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Original Research

Electrochemical Treatment of Actual Textile Indigo Dye Effluent

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Abstract

Electrochemical methods are being used increasingly as an alternative treatment process for the remediation of textile wastewaters. This study focused mainly on the color removal and chemical oxygen demand (COD) reduction of a vat textile dye (CI Vat Blue 1: indigo) from its most polluted actual effluent by electrochemical oxidation. The process was carried out in a batch-type divided electrolytic cell under constant potential using a Pt cage as anode and Pt foil as cathode. It was shown that complete colour removal was achieved in a very short time (16 mins) at pH 2 by applying a constant electrolysis voltage between the platinum electrodes. The repeated experiments indicated that extending the treatment to 40 minutes caused a considerable percentage of COD reduction (46%), occurring mainly due to indigo oxidation. It is concluded that this electrochemical method can be used effectively as a pre-treatment alternative for reducing COD and colour in industrial textile effluents before conventional treatment.

Keywords: electrochemical oxidation, indigo, actual effluent, decolorization, COD removal

Introduction

The textile industry consumes substantial volumes of water during the manufacturing process. The water that is primarily employed in dyeing and finishing operations eventually ends up as wastewater characterized by high temperature, high COD, a large amount of suspended solids, and intense color due to the extensive use of synthetic dyes [1]. The direct discharge of these colored compounds in the environment causes considerable non-aesthetic pollution and serious health-risk factors [2]. Therefore, various wastewater treatment methods, such as physico-chemical and biological methods, are applied to treat the effluent to meet regulatory discharge limits. Among these methods, coagulation and absorption are the most commonly used, but these create huge amounts of sludge that become a pollutant on its own, creating disposal problems [3]. There is a great need to develop an economic, effective, and eco-friendly way of dealing with textile dyeing wastewater at the industrial level.

Due to the drawbacks associated with conventional treatment methods, there has been a growing interest in the use of electrochemical methods for the treatment of wastewaters, as it would not generate any secondary pollutant or filtrate/sludge, and would give nearly a complete degradation of the pollutants present in the effluents [4]. Among the electrochemical treatment methods, electrochemical oxidation is of particular interest in the treatment of wastewaters polluted with organic compounds. Electrochemical oxidation of organic pollutants can be done directly using anodes with high oxygen overpotential and corrosion stability; or indirectly using appropriate anodically formed oxidants such as chloride, hypochlorite, ozone, and Fenton's reagent [5] generated at the electrode surface. This technique depends mainly on the type of anode used, and also on the properties of the wastewater and operating conditions [6].

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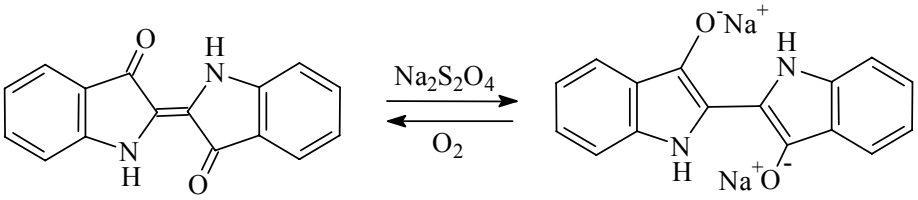

indigo leuco indigo

Fig. 1. Textile dyeing process based on the chemical reduction of indigo.

It is relatively economical, has higher treatment efficiency for color removal and degradation of recalcitrant pollutants, and shows results in a relatively short period [7, 8].

Indigo blue dye is one of the best known coloring agents. Since it shows excellent color fastness, it is extensively used in its synthetic form by modern textile industries to dye cellulosic fibres such as cotton. Although only 10 g of indigo is necessary to dye one pair of trousers, the world production of indigo is close to 10,000 t/a due to the vast annual sales of 10^9 blue jeans [9]. The textile dyeing process is based on the chemical reduction of indigo in the presence of an alkali into water-soluble leucoindigo, which has a high affinity to the cellulose fibre and can be fixed on it by the re-oxidation in air, as shown in Fig. 1 [10]. This process produces large amounts of wastewater, which must be treated with appropriate methods before its final discharge into the environment.

The removal of indigo from industrial effluents is difficult due to its resistance toward biodegradation, which causes a great environmental concern [11]. There are few reports on degradation of pure indigo dye solutions using biological [11-13] and electrochemical processes [14-16], and some recent reports on degradation of actual indigo dye wastewater using physico-chemical [17], micro filtration [18], and aerobic treatment methods [19]. However, there is no report available on the electrochemical treatment of indigo dye-containing actual wastewaters which actually describe the status of the field. In the present study, therefore, we report the investigation of the decolorization of actual field sample of textile indigo dye effluent by electrochemical oxidation and the effects of different operational parameters on color removal and chemical oxygen demand (COD) reduction.

Materials and Methods

Chemicals, Apparatus, and Instruments

A large volume of a sample of mainly polluted actual indigo dye effluent was taken from the first wash box of a cotton textile industry according to the composite sample taking rules compiled by APHA [20] as to represent the daily average effluent composition and to avoid momentarily variations. It was stored in a coloured bottle at +4ºC for instant use. The electrochemical oxidation experiments of the actual indigo dye effluent were conducted in a lab-scale batch electrolytic cell (Fig. 2). In each run, 150 cm^3 aliquot of this effluent was placed into the electrolytic cell. The cell had a total volume of 200 mL and was divided into two equal compartments with a sintered-glass disc of G3 (20-30 μm porosity) grade. It was equipped with a magnetic stirrer (IKA RO5 model, Staufen, Germany) in order to keep both the solutions in the compartments well-mixed during electrochemical oxidation. A laboratory DC power supply (RAYSEL LPS 40-5 model, Ankara, Turkey) with current-voltage monitoring was employed to provide the electric power required for electrolysis. In the electrolysis experiments, a cylindrical Pt cage electrode with a 1.7 cm diameter and 2 cm height, and a Pt foil electrode with a 2 cm^2 surface area were used as anode and cathode, respectively. A double beam UV-VIS spectrophotometer (Shimadzu-1601 PC model, Rydolmere, MSW, Australia) were used to follow color removal. pH values were measured using a digital pH-mV meter (Orion 601A model, Cambridge, MA,

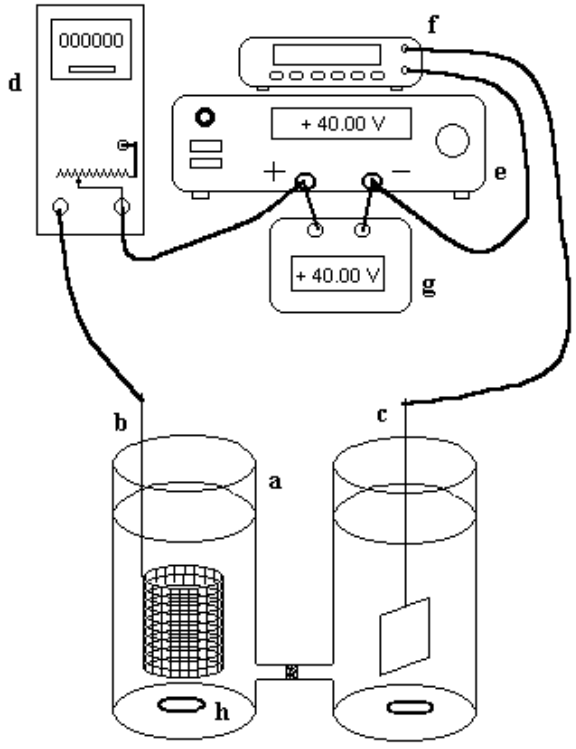

Fig. 2. Batch experimental set up: a) divided cell, b) Pt cage electrode, c) Pt counter electrode, d) electrical charge counter, e) DC Power supply, f) galvanometer, g) voltmeter, h) magnet bar.

USA), and pH adjustments were made using standard solutions of concentrated sulphuric acid. All the chemicals used were reagent grade.

Methods

The electrochemical oxidation of the actual textile indigo dye effluent taken from the textile plant was carried out under the same optimum experimental conditions (a constant potential of 40 V, a supporting electrolyte concentration of 0.24 mol/L NaCl, a treatment time of 90 minutes, and an optimum pH of 1) that were determined for the artificially prepared indigo dye effluent used in our previous work [21]. However, since the chemical composition of the actual effluent used in this study was slightly different from the artificial effluent used before, some of the working parameters such as concentration of supporting electrolyte, initial pH, and treatment time were reoptimized for maximum reduction in colour and COD. Then, the electrochemical oxidation of actual textile indigo dye effluent was carried out under the newly optimized conditions.

The electrochemical decolorization process was evaluated by spectrophotometric investigations performed in the UV-vis and especially in the visible region. In order to determine the degree of decolorization with the treatment time, 3 mL-samples of the actual effluent taken from anode compartment of the cell, and the changes in the absorbance at 666.5 nm, which is the wavelength of maximum absorbance specific for the indigo dye present in the effluent, were observed. The chemical oxygen demand was measured by an open reflux titrimetric method (5220B) according to standard methods compiled by APHA [20]. While decolorization was occurring by the electro oxidation process, changes in the COD of the actual effluent were followed by withdrawing samples from the anode compartment at determined time intervals. Each time the experiments were started over again to avoid solution level differences arising between the compartments. To eliminate possible chloride interferences during COD measurements, samples were diluted 3-10 times before refluxing, and also double amount of standard $HgSO_4$ was used as a precaution. Furthermore, primary standard grade potassium hydrogen phthalate (KHP) was used to check the reliability of the procedure. All the studies were performed at room temperature and were repeated more than twice to be sure of the repeatability of the results.

Results and Discussion

Since it is very difficult to determine the changes undergone by the target molecule during the treatment processes in a complex matrix of actual effluents, it is necessary at first to make a model study with an effluent that contains only the target molecule on an industrial scale. Then, the applicability and utility of the optimized conditions for the treatment of actual effluent can be investigated. Therefore, in this study, the previously determined parameters [21] were tested for the actual indigo dye house effluent, and it was seen as necessary to perform serial experiments in order to identify the best conditions for the treatment process.

Table 1. Comparison of initial wastewater parameters of the effluents.

	Artificial effluent[a]	Actual effluent
COD (mg O_2/L)	2299	3027
λ_{max} (nm)	681.5	666.5
A_{max}[b]	1.199	1.355

[a]Freshly prepared % 0.1 (w/v) indigo solution, which includes sodium dithionite and sodium hydroxide
[b]Measured after dilution three times

The artificial indigo dye effluent (% 0.1 w/v) used before [21] and the actual effluent used in this study are compared in terms of the wastewater parameters taken into consideration in Table 1.

It is seen from the table that the COD of the actual effluent is greater than the COD of the artificial effluent. This result can be regarded as normal, because the actual dye effluent consisted of chemicals and dyebath additives used in different sections of an indigo dyeing house, and chemicals that come from the processes undergone before dyeing the textile material. The spectrophotometric measurements showed that the color parameters of both effluents are very close to each other.

It was shown previously that for the treatment of the artificial effluent using 8.5 g/L NaCl as the supporting electrolyte, a nearly 90-minute treatment time was sufficient [21]. However, it was seen as necessary to perform serial experiments in order to adapt the experimental conditions for the actual field sample of textile indigo dye effluent because of its higher chemical load, and the importance of a shorter treatment time in a continuous system if the process is to be used on an industrial scale. Therefore, new electrochemical oxidation experiments were carried out with the actual indigo dye effluent, and results of the effects of various sodium chloride additions on the electrical charge, color removal time, and COD reduction are illustrated in Table 2.

As can be seen from the table, when 5 g NaCl was used per 150 mL of effluent, the time required for complete color removal was significantly shortened, and a considerable COD reduction percentage (46 %) was obtained when the treatment was further proceeded to 40 minutes. It is also clear from the absorption spectra of the actual indigo dye taken at 666.5 nm before and after the treatment process that the wide indigo peak disappeared almost completely after 16 minutes of electrolysis (Fig. 3).

After optimization of the supporting electrolyte concentration, electrolysis experiments were performed at pH 1, 2, 4, 5, and 7 initial values. The results of these trials are presented in Table 3.

According to the results presented in Table 3, pH 2 was chosen as the best suitable initial value based on the maximum COD reduction ratio. Then, under the determined

Table 2. Effect of sodium chloride addition on the electrochemical decolorization of the actual textile indigo dye effluent (the initial COD is 3027 mg O_2/L) at pH=2.

NaCl concentration (g/150 mL effluent)	Time (min) passed for color removal	Electrical charge (C) passed for color removal	Total treatment time (min)	Total Electrical charge (C)	COD (mg O_2/L) after treatment
0.5	160	265	182	327	2728
1.0	68	186	82	247	2759
2.0	47	186	60	250	2602
4.0	33	155	49	292	2141
5.0	16	141	40	373	1619

Table 3. Effect of initial pH values of the actual textile indigo dye effluent on the electrochemical decolorization process.

pH	Time (min) passed for color removal	Electrical charge (C) passed for color removal	Total treatment time (min)	Total Electrical charge (C)	COD (mg O_2/L) after treatment
1.0	15	124	30	313	1871
2.0	16	141	40	373	1619
4.0	24	148	45	345	1690
5.0	21	149	43	343	1855
7.0	16	164	30	375	1891

optimal study conditions (pH=2 and 5 g of NaCl per 150 mL of actual effluent), alternations in COD values were focused on to be investigated depending on the treatment time and electrical energy consumed during the electrochemical oxidation process. For this purpose, in the beginning and then at the end of 20, 35, 40, and 65 minutes of the trials performed with the actual effluent samples, 10 mL samples were taken from the anode compartment to measure the COD value of the solution. Each time the experiments were recommenced to avoid solution level differences arising between the compartments, and the related data are presented in Fig. 4.

Fig. 4 shows that the COD of the solution remediates sharply until up to 40 minutes, and then smoothly with increasing electrolysis time, while total energy consumption increases with time.

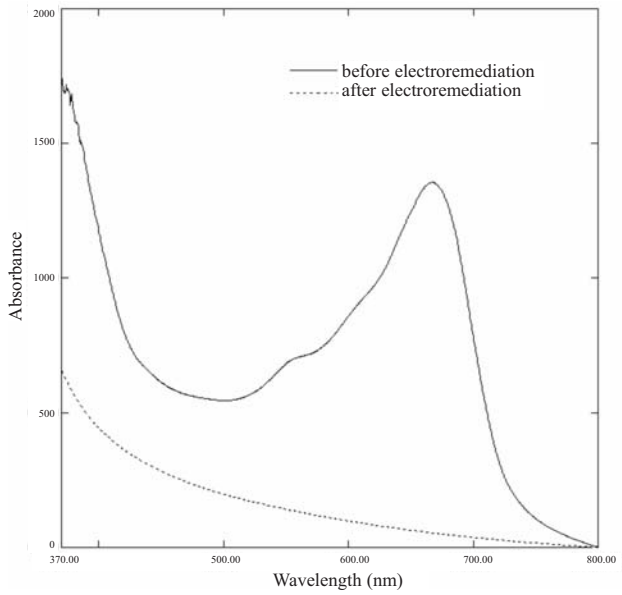

Fig. 3. UV-VIS spectra of the actual textile indigo dye effluent before and after the electrochemical treatment process (operating conditions: applied cell voltage=40 V, pH=2, NaCl concentration=5 g/ 150 mL effluent).

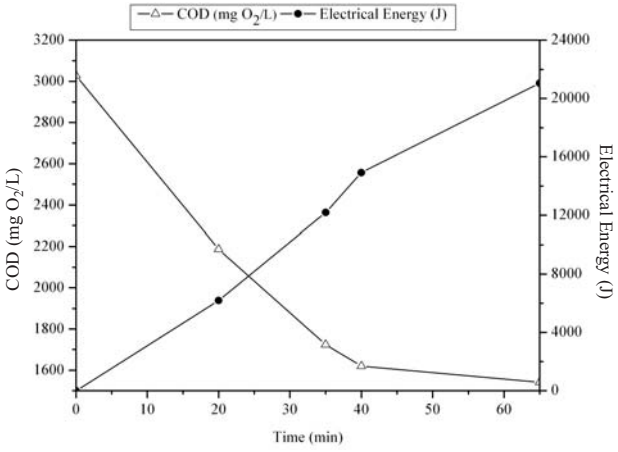

Fig. 4. Effect of treatment time on COD and electrical energy values (operating conditions: applied cell voltage=40 V, pH=2, NaCl concentration=5 g/150 mL effluent). The amounts of electrical energy consumed were calculated by multiplying electrical charge (coulomb) values by 40V.

Finally, it is proposed that if a treatment unit is set up as designed to automatically work as shown in Fig. 5, and operates to treat effluent from the indigo dye house before its mixing with the general wastewater unit, the effectiveness of the conventional treatment system of the industrial plant may be improved without using any chemical treatment. It is anticipated that stainless steel or graphite electrodes can be used on an industrial scale. Constructing and testing of this treatment unit in textile plants is planned in the near future.

In our previous study, a satisfactory irreversible color removal and COD reduction was determined during the treatment of artificial (model) indigo dye effluent. While the color was removed completely, COD decreased to 43% with an electrical charge of 390 C in 60 minutes, and greater than 60% with an electrical charge of 610 C in 90 minutes of electrolysis under optimized working conditions. And during the first five minutes of the treatment, the leuco↔indigo equilibrium shifted in favor of indigo at the oxidation potential of the anode, causing the color of the solution to darken. When the electrochemical oxidation was further proceeded, it was observed that the decolorization of the artificial effluent was nearly completed in 90 minutes [21].

In comparison with the treatment of the artificial effluent sample, the actual field sample required more NaCl concentration to achieve a similar COD and color removal efficiency in a considerably shorter period. Since the main purpose of this study was to reduce the high organic load and remove the color of the most polluted actual indigo dye effluent taken from the first wash box of the plant, the relatively high chloride concentration used here will decrease significantly during electrolysis. After electrochemical pretreatment, the actual effluent will enter the general wastewater treatment unit of the plant, and upon mixing with it the chloride concentration will be diluted at least 100-fold. Therefore, it will further decrease below the discharge standards, and probably cause no harm to the environment. On the other hand, color and COD are also between the important parameters to be monitored to meet the effluent discharge limits. Uzal et al., [18] reported no significant COD rejection of an indigo dyeing wastewater with cross-flow microfiltration (MF) experiments held at pH 7.0±0.2. MF. Khelifi et al. [19] put forward that after the application of an aerobic bioprocess to an indigo dye-containing textile wastewater, 97.5% of COD elimination and 97.3% of color removal efficiencies with a long hydraulic retention time of 4 days and low wastewater loading rate of 0.29 $g \cdot L^{-1} \cdot d^{-1}$ were obtained. Manu [17], reported 95%, 94%, and 87% decolorization of denim plant (dye bath) wastewater using alum, lime, and $FeSO_4$ at dosages of 225, 1000, and 225 mg/L, respectively. However, this physico-chemical treatment process applied to the actual indigo dye wastewater-produced sludge, which in turn causes a dewatering and disposal problem. In all these studies mentioned above, color removal and COD reduction ratios were calculated only by taking the aqueous parts of the effluent into consideration, so these calculations do not include the reduction in total COD. Therefore, in comparison with these methods, electrochemical oxidation of the actual indigo dye effluent is efficient in producing no secondary pollutants, removing color, and decreasing total COD to a reasonable extent with a small operating period.

The calculation of the energy efficiencies for the electrochemical oxidation of indigo dye is not particularly meaningful, since the reducing agents present in the effluent, such as sodium dithionite, were also oxidized during the electrolysis process. Electrical energy consumption after nearly 40 minutes of electrolysis of a 150 mL actual indigo dye effluent sample that caused complete decolorization and 46% decrease in COD can be calculated as 40 V x (~ 375 C)$\cdot 10^{-3}$ = 15.0 kJ = 0.0042 kW-h. Using this result, it can be found that approximately 30 kW-h (calculated value is 27.78 kW-h/m^3) energy is required for each ton of actual effluent treatment. The negative effect of other substances on COD is also lowered with this process and

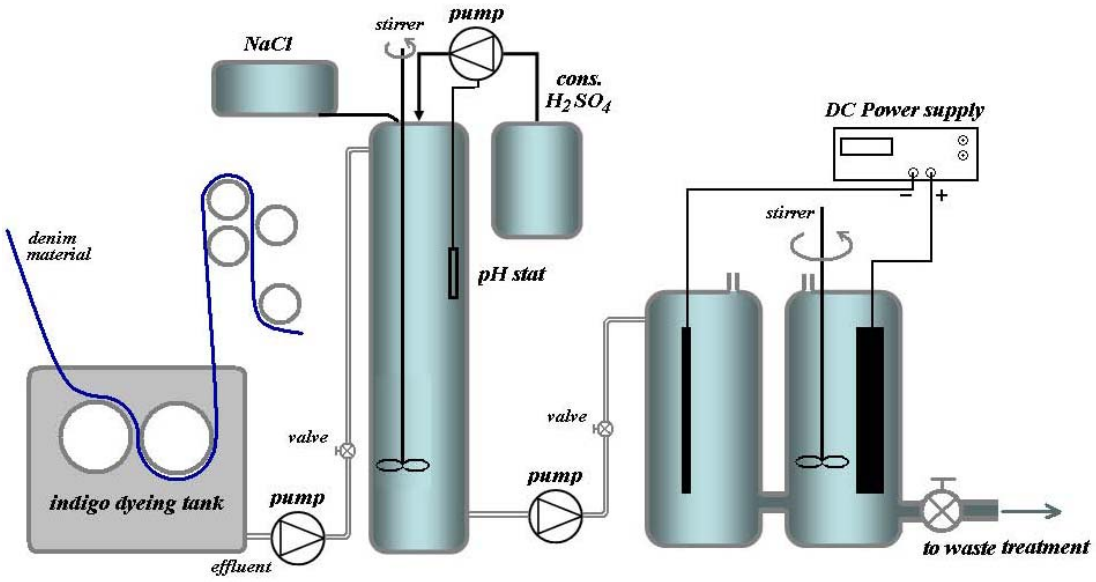

Fig. 5. A model design of an automatic unit for the electrochemical treatment of indigo dyehouse effluents.

the electrical energy consumption for these chemicals will not be a disadvantage for the total cost. Moreover, the electrical energy consumed in this study is less than in our previous model study [21]. In the model study with 150 mL of 0.1% artificial indigo wastewater by w/v, nearly 400 coulomb electrical charge passed in the same cell during 60 minutes of electrolysis for complete decolorization and 40% reduction in COD. These results indicate that the electrical energy used during the electrolysis of the actual indigo effluent is almost equivalent to the electrochemical oxidation of indigo and other auxiliary chemicals used for the preparation of the artificial (model) indigo dye effluent. The results also reveal that the general purpose chemicals entered into the actual indigo dye effluent in the plant did not affect the efficiency of the electrochemical oxidation process negatively.

Conclusion

In the present study, an effective electrochemical treatment method is put forward for a complete decolorization and chemical oxygen demand reduction of an actual indigo dye house effluent to a reasonable extent in a relatively short period of time. The cost of supporting electrolyte and pH adjustment chemicals used in this process is also at a negligible level. The negative effect of other substances on COD is also lowered with this process, and electrical energy consumption is not a disadvantage for total cost. Furthermore, this method can eliminate the dangerous solid waste problem.

We have concluded that this electrochemical oxidation method can be used as an effective pre-treatment method relative to other conventional treatment methods due to a minimal construction cost and a relatively small operating cost. It was foreseen that cheaper materials like stainless steel or graphite electrodes can be tested for industrial-scale applications. To protect surface water reserves, it is necessary to decrease the polluting properties of industrial wastewaters to below the legal limits. Therefore, further studies should be conducted to completely remove color and chemical loads of refractory organic pollutants simultaneously.

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