



Comparing the Efficiency of Nanostructured Pure ZnO and Modified ZnO with Silver Metal ion in the Photocatalytic Degradation of Acridine Orange Dye from Wastewater

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Abstract

Recently, industrialization and environmental pollution on a global scale have drawn attention to the essentiality of developing eco-friendly purification techniques. The existing wastewater treatment techniques required high capital costs for operation & maintenance. Cost-effective treatment technologies need to transform the hazardous substances into benign forms. Moreover, minimizing the adverse effects of the produced subsequent those are mostly toxic, persistent, and difficult to treat. This study describes a treatment method for acridine orange (AO) dye degradation and decolorization in wastewater under UV-Visible light utilizing both pure ZnO and Ag⁺ doped ZnO. UV-Vis spectrophotometry has been used to study the photodegradation processes of the dye. Several characterizing parameters were studied as initial dye concentration, initial pH values, amount of catalyst, and the abundance of Na₂SO₄ and NaCl. The catalysis effect of both pure ZnO Ag⁺ doped ZnO has been compared. The degradation efficiency and optimum conditions had been determined. The obtained results revealed that Ag⁺ doped ZnO is much more efficient in dye degradation than the pure form catalyst ZnO.

Key Words: Wastewater, Treatment, Acridine, ZnO, ZnO doped Ag ions, photodegradation

1. Introduction

Introduction

Water is considered as a backbone and essential requirement in all domestic, industrial and commercial activities. The generated wastewater from such processes contains a wide range of pollutants according to the type of the process. Most of the emitted effluents from these activities are intensely colored and loaded with a high concentration of organic and inorganic pollutants such as dissolved and suspended salts beside many other recalcitrant contaminants. Among the advanced oxidation processes (AOPs) the heterogeneous photocatalysis is considered a promising methods that can be used for organic pollutants degradation in water and wastewater. Some activities like textile and dyestuff industries release about (10 – 15%) of total amount of dyes that directly discharged into water streams. The safe disposal of these effluents is a major concern for environment and consequently to human health [1]. There several types of the commercial dyes that can be classified into cationic (basic dyes); anionic (direct, acid and reactive dyes) and nonionic (disperse

dyes). These dyes are characterized with having a structure of an aromatic molecular complex. Moreover, these dyes are classified based on their chromophore that refers to the component responsible colorization. Many colored dyes can be detected in wastewater effluent such as arylmethane, azo, acridine, anthraquinone, phthalocyanine, triphenylmethane, heterocyclic, nitro, nitroso, cyanine, quinone-imine, xanthene or thiazole dyes [2,3]. The cationic triphenylmethane dyes are the most famous that have been used extensively in the industrial process as colorants and antimicrobial agents [4]. Acridine orange (AO) dyes are an organic compound that serves as a nucleic acid-selective fluorescent dye with cationic properties useful for cell cycle determination. They are very similar spectrally to an organic compound known as fluorescein. They are mostly used in medicine and biology for staining solutions [5].

Different treatment methods have been extensively applied for dye-containing waste water treatment such as: biological treatment including aerobic and anaerobic techniques, incineration, AOPs including ozonation and peroxidase techniques and adsorption on solid phases. However, these treatment methods have several disadvantages and limitations. The biological treatment requires large area, long

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Receive Date: 22 November 2021, Revise Date: 04 December 2021, Accept Date: 02 January 2022

DOI: 10.21608/EJCHEM.2022.107313.4929

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periods of treatment and offensive smell; AOPs shows a short half-life, beside the presence of salts can affect ozone stability; adsorption on solid phases might be strongly affected by the change in pH and temperature. All these drawbacks may lead to contaminants transference not degradation and consequently producing sludge [6–9]. Based on the above mentioned, the heterogeneous photocatalysis represents an elegant alternative treatment for wastewater containing dyes degradation. This method exhibits many advantages over all conventional treatment techniques in dye degradation into final innocuous products [10].

Recently, the advanced oxidation processes (AOPs), that the alternative to non-destructive methods is "advanced oxidation processes" (AOPs), that based on the generation of highly reactive hydroxyl radical species that acts on oxidizing a wide range of organic pollutants in a quick and non-selective manner [11–14]. The combination of semiconductors from metal oxides such as (ZnO, TiO₂, Fe₂O₃, etc.) with UV light is considered a good example of AOPs photocatalysis systems. The importance of semiconductors are due to their metal atoms electronic structure in chemical combination, that characterized by an empty conduction band and filled valence band [15]. ZnO and TiO₂ are the most important semiconductors and ideal photocatalysts where they have a wide band gaps. Moreover, these metal oxides are chemically stable and environmentally friendly materials. However, in some cases, Zn oxides show better degradation capacity than Ti oxides [16–19]. ZnO is much favorable than TiO₂ due to its ability to absorb a larger UV spectrum fraction and consequently more light quanta [20]. Besides, the fast electron hole pair recombination in TiO₂ could also limit its efficiency. Several researches reported the higher ZnO photocatalytic activity in the degradation of organic pollutants in aqueous solutions compared to TiO₂ [21,22].

The photocatalytic efficiency of ZnO can be enhanced via different physico-chemical techniques like designed shape controlling, surface area increasing; doping another atom into the lattice leading to separation of electron-hole pairs [23 - 26]. It is known that Ag acting as electron sinks that can trap the photo-excited electrons from the semiconductor and diminishing the charge recombination process. Thus, Ag⁺ doped ZnO molecules could improve the photocatalytic activities of ZnO [27, 28].

The main aim of this study is to investigate the catalytic activity, and optimum conditions for both pure form catalyst ZnO and modified form of ZnO doped with Ag⁺ in the degradation of (AO) dye in wastewater.

From the reaction kinetics we proved that the photocatalytic degradation follows a pseudo-first

order reaction and can be expressed through the equation; $\ln(C_0/C_t) = kt$, where k is the rate constant of the apparent reaction, C_0 is AO initial concentration, t is time of the reaction and C_t is AO concentration at the reaction time t [29].

The efficiency of dye degradation can be calculated using the following equation:

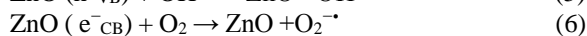
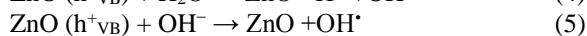
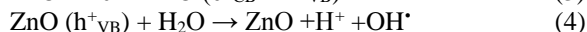
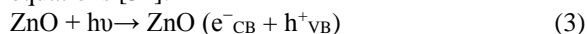
$$\text{Degradation rate (\%)} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

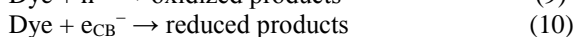
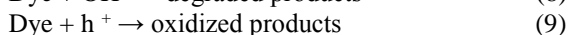
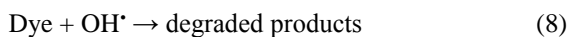
$$= \frac{A_0 - A_t}{A_0} \times 100\% \quad (2)$$

where C_0 is the initial concentration, C_t is the variable concentration at time t , A_0 is the initial absorbance, and A_t is the variable absorbance at time t .

Mechanism of Photocatalysis.

Photo-induced reaction is the actual term referring to photocatalysis process in which the reaction that could be accelerated by the catalytic [30]. The mechanism of these reactions is enhanced by photon absorption with sufficient energy that may higher than or equal to the band-gap energy (E_{bg}) of the catalyst [31]. This absorbed energy leads to a separation of the charge because of electron promotion (e^-) from the valence band to the conduction band forming a hole (h^+) generating in the valence band of the catalyst semiconductor. In case of photo catalyzed reaction the recombination between a hole and electron must be prevented as much as possible to enhance the photocatalysis process. To produce an oxidized product the reaction should occur between the generated holes and the reductant. Whereas, for producing a reduce product the reaction should occur between the activated electrons with an oxidant. The main role of the photo-generated electrons is to reduce the dye or to react with electron acceptors as oxygen molecule (O_2) that adsorbed on the surface of Zn(II). In some cases it dissolves in water, forming a superoxide radical anion $O_2^{\cdot-}$ [32,33]. However, The photo-generated holes acts on oxidizing the organic molecule to form R^+ . Also, it could produce a hydroxyl radical (OH^{\cdot}) through oxidizing H_2O or OH^- . The heterogeneous ZnO photodecomposition process of organic substrates as dyes could be due to the presence of strong oxidizing agents as peroxidase forming OH^{\cdot} radicals. These radicals have a standard redox potential of (+2.8V) that have the ability to oxidize most dye compounds to their mineral end-products. Based on the above mentioned, the relevant reactions at the surface of semiconductor causing dye degradation could be expressed from the following equations [32]:





where $h\nu$ is the required photon energy to excite the semiconductor electrons from the valence band (VB) level to conduction band (CB) level.

Materials and Methods

Materials.

All purchased chemicals were used without any further purification as-received condition.

Acridine orange dye (Sigma-Aldrich). Linear Formula: C₁₃H₉N. Molecular Weight: (179.13 g/mol). Color Index Number: 46005. CAS Number: 494-38-2. IUPAC: 3-N,3-N,6-N,6-N-Tetramethylacridine-3,6-diamine. Alternative name: 3,6-Acridinediamine.

Zinc sulfat-7-hydrat(Zn(SO₄).7H₂O) (Riedel), Silver Nitrate (AgNO₃), Sodium Carbonate anhydrouse (Na₂CO₃), NaOH, H₂SO₄ , NaCl, Na₂SO₄ and Ethanol were of analytical reagent grade and purchased from Merck.

Preparation of photocatalysts

Ag⁺ doped ZnO could be prepared by precipitation method. Dissolve Na₂CO₃ and Zn(SO₄).7H₂O separately in a double distilled water to get 0.5mol/l solutions .Slowly add Zinc sulfate solution to the vigorously stirred Na₂CO₃. Also, add AgNO₃ in the required stoichiometry to the prepared solution until a gray precipitate is formed. Then, filter the precipitate, and rinse with distilled water repeatedly. Finally, wash twice with ethanol. Dry the resultant solid product for 12h at 100 °C and make calcination for 2h at 600(+2) °C. The preparation of ZnO particle can be also performed throughout the same method but without addition of AgNO₃ solution [29].

Preparation of stock solution.

Weight ~0.05 g of Acridine orange into a 50 ml beaker. In a 1 L volumetric flask dissolve the AO dye in double distilled water and dilute it to a 1 L.

Catalyst Characterization.

In Fig. 2 the XRD patterns shows undoped ZnO and Ag⁺ doped ZnO samples. This pattern reveals the crystal structures of both oxides doped and undoped as a hexagonal primitive wurtzie structure including two oxygen and two zinc atoms per unit cell (space group P6_{3mc} (186) [1, 2]. According to the structure of hexagonal wurtzie, the intensity of the strong peak and the narrow width of the line imply a good crystallinity [3, 4]. The XRD patterns do not show peaks of metallic Ag of doped ZnO at 38.1° (111), 44.3° (200), etc., (JCPDS 89-3722). This could

be due to the low content of Ag incorporating ZnO. Silver is unusually to be found as Ag₂O in the prepared Ag⁺ doped ZnO. At 600 °C the doped oxide doped Ag has been calcined where at 400 °C the Ag₂O was decomposed to Ag. However, at annealing temperature more than 600 °C, a partially out diffusion has been occurred for the silver dopants and form silver clusters as well. Moreover, at the annealed degree of temperature ≥ 600 °C, there is no characterized peaks related to Ag could be observed. This finding could indicate the instability of Zn atom substitution by Ag ions at high degrees of temperature, which considered as a significant limitation for using Ag as the dopant of Zn oxides [5].

Ag ions might be incorporated into the lattice of ZnO either at substituent or interstitials for Zn²⁺[6].

The structural analysis of pure ZnO and d Ag⁺ doped ZnO can be shown in Table1. The least squares refinement method was used from which unit-cell parameters were calculated using 9 well-defined diffraction lines in the hexagonal system indexation. The replacement of Zn atoms by Ag ions may cause a little change of the lattice parameters; as the *c*-axis shrinked whereas the *a*-axis enlarged. Consequently, the volume of the unit cell was increased almost by 1.5% for Ag⁺ doped ZnO sample as shown in Tab.1. These lattice changes may be attributed to the substitution process of Zn²⁺ions having radius of 0.74 Å by Ag⁺ ions having radius of 1.26 Å [7].These results revealed that the obtained values are very close whether there is a slight deviation from those of pure ZnO, which referred to Ag ions were successfully occupied the sites of the lattice rather than interstitial ones. Moreover, the Ag ions formation energy on the substitutional sites was lower than those at the interstitial sites. Thus, substitutional sites were preferred to be occupied by Ag ions [8]. It is a good point to remark that for different dopants the variation of the lattice parameter is very similar [9]. The XRD patterns of the inserted portion showed that the peaks of the Ag⁺ doped ZnO samples shifted towards lower angles ($2\theta = 28 - 40^\circ$). Moreover, the peak patterns for pure ZnO and Ag⁺ doped ZnO illustrating a shifting of the lattice parameter as shown in Fig.2. There are several reasons behind this peak broadening and shifting that may be attributed to the lattice distortion, lattice mismatching, crystal strain, and the effect of the finite size.

Generally, there are several factors can affect to the beaks broadening in X-ray diffraction. We can classify such them into (i) instrumental factors that related to the resolution and the incident X-ray wavelength, (ii) sample factors that related to crystallite size and non-uniform microstrain, might cause a peak broadening [10, 11]. The peak width was smoothly varied with 2θ or *d* spacing in the case of instrumental related factors. However, in case of sample related factors the peak

broadening could have a different relationship. From which, we can estimate the relation between the crystallite size and microstrain components through gathering the Scherrer's equation for crystallite size and the Bragg's law for diffraction, as the following equation:

$$B^2 \cos^2 \theta = 16 \langle e^2 \rangle \sin^2 \theta + \frac{K^2 \lambda^2}{L^2} \quad (11)$$

where B is representing the full-width at half-maximum (FWHM) after correction of the broadening related to the instrumental factors for silicon fine powder material, θ is the diffraction angle, and K is a constant of near-unity that related to crystalline shape. For the pure ZnO and its Ag doped ZnO, Fig. 3 represents the first member plot as a function of $\sin^2 \theta$. The appeared plots were well fitted by straight lines; this finding was in agreed with Eq. (11). The value of $\langle e^2 \rangle$ could be provided from the slope of the linear fit of the data. Whereas, the value of the coherence length L could be provided from the extrapolation of $\sin^2 \theta = 0$. From which, we could estimate that the Bragg lines integral breadth of Ag doped ZnO were slightly greater than undoped ZnO, that predicts a higher microstrain content and smaller grain size as shown in Table 1.

Photodegradation experiments of dye.

A photoreactor (phocat 120.0) was used to carry out the degradation experiments by addition of photocatalyst to 100 ml dye solutions in dark for 30 min with continuous stirring under ambient conditions to achieve the adsorption equilibrium on the photocatalyst surface. Then withdraw about 5 ml of the sample from the suspended solution at time intervals for measuring the absorbance at the maximum AO dye absorption wavelength of about 487 nm. Just before any absorbance measurement a sample centrifugation should be carried out to isolate the photocatalyst from the heterogeneous solution for 10 min at 4000 rpm to completely remove the particles of the catalyst.

Results and Discussion.

The loading effect of the photocatalyst.

The kinetic degradation effect of photocatalyst on AO was investigated through applying variable concentrations doses of the photocatalyst for both pure ZnO form and Ag⁺ doped ZnO as well ranged from 0.5 to 2.5 g/l at constant initial dye concentration of 20 ppm. The obtained results showed the degradation rate of the AO was increased at the beginning of

catalyst dose concentration due to increasing the number of active sites on catalyst surface that in turn leading to the increases of the number of OH[•] and OH₂[•] radicals causing a significant increase in the photodegradation rate. However, with increasing the catalyst concentration more than a certain limit then the degradation effect was decreased this may be due to the effect of the catalyst particles aggregation causing a decrease in the active sites number of the catalyst surface. Moreover, these aggregations may cause a light scattering leading to decrease the probability of the irradiated light passage through the sample that means the reduction of the photonic flux within the irradiated solution leading to decrease in degradation rate. The obtained results from Table.2 and Figs. 4 (A&B) revealed that the optimum catalyst concentration is 1.5 g/l for both pure ZnO and Ag⁺ doped ZnO, respectively.

Effect of initial dye concentration.

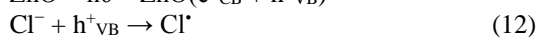
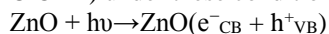
The degradation rate of AO was studied through the variation of AO concentrations from (10ppm to 20ppm) at constant catalyst loading of 1.5g/l. Table.3 and Figs. 5 (A&B) showed the maximum degradation rate was obtained at 16 ppm for both pure form of ZnO and Ag⁺ doped ZnO, respectively. However, the degradation efficiency was decreased with increasing the AO dye concentration. This adverse effect could be explained at high concentration of AO dye, the adsorption equilibrium on the surface of the catalyst active sites increases, then the competitive adsorption of H₂O, OH⁻, and O₂ on the same surface sites decrease, this will lead to a lower OH[•] radical formation, that is the main oxidant responsible for a high degradation efficiency. Whereas, with increasing the initial AO concentration levels, the light photon adsorption on catalyst particles decrease due to the decreasing of the path length of photons entering the solution, resulting in lower photon adsorption on catalyst particles and consequently a lower photodegradation rate considering the Beer-Lambert law.

Effect of Inorganic salts.

a. Effect of NaCl.

The dissolved inorganic ions are normally occurred in the industrial wastewater containing dyes. In this work we studied the effect of NaCl on the degradation rate of AO dye in the range of 0.0-2.5 g/l (16ppm) and catalyst concentration constant of 1.5g/l. The obtained results revealed that the AO degradation rate was decreased with increasing NaCl concentration for both catalysts, as shown in Table 4 and Figs. 6 (A&B) for pure form of ZnO and Ag⁺ doped ZnO consequently. The inhibition effect resulting from the

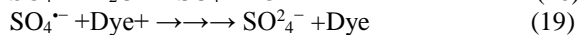
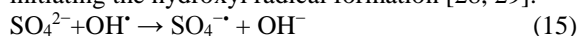
reaction between positive holes of hydroxyl radical (OH^\bullet) and ions can be explained from the equations from (12) to (14) in which h_{VB}^+ and OH^\bullet behaved as scavengers causing a prolonged color removal. The adsorbed ions might be competed with AO dye for the photo-oxidizing species on the catalyst surface causing a photocatalytic degradation preventing of the dyes [35-37]. There is an increasing probability of inorganic radical ions formation as (e.g. Cl^\bullet , $\text{Cl}_2^{\bullet-}$ and ClOH^\bullet) under these conditions [38]



Although the reactivity of these anion radicals might be taken in consideration, but they are not reactive as OH^\bullet because of their lower potentials of oxidation. Besides, the occurrence of high concentrations of scavenging radicals of (Cl^-) could drastically retard the advanced oxidation reactions [34-37].

b. Effect of Na_2SO_4 .

In this work we studied the effect of addition of different concentrations of Na_2SO_4 on the degradation rate of AO at 16ppm in the range of (0.0 - 2.5 g/l) and catalyst concentration constant (1.5g/l) for both pure ZnO and Ag^+ doped ZnO. Table.5 and Figs.7 (A&B) showed the photo-degradation efficiencies were firstly increased with increasing sulphate ions concentration. However, at high levels of sulphate ions concentration the rate of photo-degradation was decreased for both forms of pure ZnO and Ag^+ doped ZnO respectively. This might be attributed to the direct or indirect chemical formation of $\text{SO}_4^{\bullet-}$ that can explained through Eqs. (15) – (20). Previous literature studies showed that the generated in situ radicals could strongly act as efficient oxidizing agent and/or initiating the hydroxyl radical formation [28, 29].



The formed sulphate radical anion ($\text{SO}_4^{\bullet-}$) considered as a very strong oxidant ($E^0 = 2.6\text{eV}$), thus could react with dye [29,30]. Moreover, it could generate hydroxyl radicals and/or trap the photo-generated electron. These powerful oxidants could easily degrade the dye molecule, degrade [31]. Dye molecules have a great tendency to be attacked by $\text{SO}_4^{\bullet-}$ radical at various positions and then fragment them further. With increasing the concentration of sulphate ions the degradation rate was significantly decreased because of adsorption process that occurs for the excess sulphate ions on the catalyst surface causing catalyst section deactivation [32].

Effect of pH

The industrial wastewater emitted from textile facilities usually has a variable pH values. Moreover, the hydroxyl radicals' formation is also pH dependent reaction. So, pH values play an important role for both textile wastewater characterization and hydroxyl radicals' generation. The effect of pH on the photocatalytic degradation process can be hardly interpreted due to its multiple roles including the electrostatic interactions between solvent molecules, solvent molecules, surface of semiconductor, and charged radicals generated throughout the reaction process. In this work, we studied the photo catalytic degradation of AO under the effect of pH range (3.2, 5.2 (aqueous), 6.6 and 7.6) at a fixed dye concentration of (16 ppm) and catalyst loading of (1.5g/l) for both forms of pure ZnO and Ag^+ doped ZnO. The pH of the solution could be previously adjusted before the irradiation process using a dilute aqueous solution of H_2SO_4 or NaOH and not recommended to be controlled through the course of the reaction. Table 6 and Figs. 8 (A&B) for were showed that for both forms of pure ZnO and (B) for Ag^+ doped ZnO and the photocatalytic degradation of AO dye was increased at lower pH values that may be attributed to the generation of hydroxyl and sulphate radical that are powerful oxidant and have the ability to degrade the dye molecule. Whereas, with more slight increasing of pH values the degradation rate was sharply decreased due to adsorption process that may occurs near pH = 5 for the excess sulphate ions on the catalyst surface causing catalyst deactivation. However, with continuous increasing in pH (> 6.5) the degradation efficiency was significantly increased due to the presence of a huge amount of OH^- ions leading to formation of more OH^\bullet radicals, that could enhance the photocatalytic degradation of AO dye [40].

Photocatalytic degradation.

The photo-catalytic degradation for aqueous solutions of acridine orange dye (16 ppm) could be achieved by (38.0)% and (92.5)% using UV-Vis irradiation for 10 min in the presence of both forms of photo-catalysts pure ZnO (1.5 g/l) and Ag^+ doped ZnO (1.5 g/l) respectively, that can be shown in Fig.9. The degradation efficiency of pure form ZnO Ag^+ was much lower than that of doped ZnO under the same conditions. The degradation efficiency of AO dye was improved in the presence of photo-catalytic activity of Ag^+ doped ZnO than that of pure ZnO. This efficiency improvement might be attributed to the effect of Ag that has the ability to act as electron scavengers by the effect of electron trapping. This reduction potential of Ag could reduce the charges recombination and enhance the OH^\bullet production and stimulating the oxidation process. Moreover, throughout the reaction

the metallic silver was produced on the surface of ZnO and this can be easily observed from the surface darkness during the irradiation process then consequently leading to increasing the degradation efficiency [20- 23].

Conclusion

In the work, we studied the degradation efficiency of acridine orange dye in the presence of photo-catalysts of pure form ZnO and Ag⁺ doped ZnO. These photo-catalysts nanoparticles were prepared through Co-Precipitation method. The physical properties of the prepared were characterized by XRD instrument. The obtained results showed that Ag⁺ doped ZnO nanoparticles exhibited a significant improvement in the degradation efficiency of AO dye than that obtained from the pure form of ZnO nanoparticles under the same conditions and UV- Visible light. The photodegradation kinetics was performed. The first-order kinetics was observed throughout the photodegradation reactions that obviously corresponded to the assumption of the Langmuir–Hinshelwood kinetics type mechanism.

The influence of several parameters affecting the photocatalytic degradation of AO dyes using Photocatalysts were studied like catalyst concentration, initial dye concentration, pH and inorganic salt such as Cl⁻, SO₄²⁻ then consequently the optimum conditions were reported.

References

1. Ganesh K.C., Poornima M., Joveeta J.V. and Uma M. S. Decolorization and biodegradation of triphenylmethane dye, brilliant green, by *Aspergillus* sp. isolated from Ladakh, India. *Process Biochemistry*, **47**, 1388–1394 (2012).
2. Wong, Y. and Yu, J. Laccase catalyzed decolorization of synthetic dye. *Water Research*, **33**, 3512–20 (1999).
3. Aksu, Z. Application of biosorption for the removal of organic pollutants: a review. *Process Biochemistry*, **40**, 997–1026 (2005).
4. Eichlerova I, Homoika L. and Nerud F. Ability of industrial dyes decolorization and ligninolytic enzymes production by different *Pleurotus* species with special attention on *Pleurotus calyptratus* strain CCBAS 461. *Process Biochemistry*, **41**, 941–6 (2006).
5. Duxbury, D. F. The photochemistry and photophysics of triphenylmethane dyes in solid and liquid media. *Chem. Rev.*, **93**(1), 381–433 (1993).
6. Green, F. J. The Sigma–Aldrich Handbook of Stains, Dyes, and Indicators, Aldrich Chemical, Milwaukee, WI, **76** (1990).
7. Lee, J.K., Gu, J.H., Kim, M.R. and Chun, H.S. Incineration Characteristics of Dye Sludge in a Fluidized Bed Incinerator. *Journal of Chemical Engineering*, **34**, 171 (2001).
8. Garcia-Montaña, J., Torrades, F., Pérez-Estrada, L., Oller, I., Malato, S., Maldonado, M. and Peral, J. Degradation pathways of the commercial reactive azo dye Procion Red H-E7B under solar-assisted photo-Fenton reaction. *Environmental science and technology*, **42**, (17), 6663-6670 (2008).
9. Chu, W. and Ma, C.W. Quantitative prediction of direct and indirect ozonation kinetics. *Water Research*, **34** (12), 3153-3160 (2000).
10. Prado, A.G.S., Torres, J.D., Faria, E.A. and Dias, S.C.L. Comparative adsorption studies of indigo carmine dye on chitin and chitosan. *J Colloid Interface Sci*, **277**(1), 43-47 (2004).
11. Torres, J.D., Faria, E.A., Souza, J.R. and Prado, A.G.S. Preparation of photoactive chitosan–niobium (V) oxide composites for dye degradation. *Journal of Photochemistry and Photobiology*, **182**, 202-206 (2006).
12. Kuo, W. S. and Ho, P.H. Solar photocatalytic decolorization of methylene blue in water. *Chemosphere*, **45** (1), 77–83 (2001).
13. Legrini, O., Oliveros, E. and Braun, A.M. Photochemical processes for water treatment. *Chem. Rev.* **93**, 671–698 (1993).
14. Behnajady, M.A., Modirshahla, N. and Shokri, M. Photo destruction of Acid Orange 7 (AO7) in aqueous solutions by UV/H₂O₂ : influence of operational parameters. *Chemosphere*, **55**, 129–134 (2004).
15. Sohrabi, M.R. and Ghavami, M. Comparison of Direct Yellow 12 dye degradation efficiency using UV /semiconductor and UV /H₂O₂/ semiconductor systems. *Desalination* **252**, 157–162 (2010).
16. Chakrabarti, S. and Dutta, B.K. Photocatalytic degradation of model textile dyes in waste water using ZnO as semiconductor catalyst. *J. Hazard. Mater.* **112**, 269 – 278 (2004).
17. KHODJA, A., A., SEHILI, T., PILICHOWSKI, J. F. and BOULE, P. J. Photocatalytic degradation of 2-phenylphenol on TiO₂ and ZnO in aqueous suspensions. *J. Photochem Photobiol A*, **141**, 231-239 (2001).
18. DANESHVAR, N., SALARI, D. and KHATAEE, A. R. Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂ . *J. Photochem Photobiol A*, **162**, 317-322 (2004).
19. GOUVEA, C. A. K., WYPYCH, F., MORAES, S. G., DURAN, N., NAGATA, N. and PERALTA-ZAMORA P. Semiconductor-assisted photocatalytic degradation of reactive

- dyes in aqueous solution. *J. Chemosphere*, **40**, 433-440 (2000).
20. DINDAR, B. and ICLI, S. J. Unusual photoreactivity of zinc oxide irradiated by concentrated sunlight. *J. Photochem Photobiol A, Chem*, **140**, 263-268 (2001).
 21. Curri, M.L., Comparelli, R., Cozzoli, P.D., Mascolo, G. and Agostiano, A. Colloidal oxide nanoparticles for the photocatalytic degradation of organic dye. *Materials Science and Engineering C*, **23**, 285-9 (2003).
 22. Yu, J.G. and Yu, X.X. Hydrothermal synthesis and photocatalytic activity of zinc oxide hollow spheres. *Environmental Science and Technology* **42**, 4902-7 (2008).
 23. Sakthivel, S., Neppolian, B., Shankar, M.V., Arabindoo, B., Palanichamy, M. and Murugesan, V. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂. *Solar Energy Materials and Solar Cells*, **77**, 65-82 (2003).
 24. Chiu, W.S., Khiew, P.S., Cloke, M., Isa, D., Tan, T.K., Radiman, S., Abd-Shukor, R., Abd Hamid, M.A., Huang, N.M., Lim, H.N. and Chia, C.H. Photocatalytic study of two-dimensional ZnO nanoparticles in the decomposition of methylene blue, *Chemical Engineering Journal*, **158**, 345-352 (2010).
 25. Yang, L.Y., Dong, S.Y., Sun, J.H., Feng, J.L., Wu, Q.H. and Sun, S.P. Microwave-assisted preparation, characterization and photocatalytic properties of dumbbell-shaped ZnO photocatalyst, *Journal of Hazardous Materials*, **179**, 438-443(2010).
 26. Sun, J.H., Dong, S.Y., Feng, J.L., Yin, X.J. and Zhao, X.C. Enhanced sunlight photocatalytic performance of Sn-doped ZnO for methylene blue degradation, *Journal of Molecular Catalysis A*, **335**, 145-150 (2011).
 27. Kong, J.Z., Li, A.D., Li, X.Y., Zhai, H.F., Zhang, W.Q., Gong, Y.P., Li, H. and Wu, D. Photodegradation of methylene blue using Ta-doped ZnO nanoparticle. *Journal of Solid State Chemistry*, **183**, 1359-1364 (2010).
 28. Zhou, G. and Deng, J. Preparation and photocatalytic performance of Ag/ZnO nanocomposites. *Materials Science in Semiconductor Processing*, **10**, 90-96 (2007).
 29. Zheng, Y., Zheng, L., Zhan, Y., Lin, X., Zheng, Q. and Wei, K. Ag/ZnO heterostructure nanocrystals: synthesis, characterization, and photocatalysis. *Inorganic Chemistry*, **46**, 6980-6986 (2007).
 30. Anandan, S., Vinu, A., Sheeja Lovely K.L.P., Gokulakrishnan, N., Srinivasu, P.T., Moria, V. Murugesan, Sivamurugan, V. and Ariga, K. Photocatalytic activity of La-doped ZnO for the degradation of monocrotophos in aqueous suspension: *Journal of Molecular Catalysis A: Chemical*, **266** 149-157 (2007).
 31. Mills, A. and Hunte, L. An overview of semiconductor photocatalysis. *J. Photochem. Photobiol. A: Chem.*, **108**, 1-35 (1997).
 32. Carp, O., Huisman, C.L. and Reller, A. Photoinduced reactivity of titanium oxide photoinduced reactivity of titanium oxide. *Solid State Chem.*, **32**, 33-177 (2004).
 33. 32. Konstantinou, I.K. and Albanis, T.A. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—A review. *Appl. Catal. B: Environ.*, **49**, 1-14 (2004).