Research Article

Electrochemical Remediation of Phthalocyanine Dye Wastewater and simultaneous Hydrogen Production

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Abstract

In this work a continuously operated electrocoagulation process with sacrificial aluminum electrodes is presented for decolorization of aqueous solution containing nickel phthalocyanine reactive dye and simultaneous production of electrolytic hydrogen. The electrocoagulator is equipped with a gas separation tank for harvesting the electrochemically generated hydrogen gas at the cathode. Hydrogen, compared to common fossil fuels, is a clean alternative fuel of high caloric value and zero emission. The need for hydrogen has been increasing rapidly. In recent years, a major concern is to obtain hydrogen and energy from waste and industrial effluents by using them as an energy source. Electrocoagulation has proved to combine efficient removal of pollutants, such as recalcitrant dyes from wastewaters and simultaneously production of hydrogen gas at the cathode. The influence of all operating parameters on the dye removal efficiency and hydrogen production, such as wastewater pH, conductivity, current density, and inlet flow rate were investigated.Experimental results showed that the quality of the treated wastewater was very satisfactory. By working at the optimal parameters i.e. initial pH 8 and current density 10 mA/cm^2, the dye was completely removed (>99.9 %). The energy yield via the harvested hydrogen amounted to 12.5 % of the electrical energy needed for running the electrocoagulation process.

Keywords: Batch and continuous process; electrocoagulation; electrolytic hydrogen; phthalocyanine dye

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1. Introduction

Enormous amounts of water are consumed during dyeing and finishing operations. It is estimated that about 1000 m^3/day of wastewater are produced by a medium-scale textile factory. Dye-house effluents are environmentally toxic since they contain stable compounds showing enhanced resistance to conventional biological treatment and furthermore being suspected to cause carcinogenesis. During the dying procedure more than 40% of the dyes are not fixed to the textile fibres, which result in the rinse water and are discharged into the receiving water bodies more or less without treatment [1-3]. Beyond high toxicity and low biodegradability, residual dyestuffs in dyehouse effluents exhibit also an aesthetic pollution as dyestuffs are visible even at low concentrations.

Phthalocyanine is a mocrocyclic aromatic compound comprised of four iso-indole molecules bound with nitrogen atom bridges. The most representative metallic complexes are the nickel phthalocyanine (Ni-pc) and the copper phthalocyanine (Cu-pc) complexes, which are used as dyes and pigments.

Various physical and chemical methods have been applied for decolorization and abatement of dye containing wastewaters, such as coagulation-flocculation [4], adsorption [5], ultra-filtration [6], advanced oxidation [7,8] and electrochemical treatment processes.

Electrochemical processes are viable alternatives for successful treatment of recalcitrant pollutants and are mainly based on anodic oxidation at dimensionally stable electrodes [9,10] and electrocoagulation with corrodible iron and/or aluminum electrodes [11-16].

Electrochemical methods exhibit a series of advantages, such as compact equipment, immobilization of the catalyst/electrode, no generation of secondary pollution and easy control of the voltage-current variables facilitating automation of the process.

The electrocoagulation process produces metallic hydroxide flocs by electrodissolution of corrodible anodes, such as iron or aluminum. When aluminum electrodes are used the products are Al^{3+} ions at the anode and OH$^-$ ions as well H$_2$ at the cathode according the equations (1) and (2):

$$Al \rightarrow Al^{3+} + 3e^- \qquad (anode) \qquad (1)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (cathode) \qquad (2)$$

The produced Al^{3+} and OH$^-$ ions combine to a series of cationic and anionic monomeric or polymeric species, such as Al(OH)$^{2+}$, Al(OH)$_2^+$, Al$_2$(OH)$_2^{4+}$, Al(OH)$^{4-}$, Al$_6$(OH)$_{15}^{3+}$, Al$_7$(OH)$_{17}^{4+}$, Al$_8$(OH)$_{20}^{7+}$, Al$_{13}$O$_4$(OH)$_{24}^{7+}$, Al$_{13}$(OH)$_{34}^{5+}$ resulting in the formation of the gelatinous coagulant Al(OH)$_3$.

During electrocoagulation many processes occur simultaneously: anodic oxidation, cathodic reduction, particle charge neutralization/flocculation/agglomeration, adsorption by the coagulants and flotation by the hydrogen bubbles. All these processes act synergistically leading to a

quick removal of various organic and inorganic pollutants from the processed wastewater [17].

Hydrogen of high quality can be harvested, when the electrocoagulation reactor is equipped with a suitable gas separation tank in form of an up-flow anaerobic sludge bed. Hydrogen as an energy source reduces markedly the energy consumption of the electrocoagulation process. Furthermore, it can be used as reactant for various industrial applications. Phalakornkule et al., [18] reported successful electrocoagulation treatment of Reactive Blue 140 and Direct Red 23 dye containing wastewater achieving removal of color (99%), COD (93%) and TS (89%), whereas the energy yield via the electrolytic hydrogen production ranged between 8.5 and 13% of the energy demand for the electrocoagulation process. Deghles and Kurt [19] studied the hydrogen production during the electrocoagulation treatment of tannery wastewater reporting 16 % energy yield and high quality of the treated wastewater with removal of 73, 94, 100 and 51% for COD, color, Cr and NH_3-N respectively.

In the present paper a batch and continuously operated electrocoagulation process with corrodible aluminum electrodes is reported. The process combines the production of high quality treated wastewater and simultaneous energy harvesting via the recovery of the electrolytic hydrogen gas at the cathode.

2. Materials and methods

2.1. Chemicals
Commercial grade nickel phthalocyanine dye purchased from Aldrich (CAS Nr: 27835-99-0) was used for all studies. Sample dye solutions of 100 mg/L were used for all experiments. H_2SO_4, NaOH, NaCl and Na_2SO_4 of analytical grade were purchased from Merck. The required pH value was adjusted using 0.1 M solutions of H_2SO_4 and NaOH. Figure 1 shows the structure of Ni-pc dyestuff.
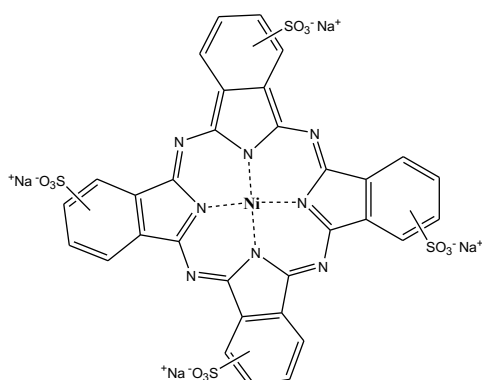
Fig. 1. Chemical structure of the reactive dye nickel phthalocyanine tetrasulfonic acid tetrasodium salt (Ni-pc), Mr: 979.40, Linear Formula: $C_{32}H_{12}N_8Na_4NiO_{12}S_4$.

2.2. Apparatus
Agilent (E3612A, USA) was used as a power supply apparatus to measure the applied current and voltage. Conductometer (WTW) and pH-meter (WTW) were used for measuring the corresponding conductivity and pH of the treated solution.

2.3. Electrochemical cell
The batch experiments were carried out at room temperature in a cylindrical acrylic reactor containing 400 mL of wastewater, which was slowly stirred at 500 rpm. Two

aluminum grid anodes and one central aluminum plate cathode, each with dimensions 10 cm x 5 cm x 0.2 cm, immersed to a 6 cm depth with an effective area 30 cm^2, served as corrodible electrodes. The distance between the electrodes was adjusted to 2 cm.

The continuous electrocoagulation experiments were conducted in a similar however, larger self made flow-through reactor containing 2 L of wastewater, three larger Al electrodes (20 cm x 10 cm x 0.2 cm) immersed to a 15 cm depth with an effective area 150 cm^2. The continuous flow-through reactor was furthermore equipped with a peristaltic pump, a flow meter, a gas collector and a gas flow meter above the central cathode to collect and measure the electrochemically generated hydrogen gas as illustrated in Figure 2:
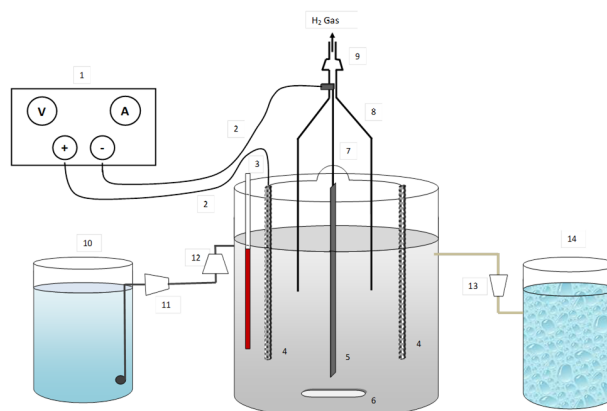
Fig. 2. Continuous electrocoagulation reactor set up (1)Power supply, (2) cables, (3) thermometer, (4) anodes, (5) cathode, (6) stirring fish, (7) cable connecting the anodes, (8) gas separator, (9) gas flow meter, (10) wastewater deposit, (11) peristaltic pump, (12) flow meter, (13) filter, (14) treated solution

2.4. Analytical Procedure
The spectroscopic determination of the phthalocyanine dye concentrations was followed and analyzed by UV-VIS Spectrophotometry (HITACHI U-2000, Japan). Samples were brought to analysis after filtration with polytetrafluorethylene filters of 0.45 μm pore size (Whatman). The supporting electrolyte was NaCl. For reproducibility all measurements were conducted in duplicate. Experiments for both, batch and continuous mode of operation were performed.

For calculation of the percent removal efficiency of dye (% R) was served equation (3):

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \tag{3}$$

where C_o is the initial dye concentration and C_t at time t.

3. Results and Discussion

3.1 Batch wise operated treatment
Various batch experiments were carried out to investigate the parameters affecting the dye removal efficiency and find optimal conditions for the electrocoagulation treatment of the wastewater samples.

3.1.1 Effect of solution pH
The initial pH value plays a significant role on the efficiency of an electrochemically treated solution. In order to show this dependence, the aqueous dye solution of various initial

pHs (2, 4, 6, 8, 10, 12) was tested at the same constant current density 10 mA/cm^2, room temperature 25 ^{0}C, same solution volume 400 mL and same dye concentration 100 mg/L.

Figure 3 shows that optimal solution pH for dye removal during the electrocoagulation treatment is the near neutral region between pH 6 and 8 displaying almost quantitative removal (>99 %). The removal percentage is very low at pH<2. It increases significantly at pH 4, remains high and almost constant between pH 6 to 10 and slightly decreases at higher alkaline pH values.

Adhoum et al. [20] and Vasuderan et al. [21] have studied the reduction of the removal efficiency in both, strong acidic and strong alkaline media. They explained it due to the amphoteric behavior of Al(OH)$_3$ that forms soluble Al^{3+} cations in acidic and soluble Al(OH)$_4^-$ anions in basic pH. These species are less stronger coagulating agents than Al(OH)$_3$ and, therefore, less suitable for wastewater treatment by electrocoagulation.
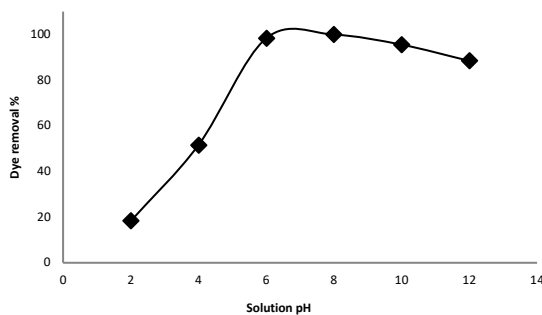

Fig. 3. Dye removal percent versus various initial solution pHs.

3.1.2. Effect of applied current density

According to the findings of Khosla *et al.* [22] and our previous work [23] the applied current density is a very important determining factor affecting immediately the rate of coagulant dosage, the production of H$_2$ bubbles and the growth and size of flocs leading to faster removal of pollutants. Electrocoagulation experiments were carried out at various current densities 5, 10 and 20 mA/cm^2, using the same initial Ni-pc concentration 100 mg/L and optimal solution pH 8. According to Figure 4, the removal rates of dye increased, as anticipated, with increasing applied current density. Namely, complete dye removal (>99.9 %) occurred in 10, 6 and 4 minutes of electroprocessing time using current densities 5, 10 and 20 mA/cm^2 respectively.
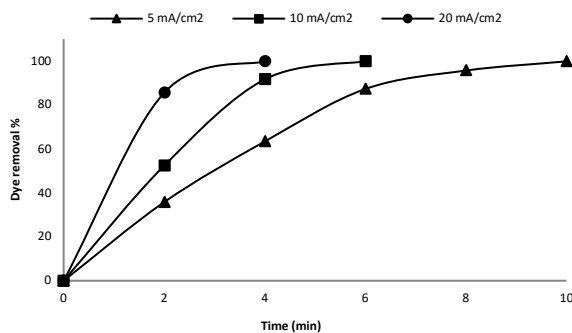

Fig. 4. Removal percentage of Ni-pc dye with time for various applied current densities

3.1.3. Effect of initial Ni-pc dye concentration

Experiments were conducted with different initial concentrations of the Ni-pc dye, keeping constant the

applied current density at 10 mA/cm^2, constant initial pH 8 and different electroprocessing time. According to Figure 5 the corresponding complete reduction of the initial due concentrations of 50, 100 and 150 mg/L appeared in 4, 6 and 10 minutes of electroprocessing time. The electrocoagulation treatment of solutions with higher initial dye concentrations certainly needs more electroprocessing time, however, the removal rate is higher than by lower concentrations. This is indicated by the abrupt change of the dye concentration at the beginning where the dye concentration is high than at the end where the dye concentration is low.
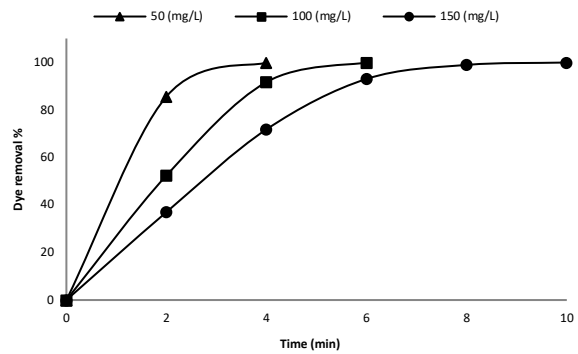

Fig. 5. Dye removal percentage versus time for various initial dye concentrations

3.2. Continuously operated treatment

The efficiency of the continuous electrocoagulation process is influenced by the same parameters as the batch wise operated process and additionally by the inlet flow rate, the wastewater conductivity and the residence time. Consequently, the investigated optimal affecting parameters pH 8 and applied current density 10 mA/cm^2 were used for the continuously operated experiments.

3.2.1. Effect of inlet flow rate

High flow rates accelerate the electrocoagulation process but reduce the residence time and influence, therefore, the dye concentration in outlet wastewater stream. The inlet flow rate of treated wastewater was increased from 15, 30, 45, 60, 75 to 90 mL/min respectively, keeping constant the current density at 10 mA/cm^2, pH 8 and room temperature 25 ^{0}C. As illustrated in Figure 6, the dye removal percent in the outlet stream remains initially very high (>99 %) for the low flow rates (15-45 mL/min) and as the flow rate further increases (60 to 90 mL/min), it begins to drop from >99 to about 71 %, whereas the residual outlet dye concentration begins to rise from 0 to 29 mg/L.

3.3 Eletrolytic hydrogen production

The electrochemical treatment of aqueous organic waste can be coupled with hydrogen production. The organic matter facilitates the electrochemical splitting of water by producing H$^+$ ions and electrons at the anode and electrolytic H$_2$ gas at the cathode [18, 19, 24, 25]. The energy harvesting via the produced hydrogen gas is calculated from equation (4):

$$E_{H2} = m_{H2} \times 122 \text{ kJ/g}_{H2} \tag{4}$$

where *m* is the mass of produced hydrogen and 122 kJ is the specific heat per g of hydrogen.
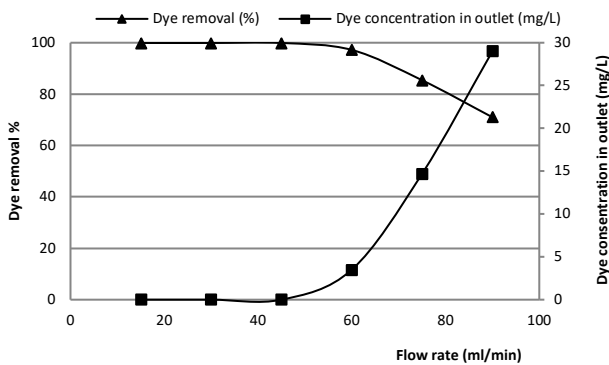
Fig. 6. Concentration and removal percent of Ni-pc dye in outlet stream versus inlet flow rate

Thus, during the continuous electrochemical treatment of the Ni-pc dye wastewater at the inlet flow rate 60 mL/min and current density 10 mA/cm^2, about 175 L hydrogen gas per m^3 of treated wastewater can be produced, which corresponds to 12.5 % energy recovery. In this way, the electrocoagulation process offers a double objective, namely wastewater remediation and energy recovery.

4. Conclusions

A batch and continuously operated electrocoagulation process with aluminum electrodes has been reported and the affecting parameters investigated. The continuous mode with inlet flow rate 60 mL/min, applied current density 10 mA/cm^2 and solution pH 8 led to complete decolorization and removal of the nickel phthalocyanine dye by >99.9 % and simultaneously 175 L hydrogen per m^3 of treated dye solution was harvested. The energy yield via the recovered H$_2$ gas was 12.5 % of the electrical energy required for running the electrocoagulation process. Thus, taking into account the significant decrease of the electrical energy demand via the hydrogen utilization and the quantitative dye removal from treated wastewater, electrocoagulation could be regarded as a useful technology for both, environmental clean-up and energy harvesting.

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