{CR}(\%) = \frac{\mathrm{ABS}_0 - \mathrm{ABS}_t}{\mathrm{ABS}_0} \times 100 \tag{1}$$

where ABS_0 and ABS_t are the instant absorbances before electrolysis and after electrolysis at time t, respectively, at the maximum visible wavelength ($\lambda_{\max}$) of the dye-contained aqueous solution. The CR % is the colour-removal percentage.

2.4. Real sample analysis

Two different water samples (a textile factory wastewater sample and a lake water sample near the same textile factory) were collected. Prior to the experiments, these samples were filtered in vacuum with the help of porous filters (pore number 4 [10–16 µm]) to remove the solid particles that may interfere the UV–vis measurements. Then, a 50 mL of each sample was taken in a beaker and pH of the water was adjusted to 6. The concentration of Na_2SO_4 in the solution was adjusted to 1.5×10^{-1} M, and 50 µg of LRG was added into it. The electrodes were immersed into the beaker and 2.5 V of potential was applied to the system.

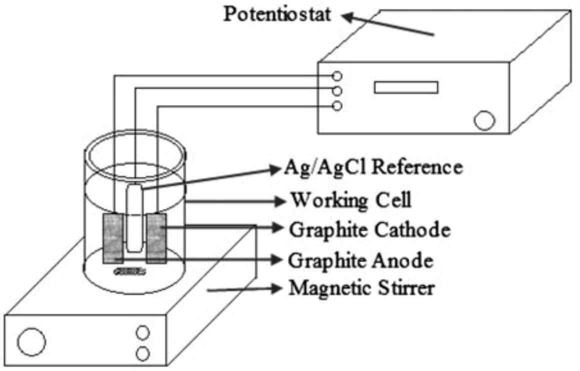

Fig. 2. Schematic diagram of experimental set-up.

3. Results and discussions

3.1. Decolourization behaviour of LRG

After dissolving Na_2SO_4, azo dye LRG gave a maximum absorbance at 492 nm. The results of UV–vis spectra of LRG before and after treatment are shown in Fig. 3. When a 2.5 V of potential (vs. Ag/AgCl, 3 M KCl) was applied to the system, the UV–vis peaks of 50 ppm LRG clearly indicated that decomposition and decolourization of dye molecules occurred on the graphite electrode surface. As can be seen from the figure, the UV/vis absorbance of dye molecule changed significantly during 20 min of electrolysis. The main absorbance peak of LRG at 492 nm started to decrease dramatically with the increasing reaction time, and did not show any new absorbance bands in the UV–vis region. These behaviours apparently confirm that the cleavage of N=N was almost completed. The weak absorbances at 325 and 371 nm were completely disappeared.

3.2. Optimization parameters of decolourization process

Optimization of the parameters such as pH, conductivity and applied potential was investigated and optimum conditions were determined. Optimization experiments were based on one variable at a time technique. The pH is the key operating factor that influences the performance of decolourization process. To examine its effect, the pH of the model solutions as well as waste waters was adjusted to the desired

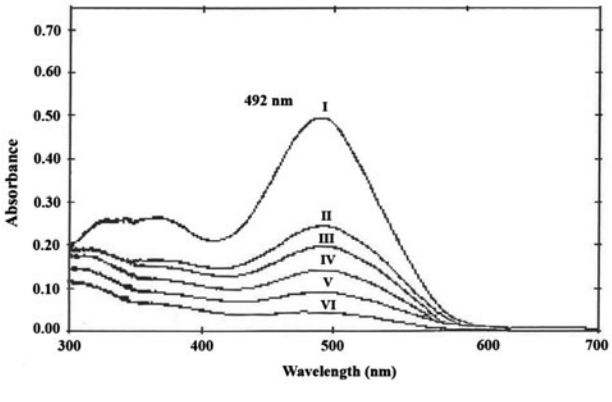

Fig. 3. UV–vis spectra of 50 ppm LRG solution after several duration of electrolysis (I: 0 min, II: 10 min, III: 12 min, IV: 16 min, V: 18 min and VI: 20 min).

value for each experiment by using different buffer solutions from pH 4 to 10. Choosing buffer solutions rather than adjusting it directly by strong acid or base was because to keep the pH of the solutions at a stable value during electrochemical treatment in which there are several reactions (O_2 and H_2 formations) that can change the pH. For this purpose, a 5 mL of buffer solution was added to 50 mL of 50 ppm dye solution containing 1.5×10^{-1} M Na_2SO_4, and the pH of the final solution was measured. Then, 2.5 V of stable potential was applied to the system up to 20 min and the results are given in Fig. 4.

Fig. 4 demonstrates that colour removal was about between 80 and 90% when pH varied between 4 and 9, but decreased to 67.8% at pH 10. The maximum efficiency of colour removal was observed at pH 6 and this value was selected as optimum. Although the variation of CR% values are close to each other against the solution pH, the small differences could be explained as the effects of pH-dependent secondary chemical reactions or other sites of the molecule possibly being reduced during electrolysis.

Another important parameter of the optimization procedure is the conductivity of the solution. Effect of conductivity on the process was determined by using different concentration of Na_2SO_4 (7.0×10^{-3}–2.0×10^{-1} mol L^{-1}) for 50 mL of 50 ppm dye solution at the optimum pH and under 2.5 V of potential (vs. Ag/AgCl, 3 M KCl) for 20 min. Table 1 and Fig. 5 describe the experimental results for the removal process with six electrolyte concentrations.

The evolution of the decolourization percentage as a function of solution conductivity displayed a sharp increase on decolourization when conductivity was increased from 7.0×10^{-3} to 7.0×10^{-2} M Na_2SO_4 followed by a plateau region about 90% at higher conductivity values (Fig. 5). According to the results, 1.5×10^{-1} M of Na_2SO_4 was enough to circulate the electrons in the cell for 50 mL of 50 ppm dye containing solution.

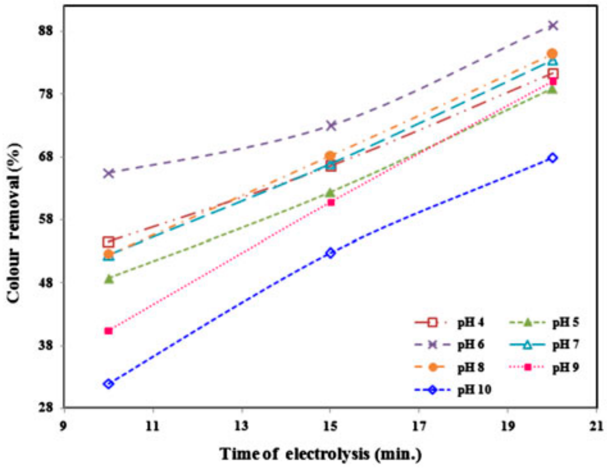

Fig. 4. Effect of pH on the decolourization of LRG, $E = 2.5$ V, $Na_2SO_4 = 1.5 \times 10^{-1}$ mol L^{-1}.

Table 1
Effect of conductivity on the colour-removal process ($n = 3$, $X_{avr} \pm SD$)

Na_2SO_4 (mol L^{-1})	Conductivity of solution (S cm^{-1}) $\times 10^{-3}$	(Time of electrolysis, CR%)		
		10 min	15 min	20 min
7.0×10^{-3}	1.5	46.1 ± 1.1	48.1 ± 2.4	54.6 ± 3.1
1.5×10^{-2}	2.5	47.0 ± 1.7	48.2 ± 3.0	55.1 ± 1.6
3.5×10^{-2}	5.8	48.9 ± 2.2	51.1 ± 3.2	58.8 ± 2.4
7.0×10^{-2}	10.8	54.2 ± 1.9	58.6 ± 1.9	68.4 ± 3.1
1.5×10^{-1}	18.5	57.0 ± 2.3	66.7 ± 1.8	89.6 ± 2.6
2.0×10^{-1}	21.1	56.1 ± 2.6	66.1 ± 1.0	88.4 ± 3.9

Effect of the applied potential on the removal of LRG was studied under optimized conditions. For this purpose, 2.0, 2.5 and 3.0 V of potentials (vs. Ag/AgCl, 3 M KCl) were applied to 50 mL of 50 ppm dye-containing cell in which the Na_2SO_4 concentration was 1.5×10^{-1} M and the pH was 6. Removal of dye percentage was determined after 10, 15 and 20 min of electrolysis and the results are summarized in Fig. 6.

As expected, removal of the dye was raised with the increase in applied potential. The colour-removal values were 48.2, 60.0 and 68.1% at 2.0 V and increased to 69.6, 75.8 and 94.2% at 3.0 V after 10, 15 and 20 min of electrolysis, respectively. But, a 2.5 V of potential was chosen as optimum at which the CR% values were 65.9, 71.9 and 89.3%. The reasons for this choice were the rapid destruction of anode electrode at 3.0 V and slower decomposition rates at 2.0 V. It was also possible to apply lower potentials for dye-removal process, but applying high cell potentials to the electrochemical cell for the simultaneous oxidation of pollutants and water improves the activity of anode material. The use of low cell potentials hinders the O_2 evolution on anode surface and some products formed by direct anodic oxidation can be adsorbed to the anode surface, and hence the anode activity reduces [5].

The surface morphology of graphite electrode surfaces was investigated by surface micrographs.

It was noted that the cathode electrode (Fig. 7(a)) had a partially smooth surface which means the electrode was slightly affected by electrolysis. On the other hand, anode electrode (Fig. 7(b)) had a rough surface covered with microcracks and deformations. Small amounts of carbon split from the surface during

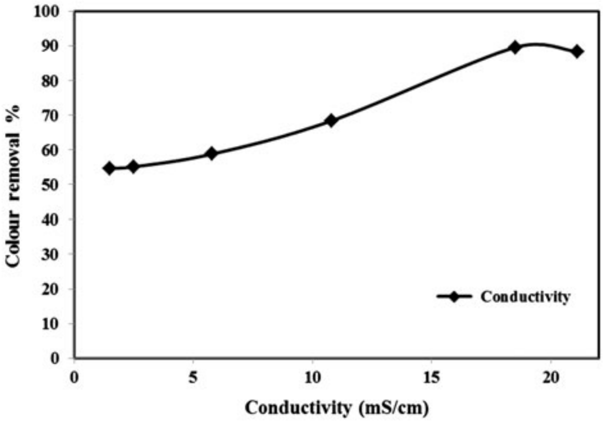

Fig. 5. Effect of conductivity on the decolourization of LRG after 20 min of electrolysis, $E = 2.5$ V, pH = 6.

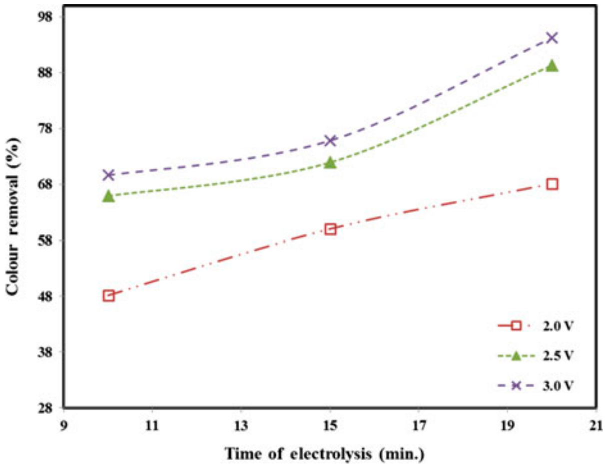

Fig. 6. Effect of applied potential on the decolourization of LRG, $Na_2SO_4 = 1.5 \times 10^{-1}$ mol L^{-1}, pH = 6.

electrolysis caused such type of structure. As a result, surface area of the anode electrode was larger when compared to that of the cathode. It is widely accepted that one of the reasons for the electrode activity enhancement is the increase in the real surface area of the electrode material [18]. The increase in the surface area can allow more interaction sites between electrode and dye molecules in the solution. So, decomposition of dye molecules may increase along with the increased active sites on the anode surface. When we analyse the Fig. 4, it is obvious that CR% values are in direct proportion to the time of electrolysis except pH 10.

It is well known that carbon-containing materials can adsorb dye molecules onto their surfaces. In order to determine the adsorption of LRG on to carbon surface, the electrodes were placed into a 50 ppm of 50 mL LRG solution and the solution was stirred for 12 h without applying potential. It was found that the colour removal was only 4.2% at an initial concentration of 50 mg L^{-1}. So, we can assume that the adsorption is insignificant for the removal of LRG.

In electrolysis process of dye removal, the anode electrode was dissolved in solution especially at higher potentials. So, the dissolution rate of the anode electrode was investigated. For this purpose, 10.0 g of Na_2SO_4 was dissolved in 100 mL of 250 ppm dye solution and the pH was adjusted to 6. The mass of electrodes was weighted and 2.5 V of potential was applied to the system for 1 h. The electrodes were washed with distilled water and dried in an oven at 105˚C for 12 h and weighed again. The consumption of anode was 62.1 mg h^{-1}, while the mass of the cathode did not change markedly.

3.3. Removal of dye in real samples

The proposed dye-removal method in aqueous solutions was applied to real samples. Applying the method on real samples can be considered as a validation of the system. The experimental results on the real samples are given in Table 2.

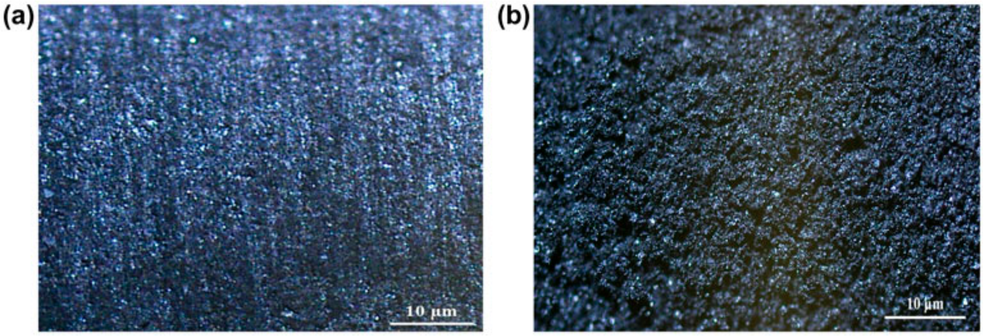

Fig. 7. Surface micrographs of graphite electrodes after 20 min of electrolysis: cathode (left), anode (right).

Table 2
Colour-removal results on real water samples (pH 6, Na_2SO_4: 1.5×10^{-1} M, $n = 3$, $X_{avr} \pm SD$)

Sample	Time of electrolysis		
	15 min	20 min	30 min
Textile wastewater (CR%)	27.6 ± 1.2	59.3 ± 2.6	89.4 ± 3.4
Lake water (CR%)	20.8 ± 2.7	51.7 ± 3.0	90.4 ± 3.1

The results indicate that about 90% of the colour was decomposed in real samples after 30 min of electrolysis. The decomposition time of LRG was more than the model samples. This may be because of the possible interfering ions in real water samples.

4. Conclusions

A series of experiments were conducted in order to find the influences of parameters for decolourization of textile dye LRG by electrochemical treatment under steady-state conditions. Dye removal by electrochemical treatment process was affected by pH, electrolyte concentration and applied potential. Anode and cathode carbon electrodes were affected by the decomposition process. The carbon rod which was connected as anode electrode was visibly reduced after electrolysis. The proposed method was also carried out on real water samples and the obtained results highlighted the efficiency of the treatment process for the removal of the dye from wastewaters.

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