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Effect of Sonication Pre-treatment of TiO_2 Catalyst for Photo-Degradation of Acid Orange 7 Azo Dye

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Abstract

In this study, Acid Orange 7 azo dye was degraded on TiO_2 catalyst layer illuminated with ultra-violet light. The TiO_2 suspension had prior been sonicated at 20 kHz before electrophoretic deposition on smooth stainless steel surfaces, with the aim of increasing the efficiency of azo dyes degradation. The effect of sonication on the TiO_2 suspension of 10 $g.L^{-1}$ and electrophoretic deposition loading to layers on surfaces was studied. Morphological properties of the electrophoretic layers from two different suspensions, Alpha and Sigma TiO_2 were characterized by Scanning Electron Microscopy to establish the specific surface properties, particle loading and crystalline sizes. A four–position reactor was used for dye degradation experiments under Ultra Violet light at 355 nm wavelength. The degradation of the azo dye was monitored at 30minutes interval for a total of 2 hours using Ultra Violet-Visible Spectrophotometer at $\lambda = 485$ nm. It was found out that 60% of dye degradation was achieved after 120 minutes without sonication pretreatment. Sonication pre-treatment resulted in 71.42% increase on the rate of photo-degradation, at a loading of 0.32 mg/cm^2. Particulate layers coated with Alpha TiO_2 showed more photoactivity compared to Sigma TiO_2. Scanning Electron Microscopy indicated that Alpha TiO_2 had 50 m^2/g surface area and 28 nm crystal size compared to Sigma TiO_2 with 10 m^2/g and 169 nm crystal size. This study shows that sonication pretreatment of Alpha TiO_2 /UV light system is most effective in photo-degrading Acid Orange 7 dye.

Keywords: sonication, photo-degradation, TiO_2 suspension, acid orange 7 dye

1. Introduction

The Acid Orange 7, *p*-(2-hydroxy-1 naphthyl azo) benzene sulfonic acid (AO7) is a monoazo dye commonly used for high temperature dyeing of wool in strong acid bath in textiles and paper manufacturing among other industrial applications. The dye is stable at normal temperature as it has a melting point of 164 ℃ and a solubility of 116 g/L in water. The presence of AO7 in effluents from these industries causes obvious environmental problems. Sonication utilizes sound of frequency above 20 kHz beyond human being hearing, leading to agitation of particles in a colloidal suspension to make a homogenous solution (Suslick, 1988, 1998). In this work, 250 cm^3 TiO_2 suspension of 10 $g.L^{-1}$was placed into a water bath and soundwaves of 20 kHz were projected for 60 seconds. Sonication improves the dissolution of solids in suspensions there by promoting “degasification” or expulsion of gases present (Mason and Lorimer, 1980). Sonication allows gas bubbles to coalesce together and easily leave the colloid thereby increase the strength of agitation which, breaks up the colloidal particles with a net effect of increasing their surface area (Mason and Lorimer, 1980). Increased particle surface area directly influences the efficiency of TiO_2 catalytic degradation rate (Cernigoj *et al.*, 2006). Electrophoretic Deposition (EPD) applies an electric field between two electrodes in a colloidal suspension of material resulting in a cathodic deposition on the electrodes (Boccaccini and Zhitomirsky, 2002, Besra and Liu, 2007). The electric-field transports the suspended charged particles to the oppositely charged electrode thereby depositing a coated layer (Zhitomirsky, 2000; Stoch*et al.*, 2001). Advantages of this technique include: -good control of layer thickness, equipment’s simplicity and short formation time (Kanamura and Hamagami, 2004). The Electrophoretic deposition of TiO_2 has been carried out in suspensions of mainly two solvents, acetyl acetone and acetone (Dor*et al.*, 2009). The process involves a two-step procedure, leading to the deposition of uniform layers on suitable substrate materials (). The charged particles move in a suspension medium followed by deposition on stainless steel plates under an electric field caused by direct current voltage (Boccaccini and Zhitomirsky, 2002; Kanamura and Hamagami, 2004, Cabanas-Polo and Boccaccini, 2015). In addition to stainless steel, other materials such as films from nanoparticles and carbon nanotubes have found practical application (Corni *et al.*, 2008; Wang *et al.*, 2000). Several investigators, (Wang *et al.*, 2000; Shrestha *et al.,* 2001; Windes *et al.,* 2002; Knote *et al.,* 2007) have reported that thin films prepared from electrophoresis display several advantages compared to other techniques. These include, corrosion resistance, versatility, simplicity, low-cost and ability to immobilize material on 3D structures and porous substrates (Knote *et al.* 2007). It has been suggested that the hardness of the thin films is dependent on the initial colloidal suspension concentration and electrophoretic deposition time (Yousefipoura *et al.* 2013).

Titanium dioxide is first illuminated with light and subsequently initiates the photo-degradation process. However, only light of wavelengths below 400nm is absorbed by TiO2 particles, e.g., 3.2eV approx. 388nm just as the organic pollutants such as dyestuffs absorbs Ultra-Violet light thereby allowing energy differential exchange between them. (Augugliaro *et al.,* 2002) Titanium dioxide as a semi-conductor photo-catalyst has found numerous applications such as in water purification, photo-voltammetry (Fernandez *et al.,* 1995, Fujishima *et al.,* 2008; Feng *et al.,* 2008). It has also found application in corrosion protection coatings, coatings in biomedicine, self-cleaning glazes and sensors (Boccaccini *et al.,* 2001; Mills *et al.,* 2003; Varghese *et al.,* 2003; Ma *et al.,* 2011; Cordero-Arias *et al.,* 2013; Wu *et al.,* 2014; Kulkarni *et al.,* 2015). Several methods to deposition TiO_2 layer on metallic surfaces have been investigated; these include plasma spraying, micro-arc oxidation (MAO), sol-gel, dip-coating and electrophoretic deposition (EPD) (Mohan *et al.,* 2012; Farnoush *et al.,* 2012). This paper reports the effect of sonication pre-treatment of TiO_2 for degradation of Acid Orange 7 dye and the analysis of the morphological properties of the deposited layers on stainless steel using Scanning Electron Microscope (SEM).

2. Materials and Methods

2.1 Chemicals and Reagents

2.1.1 Acid Orange 7 Dye (AO7)

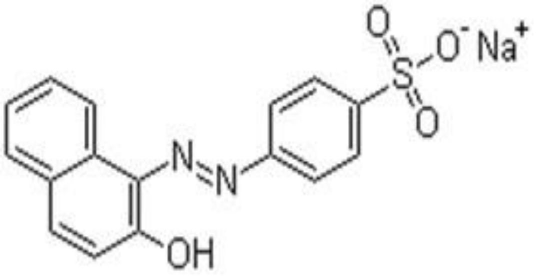


Figure 1. Structural formula of Acid Orange 7 Dye

Acid Orange 7 dye 95% purity was sourced in powder form. This was used to make a solution in water.

2.1.2 Alpha and Sigma Titanium Dioxide

Commercial Alpha TiO_2 and Sigma TiO_2 Anatase was used for the various suspensions in the methanol-water solutions for electrophoretic deposition.

2.2 Equipment and Apparatus

2.2.1 Ultra Sound Sonicator

An ultrasound Sonicator Model 150 V equipped with a probe was used on the various suspensions for pretreatment of TiO_2 suspensions**.** The Sonicator probe was immersed about 1 cm deep into the 250cm^3 solution in a beaker that was placed in a water bath, and a sound of frequency 20kHz projected for 60 seconds.

2.2.2 Electrophoretic Deposition Cell

Stainless steel plates of 7.5 cm^2 and a thickness of 3 mm were used for deposition of layers from two different powders, Alpha and Sigma TiO_2. A solution of methanol-water (80:20) of 500 cm^3 was used to make colloidal suspensions of TiO_2 at a concentration of $10g.L^{-1}$. The suspensions were stirred and then sonicated at 20 kHz for 60 seconds. The stainless steel plates were initially polished to get a mirror finish before thoroughly being washed with distilled water, rinsed, ultrasonically degreased with acetone and dried for 30 minutes. The distance between the electrodes in the cell was maintained at 10 mm and deposition was carried at time intervals, 5, 10, 30 and 60 seconds at 4 V. The coated stainless steel plates were then removed, placed on ceramic tiles and dried for a period of 48 hrs in ambient air at room temperature to constant weights. The coated layers were thereafter characterized by Scanning Electron Microscope (SEM).

2.2.3 Photo-Catalytic Reactor for the Azo Dye

A batch mode photo-catalytic reactor of capacity 2.5×10^{-5}mol $L^{-1}$was fabricated to evaluate the degradation of Acid Orange 7 dye. The photo-catalytic reactor was made of four-hole compartments, through which ultra violet light was irradiated using lamps of 18 W. The stainless steel plates coated with TiO_2 layers were suspended into the containers $25cm^3$ dye solutions maintained at constant stirring as shown in Figure 1 below.

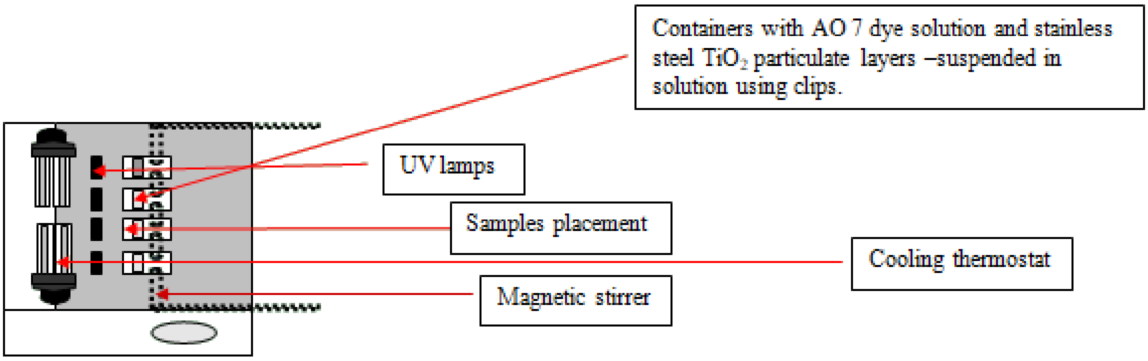


Figure 2. Four-Hole Photo-reactor for the Degradation of Acid Orange 7 Dye

2.3 Experimental– Ultra Violet TiO_2 Treatment System

A stock solution of Acid Orange 7 dye containing 1.0×10^{-4} mol. L^{-1} was made by dissolving 0.037g of the dye in 1000 cm^3water. A volume of 25 cm^3 of the solution was put in each of the four containers placed on the four-hole apparatus and stirred at 1000 rpm so as to maintain homogeneity throughout the experiment. The solutions were then irradiated with Ultra Violet light of 355nm for a duration of 120 minutes. Evaluation of photo-degradation of the dye was carried out by drawing 5 cm^3 solution from each of the container after every 30 minutes and measuring the absorbance using UV/Vis spectrophotometer at λ_{max}= 485 nm. The rate of photo-degradation of the solution was then calculated as follows;

$$J = \frac{V}{A}\frac{dc}{dt} \tag{1}$$

J (AO7mol/ (min.cm^2)

V (volume of dye solution in the containers)

A (area of stainless steel particulate layer

Containing deposited powder catalyst)

t (1hr.)

$$r_A = \frac{(c_0 - c_{60})V}{t_{60} - t_0} \cdot \frac{1}{A} \tag{2}$$

Where r_A is the rate of dye photo-degradation [(mol/ (min.cm^2)]

c_o ...initial dye concentration [mol.dm^{-3}]

c_{60} …dye concentration after 1 hour [mol.dm^{-3}]

t ….time at which irradiation started [0 hrs]

t_{60} ….time of irradiation [1 hr]

V….volume of dye in containers (0.025 dm^3)

A….irradiated geometric surface area of particulate film (0.00075 m^2)

2.4 Molar Extinction Coefficient of Acid Orange 7 Dye

The maximum absorption wavelength (λ_{max}) for the dye solution was established by scanning from 200-800nm wavelength using the UV/Vis Spectrophotometer. The Acid Orange 7 dye's molar extinction coefficient was determined by preparing solutions at concentrations of; 1×10^{-5}, 2.5×10^{-5}, 5×10^{-5}, 7.5×10^{-5} and 1×10^{-4}molL^{-1} and their absorbance measured at the established wavelength λ=485 nm. A calibration curve was then plotted and the value determined.

3. Results and Discussions

3.1 TiO_2 Morphological Characterization by Scanning Electron Microscope

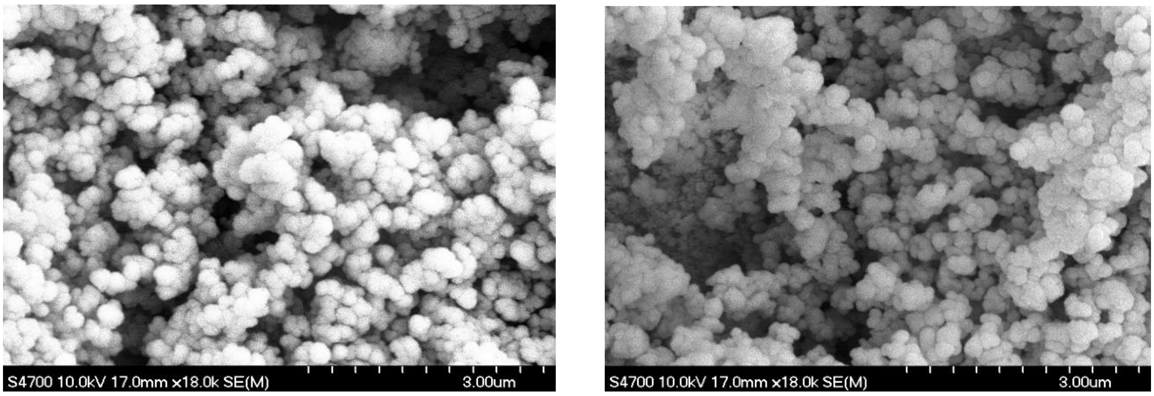
A morphological characterization of the TiO_2 powder catalysts is shown in Table 1 and Figure 3 below:

Table 1. SEM Characterization of TiO_2 Powders

Powder	**Surface area (m^2/g)**	**Particle size (nm)**
AlphaTiO_2	50	28
SigmaTiO_2	10	169

In Table 1, the Alpha TiO_2 had a greater surface area of 50 m^2/g compared to Sigma TiO_2 at 10m^2/g. Sigma TiO_2 has bigger particles sizes of about 169 nm than Alpha TiO_2's of 28 nm.

Sigma TiO_2 particles presented a surface area five (5) times lower than Alpha TiO_2 which is evident from its particle size that is six (6) times larger than AlphaTiO_2.



Alpha TiO_2 **Sigma TiO_2**

Figure 3. SEM images of TiO_2 Particulate Layers Produced by Electrophoresis

Smaller Alpha TiO_2 particle sizes corresponds to greater surface area and in this case exhibits increased crystallinity that leads to an increase in photo-degradation rate.

3.2 Effect of Electrophoresis on the Catalyst Coating

The relatioship between the electrophoretic time and amount of catalyst coating mass is shown in Figure 4 below.

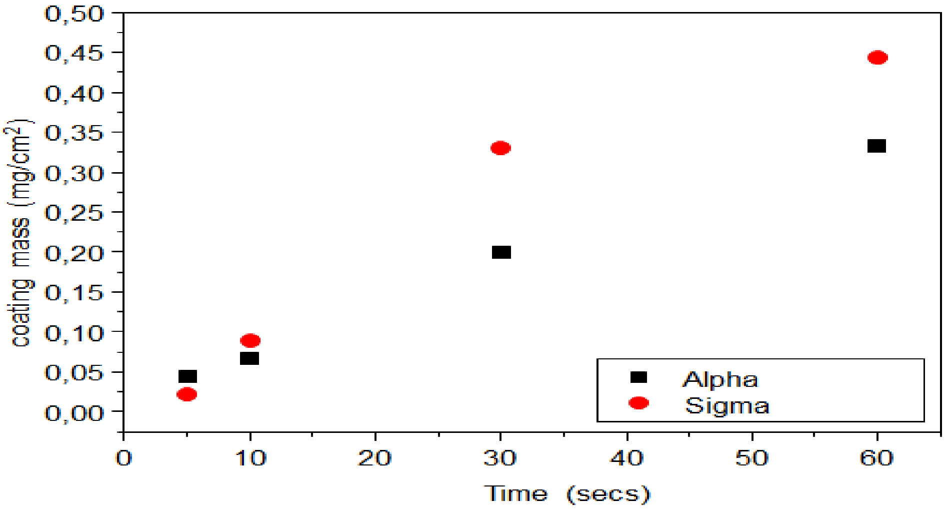


Figure 4. Electrophoresis Deposition of AlphaTiO_2 and Sigma TiO_2 per Second

After 5 seconds of Electrophoretic deposition experiments, 0.05 mg/cm^{2}Alpha TiO_2 catalyst had been deposited compared to 0.25 mg/cm^2 Sigma TiO_2 while at 10 seconds of deposition time, more of SigmaTiO_2 catalyst 0.10mg/cm^2 had been deposited compared to Alpha TiO_2 0.07mg/cm^2. After 30 seconds deposition time, the amount of Sigma TiO_2 catalyst deposited on the stainless steel coated layers was more by 0.15 mg/cm^2 compared to 60 seconds of deposition where the difference was 0.13mg/cm^2. The results obtained show that the powders have different independent rates of electrophoretic deposition under similar conditions. This is influenced by their different, concentrations, particle sizes, crystallinity, particle shape and conductivity on transport. Overall the amount of catalyst deposited in both experiments increases with electrophoretic deposition time.

3.3 Ultra Violet -Visible Spectral Analysis of Acid Orange 7 Maximum Absorption Wavelength (λ_{max})

A spectral scan between wavelength 200– 800 nm of the Acid Orange 7 dye solution carried across the UV-Visible spectrum is presented here below in Figure 5.

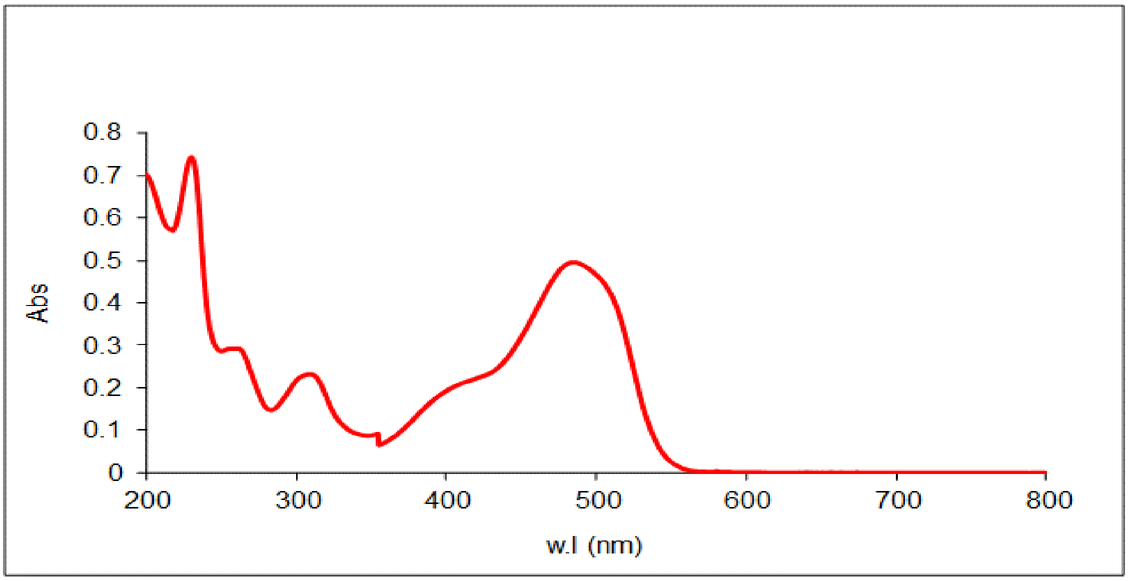


Figure 5. UV/Vis Spectrum before Photo-degradation Acid Orange 7

The scan showed a maximum absorption wavelength peak at 485 nm in the visible region.

This was similar to the value obtained by Tripathi and Srivastava, (2011). In this study, all photo-degradation experiments of the Acid Orange 7 dye solutions were measured at this wavelength λ= 485 nm.

3.3.1 Spectral Analysis Acid Orange 7 Molar Extinction Coefficient (ε)

The Molar Extinction Coefficient was determined through calibration curve plotted as shown in Figure 6 below.

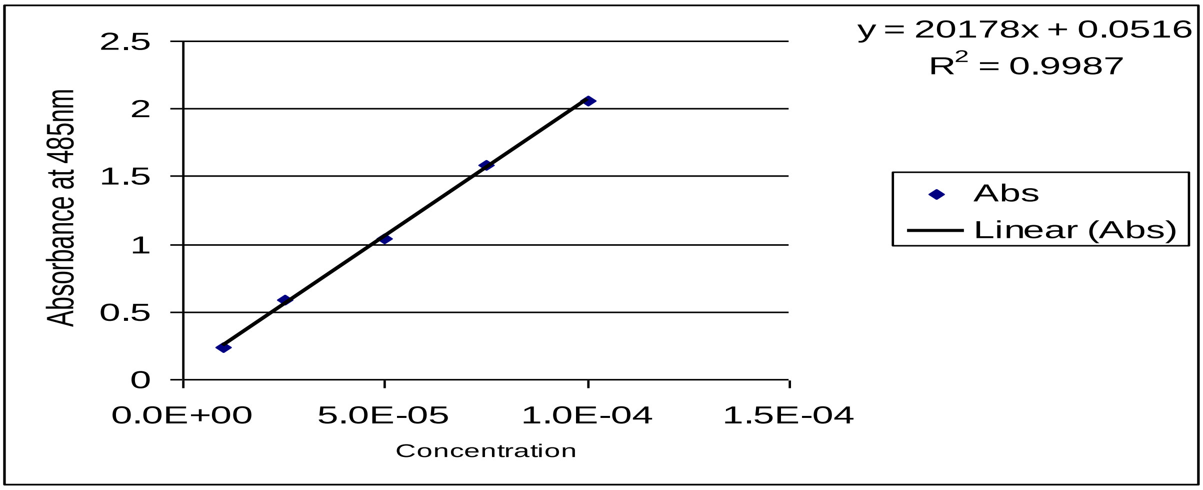


Figure 6. Calibration curve Acid Orange 7 dye

The calibration curve gave a regression of r^2 =0.9987 that yielded a Molar Absorption Coefficient **(ε)**value of 2.02×10^4 $mol^{-1}dm^3cm^{-1}$ This is close to $2.1\times10^4 mol^{-1}dm^3cm^{-1}$ reported by Ferguson and Mau (1972).

3.4 Evaluation of TiO_2 Catalyst Photo-Degradation of Acid Orange 7 Dye

Figure 7 below shows photo-degradation of 2.5×10^{-5} mol. L^{-1}Acid Orange 7 dye solution over a duration of 120 minutes without sonication pretreatment.

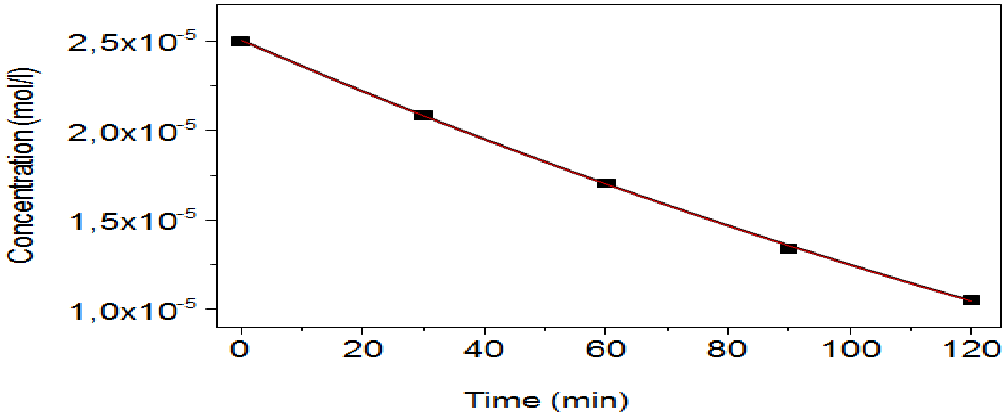


Figure 7. Photocatalytic Degradation Rate of Acid Orange 7 Dye Solution

The results show that both Alpha and Sigma TiO_2 achieved a 32% of photo-degradation in 30 minutes and 60% at 120 minutes.

3.5 Evaluation of Sonication Pretreatment of TiO_2 Catalyst on Photo-Degradation of Acid Orange 7 Dye

Figure 8 below shows the evaluation of sonication pretreatment of TiO_2 suspension on photo-degradation of Acid Orange 7 dye.

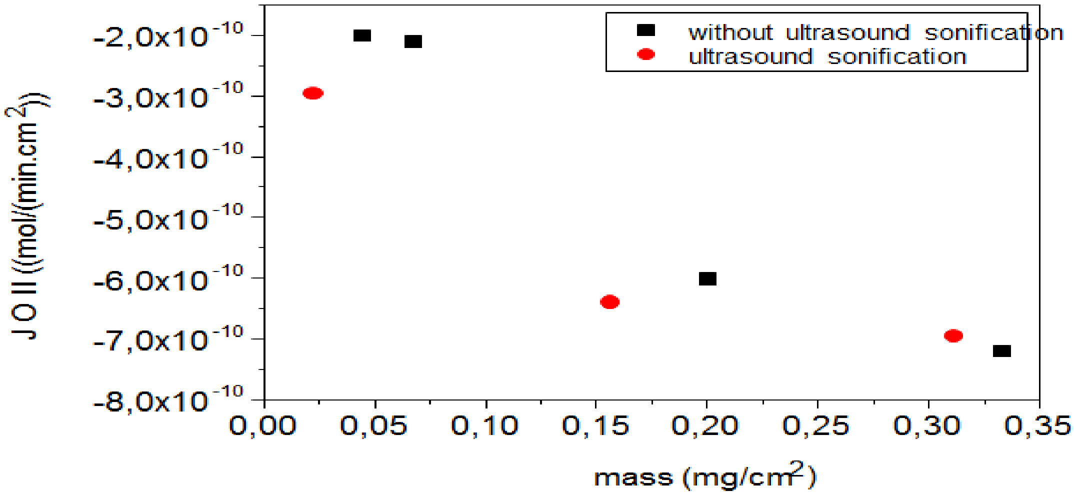


Figure 8. Effect of Sonication on the Rate of Acid Orange 7 Photocatalytic Degradation

Sonication resulted in a rate increase of Acid Orange 7 dye solution photo-degradation with 0.02 mg/cm^2 catalytic loading giving $-3.0x10^{-10}mol/min/cm^2$ compared to a -2.0×10^{-10} with a catalytic loading of 0.05mg/cm^2 of non-sonicated suspension. An increase in catalyst loading from 0.02 to 0.32mg/cm^2 led to a corresponding increase of

71.42% in dye photo-degradation.

3.6 Effect of TiO_2 Catalyst Loading on Acid Orange 7 Dye Photo-Degradation

Figure 9 below shows the relationship between Alpha and Sigma TiO_2 catalyst loading and their rates of Acid Orange 7 dye photo-degradation.

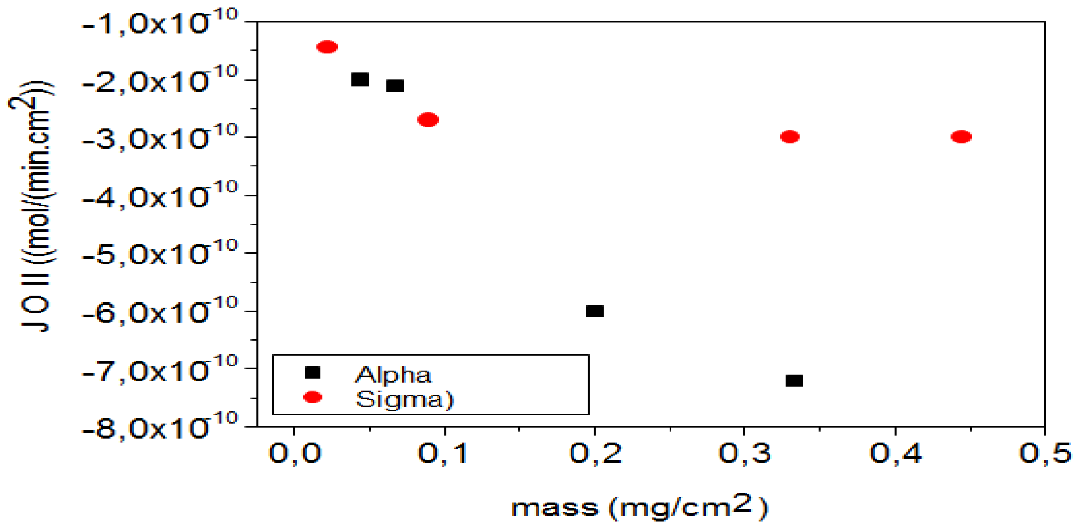


Figure 9. Effect of TiO_2 Catalyst type and Loading on Acid Orange 7 Photo-degradation Rates

At catalyst loading of 0.02-0.06 mg/cm^2 range gave a rate of dye photo-degradation for Alpha TiO_2 as -2.0× 10^{-10} mol^{-1}.min^{-1}.cm^2 while that of Sigma TiO_2 as -3.0×10^{-10} mol^{-1}.min^{-1}.cm^2. This shows that at low catalyst loadings, the degradation rates of both Alpha TiO_2 and Sigma TiO_2 are similar. At catalyst loading of 0.2 mg/cm^2, there was a significant difference in photo-degradation between the Alpha TiO_2 at -6 10×$^{-10}$mol^{-1}.min^{-1}.cm^2 compared to Sigma TiO_2 -3×10^{-10}mol^{-1}.min^{-1}.cm^2. After catalyst loading of 0.2 mg/cm^2, the rate of photo-degradation with Sigma TiO_2 remained constant at -3×10^{-10}mol^{-1}.min^{-1}.cm^2 despite further increase in catalyst loading while that due to Alpha TiO_2 reduced exponentially to -7.5×10^{-10} mol^{-1}.min^{-1}.cm^2 at a catalyst loading of 0.32 mg/cm^2.

4. Conclusion

The Acid Orange 7 dye degradation rate, using electrophoretically deposited TiO_2 photo-catalyst layer was significantly increased. The rate increase is due to the pre-treatment of TiO_2 suspension with ultrasonic sound at 20 kHz that allowed for homogenized smaller TiO_2 particles suspension and their electrophoretic deposition of uniform ultra thin layer coating on stainless steel plates. This optimizes the effective photo-degradation load to be 0.32 mg/cm^2 Alpha TiO_2 at a degradation rate of 71.42% compared to 60% of unsonicated photo-catalyst layer in 2 hrs. The sonicated layer has a smaller particle size, hence higher surface area that is effective to degrade the azo dye at a higher rate. Sonication pre-treatment of TiO_2 photo-catalytic suspension and its electrophoretic deposition increases the rate of photo-degradation of Acid Orange 7 dye.

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References

Augugliaro, V., Baiocchi, C., Prevot, A. B., Garcı´a-Lopez, E., Loddo, V., Malato, S., … Pramauro, E. (2002). Azo-dyes photocatalytic degradation in aqueous suspension of TiO_2 under solar irradiation. *Chemosphere*, *49*, 1223e30. https://doi.org/10.1016/S0045-6535(02)00489-7

Besra, L., & Liu, M. (2007). A review on fundamentals and applications of electrophoretic deposition (EPD). *Prog. Mater. Sci.*, *52*, 1-61. https://doi.org/10.1016/j.pmatsci.2006.07.001

Boccaccini, A. R., & Zhitomirsky, I. (2002). Application of Electrophoretic and electrolytic deposition techniques in ceramics processing. *CurrOpin Solid State Mater*, *6*, 251-260. https://doi.org/10.1016/S1359-0286(02)00080-3

Boccaccini, A. R., & Zhitomirsky, I. (2002). Application of electrophoretic and electrolytic deposition techniques in ceramics processing. *Curr Opinion in Solid State Mater Sci*., *6*, 251-260. https://doi.org/10.1016/S1359-0286(02)00080-3

Boccaccini, A. R., Cho, J., Roether, J. A., Thomas, B. J. C., Minay, E. J., & Shaffer, M. S. P. (2006). Electrophoretic deposition of carbon nanotubes. *Carbon, 44*, 3149-3160. https://doi.org/10.1016/j.carbon.2006.06.021

Boccaccini, A. R., Schindler, U., & Krüger, H. G. (2001). Ceramic coatings on carbon and metallic fibres by electrophoretic deposition. *Mater Lett., 51*, 225-230. https://doi.org/10.1016/S0167-577X(01)00294-4

Cabanas-Polo, S., & Boccaccini, A. (2015). Electrophoretic deposition of nanoscale TiO_2: technology and applications. *Journal of the European Ceramic Society*. https://doi.org/10.1016/j.jeurceramsoc.2015.05.030

Černigoj, U., Štangar, U. L., Trebše, P., Krašovec, U. O., & Gross, S. (2006). *Thin Solid Films*, *495*, 327-332. https://doi.org/10.1016/j.tsf.2005.08.240

Cordero-Arias, L., Cabanas-Polo, S., Gao, H. X., Gilabert, J., Sanchez, E., Roether, J. A., … Boccaccini, A. R. (2013). Electrophoretic deposition of nanostructured-TiO_2/chitosan composite coatings on stainless steel. *RSC Adv*., *3*, 11247-11254. https://doi.org/10.1039/c3ra40535d

Dor, S., Ruhle, S., Ofir, A., Adler, M., Grinis, L., & Zaban, A. (2009). *Colloids Surf. A*, *342*, 70. https://doi.org/10.1016/j.colsurfa.2009.04.009

Farnoush, H., Mohandesi, J. A., Fatmehsari, D. H., & Moztarzadeh, F. (2012). *Ceram. Int*., *38*, 6753. https://doi.org/10.1016/j.ceramint.2012.05.070

Ferguson, J., & Mau, A. W. H. (1972). Absorption studies of acid-base equilibria of dye solutions, *Chem. Phys. Lett.*, *17*, 543-546. https://doi.org/10.1016/0009-2614(72)85101-7

Fernandez, A., Lassaletta, G., Jimenez, V. M., Justo, A., Gonzale-Elipe, A. R., Herrmann, J., … Ait-Ichou. Y. (1995). Preparation and characterization of TiO_2photocatalystssupported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification. *Appl. Catal. B Environ., 7*, 49-63. https://doi.org/10.1016/0926-3373(95)00026-7

Fujishima, A., Zhang, X. T., & Tryk, D. A. (2008). TiO_2 photocatalysis and related surface phenomena. *Surf. Sci. Rep*., *63*, 515-582. https://doi.org/10.1016/j.surfrep.2008.10.001

Hachem, C., Bocquillon, F., Zahraa, O., & Bouchy, M. (2001). Decolourization of textile industry wastewater by the photocatalytic degradation process. *Dyes Pigments*, *49*, 117e25. https://doi.org/10.1016/S0143-7208(01)00014-6

Kanamura, K., & Hamagami, J. I. (2004). Innovation of novel functional material processing technique by using electrophoretic deposition process. *Solid State Ionics*, *172*, 303-308. https://doi.org/10.1016/j.ssi.2004.01.039

Knote, A., Krüger, H. G., Selve, S., Kups, T., Kern, H., & Spiess, L. (2007). Metal-ceramic composite layers on stainless steel through the combination of electrophoretic deposition and galvanic processes. *J Mater Sci., 242*, 4545-4551. https://doi.org/10.1007/s10853-006-0482-0

Kulkarni, M., Mazare, A., Gongadze, E., Perutkova, Š., Kralj-Iglič, V., Milošev, I., … Mozetič, M. (2015). Titanium nanostructures for biomedical applications. *Nanotechnol*, *26*, 062002. https://doi.org/10.1088/0957-4484/26/6/062002

Ma, R., & Zhitomirsky, I. (2011). Electrophoretic deposition of silica-hyaluronic acid and titania-hyaluronic acid nanocomposites. *J. Alloys. Comp*., *509*, S510-S513 (Suppl). https://doi.org/10.1016/j.jallcom.2010.10.111

Mary, C., & Boccaccini, A. R. (2007). Electrophoretic deposition: from traditional ceramics to nanotechnology. *J. Eur. Ceramic. Soc*., *28*, 1353-1367. https://doi.org/10.1016/j.jeurceramsoc.2007.12.011

Mason, T. J., & Lorimer, J. P. (1988). 1988 *Sonochemistry: theory, applications and uses of ultrasoundin chemistry*. Chichester, UK: Ellis Horword.

Mills, A., Hill, G., Bhopal, S., Parkin, I. P., & O'Neill, S. A. (2003). Thick titanium dioxide films for semiconductor photocatalysis. *J. Photochem. Photobiol. A Chem., 160*, 185-194. https://doi.org/10.1016/S1010-6030(03)00206-5

Mohan, L., Durgalakshmi, D., Geetha, M., Narayanan, T. S. N. S., & Asokamani, R. (2012). *Ceram. Int*., *38*, 3435. https://doi.org/10.1016/j.ceramint.2011.12.056

Narayan M. R., & Raturi, A. (2012). Deposition and characterization of titanium dioxide films formed by electrophoretic deposition. *International Journal of Materials Engineering Innovation, 3*(1), 17-31. https://doi.org/10.1504/IJMATEI.2012.044447

Shankar, V., & Grimes, P. (2008). Vertically Aligned Single Crystal TiO_2 Nanowire Arrays Grown Directly on Transparent Conducting Oxide Coated Glass: Synthesis Details and Applications. *Nano Lett.*, *8*, 3781-3786. https://doi.org/10.1021/nl802096a

Shrestha, N. K., Sakurada, K., Masuko, M., & Saji, T. (2001). Composite coatings of nickel and ceramic particles prepared in two steps. *Surf Coat Technol*., *140*, 175-181. https://doi.org/10.1016/S0257-8972(01)01045-3

Stoch, A., Brozek, A., Kmita, G. Stoch, J., Jastrzebski, W., & Rakowska, A. (2001). Electrophoretic coating of hydroxyapatite on titanium implants. *J. Mol. Struct.*, *596*, 191-200. https://doi.org/10.1016/S0022-2860(01)00716-5

Suslick, K. S. (1998). Sonochemistry. In *Kirk {Othmer encyclopedia of chemical technology*, 4th edn, 26, 517{541. New York: John Wiley.

Suslick, K. S. (ed.) (1988). *Ultrasound: its chemical, physical, and biological elects*. New York: VCH.

Tripathi, A., & Srivastava, S. K. (2011). Biodecolourisation of Azo dye, Acid Orange 10, using different bacterial strains. *2nd International Conference on Environmental Science and Technology IPCBEE, 6, IACSIT Press, Singapore, 1-6.*

Varghese, O. K., Gong, D., Paulose, M., Ong, K. G., & Grimes, C. A. (2003). Hydrogen sensing using Titania nanotubes. *Sens Actuators B Chem*., *93*, 338-344. https://doi.org/10.1016/S0925-4005(03)00222-3

Wang, Z., Shemitt, J., & Ping, X. (2000). Novel fabrication technique for the production of ceramic/ceramic and metal/ceramic composite coatings. *Scripta. Mater*., *42*, 653-659. https://doi.org/10.1016/S1359-6462(99)00414-5

Windes, W. E., & Zimmerman, I. E. (2002). Electrophoretic deposition applied to thick metal-ceramic coatings. *Surf Coat Technol*., *157*, 267-273. https://doi.org/10.1016/S0257-8972(02)00163-9

Wu, S. L., Weng, Z. Y., Liu, X. M., Yeung, K. W. K., & Chu. P. K. (2014). Functionalized TiO_2 based nanomaterials for biomedical applications. *Adv. Functional Mater*., *24*, 5464-5481. https://doi.org/10.1002/adfm.201400706

Yousefipoura, K., Akbari, A., & Bayati, M. R. (2013). The effect of EEMAO processing on surface mechanical properties of the TiO_2-ZrO_2 nanostructured composite coatings. *Ceramics Int*., *39*, 7809-7815. https://doi.org/10.1016/j.ceramint.2013.03.041

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