Three-Layer Magnetic Nanocomposite Containing Semiconductor Nanoparticles as Catalyst for Dye Removal from Water Solutions under Visible Light

Fathirad, Fariba*[+]

Department of Nanotechnology, Graduate University of Advanced Technology, Kerman, I.R. IRAN

Ziaadini, Fatemeh; Mostafavi, Ali; Shamspur, Tayebeh

Department of Chemistry, Faculty of Science, Shahid Bahonar University of Kerman, Kerman, I.R. IRAN

ABSTRACT: *In the present work, a three-layer magnetic nanocomposite containing ceria nanoparticles was synthesized as $Fe_3O_4@SiO_2@CeO_2$ by precipitation method and after characterization was used as photocatalyst for the degradation of malachite green dye from industrial wastewater under visible light. The influence parameters such as pH, initial dye concentration, photocatalyst amount, and process time on the malachite green dye removal were investigated and optimized. Under optimum conditions (pH = 9, the photocatalyst amounts of 0.05 g, the reaction time of 40 min, and the initial solution concentration of 10 ppm), the results indicated that the synthesized nanostructure has a desirable performance for dye. The removal percentage remained higher than 90% after 5 times of use and the photocatalyst could be quickly separated from the aqueous solution with the assistance of the external magnetic field. According to the calculation, the second pseudo-model was selected as the kinetic model of photocatalytic degradation.*

KEYWORDS*: Three-layer magnetic nanostructure, Semiconductor, Photocatalytic degradation, Malachite green, Visible light.*

INTRODUCTION

Environmental pollution is currently one of the most important issues facing humanity and has been highly regarded in recent years. One of the major pollutants is the dye wastewater from the textile industry that causes harm to humans and the environment [1, 2]. The very important effects of these compounds in humans can be mentioned to the effects of carcinogenicity and mutagenesis. As a result, textile dyes are considered a threat to health and the environment around the world and wastewater must be refined properly before entering the natural environment [3-5].

Malachite Green (MG) is one of the synthetic dyes that is found to be high in wastewater from various industries, including fish breeding, leather and textile industry, paper and linen. Few concentrations of this dye are visible in aquatic environments. Therefore, the effective removal of this pigment from the wastewater of the mentioned industries and preventing its penetration into underground waters is important in order to ensure human health and environmental protection [6-9]. Removal of MG from industrial wastewater was carried out by various methods

* *To whom correspondence should be addressed.*
+ *E-mail*: *f_fathirad@yahoo.com*
1021-9986/2021/6/1749-1756 *8/$/5.08*

such as ultrafiltration [10], Biotransformation [11], ion exchange [12], and adsorption on various materials such as activated carbon [13], mesoporous materials [14], graphene oxide [15], and clay [16]. But since these methods often transfer water pollution from the water phase to the solid-state and are not destructive processes, learning these techniques is not considered.

The use of photocatalysts for the removal of pollutants in most cases has been successful. Photocatalysts are referred to the catalysts that are activated in the presence of light. They are usually semiconducting solid oxides, which create a pair of electron cavities by absorbing the photons. This electron-cavity can react with molecules on the surface of the particles stimulated electrons and cavities can directly or indirectly produce radical hydroxyls that convert organic matter into minerals. Photocatalysts are used in water purification, air purification, self-cleaning glasses, anti-steam surfaces, antimicrobials, and organic molecules degradation [17, 18].

Photocatalytic degradation is biologically or so-called green and without any secondary pollution. Among the methods for eliminating environmental pollution, the use of photocatalysts is more important due to the lack of side effects. Different photocatalysts are now used to remove organic compounds from water [19, 20]. But in recent years, with the advancement of nanotechnology, the possibility of using effective and low-cost pollution elimination methods are provided [21-25]. Fe_3O_4 (magnetite) exhibits unique electric and magnetic properties based on the transfer of electrons between Fe^{2+} and Fe^{3+} in the octahedral sites. Because of its low toxicity, good biocompatibility, and tunable magnetic properties, Fe_3O_4 has received considerable attention in various areas [25]. The use of the core-shell magnetic nanostructure as a photocatalyst is a growing trend, due to the specific characteristics of these nanostructures. These nanostructures have a large surface-to-volume ratio, which significantly increases their photocatalytic capacity. In this work, a three-layer core-shell nanostructure containing Fe_3O_4 magnetic nanoparticles and semiconductor nanoparticles of CeO_2 was prepared and its application as a visible area photocatalyst was investigated.

EXPERIMENTAL SECTION

Reagents and instruments

$FeSO_4.7H_2O$, $FeCl_3.6H_2O$, NH_4OH, NaOH, ethylene glycol, ethanol, ammonia, and polyethylene glycol were purchased from Merck, and tetraethyl orthosilicate (TEOS), $Ce(SO_4)_2$, and malachite green were purchased from Sigma-Aldrich.

Product X-Ray Diffraction (XRD) data were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K_α radiation. The composition of the as-prepared photocatalyst was characterized by Transmitting Electron Microscope (TEM) model LEO-912 AB manufactured by Germany. Magnetic properties of the products were examined using a Vibrating Sample Magnetometer (VSM) at room temperature. All absorption measurements were carried out with a spectrophotometer, ultraviolet Specord 210 plus Analytikjena company in Germany after irradiation with a visible lamp (100 W, tungsten) as the radiation source.

Preparation of Fe_3O_4@SiO_2@CeO_2 three-layer magnetic nanocomposite

Iron oxide Magnetic NanoParticles (MNPs) were synthesized through the coprecipitation method and the Fe_3O_4@SiO_2 nanoparticles were synthesized through the Stöber method [26]. Iron (III) chloride hexahydrate and iron (II) sulfate hexahydrate (2:1 mmol) were dissolved in water and then, NH_4OH was added to the solution until the pH value was adjusted to 9. The precipitate was collected using a magnet, washed with deionized water, and dried at 70 °C. For Fe_3O_4@SiO_2 synthesis, ethanol solution containing magnetic powder was ultrasound and then, 5 mL of ammonia was added to the solution. 1 mL of diluted TEOS in ethanol was added dropwise, and the mixture was stirred for 24 hours at room temperature. The magnetic Fe_3O_4@SiO_2 nanoparticles were collected by a magnet, washed with distilled water, and dried at room temperature. Fe_3O_4@SiO_2@CeO_2 nanostructure was synthesized by homogeneous precipitation and subsequent calcinated. 0.5 g Fe_3O_4@SiO_2 in ethylene glycol was stirred under ultrasound waves. An aqueous solution containing 10 mM cerium sulfate tetrahydrate was added dropwise to the mixture and was stirred in the same state for 30 minutes. 3 M ammonia solution was added and stirred at 50 °C. The precipitate was separated by the magnet and dried at 80 °C. At last, the Fe_3O_4@SiO_2@CeO_2 nanocomposite was calcinated at 500 °C for 2 h.

Dye removal procedure

The photocatalytic activity measurements were conducted by removal of malachite green under visible light.

0.05 g photocatalyst was added to 20 mL of 10 ppm MG solution at pH=9. The suspension was stirred using a magnetic stirrer for 40 min under visible light. The photocatalyst was collected by magnetic separation and the solution was analyzed by UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Characterization of photocatalyst

XRD pattern of Fe_3O_4@SiO_2@CeO_2 three-layer magnetic nanocomposite is shown in Fig. 1. The peaks at the scattering angles (2θ) of 30.3, 36, 43.3, 54, 57, 63, 74 degrees and diffraction plates of (220), (311), (400), (422), (511), (440), and (533), respectively are related to the Fe_3O_4 nanoparticles. In the coating of the magnetic nanoparticles of iron oxide with the amorphous silica phase, there is no peak in the XRD pattern. Successful coating of the Fe_3O_4@SiO_2 core-shell with CeO_2 shell was confirmed with the presence of peaks at scattering angles (2θ) of 28.74, 33.28, 47.61, 56.53, 69.61, and 76.83 degrees related to the diffraction plates of (111), (200), (220), (311), (222), (400), respectively. This pattern confirmed the synthesis of Fe_3O_4, SiO_2, and CeO_2 nanoparticles, properly.

The Fe_3O_4@SiO_2@CeO_2 three-layer magnetic nanocomposite was characterized by FESEM and TEM. It was seen from Fig. 2a that the magnetic nanostructure has a spherical particle shape and some particles aggregated together. According to the TEM image (Fig 2b), the nanocomposite has a layered structure. According to the images, the size of the nanoparticles is about 40 nm.

Magnetic properties of the nanostructure were examined using VSM at room temperature. Fig. 3 shows that the Ms value of Fe_3O_4@SiO_2@CeO_2 is about 40 emu/g which is sufficient for photocatalyst collection from the reaction environment.

Investigation of photocatalytic activity in malachite green removal

Fig. 4.shows UV-Vis spectra of (a) MG solution without photocatalyst and (b) after applying the photocatalyst according to the procedure in section 2.3. As shown, in presence of Fe_3O_4@SiO_2@CeO_2 three-layer magnetic nanocomposite, the removal of malachite green dye was carried out under visible light. In this photocatalyst, the photon excitation happens and electrons are excited and transferred to the conductive band and a pair of electron-hole is created in the valence band.

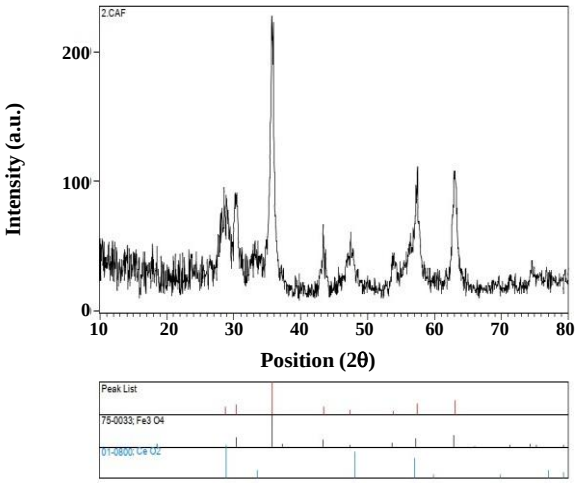

Fig. 1: The XRD pattern of Fe_3O_4@SiO_2@CeO_2 three-layer nanostructure.

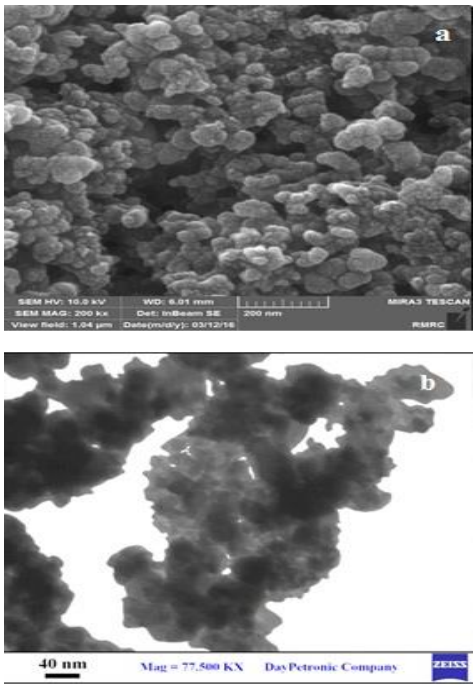

Fig. 2: (a) FESEM and (b) TEM images of Fe_3O_4@SiO_2@ CeO_2 three-layer nanostructure.

The production holes go to the photocatalyst surface and react with water molecules absorbed on the surface and form hydroxyl (OH) radicals. The electrons in the conductive band participate in reduction reactions. These electrons react with air oxygen dissolved in water and they create the superoxide anionic (O_2) radical. These free radicals enter decomposition reactions and organic dye is decomposed.

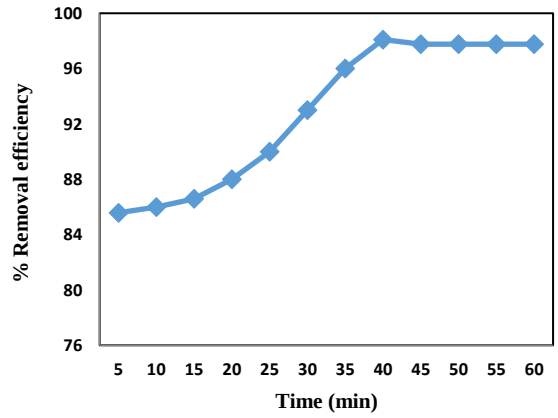

Fig. 7: Effect of radiation time on malachite green removal efficiency.

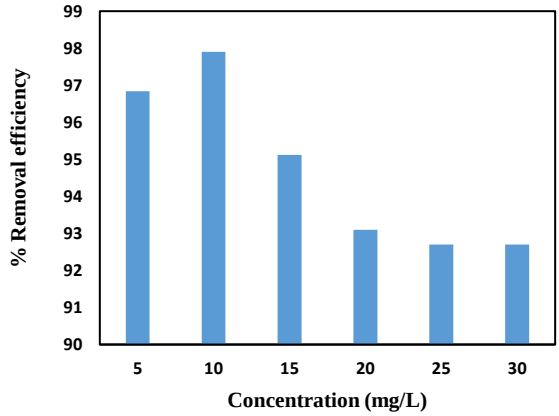

Fig. 8: Effect of solution concentration on malachite green removal efficiency.

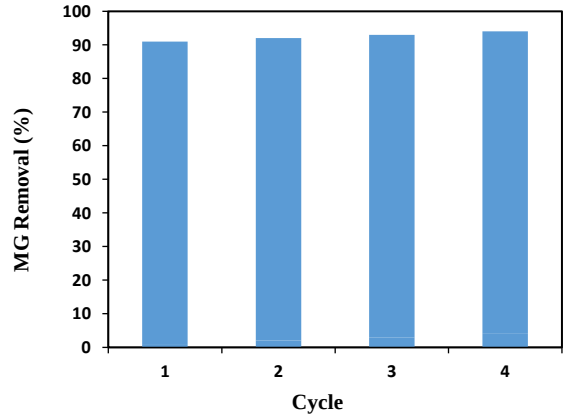

Fig. 9: Investigation of photocatalyst reusability in the malachite green removal.

Effect of different parameters on the photocatalytic removal of MG dye

Effect of pH

The dye removal efficiency was done under varying pH from 6 to 9 adjusting with HCl and NaOH. In the basic environment, the photocatalyst surface has a negative charge. Due to the cationic nature of the malachite green dye, the electrostatic gravity is generated between the photocatalyst and the cation dye and the MG removal efficiency increases at the aqueous solution. As shown in Fig. 5 the highest percentage of removal of malachite green from solution was pH = 9, which was selected as the optimum amount.

Effect of photocatalyst amount

For investigation of photocatalyst amount effect on the removal efficiency, the amount of photocatalyst was varied from 0.005 to 0.2 g, and experiments were done. The increasing amounts would make the reaction faster due to the increase in the number of active sites on the photocatalyst. In the other words, the number of hydroxyl radicals increased resulting in dye removal is better done. Further increase in photocatalyst amount above 0.05 g has a negligible effect on the MG removal efficiency, which could be due to the hindrance to the pathway of light to reach the dye molecules. The optimum value for the photocatalyst was selected 0.05 g according to Fig. 6.

Effect of reaction time

To evaluate the effect of the irradiation time on the MG removal efficiency, the solutions were exposed to visible light at 5 to 60 min. The abundance and availability of vacant sites on the photocatalysts surface results in the rapid absorption of malachite green from aqueous solutions in the first minutes and then with a gentle slope, this decomposition is continued and fixed after 40 min. As a result, the reaction reached a balance of 40 minutes (Fig. 7). Therefore, 40 min was chosen as optimal.

Effect of initial solution concentration

The effect of initial dye concentration on the removal efficiency was tested by investigation of different concentrations between 5 to 30 ppm. Based on these results and according to Fig. 8, a concentration of 10 ppm of solution malachite green was chosen as the optimal concentration.

Table 1: Parameters of First pseudo-model and Second pseudo-model equations for the removal of malachite green.

q_e(exp)	First pseudo-model			Second pseudo-model		
617.08	K_1 (min^{-1})	q_{e1} ($mg.g^{-1}$)	R^2	K_2 (min^{-1})	q_{e2} ($mg.g^{-1}$)	R^2
	0.0742	197.87	0.8349	0.0036	625	0.9836

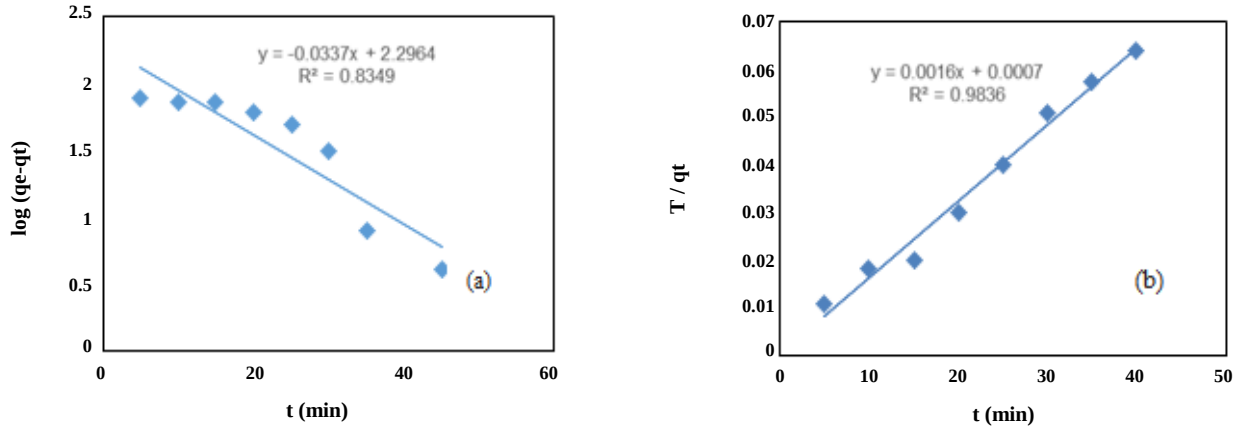

Fig. 10: Investigation of kinetic model of (a) First-pseudo and (b) Second -pseudo.

Stability and Reuse Investigation

Sustainability and reuse of three-layer magnetic nanocomposite as photocatalyst in malachite green degradation was investigated under optimum conditions. The percentage of malachite green removal with the photocatalyst remains more than 90% after 4 times of use (Fig. 9). This means that the proposed photocatalyst can be reused at least 4 times without losing a significant amount of its performance and has good stability.

Investigation of photocatalytic degradation kinetic

Equation (1) is the First-pseudo kinetic model equation in which q_e is the amount of removed dye when balancing ($mg\ g^{-1}$), q_t is the amount of deleted dye at t time (mg/g) and K_1 is the speed constant of First -pseudo order (min^{-1}).

the speed constant First-pseudo (min^{-1}).

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1 t}{2.303} \quad (1)$$

Eq. (2) is second -pseudo kinetic model equation in which k_2 is the speed constant of second-pseudo order (min^{-1}).

$$\frac{t}{q_t} = \frac{1}{q_e^2 K_2} + \frac{t}{q_e} \quad (2)$$

According to Fig. 10 the parameters of the first-pseudo and second-pseudo kinetic model can be calculated (Table 1).

According to the results, photocatalytic degradation of malachite green in the presence of the proposed photocatalyst is based on a second pseudo-model.

In describing the mechanism of MG degradation using Fe_3O_4@SiO_2@CeO_2, it can be said that the SiO_2 middle layer can block the electrons transfer from CeO_2 into the Fe_3O_4 core and help to prevent the Fe_3O_4 from being as an electron-hole recombination center. In this structure, the Fe_3O_4 and SiO_2 presented a core and shell, respectively, and both of them contacted CeO_2 in a coupled semiconductor system. The two photogenerated electrons and holes are accessible on the surface for oxidation and reduction processes. Then the generated hydroxyl radical can react with adsorbed MG, and degrade it [27].

Comparison of proposed photocatalyst with other photocatalyst

In Table 2, the proposed photocatalyst is compared with the other photocatalysts published in papers to remove malachite green dye. Fe_3O_4@SiO_2@CeO_2 three- layer magnetic nanocomposite can remove more MG with less photocatalyst consumption in shorter time under visible light in comparison with other photocatalysts.

Table 2: Comparison of proposed photocatalyst with other photocatalysts.

Photocatalyst	Concentration (ppm)	Photocatalyst Amount (g)	Time (min)	Ref
Ni-doped TiO_2	10	0.1	45	[28]
$CeFeO_3$	20	0.05	120	[29]
Nickel/magnesium ferrit	15	0.2	90	[30]
Nickel vanadate	10	0.1	100	[31]
Starfish-like La-doped ZnO/SiO2	15	0.015	140	[32]
Fe_3O_4@SiO_2@CeO_2	10	0.05	40	Present work

CONCLUSIONS

The effective removal of dyes from the industries' wastewater and preventing penetration into underground waters is important in order to ensure human health and environmental protection. Three-layer magnetic nanocomposite due to its unique properties and their surface to volume ratio has a wide application as a photocatalyst to remove industrial dyes from factory wastewater. The prepared photocatalyst has an appropriate option for pollutants removal in the environment and organic materials destruction in water due to its high photocatalytic properties, chemical stability, non-toxicity, and high activity under visible light radiation. In addition, due to its magnetic properties, it will be possible to recycle and reuse it.

Acknowledgments

The authors would like to express their sincere appreciation to Mr. Alireza Afzalipour and his wife Mrs. Fakhereh Saba, the founders of the Shahid Bahonar University of Kerman, for their foresight and generosity in training the future generations of doctors, engineers, and scientists. Also, the authors would like to acknowledge Dr. Parviz Dabiri for his support in the research activities of the chemistry and nano laboratories at the Shahid Bahonar University of Kerman.

Received : May 21, 2020 ; Accepted : Jul. 6, 2020

REFERENCES

[1] Ageena N.A., The Use of Local Sawdust as an Adsorbent for the Removal of Copper Ion from Wastewater Using Fixed Bed Adsorption, *Engineering and Mining Journal*, **28**: 224-235. (2010).

[2] Li W., Mu B., Yang Y., Feasibility of Industrial-Scale Treatment of Dye Wastewater *via* Bio-Adsorption Technology, *Bioresource Technology*, **277**: 157-170, (2019).

[3] Samsami S., Mohamadi M., Sarrafzadeh M.H., Rene E.R., Firoozbahr M., Recent Advances in the Treatment of Dye-Containing Wastewater from Textile Industries: Overview and Perspectives, *Process Safety and Environmental Protection*, **5**: 134-146 (2020).

[4] Nilsson I., Moller A., Mattiasson B., Rubindamayugi M.S.T., Welander U., Decolorization of Synthetic and Real Textile Wastewater by the Use of White-rot Fungi, *Enzyme and Microbial Technology*, **38**: 94-100 (2006).

[5] Katheresan V., Kansedo J., Lau S.Y., Efficiency of Various Recent Wastewater Dye Removal Methods: A Review, *Journal of Environmental Chemical Engineering*, **6**: 4676-4697 (2018).

[6] Mkrtchyan E., Burakov A., Burakova I., The Adsorption of Malachite Green on Graphene Nanocomposites: A Study on Kinetics Under Dynamic Conditions, *Materials Today*, **11**: 404-409 (2019).

[7] Monash P., Pugazhenthi G., Adsorption of Crystal Violet Dye from Aqueous Solution Using Mesoporous Materials Synthesized at Room Temperature, *Catalysis Today*, **15**: 390-405 (2009).

[8] Gupta V.K., Application of Low-Cost Adsorbents for Dye Removal, *Journal of Environmental Management*, **90**: 2313-2342 (2009).

[9] Ferreira T.A., Ibarra I.S., S. Silva M.L., Miranda J.M., Rodriguez J.A., Use of Modified Henequen Fibers for the Analysis of Malachite Green and Leuco-Malachite Green in Fish Muscle by d-SPE Followed by Capillary Electrophoresis. *Microchemical Journal*, **157**: 104941 (2020).

[10] Isawi H., Evaluating the Performance of Different Nano-Enhanced Ultrafiltration Membranes for the Removal of Organic Pollutants from Wastewater. *Journal of Water Process Engineering*, **31**: 100833 (2019).

[11] Wanyonyi W.C., Onyari J.M., Shiundu P.M., Mulaa F.J., Biodegradation and Detoxification of Malachite Green Dye Using Novel Enzymes from Bacillus cereus Strain KM201428: Kinetic and Metabolite Analysis, *Energy Procedia*, **119**: 38-51 (2017).

[12] Sharma G., Gupta V.K., Agarwal S., Kumar A., Thakur S., Pathania D., Fabrication and Characterization of Fe@MoPO Nanoparticles: Ion Exchange Behavior and Photocatalytic Activity Against Malachite Green, *Journal of Molecular Liquids*, **219**: 1137-1143 (2016).

[13] Sharma G., Sharma S., Kumar A., Naushad M., Du B., Ahamad T., Ghfar A.A., Alqadami A.A., Stadler F.J., Honeycomb Structured Activated Carbon Synthesized from Pinus Roxburghii Cone as Effective Bioadsorbent for Toxic Malachite Green Dye, *Journal of Water Process Engineering*, **32**: 100931 (2019).

[14] Tang Y., Zeng Y., Hu T., Zhou Q., Peng Y., Preparation of Lignin Sulfonate-Based Mesoporous Materials for Adsorbing Malachite Green from Aqueous Solution, *Journal of Environmental Chemical Engineering*, **4**: 2900-2910, (2016).

[15] Naseri A., Barati R., Rasoulzadeh F., Bahram M., Studies on Adsorption of Some Organic Dyes from Aqueous Solution onto Graphene Nanosheets, *Iranian Journal of Chemistry and Chemical Engineering IJCCE)*, **34**: 51-60 (2015).

[16] Tahir H., Saud A., Saad M., Synthesis of Kaolin Loaded Ag and Ni Nanocomposites and Their Applicability for the Removal of Malachite Green Oxalate Dye, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **37**: 11-22 (2018).

[17] Chen Y., Zhai B.Y., Liang Y.N., Li Y., Hybrid Photocatalysts Using Semiconductor/MOF/ Graphene Oxide for Superior Photodegradation of Organic Pollutants under Visible Light, *Materials Science in Semiconductor Processing*, **107**: 104838 (2020).

[18] Kampouri S., Stylianou K.C., Dual-Functional Photocatalysis for Simultaneous Hydrogen Production and Oxidation of Organic Substances, *ACS Catalysis*, **9**: 4247-4270 (2019).

[19] Shirzad Taghanaki N., Keramati N., Mehdipour M., Photocatalytic Degradation of Ethylbenzene by Nano Photocatalyst in Aerogel form Based on Titania, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*,**39(2):** 525-532 (2020).

[20] Sabonian M., Mahanpoor K., Optimization of Photocatalytic Reduction of Cr(VI) in Water with Nano ZnO/Todorokite as a Catalyst: Using Taguchi Experimental Design, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **38**: 105-113 (2019).

[21] Hedayati K., Goodarzi M., Kord M., Green and Facile Synthesis of Fe3O4-PbS Magnetic Nanocomposites Applicable for the Degradation of Toxic Organic Dyes, *Main Group Metal Chemistry*, **39(5-6)**: 183-194, (2016).

[22] Hedayati K., Azarakhsh S., Saffari J., Ghanbari D., Magnetic and Photo-catalyst CoFe2O4-CdS Nanocomposites: Simple preparation of Ni, Co, Zn or Ag-doped CdS nanoparticles, *Journal of Materials Science: Materials in Electronics*, **28**: 5472-5484 (2017).

[23] Goodarzi M., Joukar S., Ghanbari D., Hedayati K., $CaFe_2O_4$–ZnO Magnetic Nanostructures: Photo-degradation of Toxic Azo-Dyes under UV Irradiation, *Journal of Materials Science: Materials in Electronics*, **28**: 12823-12838 (2017).

[24] Naeimi A., Honarmand M., Sedri A., Ultrasonic Assisted Fabrication of First MoO_3/Copper Complex Bio-Nanocomposite Based on Sesbania Sesban Plant for Green Oxidation of Alcohols, *Ultrasonics Sonochemistry*, **50**: 331-338 (2019).

[25] Hedayati K., Goodarzi M., Ghanbari D., Hydrothermal Synthesis of Fe_3O_4 Nanoparticles and Flame Resistance Magnetic Poly Styrene Nanocomposite, *Journal of Nanostructures*, **7(1)**: 32-39 (2017).

[26] Alizadeh A., Kordestani D., Biguanide-Functionalized Fe_3O_4/SiO_2 Magnetic Nanoparticles: An Efficient Heterogeneous Organosuperbase Catalyst for Various Organic Transformations in Aqueous Media, *Journal of Materials Chemistry*, **33**: 38-42 (2012).

[27] Channei D., Wetchakun N., Inceesungvorn B., Phanichphant S., $Fe_3O_4/SiO_2/CeO_2$ Core-Shell Magnetic Nanoparticles as Photocatalyst. *International Journal of Environmental Science*, **14(10)**: 7756-7762 (2014).

[28] Parveen K., Vyas R., Photocatalytic Degradation of Non-Biodegradable Malachite Green Dye by Ni-Doped Titanium Dioxide, *Journal of Pharmaceutical and Biomedical Analysis*, **65**: 3-62 (2016).

[29] Ameta K.L., Papnai N., Ameta R., Photocatalytic Degradation of Malachite Green Using Nano-Sized Cerium-Iron Oxide, *Journal of Chemistry Society*, **6**: 14-19 (2014).

[30] Shetty K., Lokesh S.V., Rangappa D., Nagaswarupa H.P., Nagabhushana H., Anantharaju K.S., Prashantha S.C., Vidya Y.S., Sharma S.C., Designing $MgFe_2O_4$ Decorated on Green Mediated Reduced Graphene Oxide Sheets Showing Photocatalytic Performance and Luminescence Property, *Condensed Matter Physics*, **507**: 67-75 (2017).

[31] Rathore R., Ameta R., Ameta S.C., Photocatalytic Degradation of Malachite Green over Nickel Vanadate Powder, *Acta Chemica Scandinavica*, **4**: 45-58 (2014).

[32] Wang S., Chen Z., Zhao Y., Sun C., Li J., High Photocatalytic Activity over Starfish-like La-doped ZnO/SiO_2 Photocatalyst for Malachite Green Degradation under Visible Light. *Journal of Rare Earth*, Article in press, (2020).