

## Synthesis and applications of Au-Ag bimetal impregnated layered manganese oxide nanocomposite

C. Shanthi<sup>a</sup>, T. Sumathi<sup>b</sup>, R. Mayildurai<sup>c</sup>, P. Kavitha<sup>a\*</sup>, R. Kannan<sup>b</sup>

<sup>a</sup>*Department of Physics, Sona College of Technology (Autonomous), Salem-636005, Tamil Nadu, India*

<sup>b</sup>*Department of Chemistry, Sri Kumara Gurupara Swamigal Arts College, Affiliated to Manonmaniam Sundaranar University, Srivaikuntam - 628619, Thoothukudi, Tamil Nadu, India*

<sup>c</sup>*Department of Chemistry, Kumaraguru College of Technology (Autonomous), Coimbatore - 641 049, Tamil Nadu, India*

In present study, gold and silver metal nanoparticles were prepared and pillared on the manganese oxide octahedral molecular sieve type layered material. This method helps to stabilize the metal nanoparticles and for the synergetic catalytic effect of both manganese oxide and noble metal catalyst towards catalysis. Formation of layered manganese oxide in pure form and with pillaring was confirmed by XRD. Surface topology and chemical state were studied by SEM with EDS, TEM and XPS respectively. Batch studies have been conducted to evaluate the catalytic oxidative degradation of methylene blue dye using AuAg@LMO.

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### 1. Introduction

Colourants or dyes are assembly of the synthetic organic compounds that are used to impart color in the cosmetic, paper, food, textile, leather, pharmaceutical and plastic industries. New colorants such as dyes or pigments usage a variety of chromophore groups may carry a wide range of organic or inorganic compounds, both to impart the colour, and to provide the expected properties both color and durability.

Therefore, there are numerous chemical substances that are used as colour importuning agents for commercial applications. Synthetic colorants or dyes harm human beings, and they destroy the soil and aquatic environment. Additionally, during the colouring process, a lot of waste water has to be expelled. In Tamil Nadu, lot of textile and paper industries discharges these kinds of colorants especially in Erode and Tirupur Districts. The treatment of this industrial waste water is the need of hour before disposal.

Different sectors produce wastewater that is contaminated with a variety of substances, including chemical pesticides, dyes, heavy metals, and antibiotic [1,2]. Toxic chemical dyes are one of the main contaminants found in wastewater produced by the textiles paper, plastics, food, leather factories, and pharmaceutical sectors, among other hazardous chemical components [3-6]. Several common dyes used by industries to provide color include azo, basic, acidic, cationic, and others [7]. And these artificial dyes have extremely harmful, cancer-causing, and mutagenic properties [8]. Industries release their wastewater containing dyes into nearby bodies of water, such as lakes, rivers, drains, etc [9, 10].

Furthermore, some wastewater produced by other companies is utilized directly for irrigation, which degrades the quality of the land and crops [11]. The toxicity of dye molecules in water also reduces the amount of sunlight that reaches water bodies, which affects aquatic life [12]. Therefore, before effluent containing color is released into nearby water bodies, it must be properly treated. Because of its strong stability provided by its chemical structure, the dye

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\*Corresponding author: kavithap@sonatech.ac.in

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molecule is difficult to degrade into a harmless component [13].

Heavy metals such as lead, cadmium, and copper in effluent water can present substantial effects to living organisms and the ecosystem even when present in small amounts [14,15]. As a result, their removal of pollutants from different waters has become a major recurring problem. Many techniques have been developed or refined in recent years to minimize the heavy metals removal from effluent and or fresh water. These techniques include precipitation through chemicals [16, 17], the nano filtration process and ultra micro/nano filtering [18,19], chemical assist coagulation [20], carbon-based adsorption [21], and bio-chemical treatment [22, 23]. Incorporating metals and/or metal oxide nanoparticles (NPs) into porous granular materials provide a potentially active material and it showed marked solution to overcome the technical challenges associated water purification [24].

Earlier reports suggest that the octahedral molecular sieve of manganese oxide materials provides excellent activity towards for ion separation [25-28], environmental pollution management [29], and battery [30,31] and fuel cell-based energy applications. The porous, layered and defective nanostructures provide excellent platforms and active catalytic sites for the specific applications [32,33].

On the other hand, the aggregation of metal nanoparticles is one of the common problems because of their cluster nature. Due to the cluster formation the catalytic activity is lost. Hence, a number of methods have been reported, namely, capping with suitable agents like surfactants, placing in carbon and metal oxide-based supports [34]. In line with this, we made an attempt to stabilize the AuAg MNPs in Octahedral LMOs and study their catalytic activity towards organic pollutant degradation. In our earlier work we have prepared of nanostructured Gold-Silver@ carbon nanocatalyst, mono, bimetal@ C-reduced graphene oxide nanohybrids metal nanoparticles and graphene oxide-carbon nanotube metal nanoparticles [35-37].

## **2. Experimental**

### **2.1. Synthesis of octahedral layered manganese oxide**

Some modifications were done in the already reported methods [38, 39] of Octahedral Layered Manganese Oxide (OLMO) nanostructure synthesis. In brief, 20 mL of (3 M) glucose was added slowly in to the 0.38 M aqueous (50mL) potassium permanganate solution. A swift, exothermic reaction resultant in to brownish black gel within 2-5 min. After few hours, Water is separated periodically. Then the resultant solid material was dehydrated at 110°C for 24 hours.

### **2.2. Synthesis of OLMO-MNPs**

The Au, Ag and Au-Ag colloidal solutions were prepared by a reduction process using AA as the reducing agent. In brief, about 1 M AA was dispersed in DD water. To this, 10 mL of 1 mM Au and Ag precursors dissolved in DD water were added dropwise. The whole reaction was carried out at 2-3° C, covered with aluminium foil.

After complete transfer, the resultant colloidal solution contains AuAg NPs. About 2g of LMO was dispersed DD water (in 100 mL) and about 10 mL of gold –silver precursors was added dropwise and carried out in an ultrasonication bath and subjected to sonication till complete transfer. Then ultrasonication was carried out for another 5 min. to complete intercalation of MNPs into the layered structures.

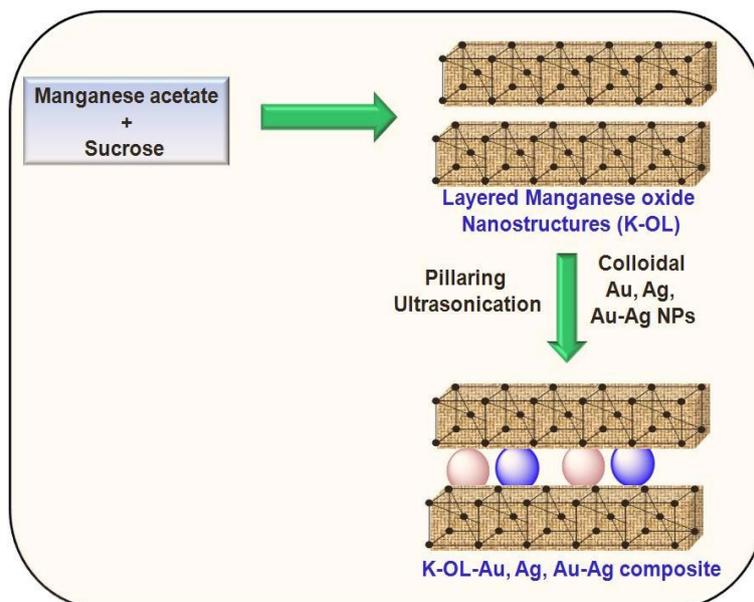


Fig. 1. Scheme of synthesis of Au-Ag bimetal impregnated layered manganese oxide nanocomposite.

### 3. Results and discussion

#### 3.1. X-ray diffraction studies

The powder XRD profile for the LMOs and MNPs pillared LMOs is shown in Figure 2. It demonstrates that the pure LMOs show fewer crystalline sharp peaks and confirms that the LMOs are highly amorphous in nature. Additionally, peaks at  $2\theta$  are  $>10$ , which indicates the formation of layered materials. The XRD profile for LMO shows peaks ( $2\theta$  is) at 9 and on further pillaring of AuAg MNPs, peak intensity is reduced from 14 to 6. For comparison silver colloidal nanoparticles pillared LMO was synthesized and tested the XRD profile indicates the peak intensity at  $2\theta$  is reduced to 14 to 9. And all the other peaks disappeared. This may be due to the ultra-sonication or hydration process.

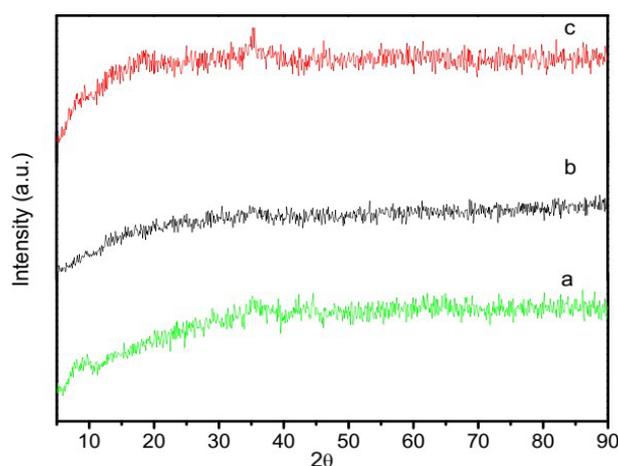


Fig.2. Powder X-Ray Diffraction profile for (a) OL Manganese oxide, (b) Silver nanoparticles pillared OL manganese oxide, (c) Gold-Silver nanoparticles pillared OL manganese oxide.

### 3.2. Topology of AuAg-LMO

The surface topology of the AuAg-LMO was characterized by SEM with EDS and TEM techniques. The SEM images (Figure 3) show metal nanoparticles are uniformly distributed and the EDX profile (Figure 4) shows the presence of Au (8%) and Ag (6%) on an average. ICP method of analysis exhibits the presence of Au (16%) and Ag (12%) in the material.

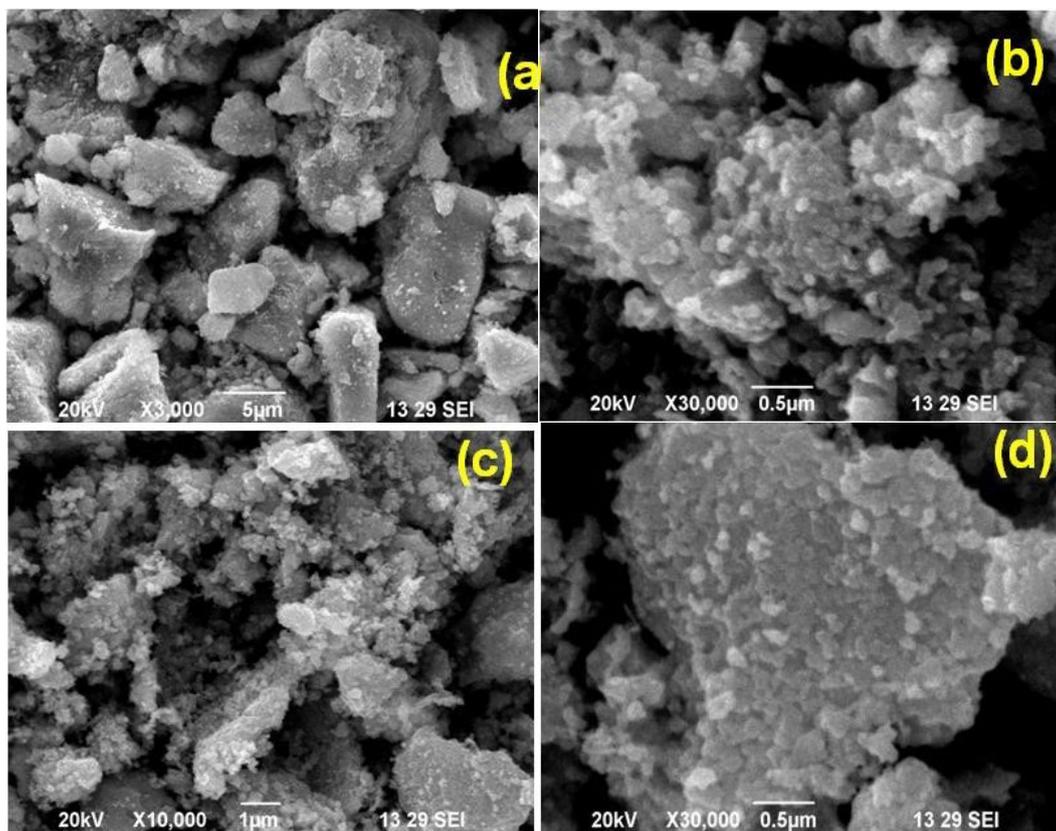


Fig. 3. Topological studies -images of the AuAg-LMO catalyst.

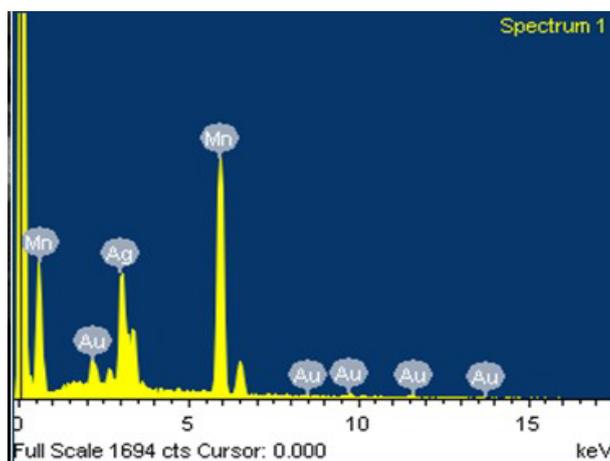


Fig. 4. EDS profile of the AuAg-LMO catalyst.

### 3.3. Transmission electron microscope studies

The TEM micrographs show that the LMO materials formed both nanosheets and nanotubes with a size range from 10-20 nm. On the intercalation of AuAg, the metal nanoparticles are distributed over the LMO material. Figure 5A (d) clearly shows the AuAg MNPs intercalated between the nanosheets of LMO materials.

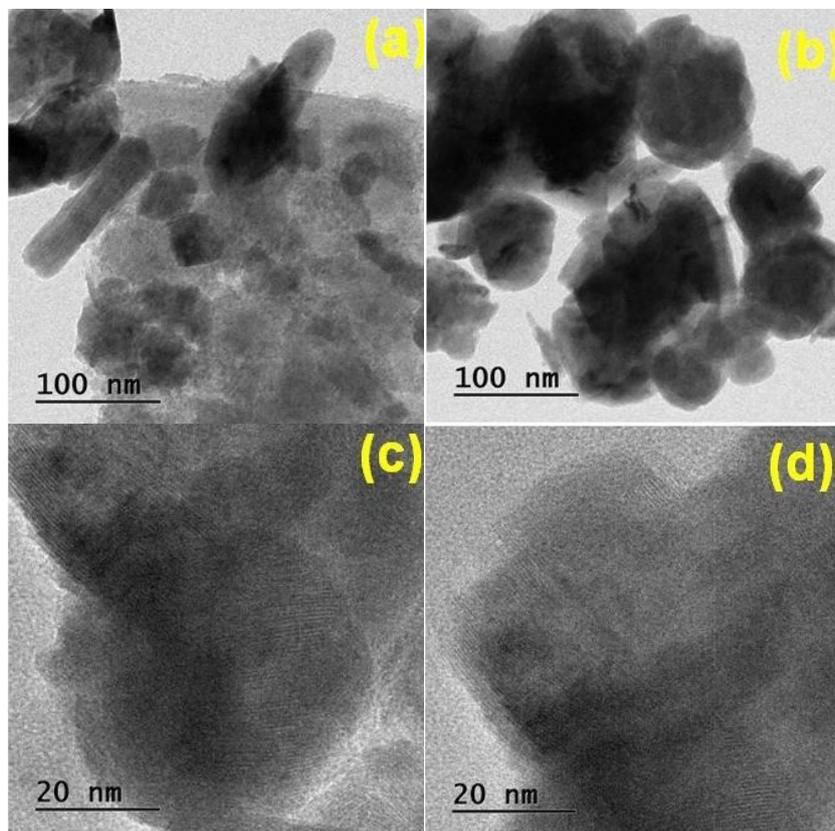


Fig.5.(a-d) (A) Electron microscopic images of the AuAg-LMO catalyst.

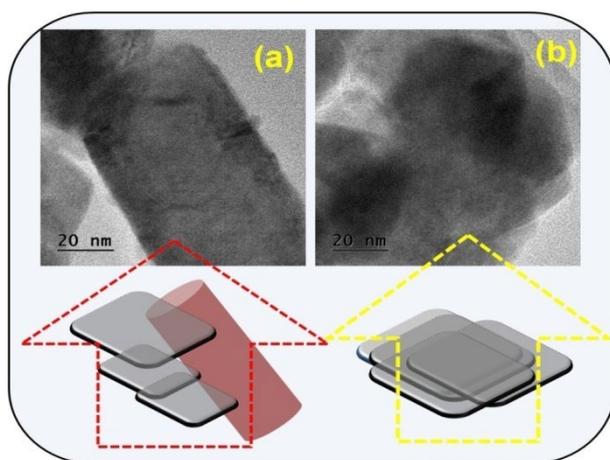


Fig.5.(B) Electron microscopic images and graphical representation of the AuAg-LMO catalyst.

### 3.4. Chemical composition and their oxidation state of the AuAg-LMO catalyst

The XPS profile for AuAg-LMO is shown in Figure 6. The chemical oxidation nature of the AuAg-LMO catalyst was further examined by XPS. Figure 6 shows the XPS spectra for Mn2p, O1s, Au4f, and Ag3d. The Mn spectra show two sharp peaks through the binding energies seen at 654.8 and 642.9 eV conforms  $Mn_2P_{1/2}$  and  $Mn_2P_{3/2}$ . Figure 6c shows a broad spectrum of 529.8 eV, which corresponds to the O1s. This material is prepared at a low temperature and expected to have more surface defects [40, 41]. Thus, the Mn and O binding energies were shifted slightly. We presumed that these surface defects would enhance catalytic activity. Further, the binding energies of Au  $4f_{7/2}$  and  $4f_{5/2}$  are 83.9 and 87.6 eV, respectively, correspond to the gold NPs.  $Ag_{3d_{3/2}}$  and  $Ag_{3d_{5/2}}$  exhibit peaks at 368 and 374.1 eV, respectively, which resemble to silver NPs. [35,40, 42-43].

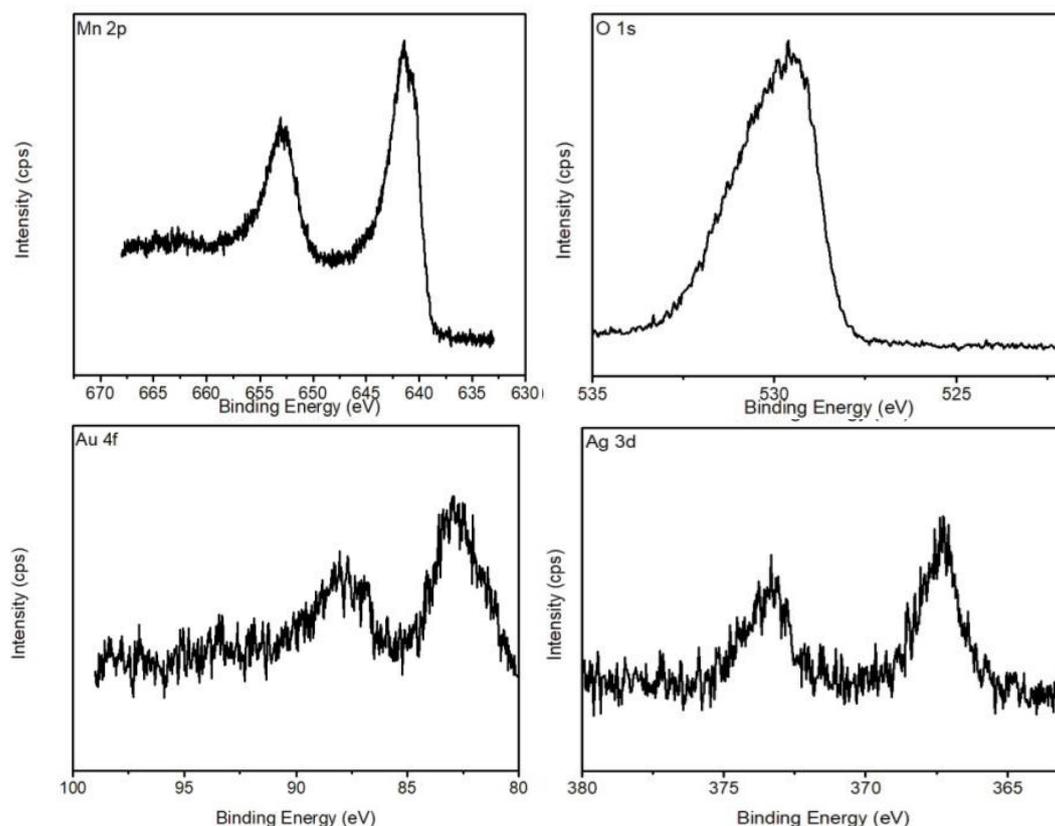


Fig. 6. XPS profile for AuAg-LMO.

### 3.5. Catalytic studies

For the catalytic reduction of 4-Nitrophenol, bimetal impregnated layered manganese oxide system performed poorly. The catalyst is not stable with the borohydrides. So, we chose dye degradation studies; both MG and MB showed almost the same results; hence we presented the MB results in detail.

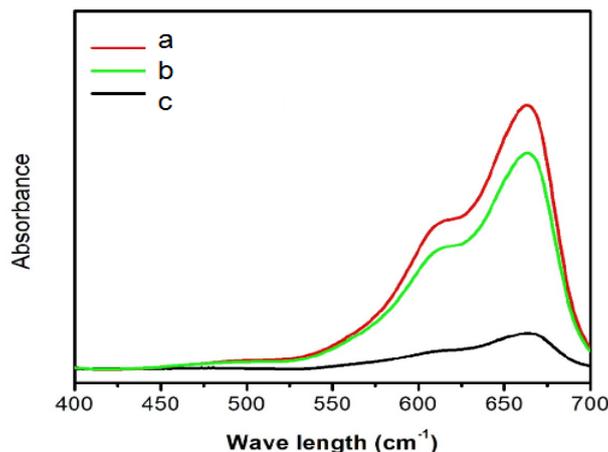


Fig. 7. UV-Vis. Spectroscopic graph of (a) Methylene Blue dye, degradation of MB dye in presence of (b) LMO and (c) AuAg@LMO with 1%  $H_2O_2$ .

The AuAg-LMO based catalytic oxidative decoloration/degradation of Methylene Blue dye has been tested in batch studies. Initially, the oxidation of Methylene Blue dye with LMO, AuAg@LMO, and  $H_2O_2$  was performed, and the effects are shown in Figure 7. It indicates that LMO and AuAg@LMO catalysts showed good catalytic activity. The UV spectra showed a 10% and 90% reduction in peak intensity with 1%  $H_2O_2$  for LMO and AuAg@LMO catalysts, respectively. It reveals that both the support and the MNPs-support contributed significantly to the catalytic activity. However, when LMO and MNPs-LMO were compared, they demonstrated remarkable catalytic activity in a short reaction time. Thus, further studies were performed with MNPs-LMOs to evaluate the effects of varying the reaction time, colourant concentration at high concentration dimer will form), catalyst quantity, and recyclability through batch studies.

Degradation was very high (0.0001 g/L) at low dye solution concentrations, i.e., approximately 95% for both LMO and AuAg@LMO. Whereas at higher concentrations (0.001 g/L and 2.0 mg/L, the reduced is changed to 1 mg/L), pure MB degrades very quickly, LMO and AuAg@LMO degrade about 50 and 60%, respectively. Similarly, for 2 mg/L, up to 29% for LMO, which is comparably higher than the AuAg@LMO (20%), is expressed in Figure 5.7. This may be accounted for by the following facts: (i) at higher concentrations, the dimers form, which hinders the peroxide from approaching the catalyst surface, or (ii) the MB dye itself reacts quickly with peroxide before reaching the catalyst surface. This type of behaviour was observed in multiple studies.

The amount of catalyst plays a vital role in the degradation process. At low extent (10 mg/L) of AuAg@LMO catalyst displays relatively low degradation associated to a high quantity (200 mg/L). It suggests that the AuAg@LMO hybrid catalyst provides a better reaction drive to interact peroxide to generate active oxygen, which is then used to degrade methylene blue dye. The extreme degradation efficiency was observed at 100 min. The reusability of the catalyst

AuAg@LMO show significant catalytic activity, and between one and five runs, 36% less catalytic activity is seen and the constancy holds well, this can be because of the adsorption of degraded by-products on the catalyst surface, and the catalytic surface may be affected by the continuous reaction, which will reduce the efficiency.

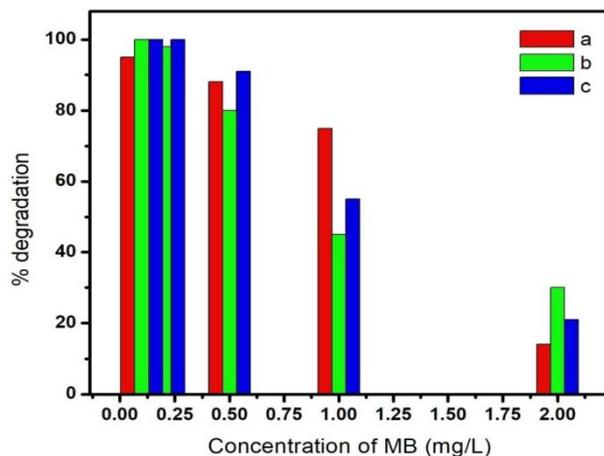


Fig. 8. Catalytic response profile of Methylene Blue with (a) LMO (b) AgLMO and (c) AuAg@LMO with 1%  $H_2O_2$ .

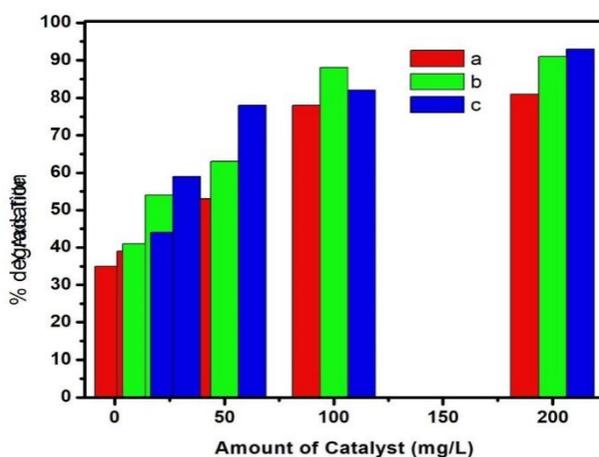


Fig. 9. Effect of catalyst amount on the MB degradation with (a) LMO, (b) Ag@LMO and (c) AuAg@LMO with 1%  $H_2O_2$ .

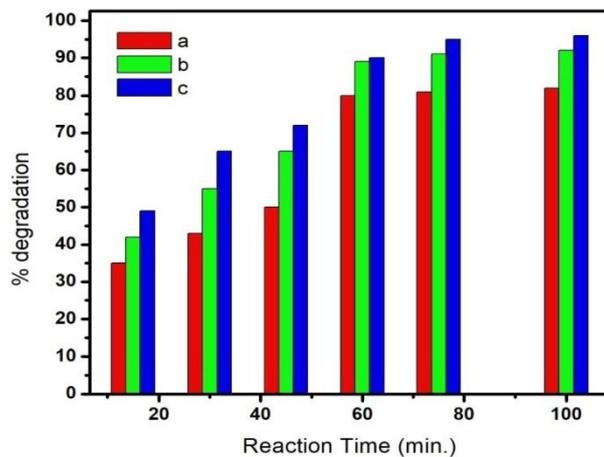


Fig. 10. Result of reaction time on the MB degradation with (a) LMO, (b) Ag@LMO and (c) AuAg@LMO with 1%  $H_2O_2$ .

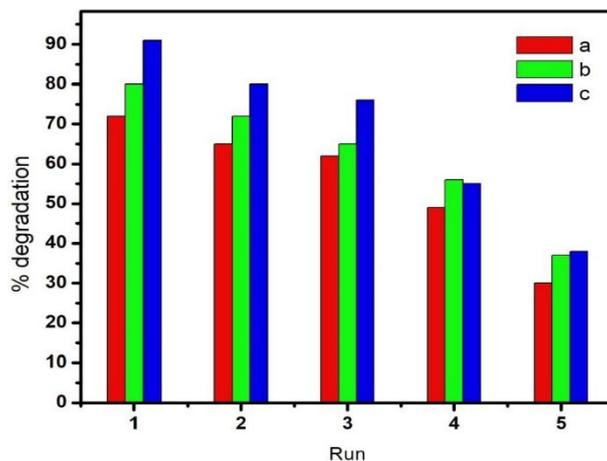


Fig.11. Catalyst reusability on the Methylene Blue dye degradation with (a) LMO, (b) Ag@LMO and (c) AuAg@LMO with 1% H<sub>2</sub>O<sub>2</sub>.

### 3.6. Effect of sodium chloride (NaCl) concentration on dye degradation

Commercial effluents degradation was carried out using artificial effluents that were mimicked using sodium chloride solution. Figure 12 shows the impact of NaCl concentration on the degradation of MB dye at ambient conditions. According to the experimental results 18% degradation revealed at 50 mol/L of NaCl solution.

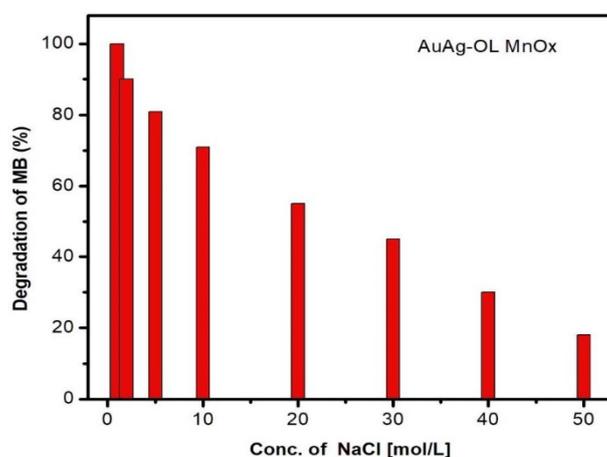


Fig.12. Impact of NaCl concentration on dye degradation.

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### References

- [1] S. Samuchiwal, D. Gola, A. Malik, A., Journal of Hazardous Materials, **402**, 123835(2021); <https://doi.org/10.1016/j.jhazmat.2020.123835>
- [2] M. Bansal, P.K. Patnala, T. Dugmore, Current Research in Green and Sustainable Chemistry, **3**, 100036(2020); <https://doi.org/10.1016/j.crgsc.2020.100036>

- [3] M. Ikram, M.I. Khan, A. Raza, M. Imran, A. Ul-Hamid, S. Ali, *Physica E: Low-dimensional Systems and Nanostructures*, **124**, 114246(2020); <https://doi.org/10.1016/j.physe.2020.114246>
- [4] C. Stone, F.M. Windsor, M. Munday, I. Durance, *Science of the Total Environment*, **718**, 134689(2020); <https://doi.org/10.1016/j.scitotenv.2019.134689>
- [5] V. Balasubramanian, S. Kalpana, R. Jeyachitra, *Journal of Ovonic Research*, **20**(1), 103(2024); <http://dx.doi.org/10.2139/ssrn.4526695>
- [6] V.T. Srisuvetha, S. Karthikeyan, P. Sangeetha, E.G. Sumangali, M. Shkir, V.R.M. Reddy, I.M. Ashraf, W.K. Kim, T. Sumathi, *Journal of Sol-Gel Science and Technology*, **106**(2), 590(2023); <https://doi.org/10.1007/s10971-023-06071-4>
- [7] M. Mathur, K.S. Vijayalakshmi, D. Gola, K. Singh, S. Chaudhary, P. Kaushik, A. Malik, *J Basic Appl Eng Res*, **2**, 1469(2015); <https://www.researchgate.net/publication/283482866>
- [8] A.V. Samrot, H.H. Ali, J. Selvarani, P. Raji, P. Prakash, *Current Research in Green and Sustainable Chemistry*, **4**, 100066(2021); <https://doi.org/10.1016/j.crgsc.2021.100066>
- [9] D. Gola, A. Bhattacharya, P. Dey, A. Malik, S.Z. Ahammad, *Journal of Health and Pollution*, **10**(26), 200610, (2020); <https://doi.org/10.5696/2156-9614-10.26.200610>
- [10] D. Gola, A. Malik, Z.A. Shaikh, T.R. Sreekrishnan, *Environmental Processes*, **3**, 1063(2016); <https://doi.org/10.1007/s40710-016-0176-9>
- [11] S. Khan, A. Malik, *Environmental Science and Pollution Research*, **25**, 4446(2018); <https://doi.org/10.1007/s11356-017-0783-7>
- [12] B. Fatima, S.I. Siddiqui, R. Ahmed, S.A. Chaudhry, *Water Resources and Industry*, **22**, 100119(2019); <https://doi.org/10.1016/j.wri.2019.100119>
- [13] D. Gola, N. Bhatt, M. Bajpai, A. Singh, A. Arya, N. Chauhan, S.K. Srivastava, P.K. Tyagi, Y. Agrawal, *Current Research in Green and Sustainable Chemistry*, **4**, 100132(2021); <https://doi.org/10.1016/j.crgsc.2021.100132>
- [14] J. Gao, S.P. Sun, W.P. Zhu, T.S. Chung, *Water research*, **63**, 252(2014); <https://doi.org/10.1016/j.watres.2014.06.006>
- [15] G. Borbély, E. Nagy, *Removal of zinc and nickel ions by complexation–membrane filtration process from industrial wastewater desalination*, **240**(1-3), 218(2009); <https://doi.org/10.1016/j.desal.2007.11.073>
- [16] K. Vallarasu, I.V. Sampathkumar, S. Manoj, K. Raja, V. Vijayalakshmi, K.M. Gopalakrishnan, K.S. Navaneethan, *J. Environ. Nanotechnol*, **12**(4), 93(2023); <https://doi.org/10.13074/jent.2023.12.234489>
- [17] J. Huang, F. Yuan, G. Zeng, X. Li, Y. Gu, L. Shi, W. Liu, Y. Shi, *Chemosphere*, **173**, 199(2017); <https://doi.org/10.1016/j.chemosphere.2016.12.137>
- [18] M. Al-Shannag, Z. Al-Qodah, Bani-Melhem, K., Qtaishat, M.R., Alkasrawi, M., 2015, *Chemical Engineering Journal*, **260**, pp.749-756; <https://doi.org/10.1016/j.ccej.2014.09.035>
- [19] H. Peng, P. Gao, G. Chu, B. Pan, J. Peng, B. Xing, *Environmental Pollution*, **229**, 846(2017); <https://doi.org/10.1016/j.envpol.2017.07.004>
- [20] M.G. Kiran, K. Pakshirajan, G. Das, *Journal of hazardous materials*, **324**, 62(2017); <https://doi.org/10.1016/j.jhazmat.2015.12.042>
- [21] S. Wan, J. Wu, F. He, S. Zhou, R. Wang, B. Gao, J. Chen, *Chemosphere*, **168**, 748(2017); <https://doi.org/10.1016/j.chemosphere.2016.10.142>
- [22] S. Rajakumar, S. Ramakrishnan, G.K. Monica Nandini, A. El-Marghany, I. Warad, M.S. Kumar, *Global NEST Journal*, **25**(6), 109(2023); <https://doi.org/10.30955/gnj.004882>
- [23] S. Wan, J. Wu, S. Zhou, R. Wang, B. Gao, F. He, *Science of the Total Environment*, **616**, 1298(2018); <https://doi.org/10.1016/j.scitotenv.2017.10.188>
- [24] S. Wan, W. Ding, Y. Wang, J. Wu, Y. Gu, F. He, *Chemical Engineering Journal*, **350**, 1135(2018); <https://doi.org/10.1016/j.ccej.2018.06.068>
- [25] Q. Feng, H. Kanoh, K. Ooi, *Journal of Materials Chemistry*, **9**(2), 319(1999); <http://dx.doi.org/10.1039/a805369c>
- [26] Q. Feng, H. Kanoh, Y. Miyai, K. Ooi, *Int. Conf. on Ion Exchange Proceedings* 141(1995).
- [27] Y.F. Shen, R.P. Zerger, R.N. DeGuzman, S.L. Suib, L. McCurdy, D.I. Potter, C.L. O'young, *Science*, **260**(5107), 511(1993); <https://doi.org/10.1126/science.260.5107.511>

- [28] Z. Wang, Y. Shi, K. Yang, H. Yang, H. Zhao, M. Xi, C. Zhang, L. Zhu, H. Jia, *Chemical Engineering Journal*, 472, p.144830(2023); <https://doi.org/10.1016/j.cej.2023.144830>
- [29] M.M. Thackeray, *Prog. Solid State Chem.*, **25**(1-2), 1(1997); [https://doi.org/10.1016/S0079-6786\(97\)81003-5](https://doi.org/10.1016/S0079-6786(97)81003-5)
- [30] X. Liu, C. Chen, Y. Zhao, B. Jia, *J. Nanomater.* **2013**(1), 736375 2013; <https://doi.org/10.1155/2013/736375>
- [31] M. Margreth, R. Schlink, A. Steinbach, *Pharmaceutical Sciences Encyclopedia: Drug Discovery, Development, and Manufacturing*, 1(2010); DOI: [10.1002/9780470571224.pse415](https://doi.org/10.1002/9780470571224.pse415)
- [32] A.J. Carrillo, P. Pizarro, J.M. Coronado, *J. Energy Storage*, **33**, 102028(2021); <https://doi.org/10.1016/j.est.2020.102028>
- [33] F. Sabaté, M.J. Sabater, *Catalysts*, **11**(10), 1147(2021); <https://doi.org/10.3390/catal11101147>
- [34] R. Rajesh, S. Lingalwar, P. Challa, P. Balla, B. Shanmugavelu V.P. Sruthi, S. Kim, S. Senthilkumar, V. Perupogu, *ACS Applied Nano Materials*, **6**(13), 12258(2023); <https://doi.org/10.1021/acsanm.3c01952>
- [35] P. Kavitha, C. Shanthi, R. Kannan, *Kuwait Journal of Science*, 49(2) 2022; <https://doi.org/10.48129/kjs.12649>
- [36] P. Kavitha, C. Shanthi, R. Kannan, *Digest Journal of Nanomaterials & Biostructures (DJNB)*, **18**(1) 2023; <https://doi.org/10.15251/DJNB.2023.181.21>
- [37] P. Kavitha, C. Shanthi, R. Kannan, *Digest Journal of Nanomaterials & Biostructures (DJNB)*, **19**(2) 2024; <https://doi.org/10.15251/DJNB.2024.192.845>
- [38] S.L. Suib, *Journal of Materials Chemistry*, **18**(14), 1623(2008); <https://doi.org/10.1039/B714966M>
- [39] R. Kannan, A. Jegan, A. Ramasubbu, K. Karunakaran, S. Vasanthkumar, *J Nanomater Biostructure*, **6**(2), 755(2011).
- [40] R. Kannan, A.R. Kim, K.S. Nahm, H.K. Lee, D.J. Yoo, *Chemical Communications*, **50**(93), 14623(2014); <https://doi.org/10.1039/C4CC06879C>
- [41] R. Kannan, H.R. Jang, E.S. Yoo, H.K. Lee, D.J. Yoo, 2015, *RSC Advances*, **5**(45), 35993(2015); <https://doi.org/10.1039/C5RA04226G>
- [42] F. Vitale, I. Fratoddi, C. Battocchio, E. Piscopiello, L. Tapfer, M.V. Russo, G. Polzonetti, C. Giannini, *Nanoscale research letters*, **6**, 1(2011); <https://doi.org/10.1186/1556-276X-6-103W>.
- [43] Ding, Y. Liu, Y. Li, Q. Shi, H. Li, H. Xia, D. Wang, X. Tao, *RSC advances*, **4**(43), 22651(2014); <https://doi.org/10.1039/C4RA03363A>