

Development of the novel poly(3,4-ethylenedioxythiophene)/TiO₂ photocatalysts with enhanced performance under solar light for azo dye degradation in wastewater

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1. Introduction – Organic synthetic dyes, specifically azo dyes, represent major environmental pollution coming mainly from textile and dye industry. They are non-biodegradable and recalcitrant pollution due to its large and complex molecular structure, which has posed a serious challenge for decolourization and complete mineralization, which are crucial to the human health and aquatic life. During the manufacturing and the processing of synthetic organic dyes approximately 12% of dyes are lost annually [1]. Advanced oxidation processes (AOPs) represent water treatment methods able to decolourize and to fully degrade organic compounds into non-toxic and non-hazardous components. Photocatalysis is established as an effective and sustainable AOP for water treatment offering a perspective for the degradation of organic water pollutants, converting them to biodegradable compounds or completely mineralizing them into carbon dioxide and water. Titanium dioxide, TiO₂, is widely used as photocatalyst but its relatively high band gap of 3,2 eV restricts its photocatalytic activity under visible light irradiation thus hindering its practical application in the water treatment processes. Attempts to excite TiO₂ under visible light (wavelength > 400 nm) were made by doping with noble metals [2] non-metal doping [3], dye sensitization [4] and enlarging surface area by particle size control [5]. Completely satisfactory solution for this problem is not found yet so finding it still remains intriguing challenge. Conducting polymers with extended π -conjugated electrons such as polythiophene and its derivatives show good light and thermal stability and high absorption coefficient in the visible light region [6] and such can act as stable photosensitizers of TiO₂ under solar light irradiation. The objective of the work was to synthesize poly(3,4-ethylenedioxythiophene) (PEDOT)/TiO₂ composite photocatalysts and to investigate its photocatalytic activities under simulated solar light irradiation. Since PEDOT/TiO₂ photocatalyst cannot be easily retrieved after the reaction due to its nanometre particle size, fly ash supported PEDOT/TiO₂ photocatalyst, was also synthesized to facilitate easier phase separation after photocatalysis.

2. Experimental. Synthesis - PEDOT/TiO₂ photocatalysts were prepared by chemical oxidative polymerization of EDOT monomer in acid environment. 7.5 mmol of EDOT and 25 mmol (2 g) of nano-TiO₂ was dispersed in 450 mL of 1.0 M HCl and stirred vigorously for 30 min. After that 50 mL of APS (3.75 mmol, 1.0 M HCl) or FeCl₃ (3.75 mmol, 1.0 M HCl) was added into mixture and polymerization reaction was carried out at room temperature for 24 h in inert nitrogen atmosphere. After polymerization precipitate was washed with water and ethanol and dried at 60 °C for 24 h. Samples prepared with APS and FeCl₃ were denoted as PEDOT/Ti-1 and PEDOT/Ti-2, respectively. For fly ash (FA) supported photocatalysts first step was immobilization of TiO₂ on FA surface by sol-gel synthesis from TiO₂ precursor tetra-n-butyl titanate (TBOT). 17 ml of TBOT was dissolved in 30 ml of ethanol and stirred 30 min at room temperature at 300 min⁻¹. Solution consisting of 28 ml of ethanol, 7 ml of deionised water and 20 ml of 3 M acetic acid was added to TBOT solution and stirred for 1 hour and left standing for 20 hour at room temperature. Afterwards it was added to 4 g of FA, dried for 12 hours at 80 °C and calcified at 400 °C for 3 hours to obtain FA-TiO₂. Chemical oxidative polymerization of EDOT monomer was carried out as described before, only 2 g of FA-TiO₂ was used instead of TiO₂. Samples prepared with APS and FeCl₃ were denoted as PEDOT/FA-Ti-1 and PEDOT/FA-Ti-2, respectively.

Characterization. Photocatalysts were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR), Perkin Elmer Spectrum One FTIR spectrometer, in the range from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1} . Thermogravimetric analysis (TGA) of studied samples was carried out using a TA Instruments Q500 analyser. The results are obtained for the temperature range from 25 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ at heating rate of 10 $^{\circ}\text{C}/\text{min}$ under the air atmosphere with a constant flow rate of 60 ml/min during analysis. Scanning electron microscopy (SEM) was utilized to determine the morphology of photocatalyst using Tescan VEGA 3 SEM, 20 kV. Samples were sputtered with Au/Pd before examining. XRD analyses were conducted at ambient temperature using a Shimadzu XRD-600 X-ray diffractometer with $\text{CuK}\alpha$ radiation. XRD spectra were recorded in the 5 $^{\circ}$ –70 $^{\circ}$ 2θ range with a scan speed 2 $^{\circ}/\text{min}$, sampling pitch of 0.02 $^{\circ}$ and a step time of 0.6 s.

Photocatalytic activity test. Wastewater containing organic azo dye C.I. Reactive Red 45 (RR45) was used to determine the degradation efficiency in terms of decolourization and total organic carbon (TOC) removal. The photocatalysts were tested in a ($V=0.1$ L and $T=25.0$ $^{\circ}\text{C}$) batch reactor which was placed under the irradiation source Oriel Arc source, Newport, USA, with Xe lamp of 450 W (operating at 425 W). The used apparatus was equipped with an Oriel AM1.5 G air mass filter, correcting the output of arc lamp to approximate the solar spectrum when the sun is at a zenith angle of 48.2 $^{\circ}$. The light intensity was measured to be 125 mWcm^{-2} using pyranometer CMP21, Kipp&Zonen, Netherland. All experiments were performed using initial RR45 concentration 30 mg/L, while photocatalyst concentration was 1 g/L. All model suspensions were prepared by using ultra-pure water with conductivity less than 1 mS/cm . Duration of each experiment was 90 min and the samples were taken periodically from and filtered using Chromafil XTRA RC (25 mm, 0.45 μm , Macherey Nagel, Germany). Before the start of the photoreactions adsorption equilibrium was reached within 30 minutes in a dark. Decolourization of RR45 was followed with a Perkin-Elmer Lambda EZ201 spectrophotometer at $\lambda_{\text{max}} = 542$ nm. Mineralization of RR45 was determined by measuring of total organic carbon content (TOC) which was performed on Total Organic Carbon analyser; Shimadzu TOC-VCPN.

3. Results and Discussion – The chemical structures of the obtained samples were elucidated by FTIR spectroscopy, which provided information about chemical composition of PEDOT/ TiO_2 and PEDOT/FA- TiO_2 samples and results are shown in Image. 1. As can be seen characteristic peaks for PEDOT are visible at all samples. The peaks at 1514 cm^{-1} and 1325 cm^{-1} are from C=C and C-C stretching of the quinoidal structure of thiophene ring and the stretching of thiophene ring, respectively, peaks at 1200 cm^{-1} , 1141 cm^{-1} and 1085 cm^{-1} originate from asymmetric and symmetric stretching of ethylene dioxy group, while those at 978 cm^{-1} and 837 cm^{-1} could be contributed to C-S stretching in the thiophene ring. [7]. Characteristic Ti-O-Ti absorption peak at around 550 cm^{-1} is outside of instruments' measuring range but fall of transmittance below 900 cm^{-1} can be attributed to that absorption. The same behaviour is visible for all synthesized samples so, it can be concluded that the FTIR spectra indicate characteristic bands for both PEDOT and TiO_2 components in composite. Samples containing fly ash have additional small peak at 695 cm^{-1} , which can be attributed to the symmetric stretching vibration of Si-O-Al linkages that have its origin in fly ash.

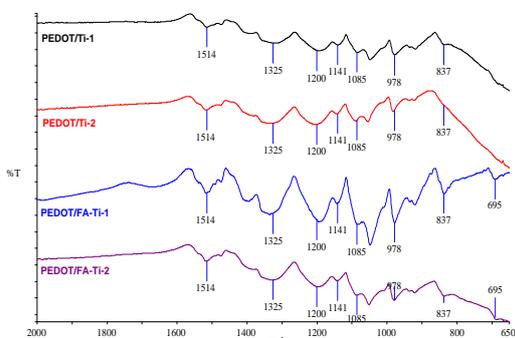


Image 1. FTIR spectra of synthesized PEDOT/ TiO_2 and PEDOT/FA- TiO_2 photocatalysts

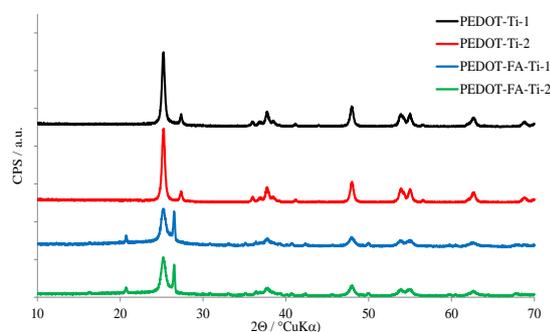


Image 2. XRD diffractograms of synthesized PEDOT/ TiO_2 and PEDOT/FA- TiO_2 photocatalysts

Results of XRD analysis are presented in Image 2. For PEDOT-TiO₂ samples characteristic diffraction lines of anatase and rutile phase of TiO₂ are present. Presence of amorphous polymeric material is not visible since TiO₂ lines dominate and broad peak of PEDOT known from literature [8] around 25° is covered by peak of anatase phase. Diffractograms of PEDOT/FA-TiO₂ samples are rather similar but some differences are visible. Anatase peak is again visible at 25.2° but new diffraction line appears at 26.5° which is attributed to quartz fraction found in fly ash. It can be seen that there is absence of rutile line at 27.5° suggesting that synthesised TiO₂ comprises purely of anatase phase. Broad hump centred at around 24° is characteristic for presence of amorphous material, most likely silica type, which is common in fly ash system [9].

SEM micrographs of all studied samples are shown in Image 3. Considerable differences are visible between samples with and without fly ash. Images 3a) and 3b) shows TiO₂ nanoparticles covered with polymer. At images 3c) and 3d) fly ash globular particles can easily be seen; some of them not totally covered by TiO₂ and polymer molecules. There is also a difference between samples depending on used oxidant. When APS oxidant is used, images 3a) and 3c), it seems that polymer amount on surface is higher.

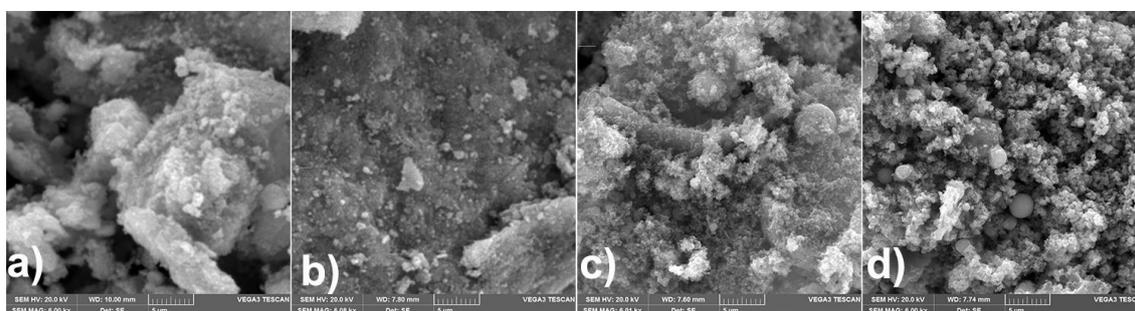


Image 3. SEM micrographs of a) PEDOT-Ti-1, b) PEDOT-Ti-2, c) PEDOT/FA-Ti-1, d) PEDOT/FA-Ti-2

Higher concentration of PEDOT polymer in the composite prepared with APS was confirmed by TG analysis and results are shown in Image 4. Thermogravimetric curves have two weight loss steps. First, small, step is visible below 100 °C and it can be attributed to the evaporation of water from samples. Main weight loss step is between 150 °C and 500 °C which corresponds to the polymer degradation. Since the fly ash and TiO₂ are thermally stable, all the weight loss comes from PEDOT degradation as organic component. It can be seen that samples prepared with APS oxidant (PEDOT/Ti-1 and PEDOT/FA-Ti-1) show higher weight loss (about 34 mass %) meaning that higher conversion of polymer is achieved as remaining weight is around 66-67 %. The samples prepared with FeCl₃ oxidant have weight loss of 12-13 mass %.

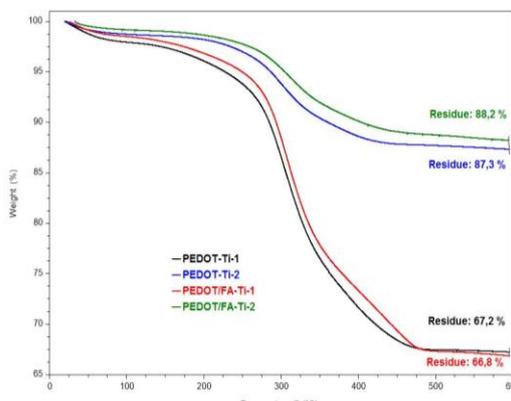


Image 4. TG curves of synthesised samples

Evaluation of photocatalytic effectiveness of studied samples is shown in Images 5 and 6 where decolourisation and total organic carbon results are presented in comparison to commercial TiO₂. TiO₂ shows slow level of adsorption of dye molecules in the dark, only 6 %, while during 90 min of photocatalysis concentration is steadily dropping to 7% of starting value. Synthesised samples show different behaviour with high level of adsorption where after 30 min almost 90% of dye molecules is adsorbed on the surface of photocatalysts. For sample PEDOT/FA-Ti-2 it is visible that concentration after 30 min at first rises, meaning that true adsorption equilibrium was not reached. Although concentration of RR45 starts to fall afterwards that sample exhibited low rate of photocatalysis in comparison to other catalysts since the final concentration is 14% of starting value. PEDOT/Ti-1 and PEDOT/Ti-2 catalysts show very similar behaviour, very high adsorption of dye onto its surface (91%)

and low rate of photocatalysis. At the end around 95% of RR45 dye was removed under the solar irradiation, which is on the same level as commercial TiO₂ photocatalyst.

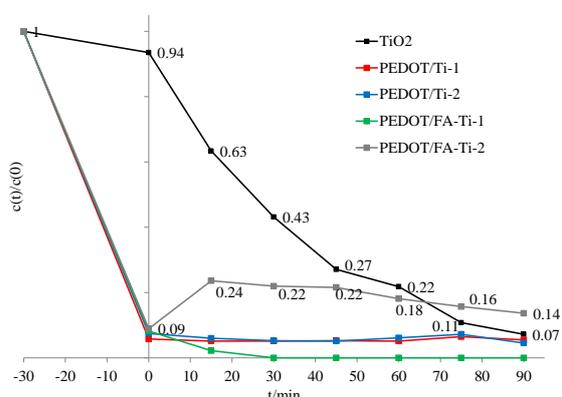


Image 5. Decolouration rate of Reactive Red 45 after adsorption and photocatalysis

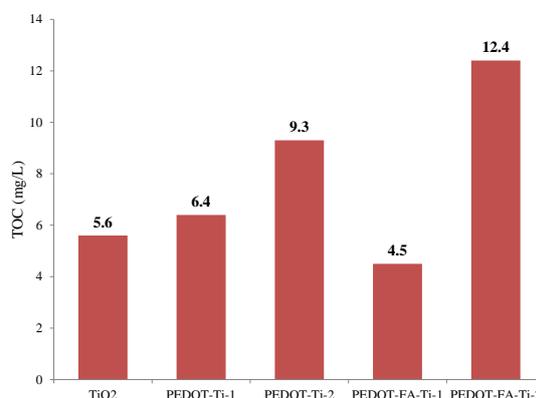


Image 6. TOC after 90 min of simulated solar irradiation; TOC (RR45, 30 mg/L) = 9.1 mg/L

Best results shows sample PEDOT/FA-Ti-1, which is able to completely remove dye after only 30 min of photocatalysis. High rate of adsorption indicate that interactions between catalyst and the RR45 are established in acid media (pH=5) as TiO₂ is positively and RR45 is negatively charged [10]. Further, strong adsorption process does not eliminate the photocatalysis as process itself is performed on the catalyst surface.

Since decolourisation itself is not sufficient to quantify photocatalysis efficiency, total organic carbon (TOC) was also measured. TOC after photocatalysis for commercial TiO₂ was 5.6 mg/L which is 38% decrease from TOC of RR45 azo dye (9.1 mg/L) at concentration of 30 mg/L. All synthesized photocatalysts have higher TOC with the exception of sample PEDOT/FA-Ti-1 that has TOC 4.5 mg/L, which is 50% decrease from starting value. The same sample showed the highest decolourization rate. It should be noted that both samples synthesized with FeCl₃ oxidant (PEDOT/Ti-2 and PEDOT/FA-Ti-2) have TOC higher than azo dye itself. Such values could be only explained by instability of PEDOT structure under solar irradiation. It is possible that PEDOT degrades and degradation products increase TOC values.

4. Conclusions – Unsupported and fly ash supported PEDOT/TiO₂ photocatalysts were successfully synthesized by chemical oxidative polymerization, which was confirmed by FTIR, XRD and SEM analysis. Polymerization yield of PEDOT was much higher with APS oxidant as proven by TG analysis. Synthesized photocatalysts showed high decolourization rate of RR45 azo dye, mainly through adsorption effect, with the exception of fly ash supported sample prepared with APS oxidant which showed excellent photocatalytic efficiency confirmed by UV/Vis spectroscopy and TOC measurement. Samples prepared with FeCl₃ oxidant showed to be unstable under simulated solar irradiation.

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5. References

- [1] S.J. Allen, B. Koumanova, *J. Univ. Chem. Technol. Metall.*, 40, (2003) p. 175.
- [2] A.L.M. Reddy, M.M. Shaijumon, S.R. Gowda, P.M. Ajayan, *J. Phys. Chem. C*, 114, (2010) p. 658.
- [3] N. Lu, H.M. Zhao, J.Y. Li, X. Quan, S. Chen, *Sep. Purif. Technol.*, 62, (2008) p. 668.
- [4] G.K. Mor, K. Shankar, M. Paulose, O.K. Varghese, C.A. Grimes, *Nano Lett.*, 6, (2006) p. 6215.
- [5] K. Shin, S.I. Seok, S.H. Im, J.H. Park, *Chem. Comm.*, 46, (2010) p. 2385.
- [6] G.K.R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, *J. Photochem. Photobiol. A*, 184, (2006) p. 234.
- [7] P. Damlin, C. Kvarnstrom, A. Ivaska, *J. Electroanal. Chem.*, 570, (2004) p. 113
- [8] M.R. Nabid, S.J.T. Rezaei, S.Z. Hosseini, *Mat. Lett.*, 84, (2012) p. 128.
- [9] S. Kurajica, I. Minga, V. Mandić, G. Matijašić, *J. Therm. Anal. Calorim.*, 124, (2016) p. 645.
- [10] I. Peternel, N. Koprivanac, H. Kušić, *Water Res.*, 40, (2006) p. 525.