Research Article

Mechanism of Degradation of Acidic Dyes in Industrial Effluents by a Nano-photo Catalytic Process with a Study of Intermediate Compounds

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Abstract The dye stuff lost in the textile industry poses a major problem to wastewater sources. This paper reports an investigation into the effect of a number of operating factors on the removal of Allura Red AC from an aqueous solution through photocatalysis Advanced Oxidation Processes (AOPs) are effective processes in treating waters polluted by a variety of harmful pollutants. This paper discusses about effect of the number of factors on removal of Allura Red AC from an aqueous solution using a photcatalytic process. The photcatalyst used in this solution was WO_3/TiO_2. Optimal dose of the photocatalyst was $0.1gL^{-1}$, color concentration was $20mL^{-1}$, and pH was 7.0. Efficiency of the photocatalyst was tested by SEM methods. Post-treatment analysis by GC-MS studies showed intermediate compunds. Photocatalysis is an effective process in decoloration because of isochronous presence of some strong oxidants and their promoting effect through production of highly reactive active hydroxyl radicals (OH).

Keywords photocatalyst, Allura Red AC, GC-MS, photo degradation

Introduction

Due to increasing population growth accompanied by industrial and agricultural developments, the world is experiencing shortage of safe water. Hence, treatment and recovery of used water is especially important [1]. As industry and technology developed, the volume of industrial wastewaters increased and huge quantities of organic and inorganic pollutions released into wastewater. Wastewaters of chemical industries contain different materials and pollutions. Dyes are the most common form of organic pollutions, which are highly problematic due to their complex and stable structure [2]. Wastewaters of dye industries are complicated effluents containing chemicals, and their disposal poses severe environmental challenges [3]. In 1987, it was estimated that of 450000 tons of dyes, 2% in the phase of production and 92% in dyeing enter the wastewater. Under these conditions, 50000tons of dyes enter wastewater every year [4]. Conventional methods for treatment of dyes such as activated sludge, flocculation and biological fouling were used to destroy unsaturated bonds existing in the structure of dyes, but the end result was not satisfactory. In contrast, advanced oxidation processes such as photo catalytic reactions, ozonation and photon emission are able to degrade organic dyes in a relatively short and to a considerable extent [5]. AOPs with the aid of highly reactive hydroxyl radicals are able to attack and eliminate oxidable pollutions effectively and non-selectively [6]. In AOPs of hydroxyl ions, O_3, H_2O_2 or air are used as oxidant and ultraviolet waves as external energy. The main advantages of this method are prevention from contamination of crops in the environment; control the hazard of increased concentration of oxidants and high velocity of the process [7]. Empirical progressin oxidation operations resulted in using photcatalytic processes. In these processes, reactive radicals are produced through absorbing light by semiconductors [8]. In catalytic reaction, semiconductors can mineralize organic compounds perfectly, do not produce sludge, and they operate under mild temperature and pressure [9]. A variety of semiconductors such asTiO_2, ZnS,ZnO,ZnO_2, SrO_2, and CdS are used as catalysts in photo catalytic reactions [10, 11]. Among these catalysts, WO_3/TiO_2 is the most stable one, used in environmental reactions [12]. Owing to their

electronic structure, semiconductors act as photosensitizers in optical oxidation-reduction processes. In addition, photo catalytic degradation process can be accelerated in presence of H_2O_2. During the reaction, it can form hydroxyl radicals in presence of superoxide radicals [13, 14]. Furthermore, WO3/TiO$_2$ serves as a conduction band for the electron acceptor and form hydroxyl radicals [10]. The main phase of these reactions is production of electron holes in semiconductors [15].

$$H_2O_2 + WO_3/TiO_2\,(e^-) \rightarrow OH^{\bullet} + OH^- \qquad (1)$$

$$H_2O_2 + h^+_{VB} \rightarrow OH_2^{\bullet} + H^+ \qquad (2)$$

$$OH^{\bullet} + OH_2^{\bullet} \rightarrow H_2O + O_2 \qquad (3)$$

Parameters of these reactions are: pH, concentration of oxygen and WO_3/TiO_2. Selection of a suitable method for decoloration depends on type and concentration of the dye. In order to select a suitable decoloration method, plus efficiency of the method, economics and finished cost of implementing the process should also be taken into consideration [16].
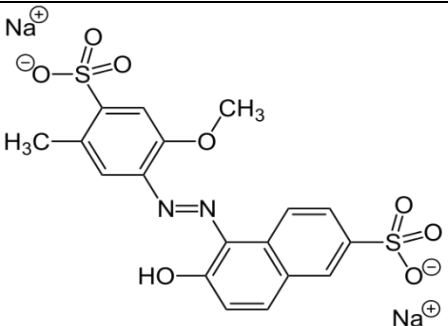
An aqueous solution including an Azo dye (Allura Red AC) was used in a photo catalysis process to analyze the effect of the number of parameters on removal efficiency of dye. The parameters are amount of photo catalyst (WO_3/TiO_2), pH, and dye concentration. A comparison was made between rates of removal by these parameters. Efficiency of the photo catalyst was tested by SEM. Also, the post treatment product was tested by GC-MS.

Experimental Work
Materials
Sulfuric acid, hydroxide acid and H_2O_2 used in the tests were procured from Merck$^{®}$ at an experimental purity grade. WO_3/TiO_2 was purchased from Mina Tajheez Aria Co. Allura Red AC with 85% purity grade was provided from Alvan Sabet Co. Table 1 shows the chemical structure of this dye (mono azo and molecular weight 350.32g/Mol). Concentration of the dye was measured by spectrophotometer Unico 4802- Double beam and by using calibration curve.

Table1: Chemical structure of dyes studied in this research

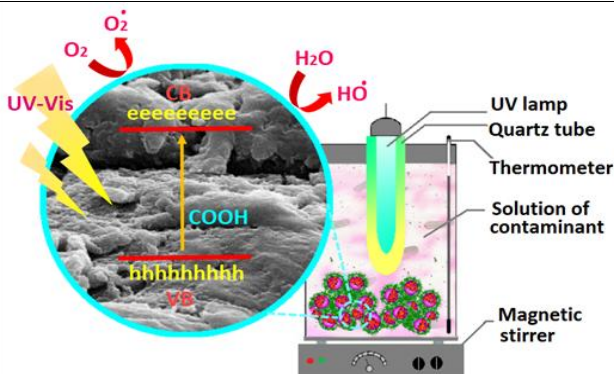| Molecular Formulae	$C_{18}H_{14}N_2Na_2O_8S_2$
Molar mass	496.42 g·mol^{-1}
CAS Number	25956-17-6
Appearance	Red powder
λ_{max} (nm)	504 nm

Figure1: Schematic representation of the reactor

Analysis products were tested through spectrophotometry (GC-MS) by GC 7890 Agilent and a capillary column HP-5 MS, 30 m x 0.25 mm equipped with Agilent Mass spectrometer 5973, functioning with an energy of 70 eV. The reactor (photo catalyst) was a 2L double glazed glass container covered by aluminum foil. A 9V lamp, purchased from Philips Co., The Netherlands, was placed in a single wall quartz tube fixed in the center of the reactor. A 4L tank connected to the reactor and a pressure pump controlled velocity of the solution flow. Figure 1 shows a schematic representation of the reactor.

Methodology

The aqueous solution was prepared by dissolving dye in distilled water. Then, WO_3/TiO_2 was added to the sample. pH of the solution was adjusted by NaOH and HCl. The sample entered the reactor and the UV lamp was put inside it.

The sample was exposed to photo catalysis process for 180 min. This was aimed to examine the number of factors on removal of Azo dyes. For this purpose, catalyst concentration, pH, and dye concentration were analyzed. The effect of catalyst concentrations ($0.02gL^{-1}$, $0.04gL^{-1}$, $0.08gL^{-1}$, $0.1gL^{-1}$, $0.12gL^{-1}$) on dye removal from solution was studied. Effect of pH was evaluated through adjustment of pH in 5 values: 2.5, 4, 6, 7, 8. To find out how dye concentration affects the rate of removal, 3 different values were used: $20gL^{-1}$, $30gl^{-1}$, $40gL^{-1}$.

Results and Discussion

Effect of Photo catalyst Concentration

When Nano photo catalyst is WO_3/TiO_2, two reactions should happen at the same time: a) oxidation from holes generated by light and b) reduction from electrons generated by light. If Nano photo catalyst remains unchanged, these processes should occur with a constant speed [17].
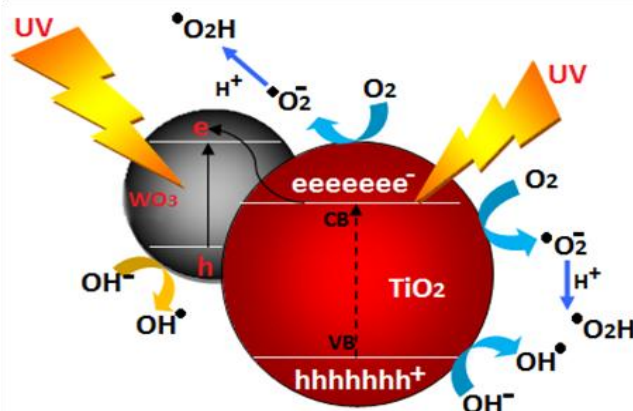

Figure2: Main process in semiconductor Nano photo catalyst of photon absorption and electron generation-hole charge separation and migration to locations of surface reaction or re-combination sites. Chemical surface reactions in reactive sites.

In the first key process in Fig. 2, photon absorption is electron hole pair generation. If an electron moves from conduction to valence balance, incident light energy should be higher than energy difference between these two bands. Success or failure of this phase depends on semiconductor band gap [17, 18].

One of the most principal factors to be noted in catalytic reactions is catalyst concentration. Effect of photocatalyston kinetic energy of degradation of Allura Red AC dye was analyzed through applying 5 doses of WO_3/TiO_2: 0.02, 0.04, 0.08, 0.1, and $0.12Gl^{-1}$. It was observed that photo catalytic degradation of azo dyes increased by using larger number of quantity of Nano particles. However, based on Fig.3, the last three values exhibit similar rate of removal. For this reason and from an economic viewpoint, $0.1gL^{-1}$ was selected as the optimal dose for suitable degradation of dye. Fig. 4 shows a comparison between speeds of dye removal. When WO_3/TiO_2 increases, decoloration also increases. Effect of quantity of photo catalyst can be explained this way. Increase in amount of photo catalyst leads to larger number of electron-hole pair, and consequently to more WO_3/TiO_2 reactive sites on the surface, resulting in higher number of $^\bullet OH$ and $^\bullet O_2$. These reactive radicals react with organic molecules and convert them to nontoxic simple materials [17, 19, 20].
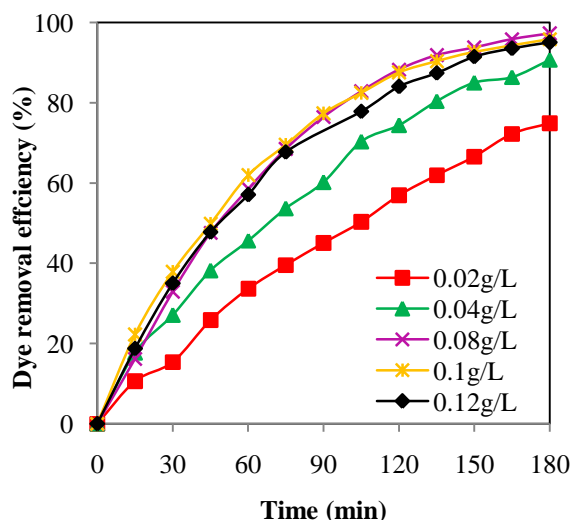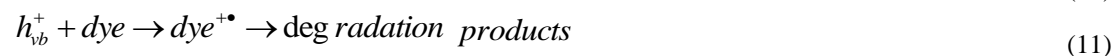
$$WO_3/TiO_2 + (hv) \rightarrow WO_3/TiO_2 + (h^+) + (e^-) \qquad (5)$$

$$h_{vb}^+ + H_2O \rightarrow {}^\bullet OH + H^+ \tag{6}$$

$$h_{vb}^+ + OH^- \rightarrow {}^\bullet OH \tag{7}$$

$$e_{cb}^- + O_2 \rightarrow O_2^{\bullet -} \tag{8}$$

$$2O_2^{\bullet -} + 2H_2O \rightarrow 2{}^\bullet OH + 2OH^- + O_2 \tag{9}$$

$${}^\bullet OH + dye \rightarrow \deg radation\ products \tag{10}$$

$$h_{vb}^+ + dye \rightarrow dye^{+\bullet} \rightarrow \deg radation\ products \tag{11}$$

Figure 3: Effect of concentration of WO$_3$/TiO$_2$ on degradation of Allura Red AC: 180min, dye concentration: 20 mgL^{-1}, pH=7, temperature=25°C)
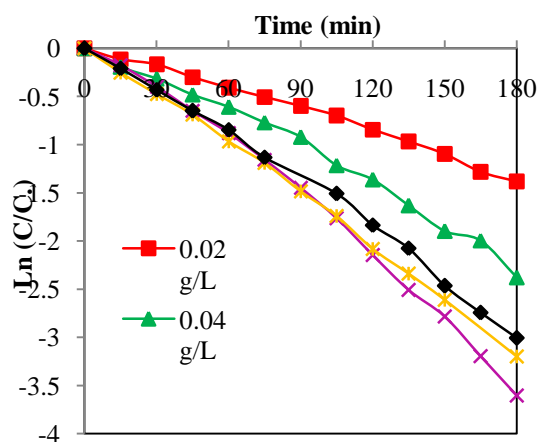

Figure4: Comparison between rates of removal for various concentrations of WO$_3$/TiO$_2$ (contact time: 180min, dye concentration: 20 mgL^{-1}, pH=7, temperature=25°C)

Effects of pH

Fig.5 shows effects of pH on removal efficiency of Allura Red AC. Five pH values were analyzed: 2.5, 4, 6, 7, 8. We observed that almost 91%, 94% and 97% of dye were removed in the following pH values: 2.5, 4, 6, respectively, after 180 min. This phenomenon can be explained in this way: as pH decreases, concentration of H ions increase, which it will lead to improved production of ${}^\bullet OH$ and ${}^\bullet O$ by photocataylist. However, it is quite clear that rate of removal is lower in pH greater than 7. This might happen because in greater pH, negatively charged surface of photocatalyst releases dye anion and reduces efficiency of phtocatalyst [21, 22].
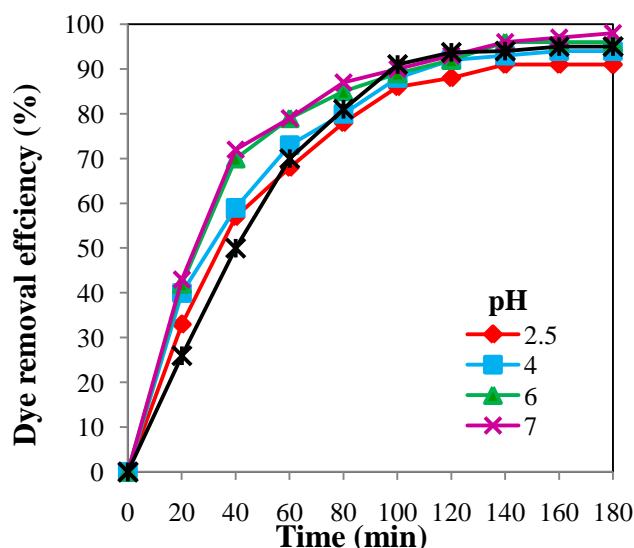
Figure5: Effect of Initial pH (i-pH) value on degradation of Allura Red AC (contact time: 180min, dye concentration= 20 mgL^{-1}, photocatalyst concentration = 0.1 mgL^{-1}, pH=7, temperature=25°C).

Effect of Dye Concentration

Three concentration values (20mgL^{-1}, 30mgL^{-1}, 40 mgL^{-1}) were used to study about effects of initial concentration of dye on efficiency of photocatalyst degradation. As shown from Fig 6, changes in initial concentration (20mgL^{-1}) will result in 97% dye removal after 180 min. However, rate of degradation reduces at greater concentrations. This is why increased dye concentration prevents photons from reaching the photocatalyst surface that itself stops formation of superoxide and hydroxyl radicals, which are responsible for absorbing dye molecules and reducing rate of removal [22-24]. Fig 6(b) shows reduction in concentration of Allura Red AC (wavelength 482 Hz in contact time from 0 to 180 min).
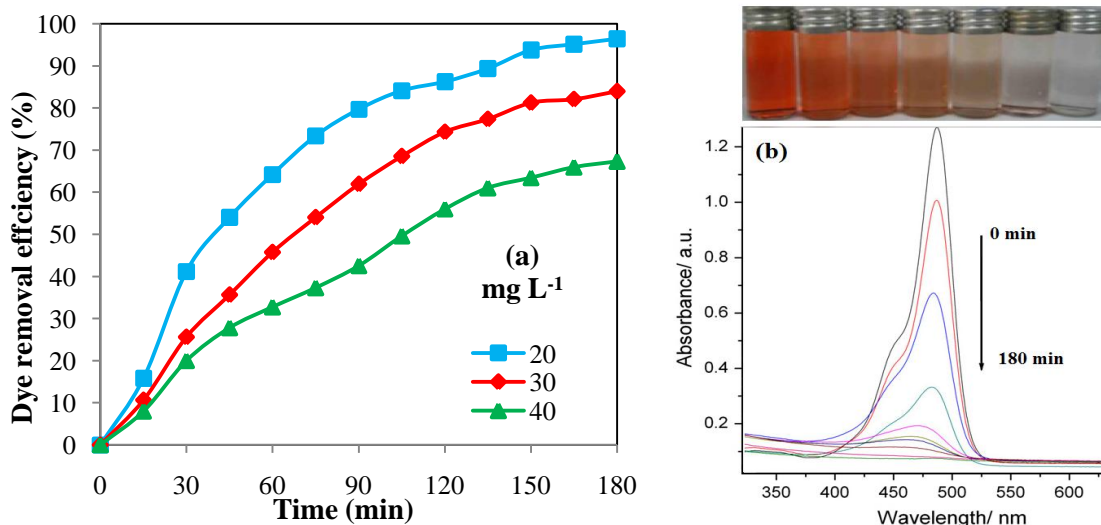

Figure 6: Effects of initial concentration on removal of Allura Red AC(contact time:180 min, photocatalyst:0.1gL^{-1}, pH=7, temperature=25°C).

Description of Photo catalysis Process: SEM Study

Composition of WO$_3$/TiO$_2$ on the Surface was determined by SEM before and after photocatalysis process. Fig 7b illustrates uniform distribution of fine particles with similar sizes. As Fig7b,c implies uniform particles of WO$_3$/TiO$_2$ are covered by dye.
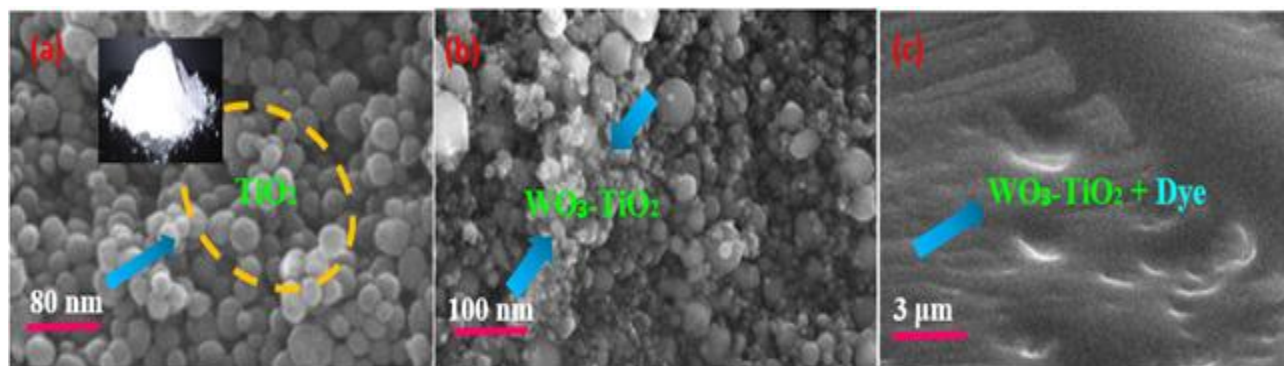
Figure7: SEM image, initial WO₃/TiO₂ (a), WO₃/TiO₂ following decoloration process

GC-SM Study

GC-SM study was carried out to identify the intermediate product produced during Allura Red AC treatment. Fig.8 shows the results about main intermediates products formed in the process.

Regarding the process, it can be said that $^•OH$ and $^•O$ attacks carbon atom in the dye molecule, which breaks down C-N bond to form 2-amino sulfonic acid (m/z 27), benzene (m/z 173), 3-amino 5 (4-amino 6-chloro-1,3,5-triazin, 2-yl) amino 4, hydroxynaphthalene-2-sulfonic acid methane ethyl (m/z 465). If photo catalysis continues, these organic compounds will be converted to CO_2, H_2O, SO_3, NO_2, NO_3, Na^+.
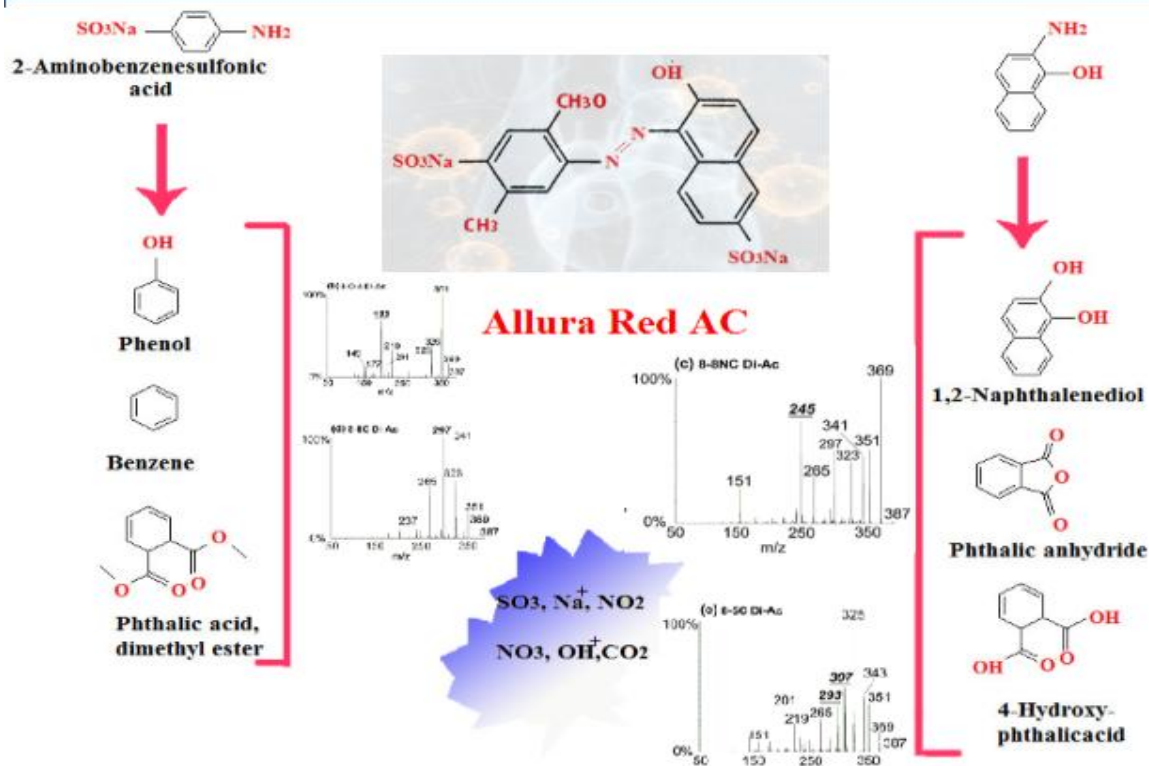

Figure 8: Mechanism of degradation of Allura Red AC (contact time:180min, dye concentration: 20 mgL⁻¹, pH=7, temperature=25°C)

Conclusion

In this study, photo catalytic degradation of azo dye (Allura Red AC) by WO₃/TiO₂ as a photocatalyst suspended in an aqueous solution was studied. Parameters of process are quantity of photocatalyst, dye concentration, and pH. It was observed that 0.1 mgL⁻¹ is the best concentration of Nano photocatalyst to remove dye and the best initial dye concentration is (20 mgL⁻¹) to remove maximum dye (97%). However, dye removal is lower in higher concentrations of photocatalyst. The efficiency of photocatlysis process was evaluated by SEM method. Post-

treatment products were tested by GC-MS studies. Consequently, intermediate compounds were identified and a reaction pathway was introduced for dye decomposition.

Reference

1. Yu C., Zhou W., Liu H., Liu Y., Dionysiou D D, 2016, Design and fabrication of microsphere photocatalysts for environmental purification and energy conversion, J Chem Eng, 287, 117-129.

2. Madhavan J., Maruthamuthu P**.**, Murugesan S., Ashokkumar M.,2009, Kinetics ofdegradation of acid red 88 in the presence of Co_2^+ ion/peroxomonosulphatereagent, Appl Catal. A., 368, 35–39.

3. Liao X., Chen J., Wang M., Liu Z., Ding L., Ye Li Y, 2016, Enhanced photo catalytic and photoelectrochemical activities of SnO_2/SiC nanowire heterostructure photocatalysts, J Alloy Compd., 658, 642-648.

4. Pandey A., Singh P. L., 2007, Bacterial decolorization and degradation of azodyes, Int. Biodeter. Biodegr., 59, pp. 73–84.

5. S. Meric, H., Selcuk M., Gallo V, 2005, Belgiorno, Decolourisation and detoxifying of Remazol Red dye and its mixture using Fenton's reagent, Desalination, 173, 239-248.

6. H Kusic., A.L Bozic., N Koprivanac, 2007, Fenton type processes for minimization of organic content in coloured wastewaters: Part I: Processes optimization, Dyes&Pigment, 74, 380-387.

7. Cheng M., Zeng G., Huang D., Lai C., Xu P., Zhang C., Liu Y, 2016, Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review, J Chem Eng., 284, 582-598.

8. Masschelein W. J., and R. G. Rice, 2002, Ultraviolet light in water and wastewater sanitation, 3-4. Lewis Publishers, Boca Raton, Fla.

9. Tachikawa T., Fujitsuka M., Majima T, 2007, Mechanistic insight into the TiO_2 photo catalytic reactions., Design of new photocatalysts, J Phys Chem. C 111, 5259–5275.

10. Bessekhouad Y., Robert D., Weber J.V, 2004, Bi2S3/TiO_2 and CdS/TiO_2 heterojunctions as an available configuration for photo catalytic degradation of organic pollutantJ., Photochem. Photobiol, A 163, 569 **.**

11. Tada H., Kokubu A., Iwasaki M., Ito S, 2004, Deactivation of the TiO_2 photocatalyst by coupling with WO3 and the electrochemically assisted high photo catalytic activity of WO_3, Langmuir 20, 4665.

12. Damodar R.A., Jagannathan K., Swaminathan Solar, T, 2007, Energy Decolourization of reactive dyes by thin film immobilized surface photoreactor using solar irradiation, Solar Energy 81, 1–7.

13. Tawabini B**.**, Zubair A, 2011, Bromate control in phenol-contaminated water treated by UV and ozone processes., Desalination, 267, 16–19.

14. Katsoyiannis I.A., Canonica S., Gunten U, 2011, Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O_3/H_2O_2 and UV/H_2O_2, Water Research, 46, 3811–3822.

15. Nosaka Y., Nakamura M., Hirakawa T,2002, Behavior of superoxide radicals formedon TiO_2 powder photocatalysts studied by a chemiluminescent probe method,Phys Chem Chem Phys, 4, 1088–1092.

16. Olya M.E., Pirkarami A., Soleimani M., Bahmaei, M, 2013, Photoelectrocatalytic degradation of acid dye using NieTiO2 with the energy supplied by solar cell: Mechanism andeconomical studies, J Environ Manage, 121, 210-219.

17. Malato S., Fernandez-Iban, P., Maldonado MI., Blanco J., Gernjak W, 2009, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends., Catal Today, 147(1), 1–59.

18. Bai S., Liu H., Sun J., Tian Y., Chen S., Song J., Luo R., Li D., Chen A., Liu C-C, 2016, Improvement of TiO_2 photo catalytic properties under visible light by WO_3/TiO_2 and MoO_3/TiO_2 composites, Appl Surf Sci., 338, 61-68.

19. Ito K**.**, Jian W., Nishijima W., Baes A.U., Shoto E., Okada M, 1998, Comparison of ozonation and AOPs combined with biodegradation for removal of THM precursors in treated sewage effluents., Water Science and Technology, 38, 179–18.

20. U F., Wei Y., Qiu Z., Sun F, 2011, Removal of Disperse Dyes from Wastewater by Nano-iron Modified Goldmine Waste-solid Assisted AOPs., Procedia Engineering, 18, 358–362.

21. Arami M., Livnaer N.Y., Mahamodi N.M., Tabrizi N.S., 2005, Removal of dyes from colourful textile wastewater by orange pell adsorbent: equation and kinetics studies, J Colloid Interface Sci, 288, 371–376.

22. Arami M., Limaee N.Y., Mahmoodi N.M., Tabrizi N.S, 2006, Equilibrium and kinetics studies for the adsorption of direct and acid of dyes from aqueous solution soya meal hull, J Hazard Mater, B. 135, 171–179.

23. Subramini A.k., Byrappa K., Ananda S., Lokanatha Rai K.M., C. Ragnathaiall C., Yoshimura M., 2007, Photo catalytic degradation of indigocaramine dye using TiO_2 impregnited activated carbon, Bull Mater Sci, 30, 37–41.

24. Goncalves M.S.T., Oliveira Campus A.M.F., Pinto E.M.M., Plesnica P.M.S., Queiroz M.J.R.P, 1999, Photochemical treatment of solution of azo dyes containing TiO_2, Chemosphere 39, 781–786.