JAPR

Vol. 01, Issue, 02, pp. 1-6, March, 2024

RESEARCH ARTICLE

Synthesis, Characterization and Photocatalytic Activity of Metal Oxide Nanoparticles

Salim Ullah Khan [a], Atif Ullah Khan [b], Muhammad Imran Khan [a]

[a] *Institute of Chemical Sciences, University of Peshawar, Pakistan.*
[b] *University of Science and Technology Bannu, Pakistan.*

ARTICLE INFO

Article History:
Received 15 *February*, 2024
Received in revised form 22 *February*, 2024
Accepted 25 *February*, 2024
Published online 10 *March*, 2024

Keywords:
Nanoparticles
Ferrites
Methylene Blue
Thymol Blue
Photocatalysis

Corresponding author: Salim Ullah Khan
E-mail addresses:
khansalim77991@gmail.com

ABSTRACT

The present research work was carried out to investigate synthesis and light induced catalytic activity of metal oxides nanoparticles. The metal oxides were synthesized through sol gel method and doped with Fe_2O_4 to enhance the photosensitization via photo Fenton's reaction. The synthesized nano sized particles were utilized in the photocatalytic degradation of two organic dyes Methylene blue (MB) and Thymol blue (TB). The morphology was characterized via scanning electron microscope (SEM) and X-ray diffraction spectrometry (XRD). The photocatalytic activity was performed under UV and sun light and the results were recorded with UV-spectrophotometer. The catalytic performance of all the catalysts was found remarkable and all the catalysts were recovered from the solution without major loss of quantity or any damage to the quality. All the catalysts were capable to be utilized several times for the degradation purpose.

1. Introduction

Water is a gift of nature occupying 70% of earth and comprising about 90% of cellular composition, but the industrial development have given rise to many issues including water contamination, leaving behind a negative impact on the environment and a serious threat to all species of organism surviving on the blue planet. The disposal of industrial wastes in water bodies make them unfit to be utilized. The waste contains chemicals that may cause fatal diseases or even death of living things. Large number of aquatic lives are wasted every year and many of the terrestrial organisms including human are proven to different types of diseases which sometimes get a pandemic situations as well [1-5]. The high concentration of heavy metals in industrial effluent is thought to be carcinogenic and mutagenic to living things [6-8]. In ancient times when scientific methods were not much developed, some simple methods like Coagulation, flocculation, sedimentation, filtration, and disinfection were used for waste water treatment, but they were time consuming and less effective. Also all these traditional methods required a large space, leave behind chemical waste and not enough developed to eliminate all harmful toxicants [9, 10]. Among the newly established water decontamination processes, advanced oxidation processes (AOPs) base on redox reactions have achieved prominence because they are considered to be the most effective approaches to degrade most of the contaminants including organic pollutants [11-15]. AOPs are non selective methods that can oxidise any kind of water pollutants into nontoxic compounds like small inorganic ions, CO_2, and H_2O. The basic mechanism of AOPs are based on the production and utilization of hydroxyl radicals (•OH), due to their high reduction potential (2.80 V vs. Normal hydrogen electrode), they can degrade a wide range of organic pollutants; including the most stable ones [16-18]. The main classes of AOPs include ultraviolet (UV) photolysis, hydrogen peroxide photo-Fenton, photo-ozonation, and heterogeneous photocatalysis. However, the popularity of heterogeneous has increased because they got the advantage of using sunlight, which is a no cost source of energy [19].

Fujishima and Honda pioneered photocatalysis research in 1972 when they used TiO_2 electrodes in water splitting [20-23]. For the degradation and removal of a wide variety of organic pollutants in contaminated water, Photocatalysis emerged as one of the most effective techniques of AOPs that can speed up the degradation of waste water. Photocatalysis utilize sunlight energy which is cost free and plentiful in nature, hence it adds to its economical values. Also photocatalysis is a low or no waste producing process, using highly reactive chemical species with high oxidation capacity to break complicated structures [24-27]. Photocatalysis via heterogeneous catalysis can completely mineralize contaminants at low temperatures and pressures, that's why it is favoured in the treatment of polluted gaseous and liquid wastes [28-34].

Metal oxides (MOs) have already been reported to be utilized for the purpose of photocatalysis. There are several reasons for this, but the most important among all is the availability and complete mineralization of the contaminants. That's why MOs are frequently used for the decontamination of industrial waste water. Although there is a limitation of higher energy band gap, i.e. to excite the electron, MOs require higher energy but the problem can be solved by doping the MOs with a metalloid possessing a lower band gap which sensitizes MOs to absorb light energy in visible region [35]. This issue can be well solved by ferric oxides as it has been reported in several research efforts. The lower band gap will help to degrade the organic dyes in the industrial effluents with much ease at lower energy or it can be done by natural sunlight rays and this adds to the economical values as well [36, 37].

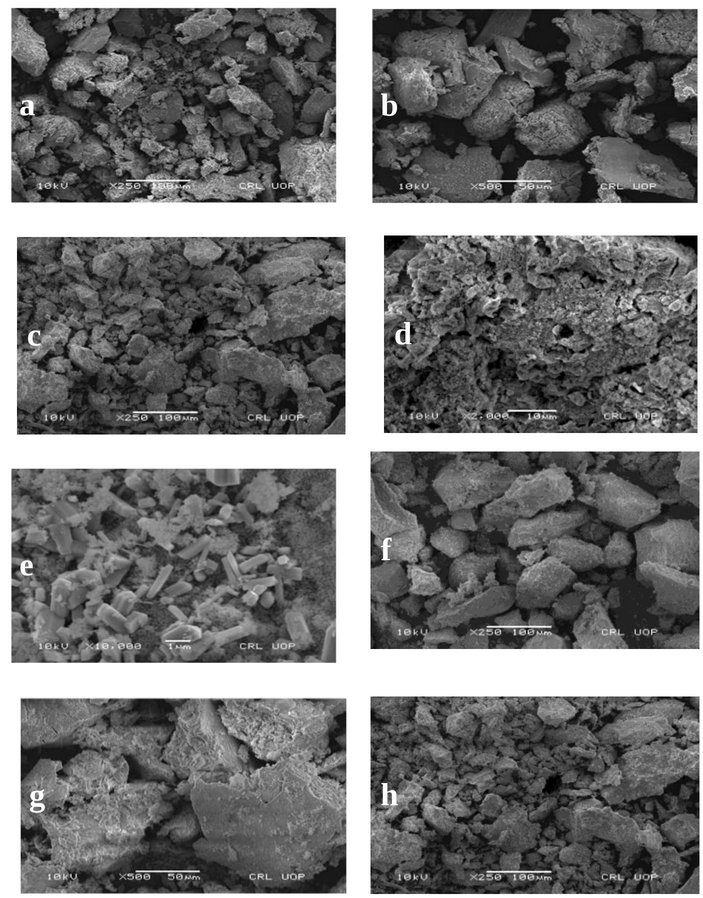
The present research effort aims the preparation and utilization of metal oxide nanoparticles (MONPs) including, Ca, Ba, Cu and Zn for the photolysis of organic dyes as a model for waste water treatment. The aforementioned metals were doped with ferric oxide for the purpose of photosensitization so that the nanoparticles could absorb light in visible range and show efficiency in the photolysis of the selected organic dyes.

2. Materials and Methods

2.1 Experimental Chemical Reagents

The chemicals utilized in this particular research work include $CaCl_2$, $BaCl_2$, $ZnCl_2$, $CuSO_4$, $FeCl_2$, KHP, NH_4Cl and NH_4OH. The dyes utilized during this research effort were Methylene Blue (MB) and Thymol Blue (TB). All chemicals were of analytical grade provided by Merck sigma and used without any further purification.

Figure 1: Scanning Electron Microscopy of Ca-Ferrites (a, b), Ba-Ferrites (c, d), Cu-Ferrite (e, f) and Zn-Ferrites (g, h) Showing Morphological Features of Metal-Ferrites



2.2 Instruments and Equipments

UV-Visible Spectrophotometer, Digital Balance, Centrifuge, Oven, pH-meter, Magnetic stirrer, Furnace, XRD and SEM. All these instruments were provided by University of Peshawar, Pakistan.

2.3 Synthesis of nanoparticles

The nano catalysts were prepared through sol gel method by dissolving calculated amounts of the above mentioned salts in 100mL distilled water to prepare 0.2M solution of $CaCl_2$, $BaCl_2$, $ZnCl_2$ and $CuSO_4$. A 0.4M aqueous solution of $FeCl_2$ was prepared by dissolving calculated amount of $FeCl_2$ in distilled water. 50mL from each solution was taken in separate beakers and mixed with 50mL of 0.4M $FeCl_2$ solution. The solutions were basified with NH_4OH and continuously stirred for two hours at 70°C.

2.4 Washing and Drying

The solutions were allowed to cool and filtered wit Wattmann filter paper and then washed several times with distilled water. The solid products were dried in an oven before calcinations.

2.5 Calcination of Product Samples

The synthesized metal oxides were heated in a muffle furnace for 6 hours at 600°C. The purpose of calcining the product was crystal growth and removal of carbonates. The sample products were allowed to cool at room temperature before characterization through SEM and XRD.

2.6 Scanning Electron Microscopy (SEM)

The morphology of the prepared nanoparticles was examined with SEM, provided by Centralized Research Laboratory (CRL) University of Peshawar (UOP). The SEM reveals porous and amorphous state for Barium nanoparticles, while Copper, Zinc and Ca showed crystalline nature with flakes of regular geometry. However, all the MONPs were porous up to some extent.

2.7 X-ray Diffraction Crystallography (XRD)

The XRD of metal nanoparticles show their structural features. It is evident that Ca, Cu and Zn show regular crystalline structures with two prominent peaks for calcium and copper ferrites and a single sharp peak for zinc ferrites, however Barium ferrites are synthesized amorphous with bunch of peaks (Figure 2).

2.8 Degradation of Organic Dyes

The catalytic activity of the synthesized nanoparticles was examined by the degradation of two organic dyes Methylene Blue (MB) and Thymol Blue (TB) under UV and sunlight radiations. The process was completed by irradiating the aforementioned dyes for 120 minutes in the presence of a calculated amount of the catalysts and recording the data with UV-visible spectrophotometer (Figure 3). In two separate flasks 3ppm solutions of the dyes were prepared and from each solution 10mL was taken in two separate vials. The dyes were then exposed with continuous stirring to light source for 10 minutes after adding 0.01g of a catalyst and the degradation was recorded with UV-visible spectrophotometer provided by ICS/UOP. These steps were repeated in the presence of UV and sunlight several times with all four catalysts for MB and TB till their solutions were got degraded. A clear solution indicated the removal of dyes. The degradation efficiency was calculated using formula:

$$\text{Degradation Efficiency (\%)} = (1-C/C_0)*100$$

3. Results

The present investigation about the synthesis of MONPs and their utilization for the treatment of industrial waste water containing organic dyes was found successful. The synthesized catalysts were found proficient to degrade MB and TB (selected as test samples) completely in a photosensitized reaction (Figure 3). The nano size catalysts were recovered from the test solutions and could be reutilized several times. The nano size of the catalysts was quit helpful in the process of degradation by providing larger surface area (Figure 1). As catalysis is a surface phenomenon, so the greater the surface area higher will be the chances for a reaction to take place. This was probably the most influencing factor for the higher catalytic efficacy of the synthesized nanoparticles. The catalytic action to decontaminate the dyes was found higher under UV radiations as compared to exposure to sun light, the possible reason may be the difference in wavelength of radiations (Figure 3). Copper and Zinc being transition metals possessing a [Ar] $3d^{10}$ $4s^1$ and [Ar] $3d^{10}$ $4s^2$ electronic configuration respectively are completely filled electronic system and considered relatively more stable than a partially filled orbital, hence it requires comparatively higher energy to excite the valence electron. All the catalysts showed their efficiency to degrade up to 80 percent of both dyes in UV and sunlight as well. The catalytic activity of copper ferrites was found to be the most efficient one followed by zinc ferrites. Calcium and Barium being the members of s-block were comparatively less efficient than copper and zinc.

4. Discussion

Photocatalysis is a completely different approach from catalysis as it requires light as an activation source, which activates the photocatalyst to accomplish the desired chemical process [4, 6]. Photocatalysis makes many reactions possible which are difficult to occur in normal conditions due to energy barriers [7]. Photosynthesis is a natural photosensitized process which can help us better understand the process of photocatalysis. Nano sized catalysts that can be sensitized through a light source is an easy, economically accepted and environmental friendly source that help to degrade organic pollutants in no time is an amazing approach for waste water treatment [11]. The present investigation is also an effort towards the understanding of photocatalysis and the possible role of metal oxide nanoparticles from alkaline earth metals and first transition series, all of them doped with ferrites for better results of oxidation activities. As already discussed the results of all the tested metal oxide nanoparticles were remarkable with transition metals comparatively more efficient [14, 22]. The prepared nanoparticles were easy to synthesize with in a lab with some basic instruments and can be tested for the degradation of any type of complex organic dyes. It's an amazing mode to decompose aqueous organic dyes and a forward step for the promotion of nanotechnology.

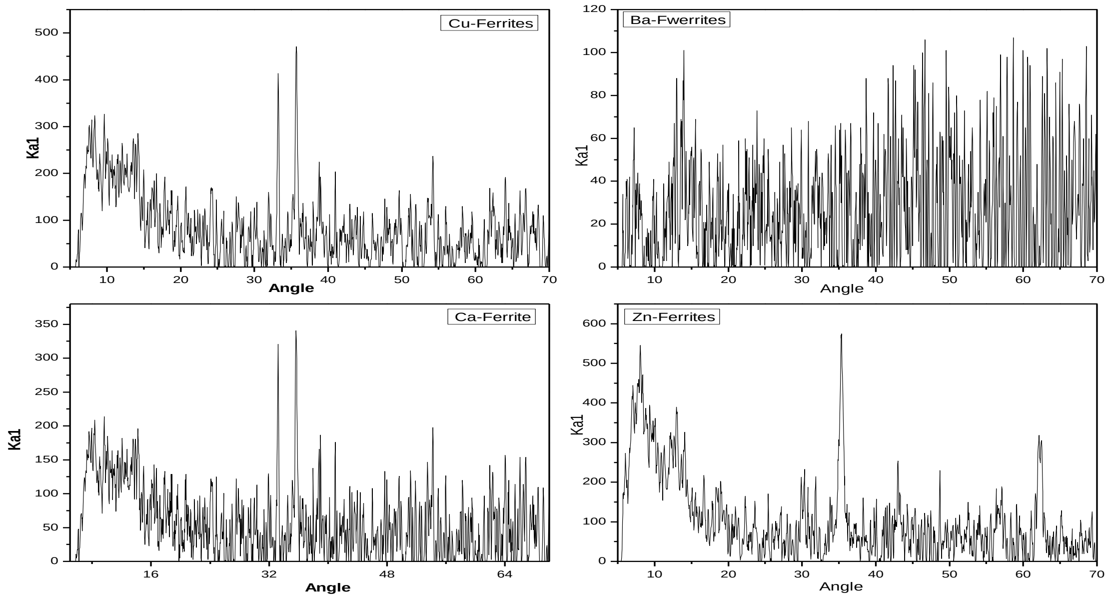


Figure 2: X-Ray Diffraction Analysis of Metal Nanoparticles

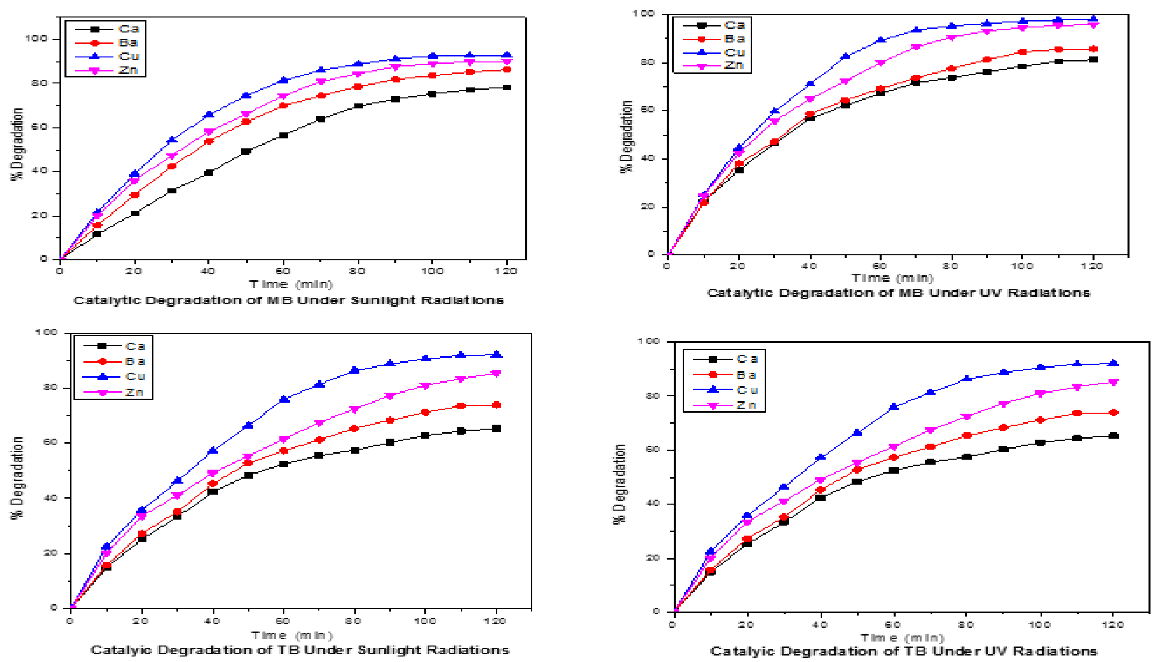


Figure 3: Catalytic Degradation of MB and TB With MONPs.

5. Conclusion

It is concluded that all the synthesized nanoparticles proved to be highly efficient source for the degradation of organic dyes and opening a new chapter of industrial waste water treatment via advance oxidation process. The catalysts activity as evident from the results section have shown Cu and Zn ferrites to be the more efficient among all four types of NPs as both of these belong to first transition series providing comparatively shorter band gap for electronic excitation. Calcium and barium ferrites also proved high efficiency but comparatively lower to that of Cu and Zn. Comparatively speaking the synthesized catalysts was excellent in their catalytic performance completing degrading the organic dyes.

Acknowledgements

The author would like to acknowledgement student of Institute of Chemical Science (ICS), University of Peshawar (UOP), Pakistan (2015-2020). This manuscript is part of Salim Ullah Khan and Muhammad Imran Khan MSc chemistry thesis.

Ethical Approval

All experimental techniques, including the handling and application of chemical reagents were authorized by the Institute of Chemical Science, (UOP), and adhered to all applicable laws and regulations in the country.

Conflict of Interest

The current study's authors all certify that they have no competing interests, either financial or otherwise.

Availability of Data and Material

No other information is at this time available.

Funding: Not applicable

Authorship contribution statement

The study's conceptualization, design, preparation of the materials, data collection, analysis, and paper writing were all done by the authors. Slim Ullah Khan, Paper writing: Muhammad Imran Khan, Atif Ullah Khan

References

[1]. Akiyama K, Nojima S, Ito Y, et al. Synthesis of a gold-inserted iron disilicide and rutile titanium dioxide heterojunction photocatalyst via the vapor-liquid-solid method and its water-splitting reaction. *ACS Omega.* 2022 doi: 10.1021/acsomega.2c04360.

[2]. Khaled Mezughi, Chedly Tizaoui, and Ma'an Fahmi Alkhatib, Effect of TiO2 Concentration on Photocatalytic Degradation of Re-active Orange 16 Dye (RO16), Advances in Environmental Biolo-gy, 2014, 8,(3), 692 – 695.

[3]. Anuar A, Marwan NF, Smith J, et al. (2021) Bibliometric analysis of immigration and environmental degradation: evidence from past decades. *Environ Sci Pollut Res.* 2021;299(29):13729–13741. doi: 10.1007/S11356-021-16470-1.

[4]. Vo Thi Thu Nhu, Do QuangMinh, Nguyen Ngoc Duy, Nguyen QuocHien, Photocatalytic Degradation of Azo Dye (Methyl Red) In Water under Visible Light Using AgNi/TiO2 Sythesized by - Irradiation Method, International Journal of Environment, Agricul-ture and Biotechnology (IJEAB),2017,2(1),529-538.

[5]. Arsad AZ, Hannan MA, Al-Shetwi AQ, et al. Hydrogen energy storage integrated hybrid renewable energy systems: a review analysis for future research directions. *Int J Hydrogen Energy.* 2022;47:17285–17312. doi: 10.1016/J.IJHYDENE.2022.03.208.

[6]. I. Poulios, A. Avrans, E. Rekliti, and A. Zouboulis, Photocatalytic oxidation of Auramine O in the presence of semiconducting oxides, J. Chem. Biotechnol.2000, 75, 205–212.

[7]. Asghar A, Raman AAA, Daud WMAW. Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: a review. *J Clean Prod.* 2015;87:826–838. doi: 10.1016/j.jclepro.2014.09.010.

[8]. Tesfay W. Gebreslassie1, Manjunatha Pattabi and Rani M. Pattabi, Review on the Photocatalytic Degradation of Dyes and Antibacte-rial Activities of Pure and Doped-ZnO, International Journal of Science and Research,2015, 4(5), 2252-2264.

[9]. Bai X, Zhang X, Hua Z, et al. Uniformly distributed anatase Ti_{O2} nanoparticles on graphene: synthesis, characterization, and photocatalytic application. *J Alloys Compd.* 2014;599:10–18. doi: 10.1016/j.jallcom.2014.02.049.

[10]. Bernabeu A, Vercher RF, Santos-Juanes L, et al. Solar photocatalysis as a tertiary treatment to remove emerging pollutants from wastewater treatment plant effluents. *Catal Today.* 2011;161:235–240. doi: 10.1016/j.cattod.2010.09.025.

[11]. Lum Sin Wan, A Study into photocatalytic degradation of meth-ylene blue and glycerol aqueous solution over copper ferrite cata-lyst, Bachelor degree thesis, Faculty of Chemical & Natural Re-sources Engineering, Universiti Malaysia, Pahang, (2015).

[12]. Bitaraf M, Amoozadeh A. The first report of covalently grafted semiconductors; n-Ti_{O2}-P25@ECH@W_{O3} as a new, efficient, robust and visible-light-responsive photocatalyst. *J Chem Technol Biotechnol.* 2021;96:963–970. doi: 10.1002/JCTB.6605.

[13]. Bruce M, Limin M. Recent advances on water pollution research in Africa: a critical review. *Int J Sci Adv.* 2021;2(3):96–375. doi: 10.51542/ijscia.v2i3.23.

[14]. Meng Z, and Juan Z. Wastewater treatment by photocatalytic oxi-dation of nano-ZnO. Global Environmental Policy in Japan,2008, 12, 1-9.

[15]. Cao SW, Yin Z, Barber J, et al. Preparation of Au-BiV_{O4} heterogeneous nanostructures as highly efficient

visible-light photocatalysts. *ACS Appl Mater Interfaces.* 2012;4:418–423. doi: 10.1021/am201481b.
[16]. Cascajares M, Alcayde A, Salmerón-Manzano E, Manzano-Agugliaro F. The bibliometric literature on scopus and wos: The medicine and environmental sciences categories as case of study. *Int J Environ Res Public Health.* 2021;18:5851. doi: 10.3390/ijerph18115851.
[17]. Chi Y, Xu S, Li M, et al. Effective blockage of chloride ion quenching and chlorinated by-product generation in photocatalytic wastewater treatment. *J Hazard Mater.* 2020;396:122670. doi: 10.1016/j.jhazmat.2020.122670.
[18]. Wan-Kuen Jo and Rajesh.J.Tayade, Recent developments in photo-catalytic dye degradation upon irradiation with energy-efficient light emitting diodes Chinese Journal of Catalysis,2014 35, 1781–1792.
[19]. Chong MN, Lei S, Jin B, et al. Optimisation of an annular photoreactor process for degradation of Congo Red using a newly synthesized titania impregnated kaolinite nano-photocatalyst. *Sep Purif Technol.* 2009;67:355–363. doi: 10.1016/j.seppur.2009.04.001.
[20]. Choudhury AKR. Technologies for the management of wastewater generated in wet processing. *Waste Manag Fash Text Ind.* 2021 doi: 10.1016/B978-0-12-818758-6.00005-3.
[21]. Chowdhary P, Bharagava RN, Mishra S, Khan N (2020) Role of Industries in Water Scarcity and Its Adverse Effects on Environment and Human Health. In: Environmental Concerns and Sustainable Development. Springer. Singapore, pp 235–256.
[22]. U.G. Akpan and B.H. Hameed, Parameter affecting he photocata-lytic degradation of dyes using TiO2 photo-catalysts: A review, Journal of Hazardous Materials, 2009,170, 520-529; DOI:10.1016/jhazmet.3009.05.030.
[23]. Coelho A, Castro AV, Dezotti M, Sant Anna GL. Treatment of petroleum refinery sourwater by advanced oxidation processes. *J Hazard Mater.* 2006;137:178–184. doi: 10.1016/j.jhazmat.2006.01.051.
[24]. Olga Sacco, Marco Stoller, Vincenzo, Vaiano, Paolo Ciambelli, Angelo Chianese, and Diana Sannino, Photocatalytic degradation of organic dyes under visible light on N-doped TiO2 photo-catalysts, International Journal of Photoenergy, 2012, pp.1-8 (2012Doi:10.1155/20121626759.
[25]. da Santos DHS, Xiao Y, Chaukura N, et al. Regeneration of dye-saturated activated carbon through advanced oxidative processes: a review. *Heliyon.* 2022;8:e10205. doi: 10.1016/j.heliyon.2022.e10205.
[26]. Dalrymple OK, Yeh DH, Trotz MA. Removing pharmaceuticals and endocrine-disrupting compounds from wastewater by photocatalysis. *J Chem Technol Biotechnol.* 2007;82:121–134. doi: 10.1002/jctb.1657.
[27]. Dewil R, Mantzavinos D, Poulios I, Rodrigo MA. New perspectives for advanced oxidation processes. *J Environ Manage.* 2017;195:93–99. doi: 10.1016/j.jenvman.2017.04.010.
[28]. Dhiman M, Sharma R, Kumar V, Singhal S. Morphology controlled hydrothermal synthesis and photocatalytic properties of ZnF_{e2O4} nanostructures. *Ceram Int.* 2016;42:12594–12605. doi: 10.1016/j.ceramint.2016.04.115.
[29]. Garrido-Cardenas JA, Esteban-García B, Agüera A, et al. Wastewater treatment by advanced oxidation process and their worldwide research trends. *Int J Environ Res Public Health.* 2020;17:170. doi: 10.3390/ijerph17010170.
[30]. Hitam CNC, Jalil AA. A review on exploration of Fe_2O_3 photocatalyst towards degradation of dyes and organic contaminants. *J Environ Manage.* 2020;258:110050. doi: 10.1016/j.jenvman.2019.110050.
[31]. Hodges BC, Cates EL, Kim JH. Challenges and prospects of advanced oxidation water treatment processes using catalytic nanomaterials. *Nat Nanotechnol.* 2018;13:642–650. doi: 10.1038/s41565-018-0216-x.
[32]. Hussain T, Wahab A. A critical review of the current water conservation practices in textile wet processing. *J Clean Prod.* 2018; 198:806–819. doi: 10.1016/j.jclepro.2018.07.051.
[33]. Khan AH, Khan NA, Ahmed S, et al. Application of advanced oxidation processes followed by different treatment technologies for hospital wastewater treatment. *J Clean Prod.* 2020;269:269. doi: 10.1016/j.jclepro.2020.122411.
[34]. A.A. Khodja, T. Sehili, J. Pilichowski, P. Boule, Photocatalytic degradation of 2 phenyl-phenol on TiO2 and ZnO in aqueous suspension, J. Photochem. Photobiol. A: Chem., Vol. 141, 2001, pp. 231-239.
[35]. N. Daneshvar, A. Aleboyeh, A. R. Khataee, The evaluation of electrical energy per order (EEO) for photooxidative decolorization of four textile dye solution by the kinetic model, Chemosphere, Vol. 59, 2005, pp.761-767.
[36]. S. sakthivel, B. Neppolian, M. V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye comparison of photocatalytic efficiency of ZnO and TiO2, Sol. Energy Mater. Sol. C, Vol. 77, 2003, pp. 65-82.
[37]. W. K. Choy, W. Chu, The use of oxyhalogen in photocatalytic reaction to remove o-chloroaniline in TiO2 dispersion, Chemosphere, Vol. 66, 2007, pp. 2106-2113.