JISSE
ISSN: 2636-4425

Journal of International Society for Science and Engineering
Vol. 3, No. 4, 88-95 (2021)

JISSE
E-ISSN:2682-3438

Photocatalytic degradation of dye wastewater with ZnO nanoparticle: Optimization

Amal Zaher[1], Heba I. Elkhouly[2]

[1] Environmental Science and Industrial Development Department, Faculty of Postgraduate studies for Advanced Sciences, Beni-Suef University, 62511 Beni-Suef, Egypt.

[2] Department of Mechanical Engineering, Faculty of Engineering, Beni-Suef University, 62511 Beni-Suef, Egypt

ARTICLE INFO

Article history:
Received:20-11-2021
Accepted:01-12-2021
Online:01-12-2021

Keywords:
Nano-ZnO
UV radiation
Dye degradation
Photocatalysis, Optimization

ABSTRACT

Treatment of effluent from dye industry by heterogeneous photocatalysis with Zinc oxide (ZnO) nanoparticle under direct solar light has been estimated. ZnO photocatalyst were prepared by sol–gel process using zinc acetate as precursor the calcination temperature was 350 °C , then characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and employed for removal of methyl orange (MO) dye from industrial wastewater. The influence of parameters such as pH, concentration of MO and photocatalyst dose was studied. 98.6% was the degradation percentage. The results showed that the degradation percent of methyl orange dye increased with increasing catalyst dosage and initial concentration up to 5 mg/l and 10 mg/l respectively, the acidic condition is favorable for photo-degradation of dye and better discoloration of it under UV light. Applied regression analysis model to estimate the effective and optimal parameter, the results shows a good agreement between the experimental and theoretical results. It was concluded that the photocatalytic process can be applied at large scale industrial wastewater

1. Introduction

Large quantities of fresh water had been consumed during the processing operations in the textile industry. Textile industry pollute the water resources and discharge of several kinds of dyes that leading to bad effect on the environment [1]. Textile wastewater contains many chemicals and dyes that make the effluents of textile industry consider as an environmental challenge [2,3]. Azo dye considers about half of the dyes applied in the textile industry and methyl orange was a typical azo dye,[4-7]. Thus, textile wastewater treatment became complicated and difficult. There are several methods for treating of wastewater. Physical methods (adsorption on activated carbon, ion exchange, coagulation….. etc.) could be applied efficiently for the removal of dyes[8] .Physical methods are methods that transfer organic pollutants from liquid to solid phase, therefore resulting in secondary pollution. Chemical methods using strong oxidants like ozone or chlorine have led to effective results, but they are considered more expensive due to using the high dosages. Biological methods are not effective methods because of the large content of aromatics compounds in the dye[9]. There are many techniques depended on advanced oxidation process (AOP) has been applied with a wide range of organic pollutants. It depended on the generation of hydroxyl radicals ($OH^{\bullet}$) which is the strong oxidizing agent and very reactive agent (E_o = 2.8 V), the ability to reduction of organic pollutants. Among these processes, heterogeneous photocatalysis was considered as an emerging destructive technology that lead to the total mineralization of most of organic pollutants [10-13]. Photo-catalysis divided into homogeneous and heterogeneous. Heterogeneous photocatalysis has showed to be an effective technology compared to other AOP[14]. Using of many semiconductors, like zinc oxide (ZnO) and titania (TiO_2) have many advantages such as high photosensitivity, high efficiency of photocatalytic degradation, non-toxic, low cost, and eco-friendly [15]. Zinc oxide is one of the promising semiconductors, that have been interested from many researchers due to its large exciting binding energy of 60 MeV and direct bandgap of 3.37 eV at 300 K [16]. ZnO is friendly semiconducting oxide material,

* Amal Zaher, Environmental Science and Industrial Development Department, Faculty of Postgraduate studies for Advanced Sciences, Beni-Suef University, Beni-Suef, Egypt, +201003603343, amal_2006z@yahoo.com

highly stable, nontoxic, inexpensive. UV light exit the ZnO nanoparticles, produce electron–hole pairs that form OH^- and O^-_2 radicals,[17].

It is important to manage the particle size, morphology, and dispersion for increment the ability of a heterogeneous catalyst, many techniques mentioned for synthesis of ZnO nanoparticles such as polymerization method [18] hydrothermal and solvothermal synthesis [19], precipitation [20], sonochemical [21] and sol–gel [22-24] technique. Researchers had been interested with the sol–gel method because of its advantages such as the low temperature of the final decomposition and ease of synthesis.

The aim of this research is removal MO dye from wastewater by photo-degradation process under UV radiation using ZnO nanoparticles which were prepared by sol–gel technique. Samples had been characterized with XRD, SEM and UV–Vis spectrophotometer. The photo degradation process was investigated in terms of optimizing the experimental conditions, e.g. pH, ZnO catalyst dose and the concentration of MO. after that the multi-component process is modeled using regression modeling, using the statistical tool for finding the optimal relationship between variables in the form of predictive equations when a combination of numerous independent parameters and their collaborations affect the preferred responses as evaluating the sensitivity functions. Murgolo, S., Franz, et al. studied performance in describing non-linear multi-component systems, which intelligent methods can solve[25]. Moreover, Hussain et al. explained the model and optimized operational factors to simulate the photolytic degradation of Sulfamethoxazole, using response surface methodology (RSM)[26].

2. Materials and methods

2.1 Materials

Sodium hydroxide, zinc acetate dihydrate, methanol and deionzied water. Zinc acetate dihydrate is applied as precursor and methanol as a reagent. Deionzied water had been applied as solvent. All chemical reagents were obtained from commercial sources.

2.2 Preparation of ZnO nanoparticles

2.2.1Sol-gel method

Zinc acetate dihydrate had been used as zinc precursor. 0.2 M zinc acetate dihydrate was mixed in methanol at room temperature by ultrasonic method for 110 min at 25℃. A clear and transparent sol had been obtained. Then 0.02 M of NaOH was added to the sol with ultrasonic stirring for 50 min, its pH was adjusted by using pH Meter between 9 and 11. The sol was dried at 100^o C for 1 hour, after that the temperature was increased up to 150^o C till gelation was happened. The sol was kept undisturbed until white precipitates settle at the bottom. After that, the precipitate was filtered then washed with methanol several time for removal of any starting material, then, dried at 80℃ for 15 min on hot plate, calcined for 4 h at 350°C and finally grinded [27].

3. Characterization

ZnO nanoparticles were characterized by XRD (Panalytical Empyrean, Sweden) with Cu^{2+} Kα radiation (wave length 1.54060 Å) for crystallinity and identification of prepared material phases. The accelerating voltage applied was 40 KV, applied current was 30 mA, range of scan angle was from 4 to 70^0 and the step of scan was 0.05^0. The microstructure of ZnO nanoparticles and morphological characterization were examined by scanning electron microscope (SEM) Germany.

3.1. Regression modeling

To estimate the associations between an independent parameter (such as Dose(A), Initial Concentration(B), and pH(C)) and a dependent variable (such as degradation), a statistical modeling technique known as regression analysis uses a collection of statistical processes called correlation analysis. There are many other types of regression analysis. Still, the most popular is linear regression, which involves finding the line (or an even more complex linear combination) that best fits the data.

3.1.1 Analysis of variance (ANOVA)

The aim of the analysis of variance (ANOVA) was to investigate which parameters significantly affected the quality characteristic. When conducting an ANOVA, it is presumed that all of the observations are normally and independently distributed with the same variance for each treatment

4. Results and discussion

4.1. XRD analysis

The diffraction patterns of X-ray for ZnO nanoparticle was shown in Figure 1. The XRD pattern for samples was displayed at 2θ = 32.5, 34.8, 36.1, 48.1, 56.5, and 62.0 result to crystal planes (100), (002), (101), (102), (110), and (103), respectively, this appear its hexagonal wurtzite ZnO structure. The appeared diffraction peaks agreed with the reported JCPDS file for ZnO (No. 89-1397).No diffraction peaks had been appeared other than ZnO, it proved that the purity of the prepared ZnO samples. The results of XRD pointed to (101) plane had been the most intense peak, also it was the preferred growth plane

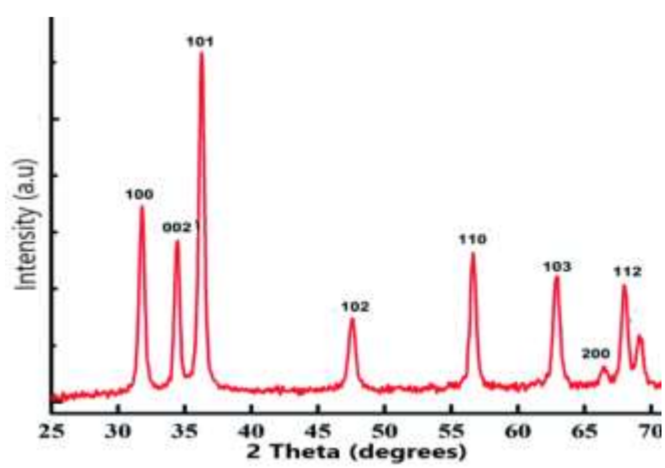

Figure 1: XRD pattern for ZnO nanoparticle

4.2. SEM analysis

SEM analysis could show the morphology of the synthesized ZnO nanoparticles by using SEM (JSM-6490LV, Japan) with accelerating voltages of 30 kV.

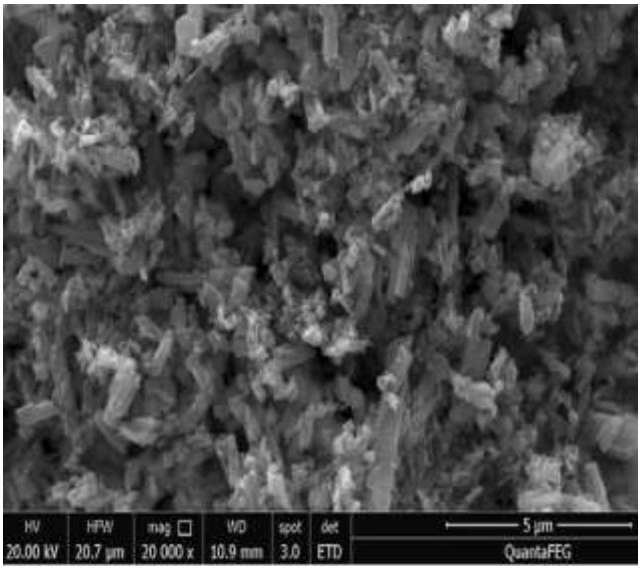

Figure 2: SEM of prepared ZnO nanoparticle

Figure 2, it showed that the prepared ZnO nanoparticle by the sol–gel process has a rod shape, which is a typical morphology of ZnO nanoparticles, [28].

5. Photocatalytic degradation study

A known amount of photocatalyst powder was mixed with MO solution (1000 mL) of given concentration in a tubular reactor which made of quartz glass. Using sodium hydroxide or hydrochloric acid to adjust the pH of the solution a pH meter is used for measuring it. The pH is adjusted around 4. For reaching the adsorption-desorption equilibrium, a solution had been kept under dark for 45 min. A UV lamp (20 W) was located 50 cm above the tube of the reactor. The solution was irradiated with continuous stirring. At interval time of 20 min, 3 ml sample of reaction solution had been taken, centrifuged at 2000 rpm for 20 min and recorded the absorbance of the clear supernatant at 464 nm by a UV-5100 spectrophotometer [29].The degradation percentage of MO had been estimated by the following equation.

$$\text{Degradation } \% = [(C_0 - C_t)/C_0]*100 \quad (1)$$

Where;

C_0 is the initial concentration and

C_t is the concentration at time t.

5.1. Effect of pH

The pH has a great effect on the degradation process. Estimating the influence of pH on the degradation of MO dye was studied at different pH from 2 to 10, as observed in Figure 3. After 120 min of irradiation the percentage of degradation was 84.0%, 96.8%, 61.0% ,43.0% and 25% at pH 2, 4,6, 8 and 10, respectively. It is observed that; degradation percentage was high at initial acidic pH of MO solution. On other hand, it was very low at high pH. [30,31]. At pH 4 high efficiency of degradation was observed. The order of efficiency is found to be pH 4 > pH 2 > pH 6 > pH 8> pH 10. This may be due to the properties of surface-charge of ZnO that associated to zero charge and the properties of MO dye. The surface of ZnO nanoparticle turn into positively charged at acidic pH [32], where several molecules of O_2 had been reduced into $O_2^{\cdot-}$ radicals due to the influence of photoelectrons since the positively charged surface of the ZnO catalyst is conducive to transport of photoelectrons to the surface of ZnO catalyst at acidic pH. This proved that the pH of the solution affect the charge of ZnO surface.

5.2. Effect of ZnO photocatalyst dose

The photocatalyst dose has a great effect on the degradation process of dye polluted water. Several concentrations of nano-ZnO in the solution was applied. As seen in Figure 4, increasing of ZnO from 1 mg/l to 10 mg/l led to increase the degradation percentage from 38% to 96.8% up to 5 mg/l. The enhancement in the degradation rate may be increase because of the number of dye molecules that adsorbed on the photocatalyst surface, while any increase in ZnO dose above 5 mg/l led to decrease in degradation percent and this may be attributed to light reflectance by molecules of catalyst and the opacity of the solution [33].Thus, 5 mg/l of ZnO was used in the subsequent work.

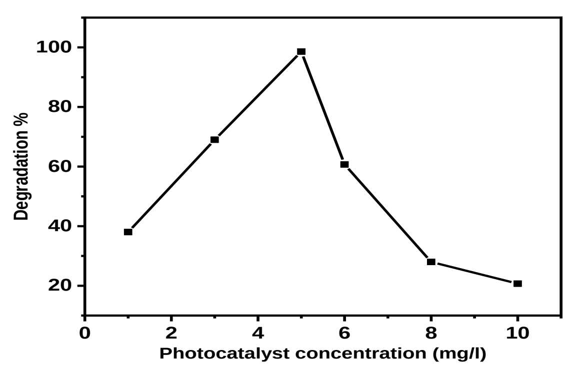

Figure 3: Effect of pH on degradation % of MO (10 mg/l MO, ZnO dose 5mg/l and contact time 120 min)

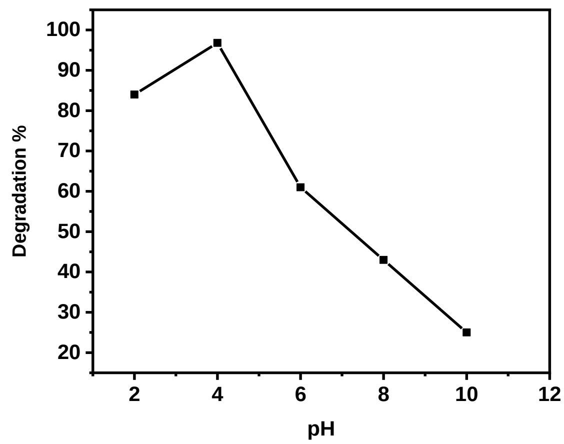

Figure 4: Effect of ZnO concentration on degradation % at pH=4, MO 10 mg/l and contact time 120 min

5.3. Initial Concentration of the dye

The influence of MO dye initial concentrations (10 to 100 mg/L) on the degradation process was critically addressed. The degradation % of MO dye after 120 min contact time was displayed in Figure 5. When other conditions were kept constant, it was observed that increasing the initial concentration of MO led to a decrease in the removal rates significantly from 96.8 to 17%. Therefore, the efficiency of removal could be enhanced by the lower initial concentration of the dye, [34,35]. This may be attributed to the adsorption of MO dye molecules on the nanoparticle catalyst surface by increasing the concentration. So several active sites had been occupied by the molecules of dye, then decreasing the adsorption of OH^- and O_2 on the ZnO. Thus, the photons couldn't reach the surface of ZnO, and the degradation percentage decreased at high initial concentrations of MO,[36].

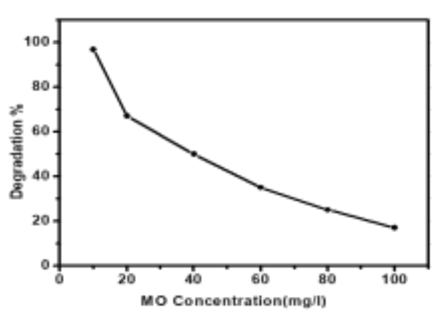

Figure 5: Effect of MO dye concentration on degradation % at pH=4, ZnO dose 5 mg/l and contact time 120 min

5.4. Development of mathematical response model

According to mathematics standards, the equations used to describe a mathematical model must include at least two variables and at least two equations. Multiple regression approaches were used to create a mathematical model in this study, thanks to the MINITAB 20 statistical program. And the regression coefficient (R^2) is R^2=90.86%, which implies that the experimental data is good. The model is shown in the following way: Objective function

$$Max\ \text{Degradation\%} = -35 + 189A - 9.8B + 2.02C - 0.69A^2 + 14.6B^2 - 3.8A * B - 0.04A * C$$

Subjected to

-≤ A ≤10

10≤ B ≤100

5≤ C≤10

5.5. Analysis of variance

Figure 6 listed ANOVA outcomes with a 5% level of significance and a 95% confidence level. In this figure, it is clear which of the important parameter has the most impact on the Degradation process. From Figure 6, it is clear that, factor B is the important significance factor then factor C.

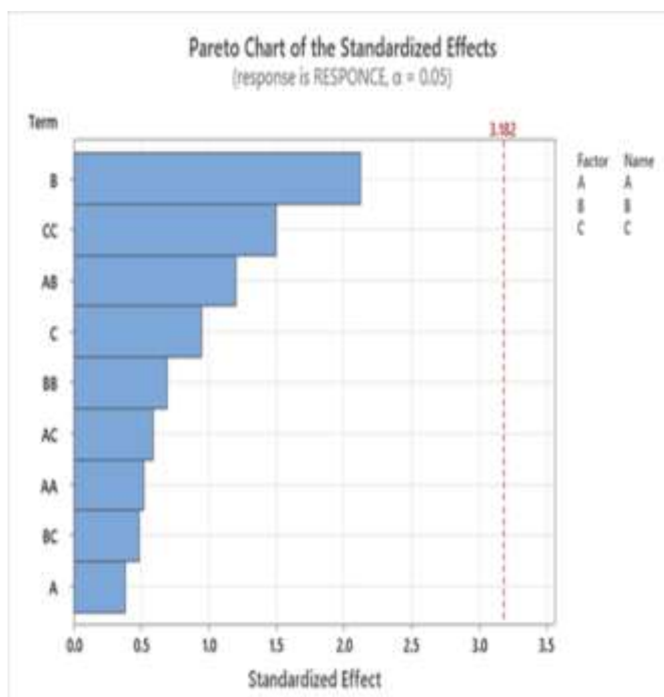

Figure 6: Pareto chart of the standardized effects

5.6. Response optimization

Objective and upper-value degradation process, while Figure 7 illustrates the optimization of degradation process reactions to changes in target values. Optimal operating settings for the input variables to optimize the decomposition process a pH of 4, an initial concentration of 10mg/l, and a dose of 5mg/l were used in this experiment, which had process desirability of 1.

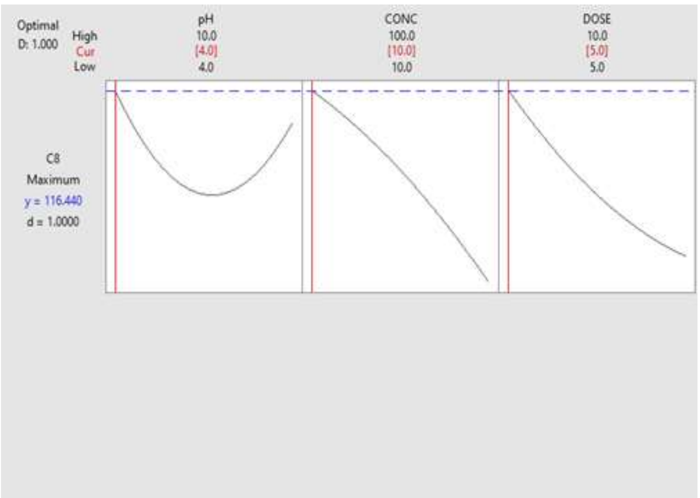

Figure 7: Optimal conditions of control variables on the degradation process

5.7. Confirmation Experiment

The experimental results presented in sections effect of pH and initial Concentration are quite close to the results obtained by (modelling analysis), i.e., the recommended and the ideal pH, concentration, and Dose (4, 10, and 5), respectively. Here between experimental and theoretical results, there is a high degree of consistency and good agreement.

6. Conclusions

The photocatalyst ZnO synthesis by sol–gel process was flexibility, simple and high efficiency for photo degradation process. Prepared ZnO at the calcination temperature of 350 °C had got good properties of photocatalytic process under UV lamp irradiation. Based on the results of XRD and SEM, Prepared ZnO nanoparticles contain hexagonal wurtzite and the size of ZnO was 20–50 nm. The percentage degradation of MO dye increasing, with increase ZnO dosage up to 5 mg/l initial concentration of the MO dye 10 mg/l and at acidic pH. As a result, the high photocatalytic efficiency and stability of ZnO nanoparticles was recommended for photocatalytic degradation. Dye concentration and pH were found to be important factors in the degradation process for each variable based on an ANOVA study of the proposed quadratic models.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgment

References

[1] J. Li, D. Wang, D. Yu, P. Zhang, Y. Li, Performance and membrane fouling in an integrated membrane coagulation reactor (IMCR) treating textile wastewater Chem. Eng. J. 240 (2014) 82–90.

[2] F. Deniz, S. Karaman, Removal of an azo-metal complex textile dye from colored aqueous solutions using an agro-residue, Microchem. J. 99 (2011) 296–302.

[3] V.P. Kamat, R. Huehn, R. Nicolaescu, A “sense and shoot” approach for photocatalytic degradation of organic contaminants in water, J. Phys. Chem., B 106 (2002) 788–794.

[4] Aleboyeh, A., H. Aleboyeh, and Y. Moussa. "“Critical” effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: Acid Orange 8, Acid Blue 74 and Methyl Orange." Dyes and pigments 57, no. 1 (2003): 67-75.

[5] Chen, You-Peng, Shao-Yang Liu, Han-Qing Yu, Hao Yin, and Qian-Rong Li. "Radiation-induced degradation of methyl orange in aqueous solutions." Chemosphere 72, no. 4 (2008): 532-536.

[6] Saravanan, R., S. Karthikeyan, V. K. Gupta, G. Sekaran, V. Narayanan, and A. J. M. S. Stephen. "Enhanced photocatalytic activity of ZnO/CuO nanocomposite for the degradation of textile dye on visible light illumination." Materials Science and Engineering: C 33, no. 1 (2013): 91-98.

[7] Nemiwal, Meena, Tian C. Zhang, and Dinesh Kumar. "Recent progress in g-C3N4, TiO2 and ZnO based photocatalysts for dye degradation: Strategies to improve photocatalytic activity." Science of The Total Environment (2021) 144896.

[8] Asaithambi, P., R. Govindarajan, Mamuye Busier Yesuf, and Esayas Alemayehu. Removal of color, COD and determination of power consumption from landfill leachate wastewater using an electrochemical advanced oxidation processes. Separation and Purification Technology 233 (2020): 115935.

[9] Gadekar, Mahesh R., and M. Mansoor Ahammed. "Modelling dye removal by adsorption onto water treatment residuals using combined response surface methodology-artificial neural network approach." Journal of environmental management 231 (2019): 241-248.

[10] I.K. Konstantinou, T.A. Albanis, Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways, Appl. Catal., B 42 (2003) 319–335.

[11] Zaher, A. Photo-Catalytic degradation of phenol wastewater: optimization using response surface methodology. Egyptian Journal of Chemistry 63, no. 11 (2020): 4-6.

[12] Li, Shengling, Qingxia Lin, Xianhua Liu, Li Yang, Jie Ding, Feng Dong, Yang Li, Muhammad Irfan, and Pingping Zhang. "Fast photocatalytic degradation of dyes using low-power laser-fabricated Cu 2 O–Cu nanocomposites." RSC advances 8, no. 36 (2018): 20277-20286.

[13] Anwer, Hassan, Asad Mahmood, Jechan Lee, Ki-Hyun Kim, Jae-Woo Park, and Alex CK Yip. "Photocatalysts for degradation of dyes in industrial effluents: Opportunities and challenges." Nano Research 12, no. 5 (2019): 955-972.

[14] Bibi, Ismat, Sabir Hussain, Farzana Majid, Shagufta Kamal, Sadia Ata, Misbah Sultan, Muhammad Imran Din, Munawar Iqbal, and Arif Nazir. "Structural, dielectric and magnetic studies of perovskite [Gd1− xMxCrO3 (M= La, Co, Bi)] nanoparticles: photocatalytic degradation of dyes." Zeitschrift für Physikalische Chemie 233, no. 10 (2019): 1431-1445.

[15] M.S. Tokumoto, V. Briois, C.V. Santilli, Preparation of ZnO nanoparticles and colon:structural study of the molecular precursor, J. Sol–Gel Sci. Technol. 26 (2003)547–551.

[16] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO2, J. Photochem. Photobiol. A 162 (2004) 317–322.

[17] Azmina, M. S., R. Md Nor, H. A. Rafaie, N. S. A. Razak, S. F. A. Sani, and Z. Osman. "Enhanced photocatalytic activity of ZnO nanoparticles grown on porous silica microparticles." Applied Nanoscience 7, no. 8 (2017): 885-892.

[18] Z.S. Hu, G. Oskam, P.C. Searson, Influence of solvent on the growth of ZnO nanoparticles, J. Colloid Interf. Sci. 263 (2003) 454–460.

[19] S.J. Chen, L.H. Lia, Preparation and characterization of nanocrystalline zinc oxide by a novel solvothermal oxidation route, J. Cryst. Growth. 252 (2003) 184–189.

[20] Rauufi, Davood. Synthesis and microstructural properties of ZnO nanoparticles prepared by precipitation method. Renewable Energy, 50(2013) 932-937.

[21] Yadav, Raghvendra S., Priya Mishra, and Avinash C. Pandey. Growth mechanism and optical property of ZnO nanoparticles synthesized by sonochemical method. Ultrasonics sonochemistry 15.5 (2008): 863-868.

[22] S.Y. Chu, T.M. Yan, S.L. Chen, Characteristics of sol–gel synthesis of ZnO-based powders, J. Mater. Sci. Lett. 19 (2000) 349–352.

[23] Zak, A. Khorsand, et al. "Effects of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified sol–gel combustion method." Ceramics International 37.1 (2011): 393-398.

[24] Khan, Shamim Ahamad, Manaal Zahera, Irfan Ali Khan, Mohd Sajid Khan, Ameer Azam, Mohd Arshad, Asad Syed, Omaima Nasif, and Abdallh M. Elgorban. "Photocatalytic degradation of methyl orange by cadmium oxide nanoparticles synthesized by the sol-gel method." Optik 251 (2022): 168401.

[25] Murgolo, S., S. Franz, H. Arab, M. Bestetti, E. Falletta, and G. Mascolo. Degradation of emerging organic pollutants in wastewater effluents by electrochemical photocatalysis on nanostructured TiO2 meshes. Water research 164 (2019): 114920.

[26] Hussain, Sajjad, Hammad Khan, Saima Gul, Juliana R. Steter, and Artur J. Motheo. Modeling of photolytic degradation of sulfamethoxazole using boosted regression tree (BRT), artificial neural network (ANN) and response surface methodology (RSM); energy consumption and intermediates study. Chemosphere 276 (2021): 130151.

[27] Wu, J., Shen, X., Jiang, L., Wang, K., & Chen, K. Solvothermal synthesis and characterization of sandwich-like graphene/ZnO nanocomposites. Applied Surface Science, 256(9) (2010) 2826-2830.

[28] Chen, C., Liu, J., Liu, P., & Yu, B. Investigation of photocatalytic degradation of methyl orange by using nano-sized ZnO catalysts. Advances in Chemical Engineering and Science, 1(01), 9(2011).

[29] Wang, Li, Zhan Li, Jia Chen, Yanni Huang, Haijuan Zhang, and Hongdeng Qiu. Enhanced photocatalytic degradation of methyl orange by porous graphene/ZnO nanocomposite. Environmental Pollution 249 (2019): 801-811.

[30] Zhu HY, Jiang R, Fu YQ, Guan YJ, Yao J, Xiao L et al Effective photocatalytic decolorization of methyl orange utilizing TiO_2/ZnO/chitosan nanocomposite films under simulated solar irradiation. Desalination 286: (2012) 41–48.

[31] Verma, Shweta, B. Tirumala Rao, J. Jayabalan, S. K. Rai, D. M. Phase, A. K. Srivastava, and R. Kaul. "Studies on growth of Au cube-ZnO core-shell nanoparticles for photocatalytic degradation of methylene blue and methyl orange dyes in aqueous media and in presence of different scavengers." Journal of Environmental Chemical Engineering 7, no. 4 (2019): 103209.

[32] Kazeminezhad, I., & Sadollahkhani, A. Influence of pH on the photocatalytic activity of ZnO nanoparticles. Journal of Materials Science: Materials in Electronics, 27(5), (2016). 4206-4215.

[33] Thomas M, Naikoo GA, Sheikh MUD, Bano M, Khan F Effective photocatalytic degradation of Congo red dye using alginate/carboxymethyl cellulose/TiO_2nanocomposite hydrogel under direct sunlight irradiation. J Photochem Photobiol A 327: (2016) 33–43

[34] Gomez-Solís, C., Ballesteros, J. C., Torres-Martínez, L. M., Juárez-Ramírez, I., Torres, L. D., Zarazua-Morin, M. E., & Lee, S. W. Rapid synthesis of ZnO nano-corncobs from Nital solution and its application in the photo degradation of methyl orange. Journal of Photochemistry and Photobiology A: Chemistry, 298, (2015) 49-54.

[35] Shakil, M., Usama Inayat, N. R. Khalid, Muhammad Tanveer, S. S. A. Gillani, N. H. Tariq, Attaullah Shah, Arshad Mahmood, and A. Dahshan. "Enhanced structural, optical, and photocatalytic activities of Cd–Co doped Zn ferrites for degrading methyl orange dye under irradiation by visible light." *Journal of Physics and Chemistry of Solids* 161 (2022): 110419.

[36] Thomas M, Naikoo GA, Sheikh MUD, Bano M, Khan F Effective photocatalytic degradation of Congo red dye using alginate/ carboxymethyl cellulose/TiO2 nanocomposite hydrogel under direct sunlight irradiation. J Photochem Photobiol A 327: (2016) 33–43