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Electro-assisted photocatalytic decolorization of Reactive Navy Blue SP-BR solution by ZnO nanoparticles immobilized on stainless steel anode

Soheil Aber[a,*], Robab Soltani-Jigheh[a], Ali Reza Khataee[b]

[a]*Research Laboratory of Environment Protection Technology, Faculty of Chemistry, Department of Applied Chemistry, University of Tabriz, Tabriz, Iran, Tel. +98 411 3393153; Fax: +98 411 3340191; emails: s_aber@tabrizu.ac.ir (S. Aber), rubab.sultani@gmail.com (R. Soltani-Jigheh)*
[b]*Research Laboratory of Advanced Water and Wastewater Treatment Processes, Faculty of Chemistry, Department of Applied Chemistry, University of Tabriz, Tabriz, Iran, email: a_khataee@tabrizu.ac.ir*

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ABSTRACT

In this study, the effect of electrical field on the photocatalytic (PC) decolorization efficiency of Reactive Navy Blue SP-BR solution using commercial ZnO nanoparticles was studied. The electrical field was applied through potential difference (ΔV) between the anode and the cathode. ZnO nanoparticles were immobilized on a stainless steel or titanium anode by electrophoretic deposition method. It was found that the electrical field could increase the decolorization efficiency. Decolorization efficiency in the dye solution with the initial concentration of 15 mg L^{-1} during 90 min was increased in electro-assisted photocatalytic (EAP) process up to 81% compared to 39% in simple PC process. Applying the potential difference of 4 V showed the highest efficiency in Reactive Navy Blue SP-BR decolorization by EAP process. The effect of working electrode material was studied by replacing the stainless steel with titanium while the other parameters were constant. EAP decolorization efficiency in the dye solution with the initial concentration of 15 mg L^{-1} and titanium anode was 64%.

Keywords: Dye removal; Electro-assisted photocatalysis (EAP); Nanosized ZnO; Textile dye

1. Introduction

The synthetic dyes used in textile industries raise concerns about color and toxicity problems. Reactive dyes are synthetic materials and extensively used for their good fixation properties [1]. Semiconductor/UV photocatalytic (PC) processes are interesting alternatives to remove the pollution of synthetic dyes. Photocatalyst particles are usually used in immobilized form in order to easily separate them from solution which makes them reusable, but the immobilized particles show lower specific surface area compared to their initial powders. Also, the easy recombination of produced electrons and holes, leads to less efficiency in PC activity [2–4]. Many researches have been done to improve the PC efficiency by preventing the electron–hole recombination, for example, by the addition of electron scavengers to electrolyte [5]. Herein, an electrical field resulted from applying a potential difference between anode and cathode, was used to increase the efficiency of Reactive Navy Blue SP-BR decolorization in the solution. Applying an electrical field between the anode on which the photocatalyst particles are immobilized and the cathode can increase the separation of the photogenerated electrons and holes. These electrons

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*Corresponding author.

and holes move in opposite directions inside the electrical field and this increases their separation by transferring the electrons to the cathode and leaving the holes in the photocatalyst [6–10].

In the present work, electro-assisted PC (EAP) process was used for Reactive Navy Blue SP-BR solution decolorization by ZnO nanoparticles immobilized on stainless steel or titanium surfaces as anode electrode while a stainless steel electrode was used as cathode. ZnO nanoparticles were immobilized using electrophoretic deposition (EPD) method.

2. Materials and methods

2.1. Immobilization of ZnO nanoparticles

ZnO suspension was prepared by the addition of 0.08 g $Mg(NO_3)_2{\cdot}6H_2O$ (Merck) and 0.25 g ZnO (Fluka) into 60 cm^3 2-propanol (Merck) [11,12]. The prepared suspension was sonicated for 90 min in ultrasonic bath (Grant, Type XB6, England, 300 W, 50 Hz). The sonication was used for breaking up the agglomerated particles [13]. This suspension was used to immobilize ZnO nanoparticles on the cathode electrode in EPD process. This electrode was used as anode in EAP process.

The EPD system comprised of two stainless steel (304) electrodes with the same size (5 cm × 5 cm), the prepared suspension of ZnO nanoparticles, and a DC power supply (Micro, Iran). To clean the electrodes before EPD process they were immersed in acetone for 5 min and then, they were dipped in to ethanol 97% for 15 min [14]. The electrodes were located as parallel in the suspension with a distance of 0.5 cm in between. A potential difference of 40 V [15] was applied between the electrodes for 7 min. To immobilize ZnO nanoparticles on titanium electrode, the cathode was changed to titanium.

2.2. Characteristics of ZnO nanoparticles before and after immobilization

To characterize the used ZnO nanoparticles, X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses were performed using a Siemens D5000 diffractometer (Germany) with Cu-Kα radiation (40 kV, 30 mA, $\lambda = 0.15418$ nm) and a Zeiss, EM10C TEM device (Germany), respectively. For the characterization of the prepared ZnO film, scanning electron microscopy (SEM) image was obtained using a SEM device (Hitachi S4 160, USA).

2.3. EAP experimental setup

The EAP system (Fig. 1) comprised of two electrodes (5 cm × 5 cm): a DC power supply (Micro, Iran), a UV-C lamp (30 W, Philips, Holland, 253.7 nm) and a chamber containing electrodes and the dye solution. The anode was ZnO/stainless steel (304) or ZnO/titanium and the cathode was stainless steel (304) without ZnO coating. The electrodes were located horizontally and arranged parallel to each other while the anode was located above the cathode. The anode was immersed 0.5 cm under the dye solution surface and the distance between two electrodes was 0.7 cm. The potential difference between the electrodes was fixed by DC power supply. The UV lamp was placed above the system and the radiation intensity was measured using a UV radiometer purchased from Cassy Lab Company (Germany). The distance between the anode electrode and UV lamp was 8 cm and it was constant all over the experiments. The amount of radiation intensity of UV lamp at this distance was obtained to be 16 Wm^{-2}.

2.4. Model dye used as pollutant

In this work, Reactive Navy Blue SP-BR organic dyestuff was used as a model pollutant (Cas No. 93050-78-3, MW: 526.5 g mol^{-1}, $\lambda_{max} = 597$ nm). Its structural formula is shown in Fig. 2. It is used in textile industry for the preparation of blue fibers. Decolorization procedure was followed by a UV–visible spectrophotometer (Perkin–Elmer 550 SE, Germany) at 597 nm.

2.5. Experimental procedure

In each experiment, 100 mL of Reactive Navy Blue SP-BR solution in thrice distilled water (15 mg L^{-1}) was transferred into the reactor. The sample was stirred for 30 min in darkness and in the absence of electrical field to eliminate the effect of surface adsorption. The solution concentration after 30 min was considered as the initial concentration in the calculation of decolorization efficiency. After the darkness stage, the lamp was turned on and the potential difference was applied to the system by the DC supply. Each EAP experiment was carried out for 90 min. Samples were withdrawn every 20 or 30 min for analysis. Photolysis experiments were conducted without electrodes in the same EAP reactor. PC experiments were performed in the same EAP reactor but in the absence of electrical field. To show the efficiency of sole electrical oxidation (EO), it was performed in the same EAP reactor while the UV lamp was off. The amount of potential difference applied in EAP and EO experiments and the current was measured using an ampere meter (DEC330FC, China). All experiments

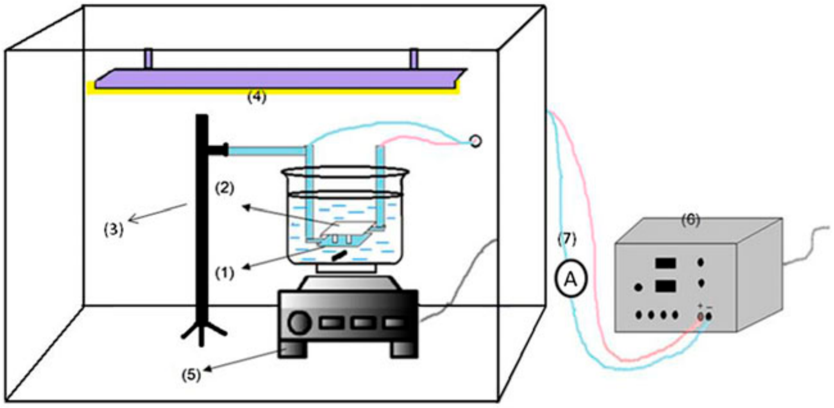


Fig. 1. Scheme of EAP setup, (1) Stainless steel cathode, (2) ZnO/Stainless steel or ZnO/titanium anode, (3) Support, (4) UV lamp, (5) Magnetic stirrer, (6) DC supply, (7) Ampere meter.

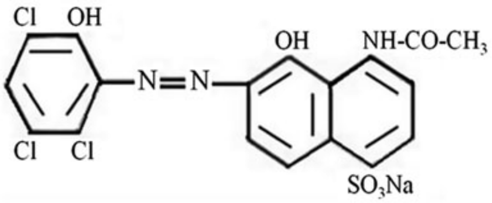


Fig. 2. The structural formula of Reactive Navy Blue SP-BR.

were performed at natural pH of the dyestuff solution, i.e. 5.4 which was measured by a pH meter (Eutech, Malaysia). To minimize the effect of EO process in decolorization, thrice distilled water which had less conductivity than regular distilled water and real water, was used for the preparation of the dyestuff solutions. Each experiment was repeated three times.

Decolorization results were shown as the plot of X vs. irradiation time. X is defined using the following equation:

$$X = \frac{c_0 - c}{c_0} \tag{1}$$

where X is decolorization efficiency at a given time, c_0 is the initial concentration (mg L^{-1}), and c is the concentration of the dyestuff (mg L^{-1}) at time t.

3. Results and discussion

3.1. Characterization results

Fig. 3(a) shows the XRD pattern of the ZnO nanoparticles. Their average crystal size was determined using Debye–Scherrer equation [16,17] approximately equal to 20 nm. According to the obtained TEM image shown in Fig. 3(b), most of the particles had a diameter less than 100 nm and were mainly round in shape. Everywhere in this manuscript, nanosize is only considered for the ZnO particles before immobilization step.

Fig. 4 shows the SEM image of stainless steel after immobilization of ZnO nanoparticles. This figure confirms the successful immobilization of ZnO nanoparticles on the surface of stainless steel by EPD method.

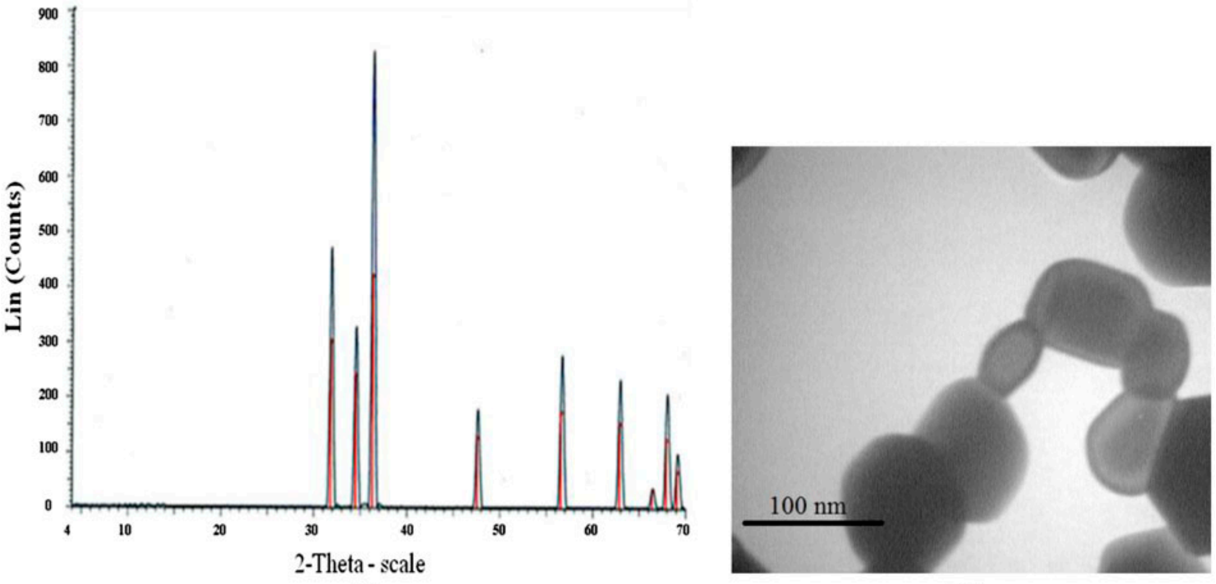
3.2. Performance of EAP process

As can be seen in Fig. 5, EAP process had better efficiency than PC and EO processes. Applying an electrical field between cathode and anode, forces the photocatalytically produced electrons and holes to move in opposite directions, so their recombination is retarded [18–20]. According to Eq. (2), UV irradiation transfers the electrons to the conduction band and leaves the holes in the valence band. By applying an electrical field, the photogenerated electrons can move to the cathode and react with water to produce H_2 and OH^- which leads to more $^{\cdot}OH$ radical production (Eqs. (3)–(6)) [18]. In the following equations, cb and vb in subscripts represent conduction band and valence band, respectively.

$$\text{ZnO/Steel} \xrightarrow[\text{Electric field}]{\text{hv}} (\text{ZnO}) - e^-_{\text{cb,anode}} + (\text{ZnO}) - h^+_{\text{vb,anode}} \tag{2}$$

$$(\text{ZnO}) - e^-_{\text{cb,anode}} \rightarrow (\text{steel}) - e^-_{\text{cathode}} \tag{3}$$

$$2((\text{steel}) - e^-)_{\text{cathode}} + 2H_2O \rightarrow H_2 + 2OH^- \tag{4}$$



(a) (b)

Fig. 3. Characteristics of the used ZnO nanoparticles: (a) XRD pattern (b) TEM image. The red lines show standard ZnO peaks.

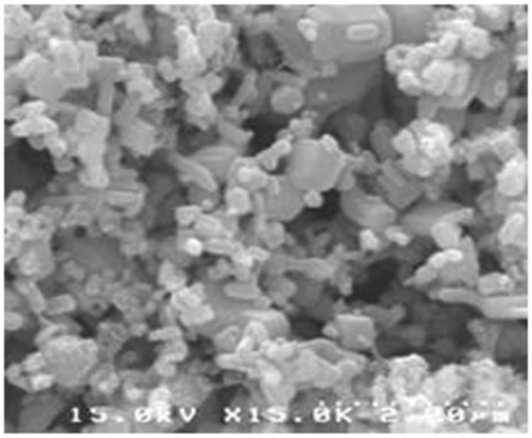


Fig. 4. SEM image of stainless steel surface after the immobilization of ZnO nanoparticles.

$$OH^- + h^+_{vb} \rightarrow {}^{\cdot}OH \tag{5}$$

$$H_2O + h^+_{vb} \rightarrow {}^{\cdot}OH + H^+ \tag{6}$$

In EO process, the electrooxidation of pollutant can occur via two mechanisms: direct oxidation of pollutant on the anode surface and indirect oxidation of pollutant by an electrochemically produced mediator [21,22]. In EAP process, as a result of direct and indirect EO reactions and also the electron–hole separation, the decolorization efficiency increases compared to solo PC and EO processes [23].

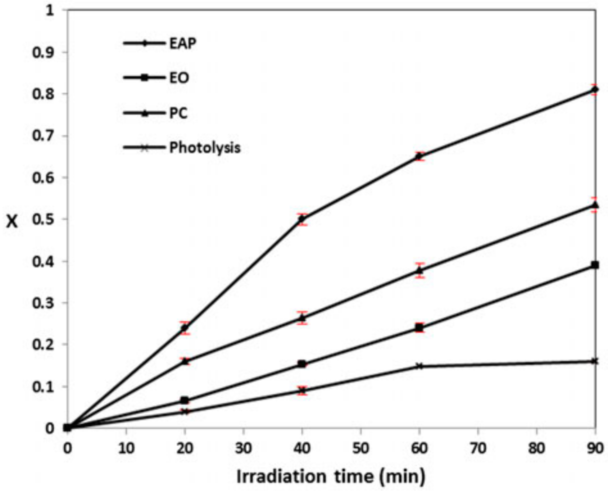


Fig. 5. The promoting effect of electrical field on the decolorization efficiency, pH = 5.4, $\Delta V = 4$ V, $c_0 = 15\,\mathrm{mg\,L^{-1}}$, $I = 16\,\mathrm{Wm^{-2}}$.

Decolorization efficiency in a solution with the initial concentration of $15\,\mathrm{mg\,L^{-1}}$ using EAP process increased to 81% after 1.5 h compared to 39% in PC process (Fig. 5) while it was 54% in solo EO process at the same condition. Accordingly, the combined technology of photocatalysis and electrooxidation enhanced the degradation of the pollutant. Similar results were obtained by Fan et al. [23] which chose Ti/SnO_2–Sb_2O_4 electrode as anode and a gas diffusion electrode as cathode for the degradation of phenol. They found that it was 65% under solo UV irradiation after 3 h. Using electrooxidation in the absence of UV irradiation, 80% of phenol was degraded at the cell voltage of 2 V after 3 h. In the presence of both UV irradiation and the cell voltage of 2 V, 100% of phenol was degraded after the same time.

To investigate the effect of electrical field in preventing the electron–hole recombination in EAP process, the curves of potential difference vs. current were plotted for ZnO/stainless steel anode and stainless steel cathode, both immersed in the dyestuff solution with initial concentration of 15 mg L^{-1} (Fig. 6). UV irradiation transfers the electrons to the conduction band and leaves the holes in the valence band. In curve (a) departed electrons under UV irradiation lead to an increase in current compared to curve (b) which has been plotted for the same electrodes in the absence of the irradiation. Curve (b) shows the current resulted from only electrolysis. In curve (a) the current is composed of two parts. First, the current resulted from electrolysis and second, the current resulted from the electrons excited by UV. Curve (c) indicates the current produced from electrons excited by UV. It shows that increasing the potential difference enhances the separation of charge carriers and so, the current increases due to restraining the electrons and holes from recombination [24].

3.3. Effect of potential difference

According to Fig. 7, increasing the potential difference between anode and cathode increased the decolorization efficiency in EAP process. Electrical field intensity has an important role in the suppression of electron–hole recombination and increases by increasing the potential difference. The direct and the indirect oxidation of the pollutant increases at higher voltage values [25], too. Liu et al. [24] reported similar results for the mineralization of methylene blue in a PC system under external bias. In their work under different biases of 0, 5, 10, and 15 V the PC efficiency was 27, 61.6, 65.7, and 76.2% after 30 min, respectively. In the present work, according to the obtained results, 4 V was chosen as the best potential difference. By decreasing the potential difference to lower than 4 V, the decolorization efficiency decreased due to the decrease in the separation of electrons and holes. At potential differences higher than 4 V, the destruction of photocatalyst film was observed. According to literature, at higher potential differences the evolution of oxygen results in the destruction of photocatalyst film [26].

To investigate the durability of the photocatalyst film, 20 successive PC experiments were performed for the decolorization of Reactive Navy Blue SP-BR solution (15 mg L^{-1}) using only one prepared photocatalyst film in all replications. Also similar EAP experiments were performed by applying the potential difference of 4 V. There was no obvious difference between the results of different replications and accordingly, the photocatalyst film was considered to be stable under the potential differences of 4 V and below.

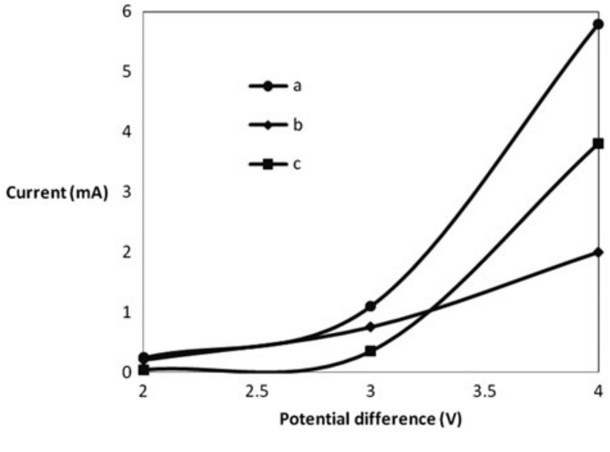


Fig. 6. "Potential difference vs. current" curves for a system containing ZnO/Stainless steel anode and stainless steel cathode in Reactive Navy Blue SP-BR solution, pH = 5.4, $c_0 = 15$ mg L^{-1}, under (a): UV irradiation ($I = 16$ Wm^{-2}) (b): darkness. Curve "c" shows the difference of curves "a" and "b".

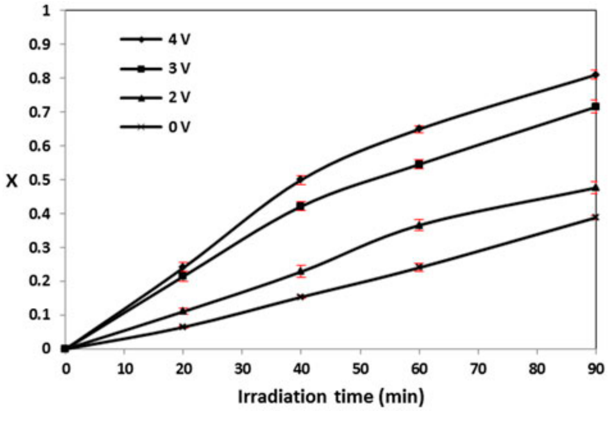


Fig. 7. Effect of potential difference on the decolorization efficiency in EAP process with ZnO/Stainless steel anode and stainless steel cathode, pH = 5.4, $c_0 = 15$ mg L^{-1}, $I = 16$ Wm^{-2}.

3.4. Effect of anode material

Stainless steel and titanium were used as anode material in EAP system and the corresponding degradation results are shown in Fig. 8. At the potential difference of 4 V, the decolorization efficiency in a dye solution with the initial concentration of 15 mg L^{-1} using stainless steel anode after 90 min was 81% while by changing it to titanium the efficiency reduced to 64%. This is probably due to the higher electrical conductivity of stainless steel than titanium. If the electrical conductivity of copper is considered to be 100%, titanium and stainless steel would have a conductivity of 3.1 and 3.5%, respectively (http://www.keytometals.com/Article122.htm, Retrieved at: 2 October 2012). As a result, the transfer of produced electrons from stainless steel anode to cathode is more convenient and this enhances the separation of the produced electrons and holes.

The effect of electrode material was investigated in the degradation of dye X-3B by Jiang et al. [7], too. In their work, stainless steel and copper were used as electrode material and they found that the degradation efficiency with copper was better than stainless steel because the electrical conductivity of copper is much higher than that of stainless steel.

3.5. Determination of electrical energy consumption

As economic considerations are very important in wastewater treatment technologies and electrical energy imposes high cost on treatment methods, its calculation is indispensable. The electrical energy consumed by EAP process is composed of two parts: first, the electricity used by UV lamp and second, the one consumed by DC supply.

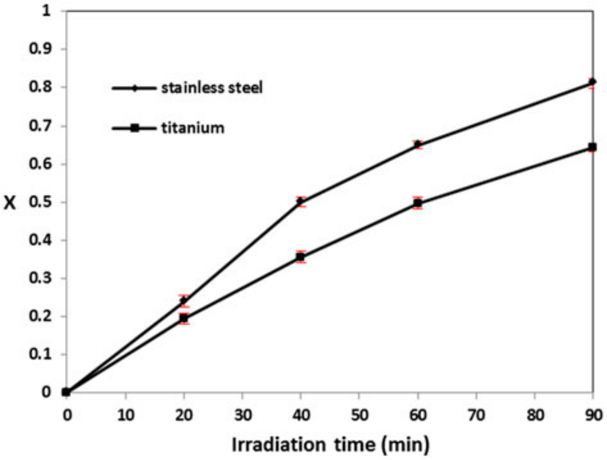


Fig. 8. The effect of anode material on decolorization efficiency in EAP process, pH = 5.4, $\Delta V = 4$ V, $c_0 = 15$ mg L^{-1}, $I = 16$ Wm^{-2}.

For UV-based processes in low pollutant concentrations, the photochemistry commission of the International Union of Pure and Applied Chemistry defined a figure of merit [27]. Electrical energy per order (E_{EO}) was proposed for use in the first-order kinetic regime. It shows the kilowatt hours (kW h) of electrical energy that is needed to decolorize contaminant by one order of magnitude in 1 m^3 of aqueous pollutant [27]. The E_{EO} values can be obtained using the following equations [28]:

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log(c_0/c)} \quad (7)$$

$$\log(c_0/c) = k \times t \quad (8)$$

where P is the lamp power (kW), t is the irradiation time (min), V is the volume of dyestuff solution (L), c_0 is the initial concentration of dyestuff (mg L^{-1}), c is the concentration of the dyestuff at time t (mg L^{-1}), and k is the first-order rate constant (min^{-1}) for the decolorization of the contaminant. According to the Eqs. (7) and (8), E_{EO} can be written as Eq. (9) [28]:

$$E_{EO} = \frac{38.4 \times P}{V \times k} \quad (9)$$

The electrical energy used by DC supply is calculated using Eq. (10):

$$W = P \times t \quad (10)$$

where W is the consumed electrical energy (kWh), P is the power (kW), and t is the time of reaction (h). To obtain the electrical energy that is necessary for the treatment of 1 m^3 of dyestuff solution, Eq. (10) is converted to Eq. (11) in which W' is the electrical energy (kWh m^{-3}) and V is the treated dyestuff solution volume (m^3).

$$W' = \frac{P \times t}{V} \quad (11)$$

$$P = 10^{-3} \Delta V \times I \quad (12)$$

Eq. (12) gives the power to be used in Eq. (11). ΔV is the potential difference (V) that is applied to the system in EAP process and I is the electrical current (A).

Herein, the E_{EO} values for decolorization in EAP and PC processes were calculated equal to 640 and

2,304 kWh m^{-3}, respectively. The electrical energy consumed by DC supply in EAP process was calculated equal to 0.348 kWh m^{-3} which can be ignored compared to the electrical energy consumption by UV lamp. By considering 0.018 USD/kWh (http://eecm.ir, Retrieved at: 23 February 2012) as electricity price in Iran, the treatment costs for 1 m^3 of the contaminated water in EAP and PC processes are 11.52 and 41.47 USD/m^3, respectively. Therefore, EAP seems to be more economic than PC from the view point of electricity consumption.

4. Conclusion

In this work, EPD method was successfully used for the immobilization of ZnO nanoparticles on stainless steel and titanium electrodes. The ability of immobilized ZnO nanoparticles in the decolorization of Reactive Navy Blue SP-BR in aqueous solution was studied in EAP, PC, and EO processes. It was found that applying electrical field increases PC decolorization efficiency. Increasing applied potential difference between anode and cathode up to 4 V results in an increase in decolorization efficiency. Stainless steel anode shows better color removal than titanium in EAP process. Regarding electrical energy consumption, the EAP is more economic than PC process.

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Symbols

ΔV	—	potential difference
C	—	concentration
E_{EO}	—	electrical energy per order
I	—	electric current
K	—	rate constant
MW	—	molecular weight
P	—	power
t	—	irradiation time
V	—	volume
W	—	electrical energy
X	—	amount of decolorization

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