Synthesis and characterization of new Ti-Bi₂O₃ anode and its use for reactive dye degradation

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Abstract

This paper reports the synthesis, characterization and application of a Ti-Bi$_2$O$_3$ anode for the electrochemical decolorization of the textile dye Reactive Red 2. The anode was synthesized by electrodeposition on a Ti substrate immersed in an acidic bismuth (III) solution at constant potential, followed by calcination in air at 600°C. Thermogravimetric Analysis (TGA), Energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) analysis revealed that the electrodeposited material was predominantly metallic bismuth, which was oxidized to pure α-Bi$_2$O$_3$ during the calcination in air. SEM micrographs revealed that the Bi$_2$O$_3$ coat at the anode surface was inhomogeneous and porous. Reactive Red 2 was completely electrochemically decolorized at the synthesized anode in the presence of H$_2$O$_2$. The applied current density, H$_2$O$_2$ and Na$_2$SO$_4$ concentration, medium pH and initial dye concentration affected the dye decolorization rate. The optimal process parameters were found to be as follows: an applied current density of 40 mA cm^{-2} using a mixture of 10 mmol dm^{-3} H$_2$O$_2$ and 10 mmol dm^{-3} Na$_2$SO$_4$ at pH 7. The dye decolorization rate was shown to decrease as its initial concentration increased. The decolorization reactions were found to follow pseudo-first order kinetics.

Keywords: coatings, electrochemical techniques, surfaces, oxidation

1. Introduction

Organic synthetic dyes are widely used as colorants in a wide variety of industries. The most commonly used dyes are reactive synthetic dyes. Wastewater originating from both dye production and industries that use them in final products presents a serious environmental problem.

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Synthetic dyes are characterized by poor biodegradability and are usually unaffected by conventional wastewater treatment systems, due to their high stability.

Electrochemical processes for the treatment of wastewater containing organic pollutants, including synthetic dyes, have many advantages. These include environmental compatibility, versatility, high energy efficiency and safety. Electrochemical oxidation of the dyes is usually accomplished by direct anodic oxidation (with direct electron transfer to the anode, which yields poor level of decontamination), or as a chemical reaction with electrogenerated species from water decomposition at the anode surface such as "active oxygen", i.e. hydroxyl radical •OH. This radical is a very strong oxidant and it is considered to be responsible for the degradation of pollutant molecules [1 - 3]. The electrogeneration of hydroxyl radical in water can often be slow and insufficient, but •OH is easily produced by the use of hydrogen peroxide in the electrochemical system; hydroxyl and hydroperoxyl radicals are electrogenerated at the electrodes in the presence of H_2O_2 and the probable mechanism of the electrochemical reaction can be as follows:

$$H_2O_2 + e^- \rightarrow •OH + OH^- \qquad\qquad \text{eq. (1)}$$

$$H_2O_2 \rightarrow HO_2• + H^+ + e^- \qquad\qquad \text{eq. (2)}$$

The oxidation of organic dyes by hydroperoxyl radicals can be ignored. However, hydroperoxyl radicals can further react with the excess peroxide, thus promoting radical chain reaction and producing highly reactive hydroxyl radicals via reaction (3):

$$HO_2• + H_2O_2 \rightarrow •OH + H_2O + O_2 \qquad\qquad \text{eq. (3)}$$

Hydroxyl radicals further react with the organics, which results in their degradation [4-6]. The anodic material is very important for the electrochemical oxidation processes. Various materials are used as anodes: Pt [7,8], boron-doped diamond [9], graphite [10] activated carbon fiber [11] and electrodes based on metal oxides, such as PbO_2, RuO_2, IrO_2, SnO_2, SbO_x etc. and their mixtures. All the above mentioned materials have a high surface area and excellent mechanical and chemical resistance even at high current densities [12-18].

Bismuth oxide (Bi_2O_3) can provide a large surface area, electrochemical stability and catalytic behavior which makes it an interesting material for the electrochemical oxidation of various organic pollutants. Bi_2O_3 micro-particles deposited onto glassy carbon electrode have been successfully used as the electro-catalyst in the electrochemical oxidation of ascorbic acid [19]. It has also been applied as a photocatalyst for the removal of other compounds, such as some organic dyes and pigments, 4-chlorophenol and gaseous NO and HCHO [20-25]. Furthermore, Bi_2O_3 can be easily prepared and its starting materials are generally low-cost.
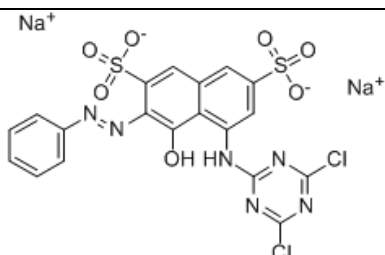
Electrodeposition is a very convenient method for material synthesis, due to its simplicity, rigid control of film thickness, uniformity, and deposition rate and is especially attractive due to low equipment cost [26]. Bi_2O_3 films and powders have been electrochemically synthesized by direct cathodic deposition from Bi (III) solutions [27-30], and by cathodic electrodeposition of bismuth metal, followed by its further anodic oxidation [31].

The aim of this work was to synthesize a Ti-Bi_2O_3 electrode and to use it for the electrochemical anodic degradation of the textile dye, Reactive Red 2 (RR2). The electrode was synthesized by an electrochemical procedure and its properties were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD) and thermogravimetric (TGA) analysis. The operational parameters for dye degradation were investigated in order to find the optimal conditions for dye degradation to occur.

2. Materials and methods

2.1. Materials

Bismuth(III)-nitrate pentahydrate, nitric acid, hydrogen peroxide and sodium sulphate

Color index name	Commercial name	IUPAC name	Chemical structure	Molecular weight (g/mol)
CI Reactive Red 2 (RR2)	Procion red MX-5B	Disodium 5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-4-hydroxy-3-(phenylazo)naphthalene-2,7-disulphonate		615.33

(Sigma Aldrich) were of reagent grade and used without further purification. RR2 was obtained

from Farbotex (Italy) and used without further purification. All solutions were prepared in

deionized water.

Table 1.Main characteristics of Reactive Red 2

2.2. Preparation and characterization of the anode

All the electrochemical experiments were carried out using an Amel 510 DC potentiostat

(Materials Mates, Italy), which was controlled by VoltaScope software package. Electrodeposition

was performed at $20 \pm 0.5°C$ in the three electrode cell with a Ti sheet (10×20 mm) as a substrate

(cathode), a Pt sheet (10×20 mm) as auxillary electrode (anode), and a saturated calomel electrode (Materials Mates, Italy) as a reference electrode. For convenience, the potentials are given as measured against the standard hydrogen electrode (SHE). The distance between the working and auxiliary electrode was 15 mm. Prior to electrodeposition, the Ti substrate was polished with different abrasive papers, etched in 1M oxalic acid at 100°C, washed with deionized water, dried and finally ultrasonically cleaned with acetone and deionized water. The bismuth (III) electrodeposition solution (0.1 mol dm^{-3}) was prepared by dissolving the required amount of bismuth nitrate in 1M HNO_3 water solution (acidic medium was used in order to avoid the addition of complexation agents needed to obtain the soluble bismuth(III) species in alkaline and neutral solutions). Electrodeposition was carried out at constant potential of 0.6 V. Electrodeposition time was 180 sec. After deposition, the Ti sheet covered with deposited film was washed with water, dried at 50°C for 12 h, calcined at 600°C for 90 minutes in air in a furnace and cooled in the open air.

The surface morphology of the electrode before and after the calcination was investigated by scanning electron microscopy (SEM) technique. The sample was attached to aluminium stubs using Leit-C carbon cement and then carbon coated in an Edwards 306 high vacuum carbon evaporator to ensure surface conductivity for EDX. Secondary electron images were taken using the lower detector of a Hitachi SU8030 cold-cathode field emission gun scanning electron microscope (FEG-SEM) at 2 kV accelerating voltage at a nominal magnification of x5000. Energy Dispersive X-ray microanalysis (EDX) was performed using a Thermo-Noran NSS system 7 with a 30 mm^2 window Ultra Dry detector. The working distance was fixed at 15 mm and an accelerating voltage of 10 kV was chosen to give adequate excitation of the K lines of the lighter elements, the L lines of Cu, Cd and Ni, and the M lines of Bi and Pb, while limiting the beam damage to the sample. Three replicate analyses were taken within a single field of view. TG studies were

performed using TGA Q5000 (TA Instruments, USA). For this purpose, another electrode was prepared in exactly the same way as the one used for the dye degradation experiments and a sample of Bi_2O_3 was carefully peeled. The sample mass used was 2.00 ± 0.50 mg. The sample was heated in air at a flow rate of 25 ml/min and heated from ambient temperature to 600°C in aluminium pan, at a heating rate of 10°C/min. The X-ray diffraction (XRD) pattern was determined using a Siemens D500 diffractometer (Germany) with a Ni filter using Cu Kα radiation ($\lambda = 0.154$ nm) and the step-scan mode with a step width of 0.02° and 1 s/step.

2.3. Dye electrolysis experiments

Dye electrolysis experiments were carried out under constant current conditions in the conventional one compartment two-electrode cell, with the synthesized Ti-Bi_2O_3 electrode as the anode and Pt sheet as the cathode, at constant temperature of 20 ± 0.5°C, using an Amel 510 DC potentiostat (Materials Mates, Italy) as a power source The working solutions were prepared by dissolving the correct amount of the dye, H_2O_2 and Na_2SO_4 in deionized water; the pH of the solutions was adjusted to the required values with $0.1/0.01$ mol dm^{-3} NaOH/HNO$_3$ solutions. The pH was measured using a pH meter (SensIon3, HACH, USA). During the decolorization experiments, the dye solutions were stirred using a magnetic stirrer. The dye concentrations were determined at $\lambda_{max} = 538$ nm using a UV-VIS spectrophotometer Shimadzu UV-1650 PC (Shimadzu, Japan). The fraction of decolorization was calculated using the equation (4):

$$\text{Percentage of decolorization (\%)} = \frac{C_0 - C}{C_0} \times 100$$

eq. (4)

Where C_0 is the initial dye concentration and C is the dye concentration at the time t.

3. Results and discussion

3.1. Characterization of the synthesized electrode

Electrodeposition was performed at a constant cathodic potential, which was chosen based on the results of a preliminary investigation. The aim was to obtain a mechanically and electrochemically stable Bi_2O_3 coat on the Ti surface in the shortest possible time. Lower electrodeposition times lead to a formation of mainly incomplete surface coats, many of them with some space between the small electrodeposited particles. Higher electrodeposition times lead to a formation of large, unstable aggregates which pealed off relatively easily and made electrode surface apparently rough. The color of the stable electrodeposited coat was gray, and after calcination in air, it changed to pale yellow.

The EDX spectral analysis of the material before calcination (Figure 1a) showed that the weight ratios of Bi and O on the examined surface were 99.10% and 0.10%, respectively, confirming that the material obtained by electrodeposition was predominantly metallic Bi. After calcination (Figure 1b), the weight ratios of Bi and O on the surface were 88.3% and 11.7%, respectively, which are close enough to their theoretical weight ratios in Bi_2O_3 of 89.70% and 10.30%, respectively), indicating that Bi_2O_3 coat was formed on the Ti surface by heating in air.
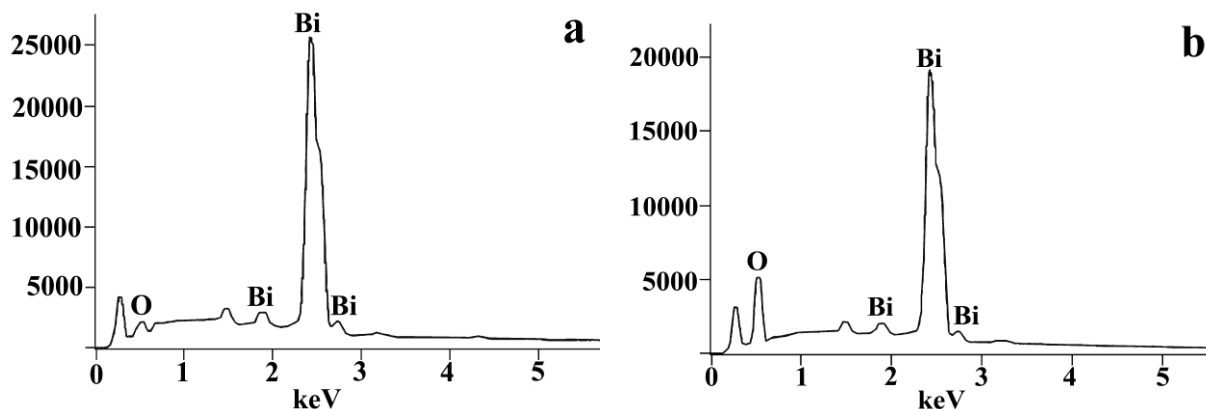
Figure 1. EDX spectra of the obtained electrode surface coat a) before heating in air and b) after heating in air

TG curves of the electrodeposited coat before (labelled Bi) and after the calcination (labelled Bi_2O_3), which were recorded in an air atmosphere, are presented in Figure 2. The weight of the non-calcined material (Bi) compared to Bi_2O_3 increased by 10.85% when heated from 25 to 600°C. This value approximately corresponds to the theoretical molecular weight difference (%) between Bi and Bi_2O_3 (11.48%), indicating that the starting material was metallic Bi, which was oxidized to Bi_2O_3 during the calcination in air. The increase in weight of the non-calcined material by 10.85% after heating in air also indicates the formation of Bismuth oxide with a theoretical formula of $Bi_2O_{2.71}$. Thus, both EDX and TG analysis confirmed the formation of the compound of approximate formula Bi_2O_3. The weight of the calcined material (Figure 2), which is assumed to be Bi_2O_3 decreased during the heating by 0.86%. This weight change is probably caused by the loss of oxygen, which might occur upon heating Bi_2O_3 at temperatures over 400°C. Both of the results are in accordance with literature data, which show that Bismuth (III)-oxide obtained at temperatures higher than 400°C is oxygen deficient [32].
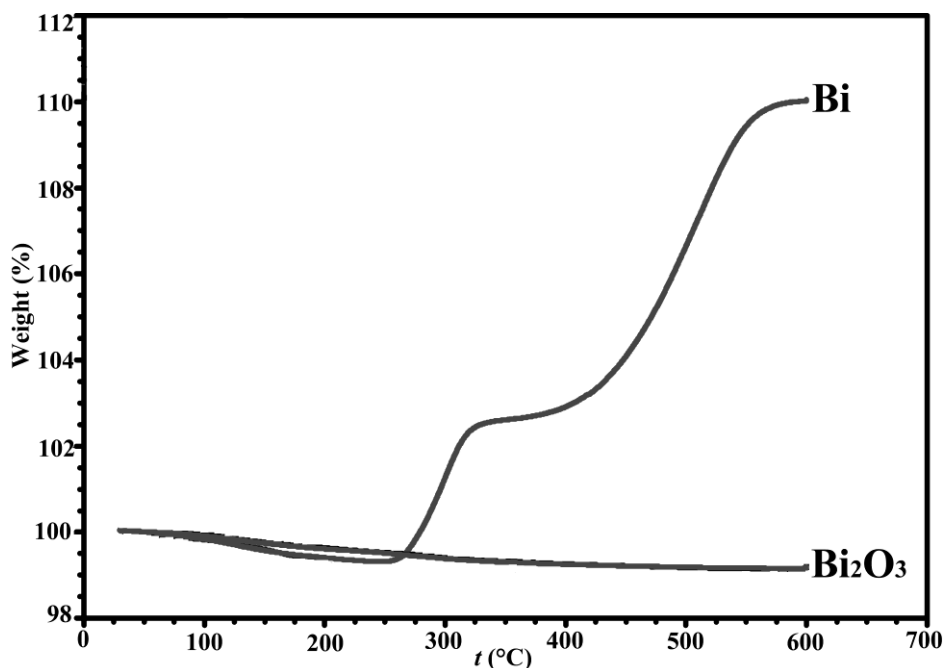
Figure 2. TG curves of the material obtained by electrodeposition from Bi (III) acidic solution before (Bi) and after the calcination in air at 600°C (Bi_2O_3)

Bi_2O_3 may exist in several polymorphous forms, such as monoclinic α-Bi_2O_3, tetragonal β-Bi_2O_3, cubic fluorite type δ-Bi_2O_3, and body-centred cubic γ- Bi_2O_3 [33]. In our case, the XRD pattern of the synthesised Bi_2O_3 (Figure 3) shows a series of diffraction peaks with characteristic 2θ values at: 27.4°, 33.3° and 46.3°, corresponding to (120), (200) and (041) reflection, respectively. These peaks are attributed to monoclinic α-Bi_2O_3 and no traces of any other crystalline form are detected, meaning that the synthesized electrode surface is covered by pure α-Bi_2O_3. This result is generally in accordance with those reported in the literature, according to which, at temperatures higher than 500°C, the formation of α-Bi_2O_3 prevails [21, 32].
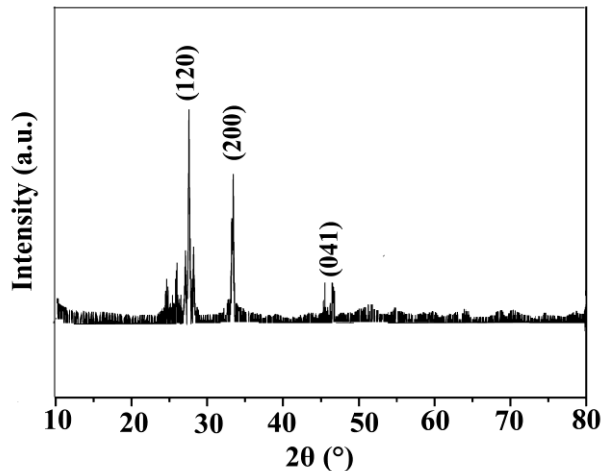
Figure 3. XRD pattern of the obtained Bi_2O_3

As expected, the formation of Bi_2O_3 on the electrode surface significantly changed its morphology (Figures 4a and 4b). A relatively compact bismuth layer was formed by electrodeposition (Figure 4a). However, its surface is apparently rough and inhomogeneous, which can be explained by the variation of the current density during electrodeposition, and by the fact that the coat was formed relatively fast. After the calcination, an apparently porous and less compact Bi_2O_3 coat was formed at the surface (Figure 4b). It is composed of small aggregates, with different shapes and sizes. There is a possibility of the formation of a thin layer of TiO_2 at some places at the electrode surface, because the electrolyte could reach Ti surface, due to the porosity of Bi_2O_3 coat. The Bi_2O_3 coat is very well held on the surface and the manufactured Ti-Bi_2O_3 electrode is thus mechanically stable and entirely safe for the common manipulation, and it is hard to peel of Bi_2O_3 coat by the use of scalpel and abrasive papers. It is also electrochemically stable under the applied dye degradation conditions.

Prior to the decoloration experiments, the stability of the electrode was tested by repeatedly exposing it to the relatively high current densities, at which the dye degradation experiments were

performed, in the presence of H_2O_2, for several hours, and neither a change in electrode mass was identified, nor was bismuth detected in solution. This indicates that it is electrochemically stable under the experimental conditions applied in this work.
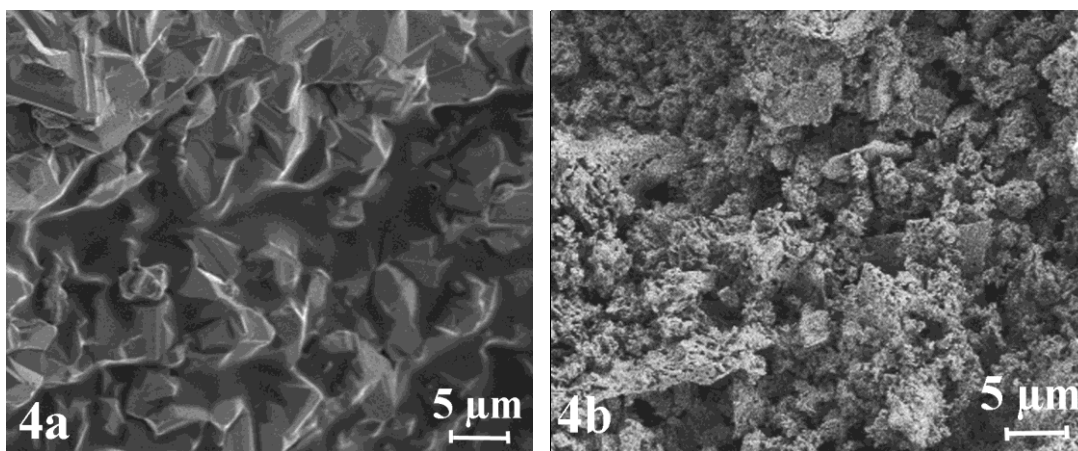

Figure 4. SEM images of the electrode surface coat a) before heating in air and b) after heating in air.

3.2. Dye decoloration

The textile dye RR2 is very stable in the presence of H_2O_2 and its initial concentration of 50 mg dm^{-3} did not appreciably change in the 10 mmol dm^{-3} aqueous H_2O_2 solution during the time period of 24 hours. Electrolysis of 50 mg dm^{-3} RR2 in 10 mmol dm^{-3} Na_2SO_4 water solution in the absence of H_2O_2 at the constant current density (j) of 40 mA cm^{-2} also gave relatively poor results: about 10% of the dye was removed after two hours. However, in the presence of 10 mmol dm^{-3} H_2O_2 solution, the dye was degraded in about 35 minutes under the same electrolysis reaction conditions. The presence of H_2O_2 in electrolytic cell significantly enhanced generation of hydroxyl radical

•OH ("active oxygen"), a strong oxidant, which attacks the dye molecule and degrades it. In the absence of H_2O_2 electrolysis proceeds at a much slower rate, probably because the concentration of "active oxygen" produced by water discharge at the anode is much lower than that obtained by H_2O_2 decomposition [6]. It is also possible that the dye is oxidized directly at the anode, but that reaction is very slow, due to the high stability of the synthetic dye molecule and it can be neglected [2]. The addition of H_2O_2 to the system permits efficient colour removal at lower current densities, at a lower background electrolyte concentration and in shorter reaction times. Taking this all into account, as well as the electrode stability, it is assumed that the synthesized Bi_2O_3 electrode is suitable anode for the RR2 dye electrochemical degradation in the presence of H_2O_2. The effect of H_2O_2 concentration, applied current density, background electrolyte concentration and pH on the RR2 decolorization at the synthesized Ti-Bi_2O_3 anode was investigated, as well as the reaction kinetics.

3.2.1. Effect of H_2O_2 concentration

The effect of H_2O_2 concentration on the decolorization of RR2 at the Ti-Bi_2O_3 anode was investigated by varying the initial H_2O_2 concentration in the system, while all the other parameters were kept constant. As can be seen (Figure 5), H_2O_2 concentration affects the decolorization rate.
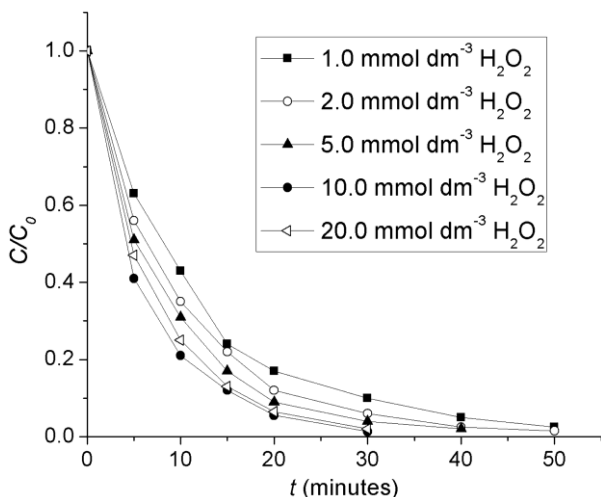
Figure 5. Effect of H_2O_2 concentration on the decolorization of RR2 at Ti-Bi$_2$O$_3$ anode (C$_0$ (RR2) = 50 mg dm^{-3}, j =40 mA cm^{-2}, C_0 (Na$_2$SO$_4$) = 10 mmol dm^{-3}, pH 7.0 ± 0.1, T = 20 ± 0.5°C)

Complete decolorization was achieved at every H_2O_2 concentration in the investigated range (from 1.0 to 20.0 mmol dm^{-3}), but its value affected the time needed for complete decolorization. As the H_2O_2 concentration increases, the concentration of hydroxyl radicals •OH increases as well, since they are generated via H_2O_2 electrochemical decomposition. Up to a concentration of 10 mmol dm^{-3} H_2O_2 the rate of decoloration clearly increases, i.e., time of decolorization decreases; for H_2O_2 concentration of 1 mmol dm^{-3} it takes almost 70 minutes for complete decolorization and for H_2O_2 concentration of 10 mmol dm^{-3} complete decolorization is achieved in less than 40 minutes. However, in the presence of 20 mmol dm^{-3} H_2O_2, the decolorization rate was lower compared to the data obtained for solutions containing 10 mmol dm^{-3} H_2O_2 and it was more than 45 minutes. The reason is probably the loss of some •OH radicals due to the scavenging effect, which occurs when the H_2O_2 concentration is relatively high. Under these conditions •OH radicals tend to react with the excess H_2O_2 to produce hydroperoxyl radicals, HO$_2$•, as shown in equation (5):

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$$H_2O_2+ \bullet OH \rightarrow H_2O + HO_2\bullet \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{eq. (5)}$$
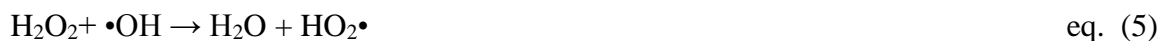
Hydroperoxyl radicals, $HO_2\bullet$ are les reactive than $\bullet OH$ radicals, and as a result the decolorization rate decreases, i.e., the time needed for complete decolorization increases [34]. The fastest decolorization time is observed with 10 mmol dm^{-3} H_2O_2, which is assumed to be the optimal concentration for the electrochemical degradation of RR2 at Ti-Bi_2O_3 anode.

3.2.2. Effect of current density

Current density is a very important parameter in electrochemical processes. Measurements of the decolorization rate of RR2 at the Ti-Bi_2O_3 anode was made under galvanostatic conditions in which the effect of current density was investigated by varying the applied constant current density to the system, while all the other parameters were kept constant.

As shown in Figure 6, the electrolysis current density has a significant effect on the decolorization rate. Complete decolorization can be achieved at any current density in the investigated range, but at different rates. At a current density of 10 mA cm^{-2}, the decolorization rate is considerably low and it takes more than 60 minutes to completely decolorize the dye solution. With increasing current density, the dye decolorization rate also increases, that is the decolorization time decreases. The effect is more significant at lower current densities and the greatest difference in rate of decolorization is observed between 10 and 20 mA cm^{-2}. When the current density reaches 40 mA cm^{-2}, the dye solution is decolorized in less than 40 minutes and any further increase in current density does not bring a significant increase in the decolorization rate, so, it is assumed that the optimal current density for the process is 40 mA cm^{-2}.
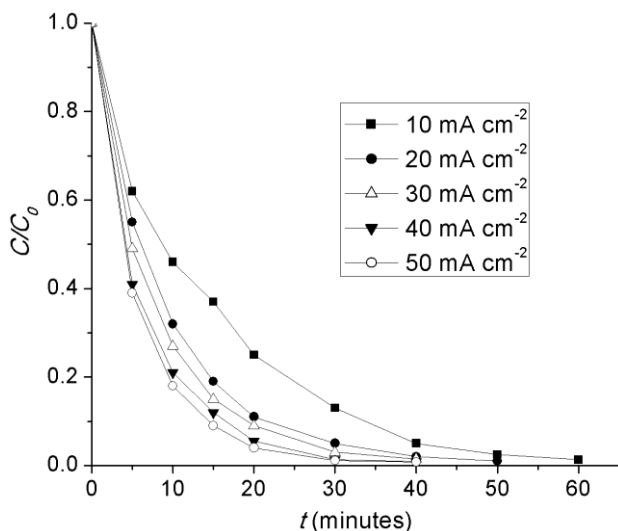
Figure 6. Effect of current density on the decolorization of RR2 at Ti-Bi$_2$O$_3$ anode (C$_0$ (RR2) = 50 mg dm$^-$3, C_0 (H$_2$O$_2$) = 10 mmol dm^{-3}, C_0 (Na$_2$SO$_4$) = 10 mmol dm^{-3}, pH 7.0 ± 0.1, T = 20 ± 0.5°C)

3.2.3. Effect of background electrolyte

Background electrolyte was added to the dye solutions in order to increase electrical conductivity. Na$_2$SO$_4$ is the most commonly used background electrolyte, due to its high electrochemical stability and neutrality in a broad potential region, good electrical conductivity, low cost and environmental compatibility. The effect of Na$_2$SO$_4$ concentration on the decolorization rate of RR2 at the Ti-Bi$_2$O$_3$ anode was investigated by varying the initial Na$_2$SO$_4$ concentration in the system, while all the other parameters were kept constant (Figure 7). As the Na$_2$SO$_4$ concentration was increased from 1 to 10 mmol dm^{-3}, the dye solution decolorization rate also increased, but the increase in its concentration from 10 to 20 mmol dm^{-3}, caused a decrease in the rate of decolorization compared to that in the presence of 10 mmol dm^{-3} Na$_2$SO$_4$. This decrease probably occurred because SO$_4{}^{2-}$ anions are also able to react with the •OH radicals, forming inorganic radicals, such as SO4$^-$ radical, according to the equation:

$$SO_4^{2-} + \cdot OH \rightarrow SO4^{\cdot -} + OH^- \qquad\qquad \text{eq. (6)}$$

 Inorganic radicals are much less reactive than •OH radicals and therefore, they practically do not participate in the dye decolorization process. Moreover the competition between the dye and the SO_4^{2-} anions with the respect to •OH radicals [34, 35] will have a significant impact upon the rate of decolorization. Thus, the optimal Na_2SO_4 concentration in the investigated system is assumed to be 10 mmol dm^{-3}. This concentration is still relatively low, and, by adding hydrogen peroxide to the system, the addition of high concentration of salt was avoided. It can be noted from Figures 5, 6 and 7 that the Na_2SO_4 concentration has smaller effect on the decolorization rate than H_2O_2 concentration and the applied current density.
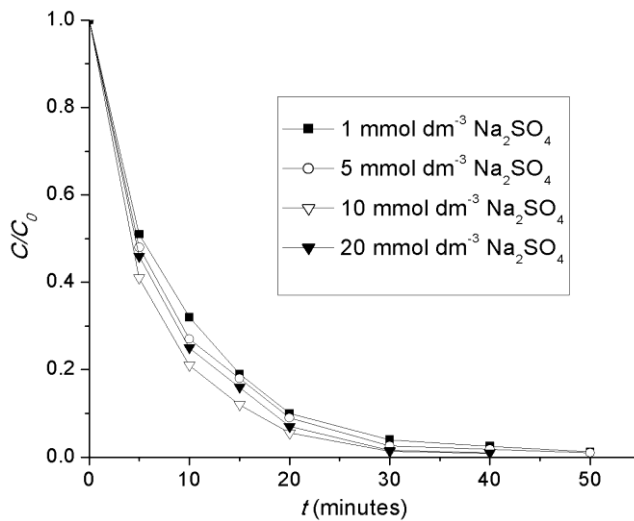

Figure 7. Effect of Na_2SO_4 concentration on the decolorization of RR2 at Ti-Bi_2O_3 anode (C_0 (RR2) = 50 mg dm^{-3}, j = 40 mA cm^{-2}, C_0 (H_2O_2) = 10 mmol dm^{-3}, pH 7.0 ± 0.1, T = 20 ± 0.5°C)

3.2.4. Effect of pH

The effect of pH on the decolorization of RR2 at the Ti-Bi$_2$O$_3$ anode was investigated by varying the initial pH in the system, while all the other parameters were kept constant. Decoloration experiments were performed in acidic, neutral and alkaline media, in the pH range, which includes the majority of real textile effluent pH values [36]. The results are shown in Figure 8. The lowest decolorization rate was observed at the pH 4, and it slightly increased when the pH was increased to 7. This was probably due to the fact that acidification of the solution, which was accomplished by the addition of HNO$_3$ resulted in a competition between the added NO$_3^-$ anions and dye molecules with respect to •OH radicals [34]. The increase of pH from 7 to 10 resulted in an insignificant increase in the decolorization rate and, in order to avoid the addition of excess alkali, pH 7 was assumed to be the optimal pH for the electrochemical decolorization of RR2 at the Ti-Bi$_2$O$_3$ anode.
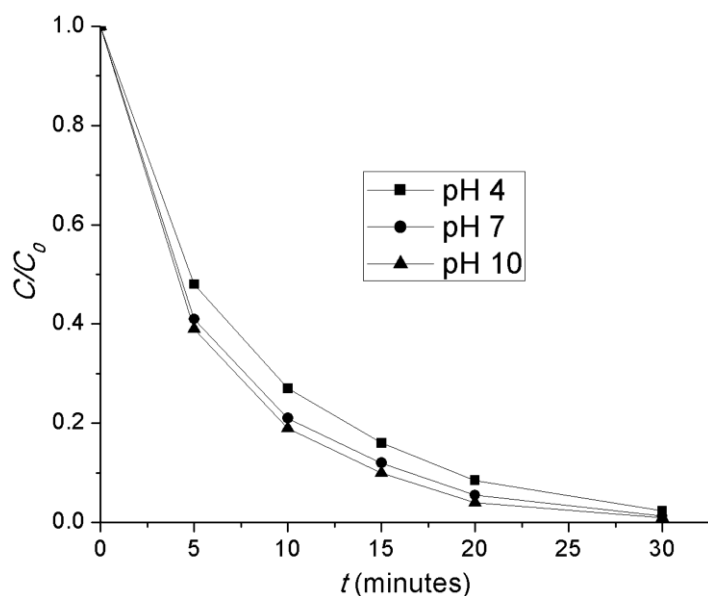

Figure 8. Effect of pH on the decolorization of RR2 at Ti-Bi$_2$O$_3$ anode (C$_0$ (RR2) = 50 mg dm^{-3}, j =40 mA cm^{-2}, C$_0$ (H$_2$O$_2$) = 10 mmol dm^{-3}, C$_0$ (Na$_2$SO$_4$) = 10 mmol dm^{-3}, $T = 20 \pm 0.5°C$)

3.2.5. Effect of initial dye concentration and the reaction kinetics

The effect of initial dye concentration on the electrochemical decolorization of RR2 at the Ti-Bi$_2$O$_3$ anode was investigated by varying the initial dye concentration in the system, while all the other parameters were kept constant at the optimal values, determined in the previous experiments. A pseudo-first-order kinetics model was used to describe the reaction kinetics [37]. It is represented in logarithmic form as:

$$\ln(C/C_0) = -kt \qquad \qquad \text{eq. (7)}$$

where C_0 is initial dye concentration, C is a dye concentration after reaction time t, and k is the reaction rate constant (min^{-1}). The plot of $\ln(C/C_0)$ against time scale for the electrochemical decolorization of RR2 at the Ti-Bi$_2$O$_3$ anode for a series of solutions containing an initial dye concentration ranging from 20 to 200 mg dm^{-3} is presented in Figure 9. As can be seen, for all these solutions, ln (C/C_0) shows a good functional linear decrease with increasing reaction time, indicating the validity of treating the process as a pseudo-first order kinetic reaction. The corresponding correlation coefficient squared (R^2) values for the initial dye concentrations of: 20, 30, 50, 100 and 200 mg dm^{-3} are: 0.995, 0.998, 0.998, 0.985 and 0.987, respectively. These values are high enough to assume that the electrochemical decolorization of RR2 at the Ti-Bi$_2$O$_3$ anode approximately follow the pseudo-first order kinetics model. This finding is in accordance with those reported in literature for the advanced oxidation processes of organic molecules, in which those molecules are oxidized by •OH radicals [34, 38, 39].

The initial dye concentration has a significant impact on dye decolorization rate. Total decolorization times for: 20, 30, 50, 100 and 200 mg dm^{-3} of the dye were about 25, 30, 35, 55, and 70 minutes, respectively and the corresponding reaction rate constants are: 0.191, 0.165, 0.146, 0.083 and 0.066, respectively. As can be observed, RR2 decolorization rate decreases as the initial

dye concentration increases. The effect of C_0 on the decolorization rate is lower for the lower initial dye concentrations (up to 50 mg dm^{-3}), i.e., the differences between the corresponding rate constants are lower. At higher dye concentrations, the reaction rate significantly decreases as the initial concentration increases. The highest decrease in k value is observed between 50 and 100 mg dm^{-3} dye concentrations. A significant decrease in the decolorization rate for the higher initial dye concentrations probably occurred because the ratio between the dye and •OH radical concentration increases, decreasing the amount of •OH available for the reaction with the dye molecules, thus prolonging the decolorization reaction time. It can also be observed that the R^2 values are little lower for the higher initial dye concentrations.
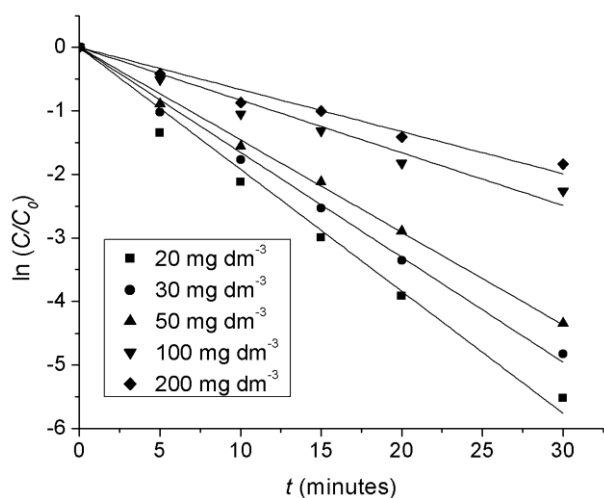

Figure 9. Effect of initial dye concentration on the decolorization rate of RR2 (C_0 (H$_2$O$_2$) = 10 mmol dm^{-3}, C_0 (Na$_2$SO$_4$) = 10 mmol dm^{-3}, current density 40 mA cm^{-2}, pH 7.0 ± 0.1, T = 20 ± 0.5°C)

4. Conclusion

In this work, the synthesis, characterization and application of a Ti-Bi$_2$O$_3$ anode for electrochemical decolorization of textile dye RR2 were performed. The anode was synthesized by electrodeposition on a Ti substrate from Bi (III) acidic solution at constant potential, followed by calcination at 600°C. The material obtained by electrodeposition was predominantly metallic bismuth, which was oxidized to pure α-Bi$_2$O$_3$ during the calcination in air. The Bi$_2$O$_3$ coat at the anode surface was inhomogeneous and porous. RR2 was completely electrochemically decolorized at the synthesized anode in the presence of H$_2$O$_2$. The applied current density, H$_2$O$_2$ and Na$_2$SO$_4$ concentration, medium pH and initial dye concentration affected the dye decolorization rate. The optimal parameters for the process are as follows: the applied current density 40 of mA cm^{-2}, 10 mmol dm^{-3} H$_2$O$_2$, 10 mmol dm^{-3} Na$_2$SO$_4$ and pH 7. Dye decoloration follows pseudo-first order kinetics, and the decolorization rate constants decrease as the initial dye concentration increases. The synthesized Ti-Bi$_2$O$_3$ anode has demonstrated good decolorization ability for the reactive dye in the presence of H$_2$O$_2$. Its preparation is fast and easy, using low-cost simple equipment and starting materials, which all makes it a promising material for further investigation and application for the removal of harmful organic compounds from water.

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