

Voltammetric Determination of Dyes

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Abstract - The applied procedure is based on the effective accumulation of Fluorotriazine dye/ Ni (II) complex onto the HMDE and the catalytic reduction of this adsorbed complex. Two double-anchor (bichlorotriazine)-based bisazo reactive dyes (Reactive Orange 12 and Reactive Red 120) were also studied by DPAdSV. In order to evaluate the effect of adding a second azo functional and/or chlorotriazine reactive groups on the AdSV property of these bisazo reactive dyeSSs, their AdSV behaviours were compared with the AdSV behaviours of structurally similar monoazo reactive dyes (Reactive Yellow 84 and Reactive Red 24, respectively). Preliminary studies indicated that for the bisazo reactive dyes, the AdSV signals for the azo and chlorotriazine groups were more enhanced, hence, their stripping voltammetric monitoring is readily achieved. In spite of the direct analysis of these bisazo reactive dyes via their enhanced azo and chlorotriazine AdSV peaks, an indirect analysis of these reactive dyes through their further Cu (II)IReactive dye complex signals is also possible. Two bichlorotriazine-based bisazo reactive dyes (Reactive Blue 171 and Reactive Red 141) formed Cu (II) IReactive dye complexes, which effectively adsorbed onto the HMDE. The subsequent stripping voltammetric measurement of the adsorbed complexes yielded a new AdSV peak related to the reduction of Cu (II) in the formed complexes.

INTRONDUCTION

Wastewater generation in huge volumes is one of the consequences of uncontrolled demand for textile articles, which causes extreme water consumption by textile industries [1]. Different wet-processing operations in the manufacturing process of textile industry result in the production of effluent which contains various pollutants including dyes, surfactants, detergents, and suspended solids [2]. Azo dyes as the largest group of organic dyes [3] constitute 20–40% of the dyes used in the textile industry [4] and are the most frequent chemical class of dyes applied to industrial scale [5]. The general chemical formula of azo compounds has been shown in the form of R-N = N-R functional group. In the structure of these compounds, the double bond between nitrogen atoms indicates the azo chromophores, while R is the aromatic ring [1] containing groups such as sulfonate and hydroxyl [3]. The relatively low degree of dye fixation to fabrics especially for the reactive dyes results in the release of unfixed dyes into the effluent [6, 7]. It has been stated that textile industries produce a strongly colored wastewater [8]. It has also been declared that even the presence of inconsiderable dye concentrations in the effluent can reduce the penetration of light into the receiving water bodies. This leads to devastating effects on the aquatic biota [9] such as photosynthetic activity of

aquatic plants [8]. The probable persistence and the long term bioaccumulation of synthetic organic dyes severely damage the health of ecosystems and living organisms [10]. A wide range of technologies for the removal of dyes from contaminated effluents can be found in literature [11]. Conventional treatment methods, i.e., physical, chemical, and biological processes, are still highly used. The physical methods mainly are practical for separating the solid pollutants, since there must be a difference between the pollutant and its media regarding the physical property. It is noticeable that chemical treatment occurs just under conditions that electrostatic property of both pollutant and coagulant is compatible [12]. Undesirable efficiency, high cost, and secondary pollutants are major shortcomings of physicochemical processes [9]. In spite of the fact that synthetic dyes have properties such as stability against light, temperature, and biodegradability [4], which makes decolorization difficult and incomplete [6], it was stated that azo dyes are non-resistant to biological treatment methods under anaerobic conditions. However, applying this method is not suggested for dye removal as the products resulted from breakdown of azo dyes can be more toxic than the dye molecules [4]. The adverse environmental and health effects of dyes and their degradation products have pushed scholars' efforts towards developing powerful and effective treatment technologies [13].

Literature Review

According to the literature review, numerous advanced methods including adsorption, biosorption, reverse osmosis, ion-exchange [6], membrane separation, electro kinetic coagulation, irradiation, ozonation [8], sonication, enzymatic treatments, engineered wetland systems [9], and advanced oxidation processes (AOPs) such as TiO₂ photo-catalysis and electrochemical methods [10] have been utilized by researchers for the efficient treatment of textile wastewater. The electrochemical advanced oxidation processes (EAOPs) have received special interest for water and wastewater remediation [13]. Among them, electrocoagulation (EC) [14], electro-oxidation (EO) [15], and electro-Fenton (EF) [16] have been frequently studied. EAOPs have some significant advantages such as simple equipment [4], easy implementation [17], close control of the favored reactions through applying optimum electrical current, on-site treatment in less space [18], and high efficiency for the degradation of persistent pollutants, while the cost of electricity used can be a drawback [19]. The presence of iron ions in the EC and EF processes leads to the sludge generation that imposes the cost of further treatment [20]. EO is the most widely used mechanism of EAOPs [21] and

anodic oxidation (AO) is the most typical kind of EO [22]. The explanation of complicated electrochemical reactions that occur during the EO treatment process and determining the definite removal mechanism of many of the contaminants do not seem an easy task [6]. EO of pollutants can occur through AO directly or indirectly, and also by the participation of chlorine-based oxidants when chloride solutions are treated [18]. In direct AO, pollutant molecules are oxidized at anode via electron transfer from the organic matter to the electrode, while in the indirect AO, the chemical reactions with electro-generated species such as hydroxyl radicals resulted from water discharge at the anode leads to the pollutant degradation [23]. It is known that direct AO leads to poor decontamination, while the effectiveness of indirect AO is dramatically dependent on the used anode. In the so-called "active" anodes which have low oxidation power, the chemisorbed "active oxygen" (MO_{x+1}) is the yield of water oxidation, while the physisorbed hydroxyl radical is the product of water discharge at the high oxidation power anodes also named "non-active". The Pt, IrO₂, and RuO₂ are some examples of the former anodes in the formation of selective oxidation products, while boron-doped diamond (BDD), PbO₂, and SnO₂ are typical kinds of the latter anodes causing complete combustion of the organic compounds (R)

"Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues" in this it was observed that the experiment was done with three agricultural residues, wheat straw, wood chips and corn-cob shreds which was tested for their ability to adsorb individual dyes and dye mixtures in solutions. Up to 70–75% colour removal was achieved from 500 ppm dye solutions at room temperature using corn-cob shreds and wheat straw. Increasing the temperature had little effect on the adsorption capacity of the residues. It was observed that dye-adsorbed residues was found to be suitable substrates for solid-state fermentation (SSF) by two white-rot fungi; *Phanerochaete chrysosporium* and *Coriolus versicolor*.

Both strains grew uninhibited and produced a maximum protein content of 16, 25 and 35 g and 19, 23 and 50 g in SSF of 100 g dry weight wood chips, corn-cob shreds and wheat straw, respectively, supplemented with ammonical nitrogen to give a C:N ratio of 20:1. And from this experiment study approach provides preliminary results for the remediation of textile effluent and the conversion of agricultural residues into soil conditioner [24].

The kinetics and mechanism of methylene blue adsorption on commercial activated carbon (CAC) and indigenously prepared activated carbons from bamboo dust, coconut shell, groundnut shell, rice husk, and straw, have been studied. In this study effects of various experimental parameters have been found by using a batch adsorption process to obtain information on treating effluents from the dye industry. In this experiment process it was observed that The extent of dye removal increased with decrease in the initial concentration of the dye and particle size of the

adsorbent and also increased with increase in contact time, amount of adsorbent used and the initial pH of the solution. This study results indicated that such carbons could be employed as low cost alternatives to commercial activated carbon in wastewater treatment for the removal of colour and dyes [25].

"Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw" This study was conducted an experiment which is done with two low-cost, locally available, renewable bio adsorbents; apple pomace and wheat straw for textile dye removal. Experiments performed at total dye concentrations of 10, 20, 30, 40, 50, 100, 150, and 200 mg/l were carried out with a synthetic effluent consisting of an equal mixture of five textile dyes.

The effect of initial dye concentration, bio adsorbent particle size, quantity of bio adsorbent, effective adsorbent, dye removal and the applicability of the Langmuir and Freundlich isotherms were examined. In the experiment they observed that One gram apple pomace was found to be a better biosorbent, removing 81% of dyes from the synthetic effluent at a particle size of 2 mm×4 mm and 91% at 600 μm. Adsorption of dyes by apple pomace occurred at a faster rate in comparison to wheat straw. Both the isotherms were found to be applicable in the case of dye adsorption using apple pomace [26].

Working Electrode (WE) Working electrode (WE) provides a site for the redox reaction of electroactive species and also for the charge transfers from and to electroactive species to take place (www.cem.msu.edu). It strongly influences the performance of the voltammetric technique. The ideal characteristics of this electrode are has wide potential range, low resistance and be able to provide a high signal-to-noise response. The WE must also has a characteristic of chemical inertness, which means it should be made from the materials that do not react with solvent and any compounds of the solutions over as wide a potential range as possible.

There are two classes of electrode for the WE, which are liquid electrode like mercury and solid electrode such as carbon, gold and platinum. Mercury electrode offers several advantages to act as the WE. Its large activation overpotential for reduction of hydronium ion to form hydrogen enables the reduction of many species in acidic solution [76]. In addition, mercury has ability to form amalgam with the most metals and provide uncontaminated surface from previous analysis due to readily formed new drops or new thin mercury films. The only disadvantage of mercury is itself oxidizing at potential of +0.3 V and cannot be used at positive applied potentials more than +0.4 V against the SCE. Figure below shows the different types of WE and their potential windows against SCE in various supporting electrolyte.

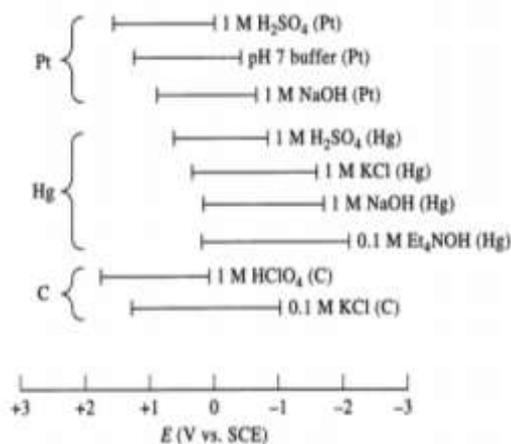


Fig - Different types of WE and their potential windows.

Apparatus needed -

Adsorptive stripping and cyclic voltammetric measurements were carried out using a Metrohm E612 voltammetric scanner and E611 voltammetric detector (Metrohm, Herisau, Switzerland) with Houston Instruments 2000 X-Y recorder, a Metrohm 663 VA Multimode Electrode stand (MME) was used in the hanging mercury drop electrode (HMDE) mode. The three electrode system was completed by means of a platinum auxiliary electrode and an Ag/AgCl (3M KCl) reference electrode. In addition, Metrohm 646 VA voltammetric processor coupled with a Metrohm 647 VA stand was also used for obtaining adsorptive stripping voltammetric measurements.

The working electrode: The working electrode is the characteristic multi-mode electrode (MME) in which three types of mercury electrodes are combined into a single design: Hanging mercury drop electrode (HMDE), dropping mercury electrode (DME) and static mercury drop electrode (SMDE).

Reference electrode: The Ag/Agel reference electrode is in many respects the most satisfactory of all reference electrodes and certainly the simplest. It consists of a silver/silver chloride wire in 3 M potassium chloride solution.

Auxiliary electrode: The third functional electrode is the auxiliary electrode, which is made of an inert material like platinum or of glassy carbon. This electrode is the current carrying electrode in the three-electrode system It is placed directly opposite the reference electrode.

For differential pulse voltammetry at the HMDE, a scan rate of 5 mVs⁻¹ and pulse amplitude of 50 mV with a pulse interval of 1 s were used. The medium stirring speed was used during accumulation with mercury drop size of 0.4 mm³. Usually reactive dyes were monitored over the voltage range from 0.0 to -1.3 V. pH measurements were made using an Orion pH meter, previously calibrated. All glassware, voltammetric cell and electrode systems were cleaned prior

to determination and washed three times with de-ionised water. De-ionised water was produced by a Maxima ultra pure water system.

Working Procedure

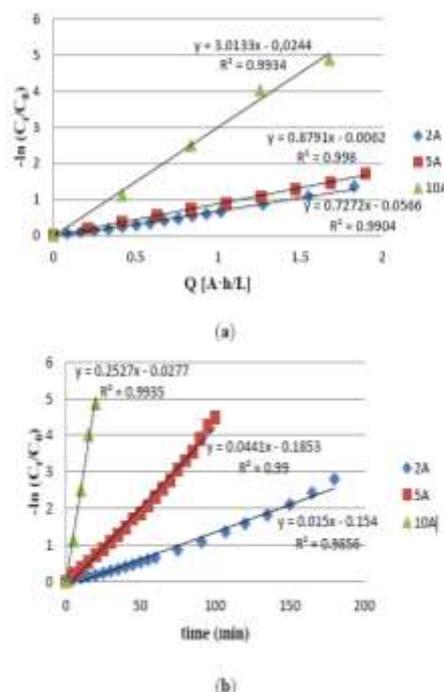
The general procedure adopted for obtaining adsorptive stripping voltammograms were as follows. A 20 ml aliquot of an appropriate buffer was placed in a clean dry voltammetric cell and the required stock solution of the test substance was added. Solutions were deoxygenated by bubbling with nitrogen for 5 min initially, while the solution was stirred at medium stirring speed. Adsorptive accumulation was carried out whilst stirring the solution. An accumulation potential at 0.0 V was applied to the working electrode for 2 min (unless otherwise stated). At the end of the accumulation period in stirred solution, the stirrer was stopped and after 20 s had elapsed and the solution had become quiescent, cathodic scans were carried out over the voltage range 0.0 to -1.3 V. Cyclic voltammetry was carried out immediately after forming a new HMDE. A new hanging mercury drop was formed after removing oxygen and after recording of the curves. All measurements were obtained at room temperature

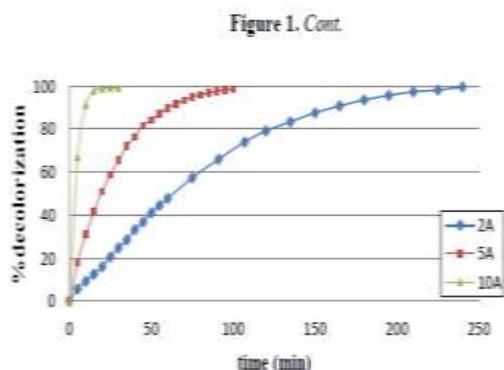
Results and Discussions

Electrochemical Treatment: Effect of the Intensity

The electrochemical kinetic rate degradation of PN dye was studied at three intensities (2 A, 5 A and 10 A). Results are plotted in Figure 1.

Figure 1. Procion Navy HEXL (PN) Decolorization with electrochemical treatments at 2 A, 5 A and 10 A. (a) PN kinetic rate in time; (b) PN kinetic rate in applied charge; (c) Evolution of PN decolorization.





The representation of $-\ln(C_t/C_0)$ vs. time (Figure 1a) showed that in all the studied cases, the dye degradation follows a first-order reaction kinetics. As expected, the treatment time required to obtain a specific degradation was shorter when the intensity applied was higher. In order to know the efficiency of the treatments, $-\ln(C_t/C_0)$ vs. the specific charge applied (A·h/L), which is a normalized parameter, were plotted in the Figure 1b. The results showed that the slopes at 2 A and 5 A were of the same order (0.73 and 0.88 respectively). In this case, the time required to achieve a fixed decolorization had an inverse linear relationship with the intensity (at constant volume). On the other hand, when the intensity is increased to 10 A, the slope becomes much higher. The time necessary to obtain the fixed decolorization is much lower than expected. Probably this higher current value promotes the generation of additional oxidant species produced from chloride oxidation (such as Cl_2 , OCl^- and chlorine radicals) or produced from water oxidation, such hydroxyl radical ($\bullet OH$), atomic oxygen ($\bullet O$), hydrogen peroxide or ozone [27].

Decolorization values of 99% can be reached with all the studied intensities (Figure 1c). The treatments at 2 A and 5 A requires a similar power consumption (29.70 W·h and 28 W·h respectively), whereas at 10 A, the consumption is reduced to 15.17 W·h to achieve the same decolorization rate. The power consumption was calculated from the corresponding voltage value for each intensity value (5.4 V, 5.2 V and 9.1 V at 2 A, 5 A and 10 A respectively). The obtained power values were multiplied by the time of treatment in hours.

Consequently, it can be stated that the decolorization treatment performed at 10 A is more efficient according to the kinetic rate, the specific charge applied and power consumption results. Therefore, the subsequent studies were carried out at this intensity.

Optimization of the Photo-Electrochemical Treatment for PN at 10 A

When an electrochemical treatment is applied to a solution which contains chloride and organic matter, small amounts of halogenated volatile compounds can be generated, mainly haloforms. In order to solve this problem, UV radiation is applied. Several studies were carried out by combining the

electrochemical treatment with UV radiation. Table 1 shows the results corresponding to the final decolorization achieved and the decolorization kinetic rate, for electrochemical treatment (treat 1) and the different combination of electrochemical and UV treatment studied on the PN effluent (treat 1+2).

The results shown in Table 1 indicate that the electrochemical treatment was the faster technique to achieve 99% of decolorization because its kinetic rate was higher. When UV radiation was applied simultaneously with the electrochemical treatment (UVEC), 99% decolorization was also achieved but the kinetic rate decreased due to the UV light degradation of the indirect oxidant compounds, generated during the electrolysis ($HClO/ClO^-$). On the other hand, it can be appreciated that the UV radiation after the electrochemical treatment enhances the dyes decolorization.

Taking into account the local regulations on discharge limits, the full decolorization is generally not required. In fact, it is commonly established that no color must be appreciated when the effluent is diluted 1/10–1/30 (this value change depending on the Country and even of the different regions). Then, the more appropriate selection is an initial electrochemical treatment followed by the UV irradiation. Among the combinations of these techniques, 5 min of electrochemical treatment provided decolorization yields around 57%. If the treatment was continued with the combined treatment UVEC, 99% of decolorization would also be achieved, whereas 66% is obtained with the UV radiation alone. For that reason, the authors decided to follow up the electrochemical treatment during 10 min (80% of decolorization) with further UV radiation to achieve 86% decolorization.

Table 1. Characterization of the electrochemical and photo-electrochemical treatments in kinetic rate, total organic carbon (TOC) removal and decolorization, applied to PN at 10 A.

Trial	Treatments	Decolorization (%)		Kinetic rate (min^{-1})		R^2	
		Treat 1	Treat 1+2	K_1	K_2	K_1	K_2
A	EC	99	-	0.2729	-	0.99	-
B	UVEC	99	-	0.1332	-	0.99	-
C	(1) 5 min EC	-	-	-	-	-	-
	(2) UVEC	55	99	0.2715	0.1598	0.99	0.99
D	(1) 5 min EC	-	-	-	-	-	-
	(2) UV	59	66	0.2738	0.0014	0.99	0.97
E	(1) 10 min EC	-	-	-	-	-	-
	(2) UV	80	86	0.2722	0.0037	0.99	0.98

Where: EC = electrochemical treatment; UVEC = electrochemical treatment with simultaneous UV radiation; EC + UV = electrochemical treatment with posterior UV radiation; K_1 : kinetic rate corresponding to treatment 1; K_2 : kinetic rate corresponding to treatment 2.

In this section, the kinetic rates expressed in charge or in time units will have the same evolution because all the experiments were run at the same intensity (10 A). Consequently, they were only reported in time units (min^{-1}).

As can be seen in Figure 2, the decolorization value was stabilized after a certain treatment time. From that moment, the decolorization value is not enhanced when the treatment time is increased.

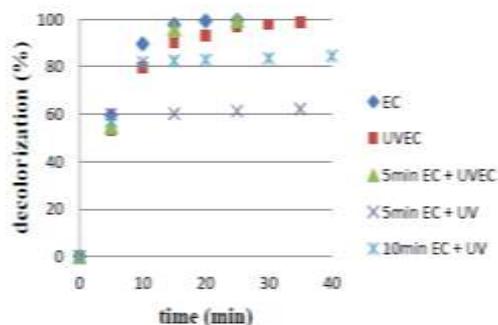


Figure 2. PN effluent decolorization evolution with different combination of electrochemical (10 A) and photo-electrochemical treatments.

The samples for haloforms detection were collected when the higher decolorization value was achieved. Chloroform was the unique halogenated compound detected by the GCMS analysis. The concentration of this compound generated in the different treatments is plotted in Figure 3.

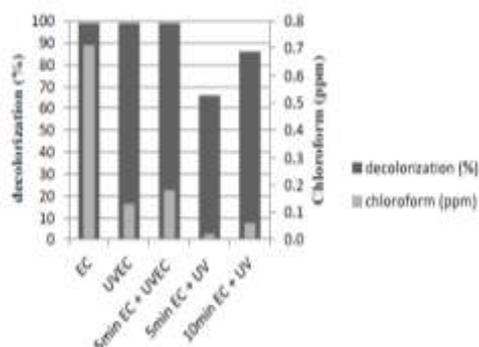


Figure 3. Final decolorization of PN effluent and chloroform generated versus the different electrochemical (10 A) and photo-electrochemical treatments.

According to Figure 3, it can be seen that the electrochemical treatment alone is able to achieve 99% decolorization, but at the same time, 0.7 ppm of chloroform are generated. A clear reduction of this concentration is achieved with the UV radiation treatments, both applied simultaneously during the electrochemical treatment or after it, as a final treatment. UV treatment is able to reduce chloroform concentration below 0.2 ppm.

Taking into account all the results obtained, including decolorization and chloroform removal, we consider that the best method is the trial E, where the electrochemical treatment was applied until 80% of decolorization, with posterior UV radiation (10 min EC + UV). This procedure achieved 86% effluent decolorization (which is already an acceptable value for the subsequent discharge).

Under these conditions, the final chloroform concentration was lower than 0.1 ppm and the final dye concentration was lower than 0.5 ppm, which is acceptable for the reuse step. In addition, in the case of effluent discharge, this concentration is not appreciated by the human eye after a 1/10 dilution which corresponds to the mixture of the dyeing bath with the rest of effluents (rinsing and washing baths).

Conclusion

The electrochemical treatment achieved 99% of dye decolorization at all the studied intensities, although it was more efficient at the higher current intensity, 10 A. When this technique was applied with simultaneous UV irradiation, the decolorization kinetic rates decreased, whereas dye decolorization was enhanced by the application of UV after the electrochemical treatment. In any case, the UV irradiation reduced the chloroform content.

The most efficient combination to treat reactive dye effluents is the electrochemical treatment up to 80% decolorization followed by UV irradiation. In this way, the chloroform concentration was lower than 0.1 ppm except for PMX-2R. No influence of the number of functional groups in the dye molecule was evidenced.

It was also demonstrated that the complete dye mineralization was not necessary to reuse the treated effluent in new dyeing processes. Decolorized effluents with only 4% TOC removal provided color differences into the acceptable range (DECMC (2:1) < 1), which resulted in reducing significantly effluent salinity and saving 70% water.

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