

Comparative Study on Degradation of Anionic and Non-Ionic Textile Dyes Using TiO₂/CAC Nano-Composites

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ABSTRACT

The synergistic relation among TiO₂ and Commercial Activated Carbon (CAC) was investigated for treatment of existing organic contaminants in Textile wastewater. TiO₂ nanoparticles and TiO₂/CAC composites varying the amount of CAC in composite were prepared by Liquid Impregnation method. Relevant techniques were used for the characterization (i.e. particle size, crystallinity and surface morphology) of prepared catalysts with anatase phase dominant in all catalysts. Drimarene Brilliant Red (K-4BL-CDG), Disperse Blue and Cibacron Orange were used as model contaminants having different chemical structure and response towards catalysts. The remaining concentration of dye in solution was checked by UV-Visible Spectrophotometer. Drimarene Brilliant Red and Cibacron Orange (anionic dyes) showed the highest of 95% and 84% removal respectively within 90 min after the treatment with TiO₂/CAC composite as compared to TNPs and only CAC. It was found that addition of CAC improves the photocatalytic efficiency of TNPs by increasing the surface area. For Disperse Blue (non-ionic dyes), the maximum removal efficiency (75%) was achieved when treated with CAC as compared to pure TNPs and TiO₂/CAC composite. The study demonstrated that photocatalytic efficiency was based on the active group in the structure of different dyes.

Keywords: Titania Nanoparticles (TNPs), Commercial Activated Carbon (CAC), Disperse Dye, Photocatalytic Degradation

1. INTRODUCTION

Textile industry is considered as a main consumer of water. Due to different processes in Industrial sector, dyes make their path directly into wastewater channels depending on their chemical structure as well as fabric quality. Dyes are classified as Anionic (reactive, acid and direct dyes), Non-ionic (all dispersed dyes) and Cationic (basic dyes) depending on their molecular structure, especially the presence of active/functional group (Hemsas et al. 2014).

Anionic dyes (Reactive dye) are bright colored compounds, easily soluble in water and fixed to the fabric by means of covalent bond. While the non-ionic dyes (Disperse dyes) do not ionize in solution and persist in colloidal form with the reason to less soluble in water (Yagub et al. 2014). Disperse dyes are characterized by anthraquinone and sulfide structures having $-NH$, $-C=O$ and aromatic groups. Reactive dyes are more stable as compare to disperse dyes due to the presence of azo bonds ($N=N$) along with $-OH$, $-SO_3^-$ and $-COO^-$ groups (Kim et al. 2004). During dyeing, some dyes make their way directly in wastewater streams as they do not get fixed with polymer and result in polluting environment (Kim et al. 2004; Zangeneh et al. 2015). Their removal require special treatment processes due to less solubility and degradation in wastewater streams (Asilturk and Sener, 2012).

Dye removal through biological treatment of effluent does not work due to their slow biodegradation. Some other conventional techniques like coagulation and adsorption play their role in the treatment of such effluents but they result in the formation of byproducts rather than their complete elimination (Zhong et al. 2014). The Advanced Oxidation Process (AOP) is an emerging technique for dye degradation using sunlightwa. Among this, use of TNPs is significant for low cost, stable nature and suitable band gap energy (Garcia-Munoz et al. 2014).

The efficacy of TNPs has been increased while making composites with materials, porous in nature in order to enhance the number of active sites by increasing the surface area. These composites include TiO_2 /zeolite (Shankar et al., 2006), TiO_2/SiO_2 (Van Grieken et al., 2002; Sayilkan et al., 2007; Zhang et al., 2013), TiO_2 /clay (Mogyorosi et al., 2003, Awate and Suzuki, 2001), TiO_2 /graphene (Li et al., 2013; Li et al., 2012; Kim et al., 2012), TiO_2 /perlite (Hosseini et al., 2007) and TiO_2 /activated carbon (Chen et al., 2010; Tryba et al., 2003; Velasco et al., 2010). Due to this CAC along with anatase phase of TiO_2 thus displays a synergistic behavior for the removal of organic and inorganic pollutants from wastewater stream (Benjwal and Kar, 2015; Fariaand Wang, 2009). In this way, CAC acts as a supporting material in photocatalytic degradation of organic pollutants. It brings the pollutants come close to the active sites of TNPs where hydroxyl radicals (OH^\cdot) are present for effective degradation expressing synergistic effect (Mahmoodi et al., 2011).

In previous studies some other titania based nanocomposites have been used having greater adsorbing capacity as well as photocatlytic efficacy when compare with pure TNPs. The current study focused on the use of CAC coupled with TNPs for the removal of selected textile dyes in which TiO_2 trigger reaction when dye adsorb on the

surface of CAC. Response Surface Methodology (RSM) was used to investigate the best photocatalyst for the removal of selected textile dyes.

2. MATERIALS AND METHODS

2.1. Preparation of Titania Nanoparticles

General purpose TiO_2 was added in distilled water and kept stirring overnight following by settling the mixture at room temperature. The obtained material was dried in oven at 105°C in order to remove moisture. The dried sample was placed in muffle furnace for calcination (500°C for 6 h) after grinding.

2.2. Preparation of TiO_2 /CAC Composite

For preparing composite, 0.99g of TNPs were mixed with required amount of CAC and magnetically stirred in 300 ml of distilled water and filtered the material (Rioja et al., 2012). After drying the black and white powder was calcined in a furnace at 400°C for 4 h. The other composites with 0.2, 0.4, 1, 2, 5, 7.5 and 10% of CAC were prepared by the same process and stored in air tight bottles for further use.

2.3. Photocatalytic Study

To check photocatalytic activity, different dye solutions were degraded under UV-A lamp. 500 ml Pyrex cylinder (covered with foil) at room temperature was used for this study. The required quantity of nanocomposite was mixed in 15 mg/L dye solution. The whole set up was positioned on a stirrer and after regular interval color removal was observed using UV-Visible Spectrophotometer (T-60U PG Instruments, UK). The λ_{max} for Drimarene Brilliant Red (542 nm), Disperse Blue (550 nm) and Cibacron Orange (435 nm) was identified before proceeding to experiment.

3. RESULTS AND DISCUSSION

3.1 Experimental Design

In Response Surface Methodology (RSM), the face centered design was used for the investigation of best suitable photocatalyst in this study. Three factors were listed as: type of catalyst, type of dye and photodegradation time having three level for each factor corresponding to their low, medium and high value as shown in Table 1.

Table 1. Coded values and Actual titles corresponding to various factors in RSM software for degradation of textile dyes

Coded value	Actual Title	
	Time	Dyes
-1	30	Drimarene Brilliant Red (DBR)
0	60	Disperse Blue
1	90	Cibacron Orange

3.1.1. Photocatalytic Degradation Using UV+TNPs

When dye solutions were treated with optimal amount of pure TNPs under UV-A lamp, dyes behaved in different manner depending on their chemical structure. **Fig. 1** showed the interaction between removals of different dyes at various time interval. It was observed that at constant dose of TNPs, 80%, 54.2% and 80.6% removal was observed after 90 min for DBR, Disperse Blue and Cibacron Orange respectively. The significant difference in the structure of these dyes might be the absence of azo group (-N=N-) in Disperse Blue (**Khataee and Kasiri, 2010**). With UV light, the hydroxyl radicals are generated on the surface of TNPs (semiconductor). These radicals having oxidizing power breakdown the azo group present in reactive dye (**Neppolian et al., 2002**). Azo group is more susceptible to photocatalytic degradation. That is why reactive dyes have better removal efficiency as compared to disperse dye. The anthraquinone group in disperse dye is less susceptible to photocatalysis, resulting in less removal efficiency when treated with pure TNPs (**Khataee and Kasiri, 2010**).

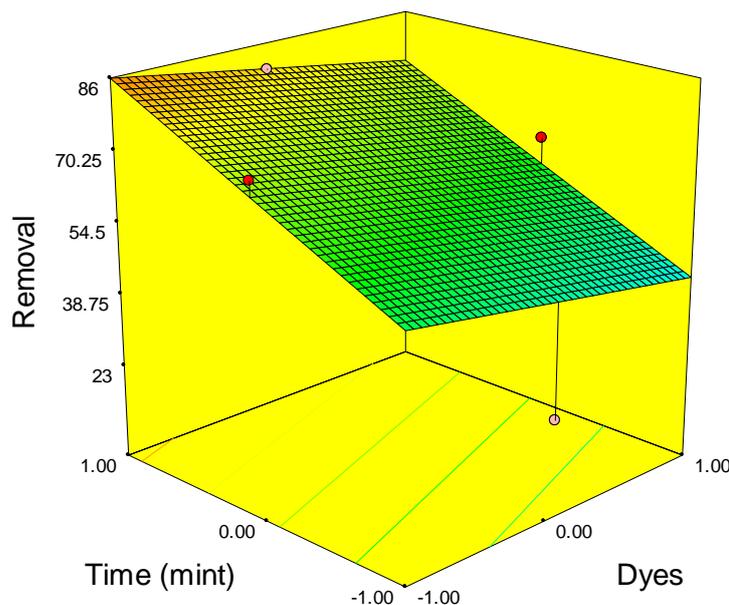


Fig. 1. Photocatalytic degradation of DBR, Disperse Blue and Cibacron Orange using UV + TNPs (dye concentration; 15 mg/L and catalyst dose; 150 mg/L).

3.1.3 Photocatalytic Degradation Using UV+CAC

All three dyes showed good degradation when treated with CAC as compared to pure TNPs. For DBR 90.7 % removal efficiency was observed while 75.2 % and 85.2 % in case of disperse Blue and Cibacron Orange respectively (**Fig. 2**) when treated with optimum dose of CAC for 90 min under UV lamp. The minor difference in

the degradation rate might be attributed to various factors. Generally, at neutral pH (6-8), most of the particles (e.g. dyes, clays, humic acid and bacteria) are negatively charged in natural water (Kim et al., 2004). Similarly all the dye molecules in aqueous solution are negatively charged while CAC maintains a net positive charge on its surface. The difference in electrostatic interaction among the negatively charged dye molecules and positively charged CAC is responsible for adsorption phenomenon (Silva et al., 2006). The reactive dye (DBR and Cibacron Orange) are strongly charged as compare to Disperse Blue and also the conductivity of reactive dye is much higher than disperse dye (Kim et al., 2004). That could be the reason that DBR and Cibacron Orange has somewhat greater removal efficiency as compared to disperse one.

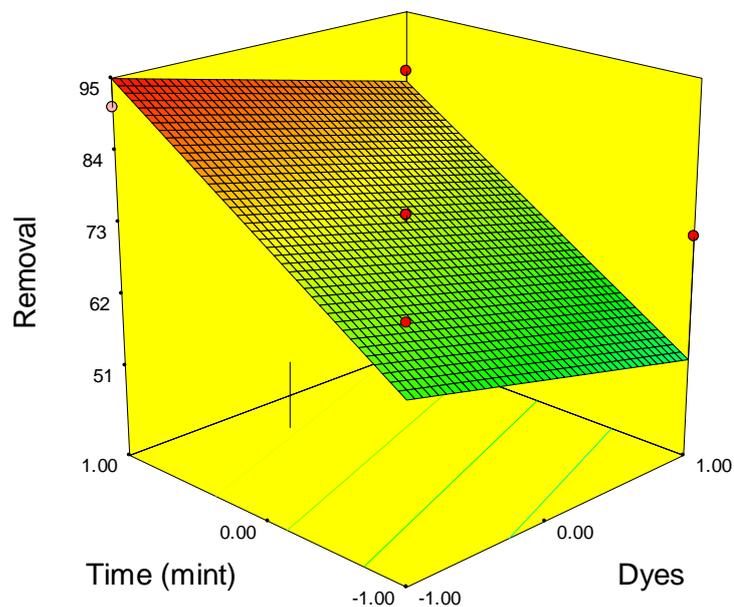


Fig. 2. Photocatalytic degradation of DBR, Disperse Blue and Cibacron Orange using UV + CAC (dye concentration; 15 mg/L and catalyst dose; 150 mg/L).

3.1.4 Synergistic Photocatalytic Degradation Using UV+TiO₂/CAC Composite

The plot of RSM for photocatalytic degradation using TiO₂/CAC was shown in Fig. 3. The results for the removal of DBR showed strongly synergy effect by adding CAC in TNPs. Within 30 min more than half of the dye was removed and maximum degradation (95.5 %) was obtained after 60 min and remained same with increasing time up to 90 min. While for Cibacron Orange 84% removal was observed after 90 min. It states that nanocomposite has superior photocatalytic efficacy as compared to TNPs and CAC separately. Actually due to CAC available active site on TNPs increases, resulting in greater photocatalytic efficiency (Benjwal and Kar, 2015). The TNPs attach with porous CAC and enable them to adsorb dye molecules, assisting in photocatalytic degradation (Yuan et al., 2007; Yap et al., 2011). It could be

demonstrated that TiO₂/CAC composite increases the active sites for reactive agents to take part in photocatalytic degradation (Muthirulan et al., 2013).

Besides this, all the intermediate products also adsorb on the surface of CAC during photocatalysis and thus prevent their dissolution again in to the water (Zhang et al., 2005). Benjwal and Kar (2015) reported that TiO₂/CAC neutralized all the intermediates in photocatalysis. But in case of pure TNPs, the intermediates do not attach to the surface of TiO₂ and make their way in to the water again. By adding CAC to the TNPs, the crystallite size of the TNPs is reduced. The reduction in particle size, improves the photocatalytic efficiency by reducing the recombination of electron-hole pairs.

The synergistic relationship of TNPs and CAC was not strongly illustrated in case of Disperse Blue, might be attribute to various factors such as difference in chemical structure and solubility in water. Another reason might be the absorption of photons by dye molecules, resulting in less number of photons for the generation of hydroxyl radicals (Damodar et al., 2007). Kim et al. (2004) reported that disperse dyes can be easily removed by coagulation due to their less stability and solubility in aqueous solution.

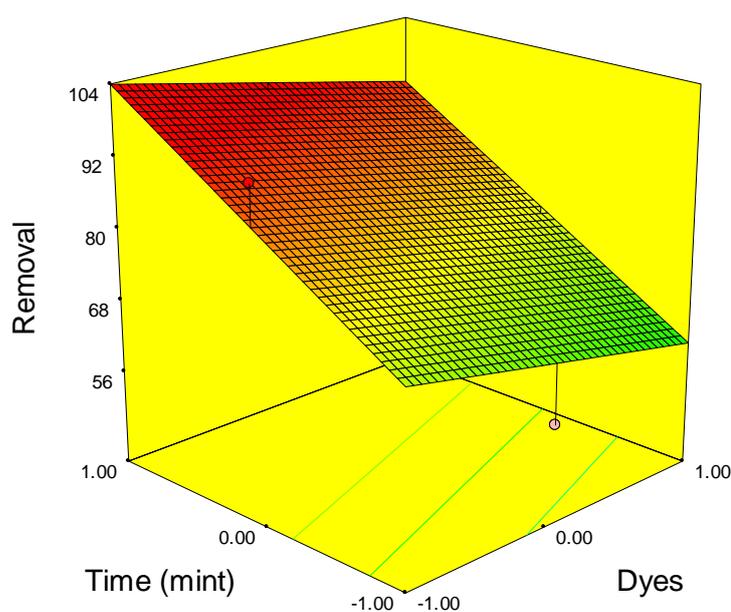


Fig. 3. Photocatalytic degradation of DBR, Disperse Blue and Cibacron Orange using UV + TiO₂/CAC (dye concentration; 15 mg/L and catalyst dose; 150 mg/L).

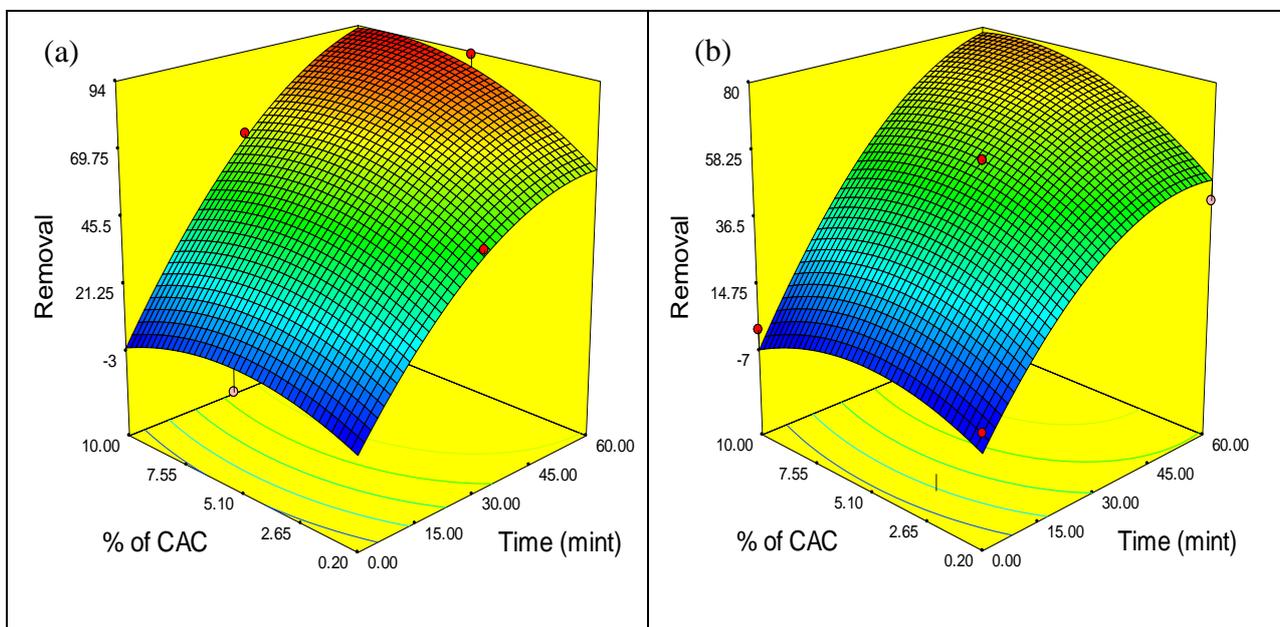
3.1.5 Photocatalytic Degradation Using varying amount of CAC in TiO₂/CAC Composite

The experiment was also performed by varying the amount of CAC (0.2% to 10%) in composite and Fig. 4 represents that increasing the amount of CAC in composite affects the penetration of radiations and number of active sites on the

surface of semiconductor. As the percentage of CAC in TiO₂/CAC increases, the removal of DBR decreases but in case of Disperse Blue and Cibacron Orange, the degradation rate almost remains constant. The decrease in the removal efficiency of DBR is due to the reflectance of UV radiations by CAC (Rajamanickam and Shanti, 2014). Although the CAC increases the active sites for photodegradation but the shielding effect of CAC loading decreases the penetration of UV radiations resulting in the decrease of removal efficiency (Muthirulan et al., 2012b). It might be attributed that excessive CAC contacting directly to the surface of TNPs, resulting in the reduction of active sites for photocatalysis (Silva et al., 2006). So it is understood that optimum amount of CAC in composite is required for the maximum photocatalytic degradation because too much contents of CAC in composite results in the reflectance of radiations by CAC. Table 2. Shows the low, medium and high value corresponding to various factor for determining the optimized value of CAC in composite.

Table 2. Coded values and Actual titles corresponding to various factors in RSM software for optimization of CAC in TiO₂/CAC

Coded value	Actual Title	
	Time	% of CAC in composite
-1	0	0.2
0	30	5.1
1	60	10



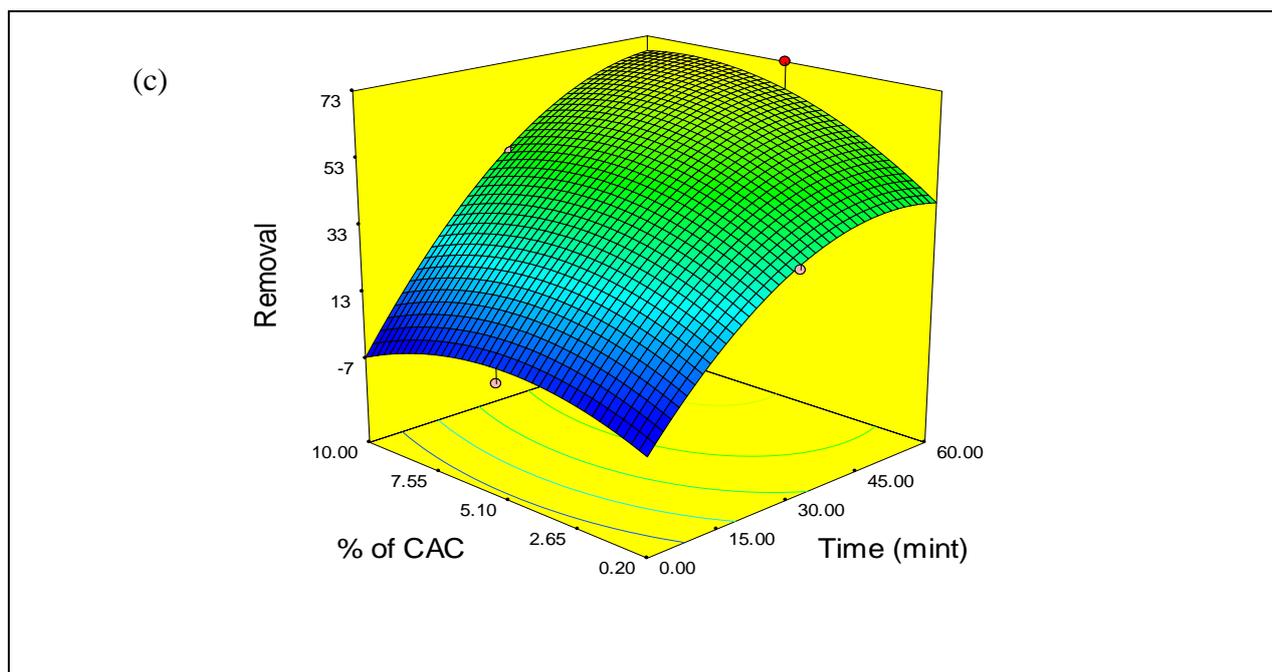


Fig. 4. Photocatalytic degradation of (a) DBR, (b) Disperse Blue and (c) Cibacron Orange by varying amount of CAC in TiO_2/CAC (dye concentration; 15 mg/L and catalyst dose; 150 mg/L).

4 CONCLUSIONS

Addition of CAC to the TiO_2 catalyst proves to be a useful technique for improving the efficiency of TNPs. The present study shows that DBR, Disperse Blue and Cibacron Orange behave in a different manner when treated with the same catalyst depending on their molecular structure especially the presence of active/functional group. The purpose of this study was the enhancement of photodegradation rate by mutual linking of CAC and TNPs to make a unique composite having greater surface area. We observed that photodegradation rate of DBR (Anionic) is greater when treated with TiO_2/CAC composite due to the presence of azo group. Disperse Blue (Non-Ionic) has maximum removal while treating with CAC might be attributed to the absence of azo group. While Cibacron Orange depicts almost same removal rate for CAC and TiO_2/CAC .

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REFERENCES

- Asiltürk, M., and Şener, Ş. (2012). TiO₂-activated carbon photocatalysts: preparation, characterization and photocatalytic activities. *Chemical Engineering Journal*, 180, 354-363.
- Awate, S. V., and Suzuki, K. (2001). Enhanced adsorption capacity and photocatalytic oxidative activity of dyes in aqueous medium by hydrothermally treated titania pillared clay. *Adsorption*, 7(4), 319-326.
- Benjwal, P., and Kar, K. K. (2015). Simultaneous photocatalysis and adsorption based removal of inorganic and organic impurities from water by titania/activated carbon/carbonized epoxy nanocomposite. *Journal of Environmental Chemical Engineering*, 3(3), 2076-2083.
- Chen, K., Li, J., Li, J., Zhang, Y., and Wang, W. (2010). Synthesis and characterization of TiO₂-montmorillonites doped with vanadium and/or carbon and their application for the photodegradation of sulphorhodamine B under UV-vis irradiation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 360(1), 47-56.
- Damodar, R. A., Jagannathan, K., and Swaminathan, T. (2007). Decolourization of reactive dyes by thin film immobilized surface photoreactor using solar irradiation. *Solar Energy*, 81(1), 1-7.
- Faria, J. L. and Wang, W. (2008) Carbon Materials in Photocatalysis, in *Carbon Materials for Catalysis* (eds P. Serp and J. L. Figueiredo), John Wiley and Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9780470403709.ch13
- García-Muñoz, P., Carbajo, J., Faraldos, M., and Bahamonde, A. (2014). Photocatalytic degradation of phenol and isoproturon: Effect of adding an activated carbon to titania catalyst. *Journal of Photochemistry and Photobiology A: Chemistry*, 287, 8-18.
- Hemsas, S., Belbeki, Z., and Benrachedi, K. (2014). Removal of Dispersed Dyes from Aqueous Solution Using Activated Carbon Prepared from Olive Stones. *Journal of Agricultural Science and Technology*, (4), 414-421.
- Hosseini, S. N., Borghei, S. M., Vossoughi, M., and Taghavinia, N. (2007). Immobilization of TiO₂ on perlite granules for photocatalytic degradation of phenol. *Applied Catalysis B: Environmental*, 74(1), 53-62.
- Khataee, A. R., and Kasiri, M. B. (2010). Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: influence of the chemical structure of dyes. *Journal of Molecular Catalysis A: Chemical*, 328(1), 8-26.
- Kim, C. H., Kim, B. H., and Yang, K. S. (2012). TiO₂ nanoparticles loaded on graphene/carbon composite nanofibers by electrospinning for increased photocatalysis. *Carbon*, 50(7), 2472-2481.
- Kim, T. H., Park, C., Yang, J., and Kim, S. (2004). Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. *Journal of hazardous materials*, 112(1), 95-103.
- Li, K., Chen, T., Yan, L., Dai, Y., Huang, Z., Guo, H., and Song, D. (2012). Synthesis of mesoporous graphene and tourmaline co-doped titania composites and their photocatalytic activity towards organic pollutant degradation and eutrophic water treatment. *Catalysis Communications*, 28, 196-201.

- Li, K., Chen, T., Yan, L., Dai, Y., Huang, Z., Xiong, J., and Zeng, Z. (2013). Design of graphene and silica co-doped titania composites with ordered mesostructure and their simulated sunlight photocatalytic performance towards atrazine degradation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 422, 90-99.
- Mahmoodi, N. M., Arami, M., and Zhang, J. (2011). Preparation and photocatalytic activity of immobilized composite photocatalyst (titania nanoparticle/activated carbon). *Journal of Alloys and Compounds*, 509(14), 4754-4764.
- Mogyorosi, K., Dekany, I., and Fendler, J. H. (2003). Preparation and characterization of clay mineral intercalated titanium dioxide nanoparticles. *Langmuir*, 19(7), 2938-2946.
- Muthirulan, P., Meenakshisundaram, M., and Kannan, N. (2013). Beneficial role of ZnO photocatalyst supported with porous activated carbon for the mineralization of alizarin cyanin green dye in aqueous solution. *Journal of Advanced Research*, 4(6), 479-484.
- Muthirulan, P., Naganathan, G., Sundaram, M. M., and Kannan, N. (2012b). Beneficial role of commercial activated carbon for the decoloration of Safranin dye on TiO₂ and ZnO/UV system for the application of effluents treatment from wastewater. *Indian J. Environ. Prot.*, 32, 546-553.
- Neppolian, B., Choi, H. C., Sakthivel, S., Arabindoo, B., and Murugesan, V. (2002). Solar light induced and TiO₂ assisted degradation of textile dye reactive blue 4. *Chemosphere*, 46(8), 1173-1181.
- Rajamanickam, D., and Shanthi, M. (2014). Photocatalytic degradation of an azo dye Sunset Yellow under UV-A light using TiO₂/CAC composite catalysts. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 128, 100-108.
- Rioja, N., Benguria, P., Scifo, L., and Zorita, S. (2012). Synergy effect in the photocatalytic degradation of pharmaceuticals on a suspended mixture of titania and activated carbon Nanocon, Brno, Czech republic, EU. <http://nanocon2013.tanger.cz/files/proceedings/04/reports/633.pdf>.
- Sayilkan, F., Asilturk, M., Sener, S., Erdemoglu, S., Erdemoglu, M., and Sayilkan, H. (2007). Hydrothermal Synthesis, Characterization and Photocatalytic Activity of Nanosized TiO₂ Based Catalysts for Rhodamine B Degradation. *Turkish Journal of Chemistry*, 31(2), 211.
- Shankar, M. V., Anandan, S., Venkatachalam, N., Arabindoo, B., and Murugesan, V. (2006). Fine route for an efficient removal of 2, 4-dichlorophenoxyacetic acid (2, 4-D) by zeolite-supported TiO₂. *Chemosphere*, 63 (6), 1014-1021.
- Silva, C. G., Wang, W., and Faria, J. L. (2006). Photocatalytic and photochemical degradation of mono-, di- and tri-azo dyes in aqueous solution under UV irradiation. *Journal of Photochemistry and Photobiology A: Chemistry*, 181(2), 314-324.
- Tryba, B., Morawski, A. W., and Inagaki, M. (2003). Application of TiO₂-mounted activated carbon to the removal of phenol from water. *Applied Catalysis B: Environmental*, 41(4), 427-433.

- Van Grieken, R., Aguado, J., López-Muñoz, M. J., and Marugán, J. (2002). Synthesis of size-controlled silica-supported TiO₂ photocatalysts. *Journal of Photochemistry and Photobiology A: Chemistry*, 148(1), 315-322.
- Velasco, L. F., Parra, J. B., and Ania, C. O. (2010). Role of activated carbon features on the photocatalytic degradation of phenol. *Applied Surface Science*, 256(17), 5254-5258.
- Yagub, M. T., Sen, T. K., Afroze, S., and Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: a review. *Advances in colloid and interface science*, 209, 172-184.
- Yap, P. S., Lim, T. T., and Srinivasan, M. (2011). Nitrogen-doped TiO₂/AC bi-functional composite prepared by two-stage calcination for enhanced synergistic removal of hydrophobic pollutant using solar irradiation. *Catalysis Today*, 161(1), 46-52.
- Yuan, R., Guan, R., Liu, P., and Zheng, J. (2007). Photocatalytic treatment of wastewater from paper mill by TiO₂ loaded on activated carbon fibers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 293(1), 80-86.
- Zangeneh, H., Zinatizadeh, A. A. L., Habibi, M., Akia, M., and Isa, M. H. (2015). Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium dioxides: A comparative review. *Journal of Industrial and Engineering Chemistry*, 26, 1-36.
- Zhang, X., Zhou, M., and Lei, L. (2005). Preparation of photocatalytic TiO₂ coatings of nanosized particles on activated carbon by AP-MOCVD. *Carbon*, 43(8), 1700-1708.
- Zhang, Y., Liu, F., Lu, Y., Zhao, L., and Song, L. (2013). Investigation of phosphorylated TiO₂-SiO₂ particles/polysulfone composite membrane for wastewater treatment. *Desalination*, 324, 118-126.
- Zhong, J., Li, J., Zeng, J., Huang, S., Hu, W., Chen, J., ... and Zhang, S. (2014). Enhanced photocatalytic activity of sulfated silica-titania composites prepared by impregnation using ammonium persulfate solution. *Materials Science in Semiconductor Processing*, 26, 62-68.