

A strategy for degradation of 2,5-dichlorophenol using its photoelectrocatalytic oxidation on the TiO₂/Ti thin film electrode

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ABSTRACT

In this work, the photoelectrocatalytic (PEC) degradation of 2,5-dichlorophenol can be used for its removal from aqueous solution. To study this activity, a TiO₂ thin film modified titanium sheet (TiO₂/Ti) was fabricated by anodizing Ti plates using a two electrode system under the constant bias voltage of 20 V for 20 min in a solution of 0.2% (v/v) HF followed by calcination at 500 °C for 2 h. Then, the electrochemical properties of 2,5-dichlorophenol were compared on the surface of the TiO₂/Ti and unmodified Ti electrodes. Consequently, the TiO₂/Ti was applied for PEC degradation of 2,5-dichlorophenol. It was found that 2,5-dichlorophenol could be degraded more efficiently by this photoelectrocatalysis process than the sum of degradation obtained by photocatalytic (PC) and electrochemical (EC) oxidation so that the amount of 2,5-dichlorophenol degraded by PEC, PC and EC oxidation were equal to 51%, 39% and 5% respectively under the 0.4 V voltage in 60 min. The effect of various parameters was studied and the highest degradation percentage of 2,5-dichlorophenol was obtained at pH 6.0, the initial 2,5-dichlorophenol concentration of 7.0 mg L⁻¹ and applied potential of 1.2 V.

Keywords: 2,5-Dichlorophenol, Degradation, Photoelectrocatalysis, TiO₂/Ti electrode.

1. Introduction

Advanced oxidation processes (AOPs) were broadly applied in the treatment of water because of their ability for pollutions removal [1-3]. Among the various AOP techniques, semiconductor mediated photocatalysis has achieved great importance over the last few years due to its potential to destroy a wide range of organic and inorganic pollutants at ambient conditions, without the production of harmful products [4-6]. In this process, irradiating a semiconductor generates electron-hole (e⁻/h⁺) pairs which finally produce the hydroxyl and superoxide radicals in order to be used in initiating oxidation and reduction reactions [3-6]. TiO₂-based photocatalysis as one of the AOP methods have been extensively employed by several researchers in environmental applications, containing the purification of polluted air, water and wastewater due to low price, good chemical stability, non-toxicity and non-photo-corrosion [7-10].

Unfortunately, TiO₂ has a band gap of 3.2 eV, it can only be activated by UV radiation ($\lambda < 387$ nm), and thus the use of sunlight as an energy source is limited due to its large band gap [2]. Moreover, a low quantum yield rate, because of recombination between electrons/holes pairs, has limited its practical application to environment science. In order to enhance the photocatalytic (PC) efficiency, many modifications such as metal or nonmetal doping [11,12], supporting TiO₂ on polymeric fibers [13] and clays [14], coupled semiconductors [14], dye sensitization [15], etc. improved photocatalytic efficiency of TiO₂ has been performed by many researchers. Neamen [16] described doping as the process of adding foreign or impurity atoms into the crystal lattice of a semiconductor material. In the supporting method, TiO₂ was immobilized on various substrates to prevent the electron-hole recombination [14]. The coupling of semiconductors results in the balance of their Fermi levels (i.e., energy midway between the conduction and the valence band edges) such that the electron flow is from the semiconductor with the higher Fermi level to the one with the lower Fermi level [17]. Also, dye sensitization is a means of

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increasing absorption toward the visible light region through the inducement of the photo-excited dye molecule [18]. Photocatalytic oxidation of organic compounds can be obtained either using the form of TiO_2 slurry or film in aqueous solution. The utilizing of TiO_2 in the form of film is preferred because this technique has not problems such as difficulty in photocatalyst recovery. However, the application of the former method reduces the quantum efficiency because of the reduction of active surface area [19,20]. Moreover, the rapid recombination of photo-produced holes and electrons as an important factor in quantum efficiency reduction at TiO_2 during the photocatalytic process is a practical obstacle [21]. Photoelectrocatalysis as a new strategy withdraws electrons to counter electrodes by the external bias potential [22-27]. As a result, it decreases the recombination of photoholes and photoelectrons and promotes the photocatalytic degradation of organic pollutants.

Chlorophenols as members of phenolic compounds are applied widely in the environment because of their various antimicrobial properties. Their applications contain disinfectants, wood preservation, pesticides, dyes, and as intermediates in production of pharmaceuticals [28]. Due to the harmful effects of phenolic compounds (and in general for all organic/inorganic pollutants) removing of such water pollutants has been subjected by environmental chemists [29-31]. In this study, 2,5-dichlorophenol was selected to degrade PEC. This compound has been monitored in effluent of certain industrial wastewater and groundwater. In addition, it has also been distinguished as a potential environmental risk stressor in surface water [32]. Furthermore, 2,5-dichlorophenol is not very biodegradable due to its recalcitrant properties [33]. 2,5-dichlorophenol is not only problematic to the environment but also to human health. It is determined as an endocrine disrupting chemical, and it has been associated with increased obesity [34], type 2 diabetes [35], and food allergies [36] in adults, teenagers, and children, as well as reduced birth weights in boys [37]. Thus, degradation of 2,5-dichlorophenol is a matter of great interest, however, there are few studies about its degradation [33,38].

In this study, the PEC removal of 2,5-dichlorophenol was performed using TiO_2 film modified titanium foil photoelectrodes (TiO_2/Ti). The TiO_2/Ti thin film electrode was provided by anodizing a Ti plate in aqueous solution. Also, the photoelectrochemical behavior of 2,5-dichlorophenol toward the TiO_2/Ti and the effect of different factors (pH of solution, initial 2,5-dichlorophenol concentration and used bias

potential) were studied on 2,5-dichlorophenol degradation. The simplicity of TiO_2/Ti electrode preparation, using only a 4 W medium pressure mercury lamp for 2,5-dichlorophenol PEC degradation and application of the carbon paste electrode as a cost and available sensor for monitoring of 2,5-dichlorophenol concentration variations in various removal methods, can be considered as advantages of this research work.

2. Experimental

2.1. Apparatus

A photoreactor system was designed as observed in Fig. 1 containing a cylindrical shaped quartz reactor (3.0 diameter \times 8.0 height with a 1.8 mm wall), a TiO_2/Ti electrode as photoanode, Pt rod electrode as the cathode, an $\text{Ag}/\text{AgCl}/\text{KCl}$ (3M) as the reference electrode and a 4 W medium pressure mercury lamp as a UV light source. The reactor and the UV lamp were put in a black box to keep away from extraneous illumination. The three electrodes were set in the center of the reactor in parallel and connected with the potentiostat (μ Autolab Type III). Scanning electron microscopy (SEM) (Philips Corp., XL30 model) was used for seeing of the surface morphology of the TiO_2 unmodified and modified titanium electrode. Also, concentration variations of 2,5-dichlorophenol in different processes were measured through differential pulse voltammograms using a carbon paste electrode. A carbon paste electrode (CPE) was utilized as a working electrode for electrochemical examination of 2,5-dichlorophenol concentration variations in the different processes such as photoelectrocatalysis by measurements of the peak current (I_p) decay at the peak potential (E_p) oxidation of 2,5-dichlorophenol in its differential pulse voltammograms over various times. The scan rate for recording DPVs was 10 mV s^{-1} . The photoactive surface of the anode (TiO_2) was illuminated by a 4 W medium pressure mercury lamp with a power intensity of 0.4 mW cm^{-2} as UV light source.

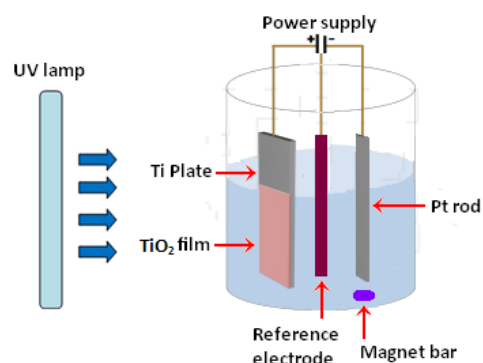


Fig. 1. Schematic of the photoelectrocatalytic batch reactor set-up.

Scanning electron microscopy (SEM) (Philips Corp., XL30 model) was used for seeing the surface morphology of the TiO₂ modified carbon electrode. Measurements of pH were made with a Denver Instrument Model 827 pH meter equipped with a Metrohm glass electrode. Zeta potential of the TiO₂ was measured using a Zeta potential meter (Stabino, Particle Mertix Company, Germany). X-ray diffraction (XRD) was conducted on a X-ray diffractometer (XRD, GBC MMA Instrument) with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$).

2.2. Reagents

In this investigation, double distilled water was applied as solvent. 2,5-dichlorophenol and titanium foils (0.25 mm thickness, 99.7% purity) were purchased from Fluka and Sigma-Aldrich respectively. Hydrofluoric acid (99.5%, Fluka) and nitric acid (66%, Fluka) were used as received. H₃PO₄ (99%, Fluka) and its salts were employed for fabrication of buffer solutions. Paraffin oil (density: 0.88 g/cm³) and graphite powder (particle diameter 0.1 mm) were obtained from Fluka.

2.3. Construction of the TiO₂/Ti and carbon paste electrodes

To prepare the TiO₂/Ti electrode, Ti sheet (3.0 × 3.0 cm²) was mechanically polished with 220# and 1500# abrasive papers respectively. Then, the Ti plate was immersed in an ultrasonic bath containing distilled water, chemically etched by sinking aqueous solution containing 3.0 mL HF (99.5%), 12.0 mL HNO₃ (66%) and 15.0 mL double distilled water and cleaned thoroughly with acetone and deionized water. After that, the Ti sheet was anodized as an anode in the presence of Pt rod as the cathode using a two electrode system under constant bias voltage of 20 V for 20 min in a solution of 0.2% (v/v) HF. Finally, the TiO₂/Ti electrode was then rinsed with distilled water, dried in air and calcinated in a furnace at 500 °C for 2 h.

The carbon paste electrode was fabricated according to same procedure, with adding paraffin oil (0.40 g) to graphite powder (1.0 g). A portion of the carbon

paste was filled firmly into one end of a glass tube (internal radius 3 mm), and a copper wire was inserted through the opposite end to establish an electrical contact. The surface of the carbon paste electrode was polished on a piece of weighing paper to obtain a smooth surface just before use.

3. Results and Discussion

3.1. The photoelectrode characterization

SEM was used to investigate the TiO₂/Ti electrode surface. Fig. 2 indicates the SEM photos of the unmodified and TiO₂ modified Ti electrodes. It can be shown from Fig. 2B that TiO₂ coverage was formed and almost distributed as a uniform texture on the surface of Ti substrate, although some ups and downs were sometimes observed on the surface.

XRD patterns were taken in the range of 2 θ between 20° and 70° with a scanning rate of 0.05°/s (Fig. 3). As seen, TiO₂ films can be successfully developed on Ti substrate containing peaks that are attributed to both the anatase and rutile phases because the diffraction peaks of TiO₂/Ti electrode were in agreement with its standard patterns of Ti metal phase (JCPDS 44-1294), the TiO₂ anatase (JCPDS 21-1272) and rutile phases (JCPDS 21-1276) [39]. Phase composition was estimated by the integral intensities of anatase (101) and rutile (110) reflections [40] and it was found to be about 75% and 25%, respectively. The primary crystallite size of TiO₂ was estimated at 25 ± 3 μm applying the Scherrer's equation [40-42].

3.2. Photoelectrochemical properties of the photoelectrode

Some basic reactions involved in the photocatalysis are summarized in Table 1. In a semiconductor catalyst, UV irradiation with enough energy creates electrons and holes due to excitation electrons from the valence band (VB) to conduction band (CB) (Fig. 4A and Eq. 1 in Table 1) [43].

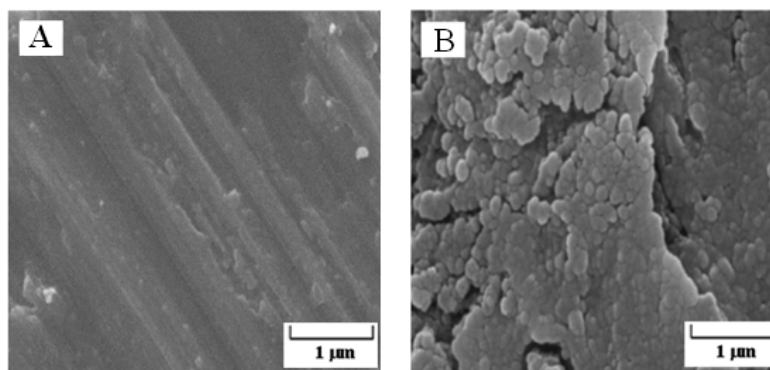


Fig. 2. A typical SEM micrographs of (A) Ti and (B) TiO₂/Ti electrodes.

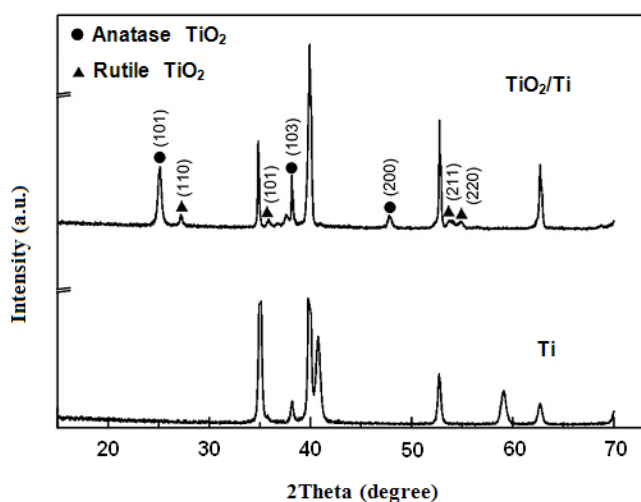


Fig. 3. XRD patterns of Ti and TiO₂/Ti electrodes.

Table 1. Some basic reactions involved in the photocatalysis process.

Reaction equation	Number
$\text{TiO}_2 + h\nu \rightarrow e_{\text{CB}}^- + h_{\text{VB}}^+$	(1)
$h_{\text{VB}}^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$	(2)
$e_{\text{CB}}^- + \text{O}_2 \rightarrow \text{O}_2^{\cdot-}$	(3)
$\text{O}_2^{\cdot-} + \text{H}^+ \rightarrow \text{HO}_2^{\cdot}$	(4)
$2\text{HO}_2^{\cdot} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	(5)
$\text{H}_2\text{O}_2 + \text{O}_2^{\cdot-} \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2$	(6)
$e_{\text{CB}}^- + h_{\text{VB}}^+ \rightarrow \text{TiO}_2 + \text{heat}$	(7)
$e_{\text{CB}}^- + \cdot\text{OH} \rightarrow \text{OH}^-$	(8)

As shown in this figure, these powerful species can move towards the catalyst surface and react with pre-adsorbed materials such as H₂O and pollutants (Eq. 2). When holes react with H₂O (or OH⁻) as a hole scavenger, hydroxyl radicals are formed. Likewise,

the photoinjected electron can create other oxidizers such as O₂^{·-}, HO₂[·] and H₂O₂ with less strength and more ·OH based on Eqs. (3)-(6). Organic pollutants can be oxidized using holes or hydroxyl radicals. As observed in Fig. 4A and Eqs. (7) and (8), the recombination of electrons and holes can decrease concentration of this photo-generated species and subsequently, it is considered as an important problem in photocatalysis. In photoelectrocatalysis, the application of bias voltage can separate the electrons and holes pairs. This potential conducts the electrons to the counter electrodes and the holes remained at the surface of the TiO₂/Ti electrode (Fig. 4B). As a result, the photoelectrocatalysis technique can present much higher efficiency for organic compounds oxidation.

To confirm the photoelectrochemical answer of the TiO₂/Ti electrode, hydrodynamic amperometry was carried out at an applied potential of 0.5 V in 0.1 M buffer solution under UV light (Fig. 5A). As shown in this figure, the ascent and fall of the photocurrent reacted well to the illumination being turned on and off. This pattern of photocurrent can be greatly reproduced for on-off cycles of radiation. A certain increase seen in the photocurrent under illumination shows that photogenerated electrons on the Ti/TiO₂ electrode can be adequately directed to the auxiliary electrode utilizing applied positive potential, which would be crucial for banning of the charge recombination. Furthermore, for studying the photoelectrochemical activity of the TiO₂/Ti electrode and to make sure its ability to oxidize 2,5-dichlorophenol by photoelectron-catalysis method, cyclic voltammetry experiments in the dark and under UV light illumination were carried out both with and without 2,5-dichlorophenol (Fig. 5B).

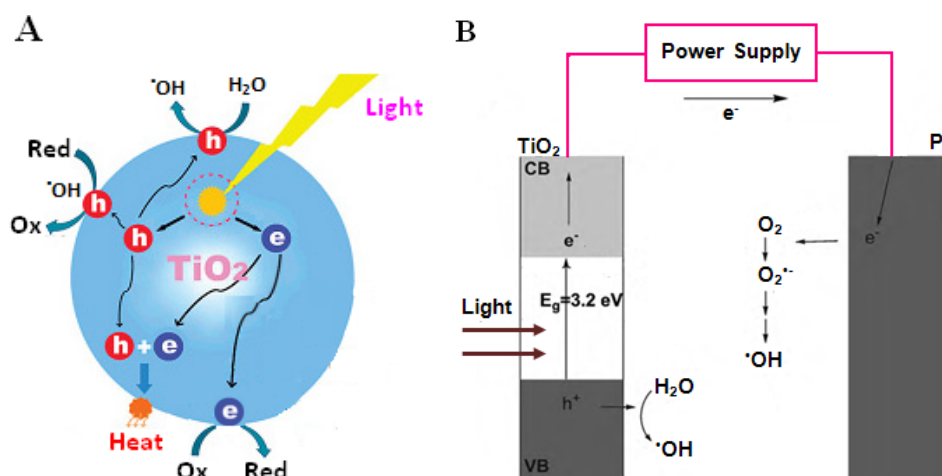


Fig. 4. Schematic photoexcitation, recombination and reaction processes of a semiconductor particle (A) and effect of applied potential on separation electron-hole at the surface of the TiO₂/Ti electrode in photoelectrocatalysis process (B).

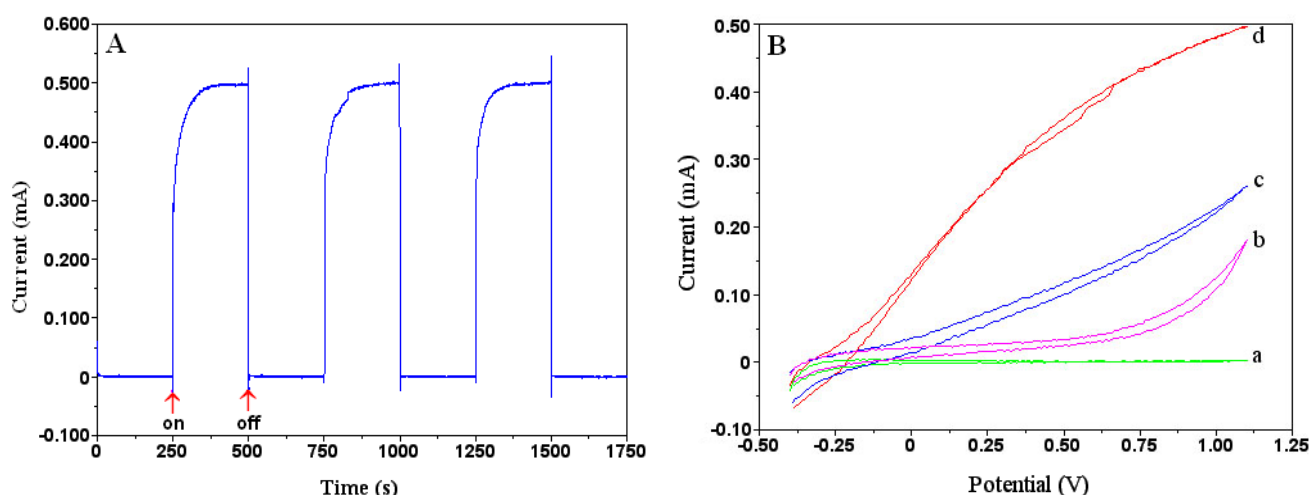


Fig. 5. A) Photocurrent-time response of TiO₂/Ti electrode at a biased potential of 0.5 V vs. reference electrode under on-off cycles of irradiation in 0.1 M phosphate buffer solution (pH 7.0). B) Cyclic voltammograms of 70 mg L⁻¹ 2,5-dichlorophenol at the unmodified Ti electrode surface (a) in dark and (b) under UV irradiation, (c) and (d) as a and b at the TiO₂/Ti electrode surface respectively at a scan rate 10 mV s⁻¹.

As can be observed in Fig. 5B, the TiO₂/Ti electrode cannot oxidize 2,5-dichlorophenol in the darkness (Fig. 5B-a). However, in similar conditions, the small current is generated due to 2,5-dichlorophenol oxidation at the Ti foil surface (Fig. 5B-b). These results can be attributed to electrical conductivity difference of TiO₂ and Ti materials as a semiconductor and metal respectively. On the other hand, under UV illumination, 2,5-dichlorophenol oxidation produces much higher photocurrent at the TiO₂/Ti electrode surface than that of unmodified Ti foil electrode (Fig. 5B-c,d). This demonstrates that 2,5-dichlorophenol as a hole scavenger by obtaining holes could be viably oxidized and as a result this would be positively effective in electron-hole separation. The photocurrent generation at the surface of unmodified Ti foil electrode might be due to the illumination energy which is greater from the work function of the Ti (about 4.3 eV), and consequently, light can create the photoelectrons.

3.3. Comparison of different methods for 2,5-dichlorophenol removal

Tests on photoelectrocatalytic (PEC), photocatalytic (PC), electrochemical (EC) and direct photolytic (DP) degradation of 2,5-dichlorophenol were performed to compare removal efficiencies in four methods (Fig. 6A). Also, the concentration variations of 2,5-dichlorophenol in different processes were measured with relationship between the final and initial peak currents as C/C_0 through differential pulse voltammograms using a carbon paste electrode with the scan rate of 10 mV s⁻¹. Apart from renewability by simple polishing, the application of carbon-paste electrode presents several other advantages including very low Ohmic resistance,

better reproducibility and stability, easy preparation and adequate robustness in aqueous solutions [44]. The percentage of 2,5-dichlorophenol degradation is calculated by the following formula:

$$\% \text{Degradation} = [(C_0 - C)/C_0] \times 100 \quad (9)$$

Fig. 6A shows, almost no 2,5-dichlorophenol degradation (about 5%) in the EC technique under 0.4 V voltage in 60 min. The DP, PC and PEC processes degraded 30%, 39% and 51% of 2,5-dichlorophenol within the similar times, respectively. Therefore, the obtained experimental results proved that the degradation efficiency and the rate of 2,5-dichlorophenol in the PEC method were more than those in the PC, DP and EC methods. In addition, the degraded 2,5-dichlorophenol amount in the PEC process is significantly greater than the total of degraded 2,5-dichlorophenol amounts relating to the EC and PC processes. That means that the synergistic effect was observed in the PEC method. On the other hand, according to the Langmuir-Hinshelwood kinetic model, the obtained experimental results can fit the first-ordered reaction model equation, $\ln(C_0/C) = f(t) = kt$ (k as rate constant) (Fig. 6B) [45]. The corresponding reaction rate constants, k , can be calculated for evaluation of the degradation efficiency of 2,5-dichlorophenol in the PEC, PC, DP and EC processes utilizing the slope of the curves. The experimental results demonstrated that the reaction rate of 2,5-dichlorophenol degradation in the electrochemically assisted photocatalysis process was faster than that of PC, DP and EC oxidation (Table 2).

There are various important factors in choosing a waste-treatment technology, inducing economics, economy of

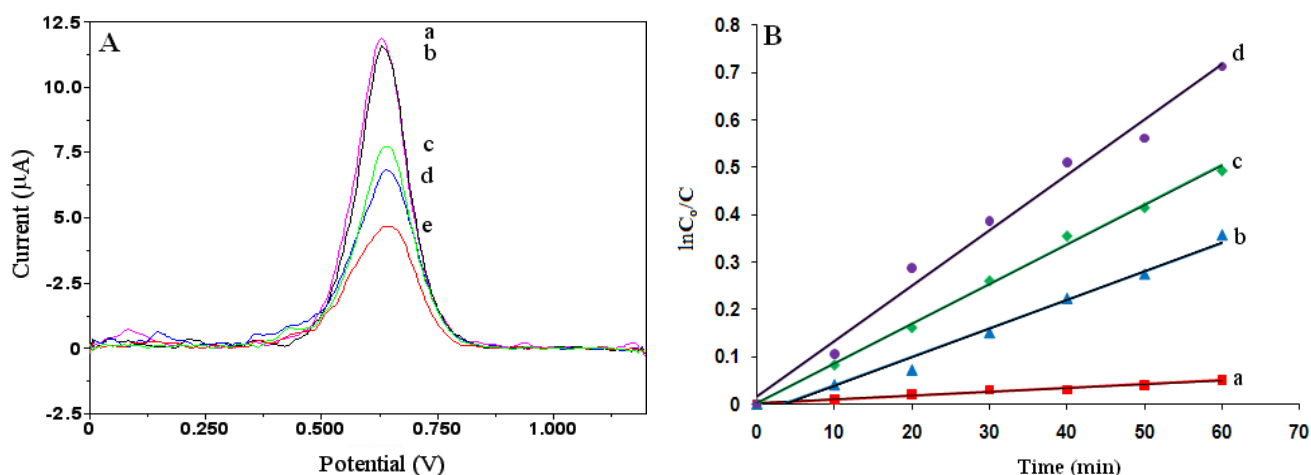


Fig. 6. A) Differential pulse voltammograms of 7.0 mg L⁻¹ 2,5-dichlorophenol at the TiO₂/Ti electrode surface before (a) and after (b) EC, (c) DP, (d) PC and (e) PEC degradation processes, in 0.1 M phosphate buffer solution (pH 7.0) and E = 0.4 V vs Ag/AgCl/KCl (3M). B) Comparison of (a) PEC, (b) PC, (c) DP and (d) EC degradation of 2,5-dichlorophenol based on plot of lnC₀/C as a function of time.

scale, regulations, effluent quality aims, operation (maintenance, control, safety) and robustness (flexibility to change/upsets). Despite the fact that these factors are necessary, financial aspects are frequently paramount. Since the photodegradation of aqueous organic pollutant is an electric-energy-intensive process, and electric energy can represent a noteworthy portion of the operating costs, simple figures of merit based on electric energy consumption can be very useful and informative. Recently, the international union of pure and applied chemistry (IUPAC) has proposed two figures-of-merit for advanced oxidation processes (AOPs) on the utilization of electrical energy. In the zero-order range, the appropriate figure-of-merit is the Electrical Energy per Mass (E_{Em}) defined as the kW h of electrical energy required for degradation of one kg of the pollutant [46]. In the case of low pollutant concentrations, which applies here, the appropriate figure-of-merit is the electrical energy per order (E_{Eo}), defined as the number of kW h of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in 1 m³ of contaminated water. The E_{Eo} (kW h m³ order⁻¹) can be determined from the following equations:

$$E_{Eo} = P \times t \times 60 \times 1000/V \times \ln(C_0/C) \quad (10)$$

$$\ln(C_0/C) = k \times t \quad (11)$$

where P is the rated power (kW) of the AOP system, t is the illumination time (min), V is the volume (L) of the water in the reactor, C₀ and C are the initial and final pollutant concentrations and k is the pseudo-first-order rate constant (min⁻¹) for the decay of the pollutant concentration [47,48]. From Eqs. (10) and (11), E_{Eo} can be written as follows:

$$E_{Eo} = (38.4 \times P)/(V \times k) \quad (12)$$

The calculated E_{Eo} values for PEC, PC, EC and DP degradation of 2,5-dichlorophenol are shown in Table 2. As it is clear, the amount of electrical energy consumed in PEC degradation process to reduce the concentration of a pollutant by 90% in 1 m³ of contaminated water is less than the other three processes. Therefore, the efficiency of photoelectrocatalysis process is higher than other degradation processes.

3.4. Effect of pH amount

Fig. 7A displays the effect of pH on the degradation rate of 2,5-dichlorophenol in initial 2,5-dichlorophenol concentration 7.0 mg L⁻¹ within 0.4 V voltage over 60 min illumination.

Table 2. Rate constants (k) and electrical energy per order (E_{Eo}) compared PEC degradation of 2,5-dichlorophenol with PC, DP and EC removal processes.

Process	k, min ⁻¹	Correlation coefficient, R ²	E _{Eo} , kW h m ³ order ⁻¹
PEC	0.0117	0.9868	657
PC	0.0085	0.9896	904
DP	0.0060	0.9845	1280
EC	0.0008	0.9758	9600

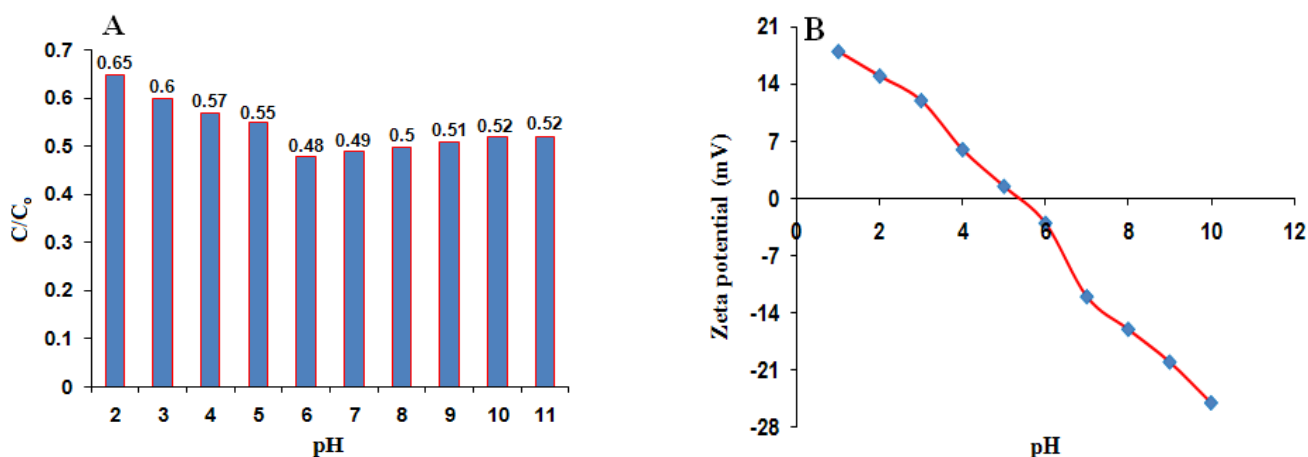
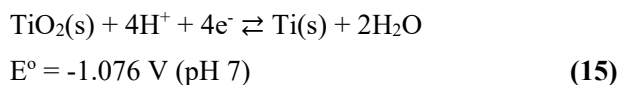
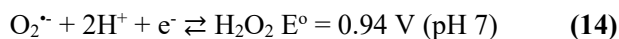
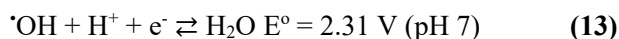


Fig. 7. A) Influence of pH on PEC removal of 7.0 mg L⁻¹ 2,5-dichlorophenol at the TiO₂/Ti electrode surface with bias potential 0.4 V vs Ag/AgCl/KCl (3M) over 60 min illumination. B) The Plot of zeta potential for TiO₂ nanoparticles suspended in phosphate buffers as a function of the pH of the suspension.

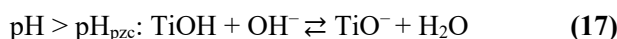
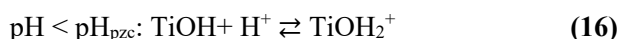
As shown in this figure, the amount of 2,5-dichlorophenol degraded increased to pH 6, however, it slightly decreased to 8 and is almost constant after this pH. pH is a common factor that influences the removal of pollutants in many processes. The change of pH modifies the position of the TiO₂ conduction band (-60 mV per pH unit) [49]. Therefore, when the pH amount is raised, the ability of holes as the powerful oxidizing elements decreases. As shown previously in Fig. 4A, the strong oxidation power of the hole enables a one-electron oxidation step with water to produce a hydroxyl radical (Eq. 3 in Table 2). Also, oxygen can act as an electron acceptor, and be reduced by the promoted electron in the conduction band to form a superoxide ion. Standard reduction potential (E°) of •OH and O₂^{-•} radicals and TiO₂ as oxidizing agents along with their reduction present reactions as follows [50,51]:



It is clear, TiO₂ is not an oxidizing agent in the absence of light. During illumination with hole formation, TiO₂ acts as a strong oxidizing agent lowering the activation energy for the decomposition of organic and inorganic compounds. As pH increases, the oxidizing power of •OH and O₂^{-•} radicals decreases (Eqs. 13 and 14)

On the other hand, since the surface charge of the TiO₂/Ti electrode is influenced by the pH of the solution and by dissolved species, the electrophoresis method has been used to determine the changing in the isoelectric point of TiO₂. The isoelectric point is the pH at which zeta potential of a molecule or surface is equal to zero [52].

Fig. 7B shows the results of measuring the zeta potential for suspended TiO₂ particles as a function of the pH of the suspension. The pH of the iso-electric point for TiO₂ was found to be almost 5.04. Hydroxyl groups on TiO₂ surface undergo the following reactions under various pH conditions [53]:



It is worth noting that, in the simplest case, if the specific sorption of ions and dissociation of counterions are neglected, then point of zero charge (pH_{pzc}) coincides with the isoelectric point (pH_{iep}) [52]. Since the point of zero charge (pH_{pzc}) of the TiO₂ is around 5.04, so the TiO₂ surface in pH < pH_{pzc} and pH > pH_{pzc} is positively and negatively charged respectively [54]. In aqueous solution, at pH higher than pH_{pzc}, the catalyst surface is negatively charged and thus the adsorption of cations is favored and as a consequence, the oxidation of cationic electron donors and acceptors are favored. At pH lower than pH_{pzc}, the adsorbent surface is positively charged and thus the adsorption of anions is favored [55]. Since 2,5-dichlorophenol is a weak organic acid in water (pK_a 7.51), therefore, depending on the pH value in the solution, 2,5-dichlorophenol can be presented as neutral molecules or anions. In this way, pH affects the adsorption ability of the target material on the TiO₂ photocatalyst [56]. At pH < 5, repulsion force between the protonated 2,5-dichlorophenol molecules with positively charged surface reduces the degradation extent. As pH increases, these interferences tend to decrease and the PEC degradation extent tend to increase almost till pH 6.0. On the other hand, the constant potential of 0.4 V was applied to the TiO₂/Ti electrode in all pHs, so the electrode gets constant positive charge. It is likely, this positive charge

increases the effect of positive charge which is dependent on pH at $\text{pH} < 5$, and as a result, the degradation of 2,5-dichlorophenol decreases further than that of the absence of voltage. However, in $5 < \text{pH} < 8$, voltage generating positive charge is in conflict with negative charge which is dependent on pH and the surface of the electrode gets uncharged. The mentioned charge balance can be related to the low negative charge depending on pH in $5 < \text{pH} < 8$ unlike pH generated high negative charge in $\text{pH} > 8$. Thus, 2,5-dichlorophenol degradation efficiency in pH 6 was highest. Due to 2,5-dichlorophenol neutrality, its absorption is probably higher on the electrode surface at pH 6 than that of $\text{pH} < 6$. Also, the opposite effects of pH on E° of $\cdot\text{OH}$ and surface charge changes of TiO_2 may result in the best degradation efficiency at pH 6. In $\text{pH} > 8$, it is expected, 2,5-dichlorophenol oxidation get easier due to losing its protons and also presence of large amounts of hydroxyl radicals [57]. However, a minor increase in removal rate was seen under alkaline conditions. In this case, as pH increases, pH generated negative charge is more than its voltage producing charge positive. In pH greater than 8, there may be a balance between the adsorption ability decrease of 2,5-dichlorophenol on the TiO_2 surface and the increase of hydroxyl radicals in alkaline medium. Therefore, the repulsive force between negatively charged surface of the catalysts and the anionic dominant form of 2,5-dichlorophenol repels 2,5-dichlorophenol from the catalysts surface, resulting in the decrease in the degradation extent.

3.5. Effect of initial 2,5-dichlorophenol concentration

The initial 2,5-dichlorophenol concentration effect on its removal was investigated at different initial concentrations of the 2,5-dichlorophenol. The experiments were performed in phosphate buffer solution (pH 6.0) containing 7.0 to 13.0 mg L^{-1}

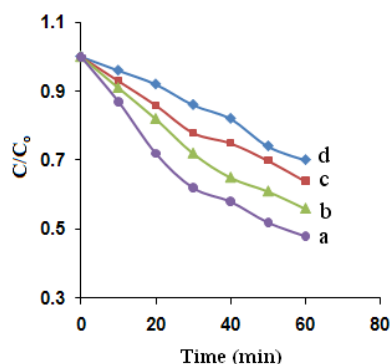


Fig. 8. Effect of the different initial 2,5-dichlorophenol concentration on its removal: (a) 7.0, (b) 9.0, (c) 11.0 and (d) 13.0 mg L^{-1} in phosphate buffer solution (pH 6.0) on a TiO_2/Ti electrode with bias potential 0.4 V vs $\text{Ag}/\text{AgCl}/\text{KCl}$ (3M).

2,5-dichlorophenol on a TiO_2/Ti electrode biased at $E = 0.4$ V vs. reference electrode. It can be observed in Fig. 8, when the initial 2,5-dichlorophenol concentration increased the value of the PEC 2,5-dichlorophenol removal increased but the reaction rate reduced sharply. Since the PEC oxidation occurred on the catalyst surface, not in the bulk of the solution [58], the reduction in degradation rate at higher initial 2,5-dichlorophenol concentrations can be clarified by the fact that at these concentrations, the light intensity reaching the TiO_2 film surface reduced due to the lower transparency of the solution.

3.6. Effect of bias potential

When a potential gradient over the titania film is applied, the photogenerated charges separation increases and forces the photogenerated holes and electrons to move in inverse directions. Therefore, the degradation rate increased significantly when the employed cell potential increased. According to Fig. 9, to investigate the effect of bias potential on 2,5-dichlorophenol degradation rate, experiments were carried out in the phosphate buffer solution (pH 6.0) in presence of 2,5-dichlorophenol 7.0 mg L^{-1} within 60 min using six cases of bias potential, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 V. As shown in the figure, the degradation rate increases as a function of applied potential up to $E = 1.2$ V. These outcomes demonstrate that higher voltage situations accelerate the production and separation of electron-hole pairs. The majority of the photogenerated electrons at the TiO_2/Ti surface were removed either by the electric field or by the reaction with dissolved oxygen. When the applied potential was increased beyond 1.2 V as an optimum voltage, a decrease in degradation occurred. The more oxidation of water molecules using the photogenerated holes can probably be mentioned as the reason of this phenomenon [59].

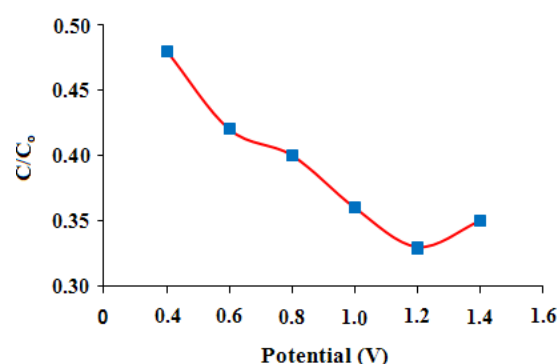


Fig. 9. PEC removal of 2,5-dichlorophenol as affected by the applied potentials on PEC degradation of 7.0 mg L^{-1} 2,5-dichlorophenol in phosphate buffer solution (pH 6.0) over experimental time 60 min.

4. Conclusions

The results confirmed that the PEC degradation of 2,5-dichlorophenol using the TiO₂ modified Ti foil (TiO₂/Ti) and UV light was found to be an efficient technique. Experimental results demonstrated that PEC degradation rate of 2,5-dichlorophenol was greater than DP, EC and PC removal. Also, the total of degraded 2,5-dichlorophenol amounts in the EC and PC processes was considerably lower than that of the PEC process. Besides, the obtained results indicated that the PEC degradation rate of 2,5-dichlorophenol was affected by the pH of solution, the initial 2,5-dichlorophenol concentration and the amount of applied potential.

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