Hydrothermal Green Synthesis of Silver Doped Molybdenum Nanocomposites Using Citrus Limetta Extract for Photo Catalytic Properties

Kanwal Iqbal Alvi,[1] Muhammad Suleman,[1] Farzana Batool,[1] Sarfraz Iqbal,[2] Freeha Hafeez,[1*] Amna Afzal,[1] Saba Afzal,[1] Hafiz Abdul Mannan,[1] Muzammil Hussain,[1] Muhammad Bilal,[1] Soha Saddique[1]

1. Riphah International University, Faisalabad Campus, Pakistan.
2. Department of Urology, Guangdong Medical University.

ABSTRACT

Synthetic dyes are extensively used in various articles of daily use ranging from foods, drinks, clothes, fabric to furniture. These toxic synthetic dyes are discharged in aquifers posing serious health issues. Even when they are treated in water treatments plants with disinfectants, the break down chemicals ends as chlorinated xeno-chemicals. There is an urgent need to eliminate these carcinogenic toxic dyes from water. This study deals with the synthesis of photocatalyst with a potential to eradicate harmful synthetic dyes from wastewater. This research work shows Ag based Mo nanoparticles from *Citrus Limetta* (Mousami) extract by hydrothermal green synthesis method. The synthesized photocatalyst was studied by different analytical techniques where SEM showed the development of crystalline particles, EDX evidenced the existence of Mo and Ag metals in large amounts and XRD pattern explained the phase and crystallinity in the prepared nanocomposites by giving distinct peaks for molybdenum and silver metals. Photocatalytic tests were performed by using Methylene Blue (MB) and Methylene Orange (MO) dyes by using UV-vis spectrophotometer. Absorbance values obtained were plotted against time and wavelength for assessing the degradation efficiency of the prepared nanocomposites. The prepared photo catalyst exhibited good ability to degrade synthetic dyes and could be effectively used for water purification. Hence, hydrothermal green synthesis proved to be an effective, cost free and safe method for the synthesis of silver doped molybdenum nanocomposites possessing remarkable photocatalytic activity.

Keywords: Rutaceae, nanoparticles, nanocomposites, *Citrus limetta*, silver nitrate, ammonium hepta molybdate, photocatalyst

Introduction

Nanotechnology is a versatile field that uses particles ranging from 1 to 100 nanometers with modified surfaces that give rise to promising physico-chemical properties. Despite the scale up challenges, complicated synthesis and lack of reproducibility the future of the nanotechnology appears to be bright (Hulla, Sahu, & Hayes, 2015). They possess remarkable photocatalytic activity due to large surface to volume ratio (Reverberi, Kuznetsov, Meshalkin, Salerno, & Fabiano, 2016), Optimization of various manufacturing parameters can lead to form nanoparticles with diverse shapes and structures (Iravani, 2011). Due to these properties, nanoparticles have found use in

everyday life such as in medicines formulation, controlling pollution , textile sector, crop protection and in making hydrogen fuel cells (Nasrollahzadeh, Sajadi, Sajjadi, & Issaabadi, 2019).

Many different organic and inorganic chemicals are used for dyeing in different industries through varied processes. Textile industry consumes water and energy in production processes which involve wet as well as dry processes. During these processes various types of wastes are produced which are mostly discharged in water sources resulting in serious contamination of water. These processes are giving us good production of clothing but at the same time their main drawback is contamination of water which must be controlled (Ozturk, Karaboyacı, Yetis, Yigit, & Kitis, 2015). It is unfortunate that toxic industrial chemical wastes are discharged in water, including dyes such as Methylene Blue and Methylene Orange, which are highly carcinogenic azo dyes posing serious health issues (Chand et al., 2020). Many different physical processes can be utilized for eradicating colored chemicals from water such as activated carbon, adsorption, ultrafiltration, but these techniques often seem to fall short of getting the required outcome. In the back drop of ever increasing population of the world, protection of water aquifers becomes even more important and we need to find more resources of clean water (Kunduru et al., 2017). Several methods have been developed to purify water where adsorption is often used to remove pollutants effectively (Li, Zhang, Fakhri, Gupta, & Agarwal, 2019) Different chemical processes such as chlorination, ozonation and oxidation have been used in the past. Various photocatalytic methods and biological techniques (both based on whole organisms and enzymatic) are being explored for the treatment of wastewater. (Ajmal, Majeed, Malik, Idriss, & Nadeem, 2014). There is a need to find chemicals which don't pose a lethal effect after treatment and are not too expensive. This is a space which is currently being championed by non-toxic nanoparticles synthesized through green chemistry which are capable of degrading dyes. (Gudikandula & Charya Maringanti, 2016) (Opris et al., 2019).

Nanocomposites are multi-fabricated materials having multifunctional characteristic properties. Scientists are exploring the methods for utilizing bio-renewable sources in the synthesis of material particles (Ates, Koytepe, Ulu, Gurses, & Thakur, 2020). Catalytic, magnetic, electrochemical and optical properties of nanomaterials are quite diverse than the component materials from which they are prepared (Petronella et al., 2017). Nanoparticles of molybdenum metal are largely used to degrade the synthetic organic dyes because they exhibit outstanding catalytic activity towards the oxidation of various chemicals (Manivel et al., 2015). Among various approaches being used, green synthesis proved to be one of the efficient method for the preparation of different nanoparticles for use as photo catalyst during dye degradation (Saif, Adil, Chaudhry, & Khan, 2022). Bioactive molecules found in plants act like capping agents and have the potential to modulate toxicity for environmental and healthcare applications (Ying et al., 2022). , Molybdenum and silver act as heterogeneous photocatalyst. The oxidation reaction to degrade the dye is carried out under light to produce fee radicles, thus producing CO_2 and H_2O. Electron-hole pairs are easily generated because of the reduced band gap of the prepared photocatalyst. Due to presence of more active sites, small size and porous nature of particles, photocatalysis is facilitated. Silver particles due to large surface to volume ratio exhibit outstanding antibacterial as well as photocatalytic features even in minor amount.(Thekkethil, Sreekuttan, & Madhavan, 2021). Methods used by the researchers in the past seemed to be expensive and time consuming. Hence, there

is a need to introduce a novel, cost free and environment friendly methods to prepare nanoparticles for water treatment.

In the present research work, silver doped molybdenum nanoparticles were prepared through green synthesis by using *Citrus Limetta*, commonly called sweet lemon pith extract by using hydrothermal green synthesis approach to get pure composite for effective dye degradation. The prepared nanoparticles were then characterized by X-Ray Diffraction (XRD), Energy Dispersive X-Ray (EDX) and Scanning Electron Microscopy (SEM). Further, photocatalytic activity was studied with two model synthetic dyes: Methylene Blue and Methylene Orange.

MATERIALS AND METHOD

2.1Apparatus

Beakers, Conical Flasks, Whatman filter paper No.1, Funnel, Magnetic stirrer, watch glass, Spirit lamp, Hematocrit having 5000 rpm UTD 5 B centrifuge (China), Teflon coated autoclave, Glass cuvette, Electric oven, Eppendorf tubes UV-VIS Spectrophotometer Perkin Elmer Lambda 950. UV-VIS spectrophotometer (USA)

2.2 Materials

Silver nitrate salt ($AgNO_3$), concentrated HCl, Ethanol, Distilled water, Methylene blue (MB), Methylene orange (MO), Ammonium heptamolybdate salt $(NH_4)_2Mo_7O_{24}$), Citrus Limetta

2.3 Preparation of pith extract from Citrus Limetta

Citrus Limetta fruit was washed with distilled water two to three times to clear dust and other impurities. After washing, fruit was cut into two parts and slushy portion was taken out by using a cutter and was minced into tiny parts. These tiny parts were put in a large conical flask with broad neck and heated with 100ml of distilled water at 70°C for few hours. The hot extract was kept for some time to cool down and filtered with the help of filter paper in a glass funnel.

2.4 Preparation of molybdenum nanoparticles

0.3 M solution of molybdate was prepared in distilled water with the help of Ammonium heptamolybdate salt acing as a precursor. Then, 10mL of the prepared molybdate solution was transferred to another beaker drop after drop while continually being stirred at room temperature for 80 minutes, temperature was raised to 40°C and solution was further stirred for 80 minutes. At high temperature, color of solution altered from light green to dark green and finally to black, at which point stirring was stopped and solution was allowed to cool down. Centrifugation was carried out for 30 minutes at 4500 rpm nanosized particles of molybdenum were obtained. The prepared nanoparticles of Mo were washed with distilled water and ethanol solution. Then, nanoparticles were dried at 50 °C in an electric oven. In this way, molybdenum nanoparticles of good purity were formed. The schematics can be found in Figure 1.

2.5 Preparation of Ag based Mo nanocomposites

The above synthesized nanoparticles were utilized to make 0.3 M molybdate solution with distilled water and stirring was carried out at room temperature with the addition of 0.2M silver nitrate in the solution. After that, stirring was further done for 40 minutes. Then, mixture was transferred to a Teflon coated stain less steel autoclave for heating for 5 to 6 hours at 190°C to prepare the required

nanocomposites. On completing the heating of the material, solution was kept at room temperature to get cooled and then centrifuged. The nanocomposites formed were washed with distilled water and ethanol. Then, final prepared product was dried in an oven at 50°C for few hours. Dried product was stored in glass vials and Eppendorf tubes.

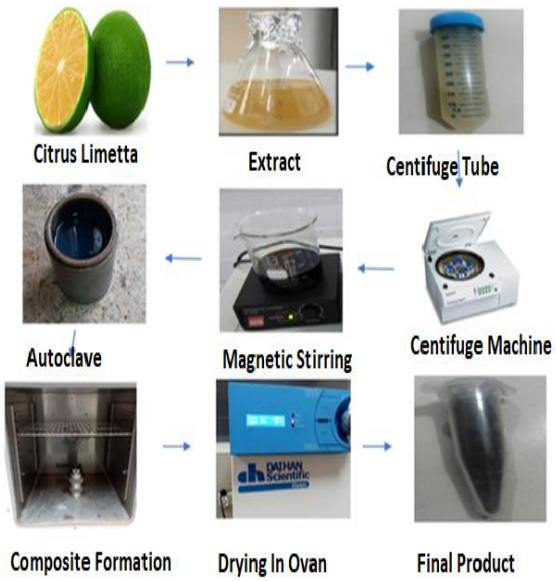


Figure 2.1 Steps for synthesis of nanocomposites

2.6 Photocatalytic application

Photocatalytic experiment was performed with the help of UV-visible spectrophotometer by using Mercury vapor lamp with the intensity of 100 $mWcm^{-2}$. Both dyes were separately dissolved in water to form colored solution. Each dye solution was placed in darkness by adding small amount of the catalyst. Observation indicated that no significant color change occurred for each dye solution in dark. Photocatalytic efficiency of the synthesized catalyst was investigated by mixing about 9—12 mg of the prepared nanocomposites in 70mL of every dye solution separately and each dye solution was subjected to magnetic stirring in the absence of light for 40 minutes to establish good adsorption equilibrium. After stirring, dye solution with the catalyst was exposed to Ultraviolet light source for degradation. After every 20 minutes about 5ml of the solution of dye sample was used to find out the absorbance values by using UV-visible spectrophotometer.

2.6 Characterization

The synthesized nanocomposites were studied with the help of different techniques such as SEM, EDX and XRD analysis to get valuable details related to the structural arrangement, composition, nature, morphology and distribution of particles in the prepared sample. SEM proved to be an effective technique for obtaining information on shape and morphology of particles (Kim & Tasan, 2019).

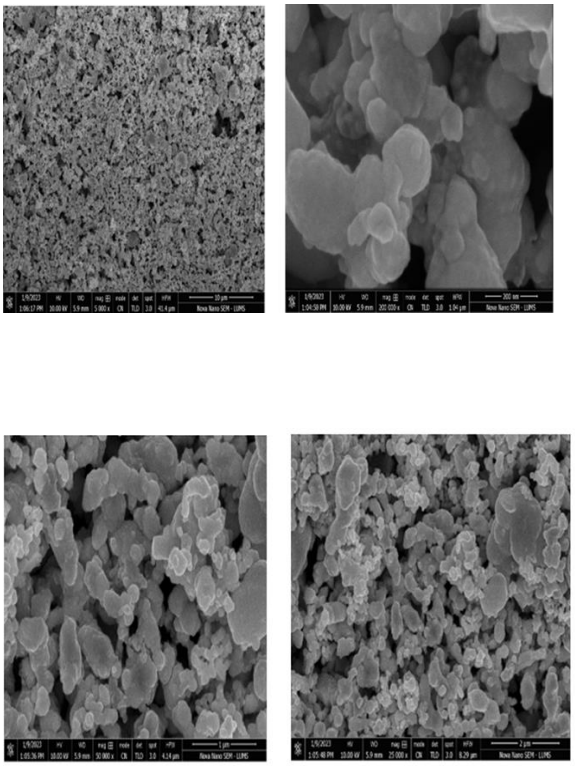
EDX in combination with SEM allows investigation of the elemental composition of the prepared nanocomposites. Accuracy of EDX spectrum is related to the precision for measuring the characteristics X-rays released from the specific elements. (Abd Mutalib, Rahman, Othman, Ismail, & Jaafar, 2017). In EDX characterization, a silicon drift type detecting instrument is used with resolution capacity 127eVFWHM and range used for detection was almost 1 atomic % from depth of 0.4-4 μm. In the spectrum of the prepared sample, higher peak is obtained for the elements present in large quantities in the material. (Hodoroaba, 2020).

XRD is a very useful characterization technology which is extensively used by the researchers to obtain valuable details about the structures and geometries of the prepared sample material. Sample could be scanned through range 2θ angles to obtain all kind of diffractions due to random positioning of sample material. Diffractions peaks are transformed to d-spacing for proper identification of prepared

sample because each sample possess a distinct set of d-spacing (Chauhan & Chauhan, 2014).

RESULTS AND DISSCUSSION

The present experimental work shows the preparation of silver doped molybdenum nanoparticles by using *Citrus Limetta*. SEM photographs show clusters of nanocomposites dispersed in the prepared sample, showing the development of spherical shaped nanoparticles. Cross-sectional view of the prepared nanocomposites could be observed in figure 3.1 that indicated 3-dimensional image of nanocomposites having spherical beads with size ranging from 50 to 80 nm in diameter. At some places, nanoparticles were arranged one above the other longitudinally and at some other places, the particles were stacked together in circular manner.



Figs 3.1 *SEM images of nanocomposite material (a)10kv,magnified to 10000X, while bar sizes are 5.9mm (b)10kv,magnified up to 100,000X,bar sizes of 5.9mm,(c)10kv,magnified up to 50,000X bar size is 5.9mm,(d)10kv,magnified up to 25,000X bar size is 5.9mm*

Energy Dispersive X-ray (EDX)

While doing the SEM and EDX analysis, prepared nanocomposites in powder form was put on a glass plate. Due to this reason, spectrum contained silicon peaks because of the glass material being used. EDX spectrum showed the existence of carbon and oxygen because of bioactive molecules found in the extract. Carbon and oxygen may be due to vitamin C found in *Citrus Limetta* extract. Silver and Molybdenum metals showed higher percentage indicating their large concentration in the final product. Data in table showed that molybdenum concentration in the prepared material was 79.82% and silver was found 10.19% indicating the precision of the experiment.

Table: 3.1 *Weight percentage of elements by EDX analysis*

Sr. No	Elements	Spectral series	Weight %	Atomic %
1	C	K-series	4.46	0.81
2	O	K-series	3.52	0.69
3	Mo	L-series	79.82	1.05
4	Ag	L-series	10.19	1.33
5	Au	M-series	3.02	0.1

Each peak in the spectrum was indicative of each individual element in the sample. Element showing the highest peak meant that element was found in the greatest concentration. EDX characterization

indicated that the nanocomposites sample contained Mo and Ag metals with minor amounts of carbon (C), oxygen (O) and gold (Au). Clear peaks for molybdenum (Mo) with percentage weight (wt. %) of 79.82 and silver (Ag) having wt. % of 11.28 were noted in the EDX spectrum of the sample.

XRD analysis measured angle 2θ with the range of 15° to 70° indicating sharp distinct peaks. The characteristics peaks were observed for molybdenum metal at an angle of 20.35°. Slight shifting of peak from its actual value of 20° was because of enhanced d spacing. On plotting the spectrum intensity versus 2θ, it was observed that the prepared nanocomposites were found to be crystalline due to the formation of sharp peaks as shown in figure 3.3. Doping of transition metal resulted in certain deviation in peak positions. In XRD spectrum, no prominent contamination was noticed that suggested strong indication for doping of Ag into Mo nanoparticles forming the desired nanocomposites.

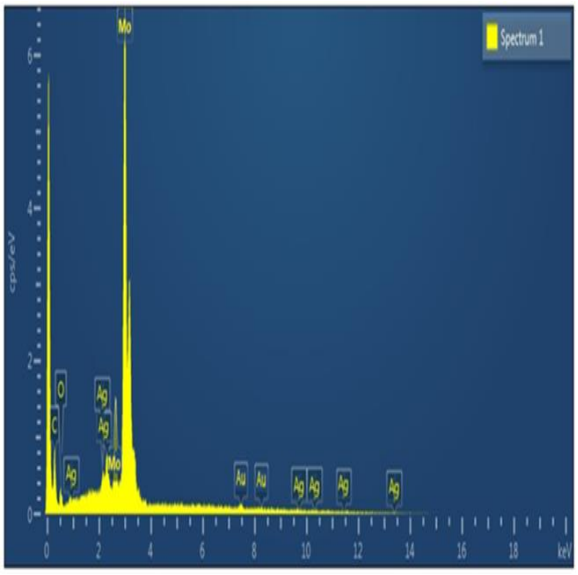


Figure 3.2 *EDX spectrum for nanocomposites material*

Peaks at 2θ =13.23°, 20.02°, 24.21°and 26.30° with intensities 020,101,040 and 131 respectively, corresponds with JCPDS card no.01-074-1389 suggested the presence of orthorhombic crystals of Mo nanoparticles in XRD spectrum. On the other hand, peaks at 2θ=38.22°and 44.41° with intensities 110 and 200 respectively showed the existence of face centered cubic Ag in the nanocomposites matching with JCPDS file card no.04-0783. It was found that in some areas of spectrum peak intensity seemed broader suggesting a reduction in crystallinity because of minute quantities of C and O atoms in the prepared material. XRD peak arrangement of Ag-doped Mo nanocomposites showed the crystalline structure of the prepared nanocomposites. Hence, in this way it was established that the prepared sample was a composite containing two metals. XRD diffraction of peaks of the nanocomposites was obtained with the help of XRD diffractometer using Cu Kα λ=1.78897Å radiation.

Photocatalytic application

The photocatalytic degradation efficiency of the catalyst was observed with the help of two toxic azo dyes, methylene blue (MB) and methylene orange (MO). These dying chemicals are largely being discharged in the water bodies causing serious health hazards.

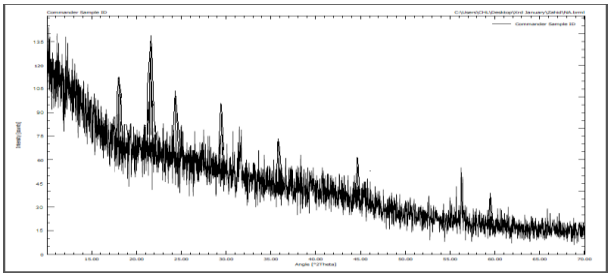


Fig3.3 *XRD spectrum of nanocomposites*

Maximum absorbance was used for investigating the catalytic activity of the sample. The value of absorbance maxima was 650nm in case of methylene blue. For

methylene orange (MO), absorbance maxima value was 455nm as seen in the figure 3.5.

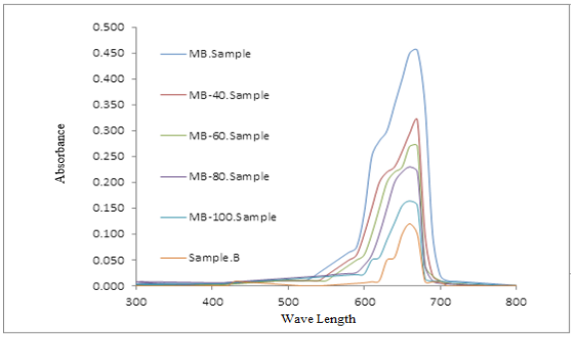


Fig. 3.4 Absorbance spectrum of methylene blue dye

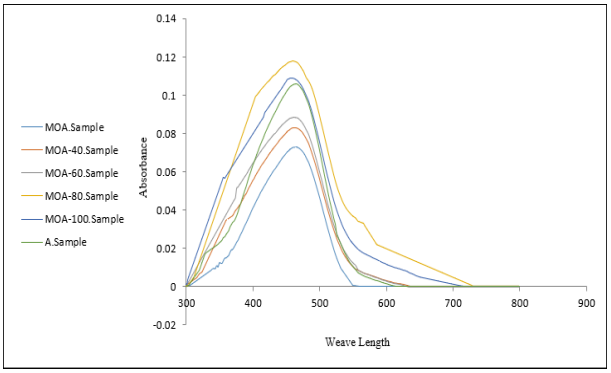


Figure 3.5 *Absorption versus wavelength spectrum for MO dye*

After every 20 minutes of irradiation, 5ml of sample solution was shifted to a glass cuvette for measuring the absorbance values with the help of spectrophotometer. Values of absorbance were compiled for each dye separately. It was found that the dye degraded in a timely manner. The absorbance readings observed by spectrophotometer at different time intervals could be shown in table 3.2.

Table: 3.2 *Absorbance values of methylene blue and methylene orange dyes with time*

Sr. No	Time Minutes	Methylene blue (Absorbance) Nm	Methylene orange (Absorbance) Nm
1	20	2.76	1.27
2	40	1.0916	0.4749
3	60	0.34	0.1129
4	80	0.054	0.0718
5	100	0.0213	0.0162

Absorbance values of each of the dye was measured at 20, 40, 60,80 and then after 100 minutes of light irradiation .It was found that as time changed ,absorbance values were also altered until remarkable and prominent photocatalytic degradation of dye was observed. Increased photocatalytic degradation of both dyes was because of reduced band gap and remarkable photocatalytic applications of the prepared sample material acting as photocatalyst during degradation of dyes.

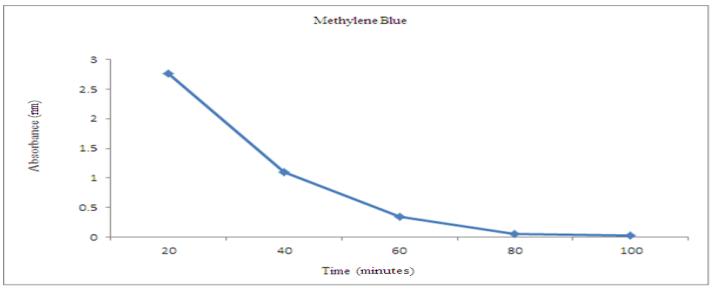


Figure 3.6 *Absorbance versus time graph for methylene blue (MB) dye*

The solution of each organic dye with some amount of prepared catalyst was placed under ultraviolet light source for certain time, then it was noted that there occurred some electronic transition due to absorbance of light radiations. Falling down

of curves in graph indicated a decline in absorbance reading of dyes with the passage of time showing the completion of degradation of dyes.

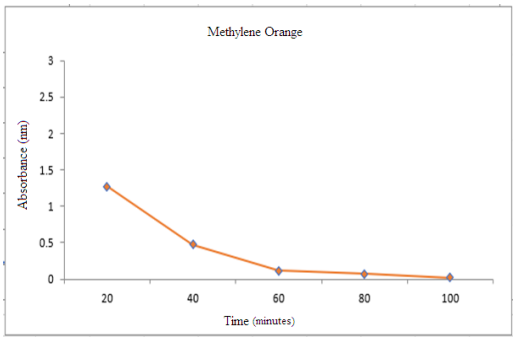


Figure 3.7 *Absorbance versus time graph for methylene orange (MO) dye*

Degradation abilities of both dying chemicals being used were found to be different due to diverse molecular structures and composition of each dye. The discrepancy in the position of curve of methylene blue (MB) and methylene orange (MO) dyes suggested that decolorization process of dyes depend on the molecular structure and type of dye used. Hence, with the same photo catalyst, different dyes are decolorized to different extent. Methylene blue (MB) and methylene orange (MO) dyes exhibited different nature, composition and structural formula which caused a variation in the absorbance tendency of two dyes with the passage of time as indicated in figure 3.8

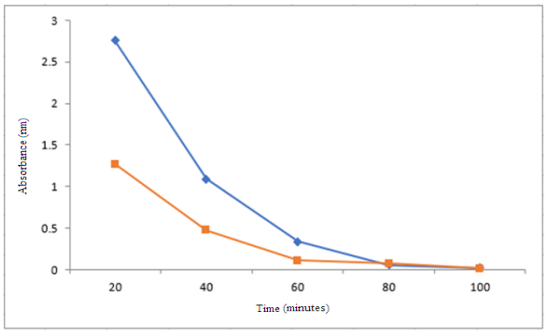


Figure 3.8 *Comparative study of absorbance versus time graph for MB and MO dyes*

The results of characterization indicated the efficiency of the nanocomposites prepared for decolorization of organic dyes. Nanoparticles of silver doped molybdenum proved to be efficient and less expensive photo catalyst as compared to the previously used photocatalytic material with no adverse effects. Many harmful and carcinogenic dying chemicals are extensively are in use in various industries like in textile industry, paper industry, pharmaceuticals etc. Therefore, it is considerably required to eradicate these pollutants and toxic contamination from wastewater. The method studied in the present research work proved to be an efficient, economical and eco-friendly for eliminating methylene blue (MB) and methylene orange (MO) dyes from polluted water.

Conclusion

The present study described green synthesis method to prepare silver doped molybdenum nanocomposites with the help of Citrus Limetta pith extract. The synthesized nanoparticles were characterized by SEM, EDX and XRD analysis. The results of characterization confirmed the formation of uniform, spherical, well distributed nanoparticles having high percentage of molybdenum and silver metals. The catalytic activity of the prepared photocatalyst was investigated by studying the degradation of organic dyes, Methylene Blue (MB) and Methylene Orange (MO) under UV-light irradiation. The results indicated that the prepared photocatalyst could be effectively used for the treatment of wastewater degrade the synthetic dyes remarkably.

References

Abd Mutalib, M., Rahman, M., Othman, M., Ismail, A., & Jaafar, J. (2017). Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy. In *Membrane characterization* (pp. 161-179): Elsevier.

Adeel, M., Ma, C., Ullah, S., Rizwan, M., Hao, Y., Chen, C., . . . Wang, L. (2019). Exposure to nickel oxide nanoparticles insinuates physiological, ultrastructural and oxidative damage: A life cycle study on Eisenia fetida. *Environmental Pollution, 254*, 113032.

Ajmal, A., Majeed, I., Malik, R. N., Idriss, H., & Nadeem, M. A. (2014). Principles and mechanisms of photocatalytic dye degradation on TiO 2 based photocatalysts: a comparative overview. *Rsc Advances, 4*(70), 37003-37026.

Ates, B., Koytepe, S., Ulu, A., Gurses, C., & Thakur, V. K. (2020). Chemistry, structures, and advanced applications of nanocomposites from biorenewable resources. *Chemical Reviews, 120*(17), 9304-9362.

Chand, K., Cao, D., Fouad, D. E., Shah, A. H., Dayo, A. Q., Zhu, K., . . . Dong, S. (2020). Green synthesis, characterization and photocatalytic application of silver nanoparticles synthesized by various plant extracts. *Arabian Journal of Chemistry, 13*(11), 8248-8261.

Chauhan, A., & Chauhan, P. (2014). Powder XRD technique and its applications in science and technology. *J Anal Bioanal Tech, 5*(5), 1-5.

Gudikandula, K., & Charya Maringanti, S. (2016). Synthesis of silver nanoparticles by chemical and biological methods and their antimicrobial properties. *Journal of experimental nanoscience, 11*(9), 714-721.

Hodoroaba, V.-D. (2020). Energy-dispersive X-ray spectroscopy (EDS). In *Characterization of Nanoparticles* (pp. 397-417): Elsevier.

Hong, N. H. (2019). Introduction to nanomaterials: basic properties, synthesis, and characterization. In *Nano-sized multifunctional materials* (pp. 1-19): Elsevier.

Hulla, J., Sahu, S., & Hayes, A. (2015). Nanotechnology: History and future. *Human & experimental toxicology, 34*(12), 1318-1321.

Iravani, S. (2011). Green synthesis of metal nanoparticles using plants. *Green Chemistry, 13*(10), 2638-2650.

Kim, J., & Tasan, C. C. (2019). Microstructural and micro-mechanical characterization during hydrogen charging: An in situ scanning electron microscopy study. *International Journal of Hydrogen Energy, 44*(12), 6333-6343.

Kunduru, K. R., Nazarkovsky, M., Farah, S., Pawar, R. P., Basu, A., & Domb, A. J. (2017). Nanotechnology for water purification: applications of nanotechnology methods in wastewater treatment. *Water purification*, 33-74.

Li, X., Zhang, Z., Fakhri, A., Gupta, V. K., & Agarwal, S. (2019). Adsorption and photocatalysis assisted optimization for drug removal by chitosan-glyoxal/Polyvinylpyrrolidone/MoS2 nanocomposites. *International journal of biological macromolecules, 136*, 469-475.

Manivel, A., Lee, G.-J., Chen, C.-Y., Chen, J.-H., Ma, S.-H., Horng, T.-L., & Wu, J. J. (2015). Synthesis of MoO3 nanoparticles for azo dye degradation by catalytic ozonation. *Materials Research Bulletin, 62*, 184-191.

Nasrollahzadeh, M., Sajadi, S. M., Sajjadi, M., & Issaabadi, Z. (2019). Applications of nanotechnology in daily life. *Interface science and technology, 28*, 113-143.

Opris, R., Toma, V., Olteanu, D., Baldea, I., Baciu, A. M., Lucaci, F. I., . . . Clichici, S. (2019). Effects of silver nanoparticles

functionalized with Cornus mas L. extract on architecture and apoptosis in rat testicle. *Nanomedicine, 14*(3), 275-299.

Ozturk, E., Karaboyacı, M., Yetis, U., Yigit, N. O., & Kitis, M. (2015). Evaluation of integrated pollution prevention control in a textile fiber production and dyeing mill. *Journal of cleaner production, 88*, 116-124.

Petronella, F., Truppi, A., Ingrosso, C., Placido, T., Striccoli, M., Curri, M., . . . Comparelli, R. (2017). Nanocomposite materials for photocatalytic degradation of pollutants. *Catalysis Today, 281*, 85-100.

Reverberi, A., Kuznetsov, N., Meshalkin, V., Salerno, M., & Fabiano, B. (2016). Systematical analysis of chemical methods in metal nanoparticles synthesis. *Theoretical Foundations of Chemical Engineering, 50*(1).

Saif, S., Adil, S. F., Chaudhry, A., & Khan, M. (2022). Microbial synthesis of magnetic nanomaterials. In *Agri-Waste and Microbes for Production of Sustainable Nanomaterials* (pp. 323-356): Elsevier.

Sarkar, S., Chakraborty, S., & Bhattacharjee, C. (2015). Photocatalytic degradation of pharmaceutical wastes by alginate supported TiO2 nanoparticles in packed bed photo reactor (PBPR). *Ecotoxicology and Environmental Safety, 121*, 263-270.

Thekkethil, A. J., Sreekuttan, S., & Madhavan, A. A. (2021). *Application of nano molybdenum trioxide in thermal storage and photocatalysis.* Paper presented at the Journal of Physics: Conference Series.

Ying, S., Guan, Z., Ofoegbu, P. C., Clubb, P., Rico, C., He, F., & Hong, J. (2022). Green synthesis of nanoparticles: Current developments and limitations. *Environmental Technology & Innovation, 26*, 102336.