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Catalytic Reduction of Rhodamine B and Crystal Violet using SnO_2 – SiO_2 Nanocomposite Derived from Rice Husk

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Abstract - *In this study, simple preparation of the biogenic silica from rice husk was used to prepare tin oxide – silica nanocomposite (TOS). The amorphous silica extracted from rice husk using the acidic route, and then nanocomposite was done using a wet imprecation method. SnO_2 – SiO_2 nanocomposite composition and morphology was characterized by various techniques such as ultraviolet-visible spectroscopy, X-ray diffraction, energy dispersive X-ray, Scanning electron microscopy. The nanocomposite exhibited exceptional catalytic activity in reducing Rhodamine B (90%), and Crystal violet (93 %) dyes under optimal conditions. Thus, overall dye degradation studies were more efficient, quick, economically low cost, a feasible protocol with recyclable nanocomposite.*

Key Words: Rice husk 1, Silica 2, nanocomposite 3, Dye 4, Reduction 5, Catalyst 6.

1. INTRODUCTION

Industrial activities bring more amounts of contamination into an aquatic environment, which may affect the ecosystem more. Dyes in wastewater come from food industries, dyeing, printing, textiles and printing, resulting in adverse effects.[1,2] Therefore, it needs to find the most effective methods to remove these contaminations.[3] Now a day's reduction process using metal nanoparticles with sodium borohydride is a new efficient technique to remove dyes from water.[4] The metal nanoparticle reactivity is more than the particular metal counterpart because of their larger surface area and smaller size. Tin oxide nanoparticle is industrially an important semiconductor[5], because of low thermal stability and aggregation[6], which can be overcome by incorporating amorphous silica to form SnO_2-SiO_2 nanocomposite. There are several studies using SnO_2-SiO_2 nanocomposite such as nano films[7], nanotubes[8], xerogel[9], sensors[10], photocatalyst[11].

This work aims to synthesize SnO_2-SiO_2 nanocomposite from amorphous biogenic extracted from rice husk. SnO_2 – SiO_2 nanocomposite's composition and morphology was characterized by various techniques with ultraviolet-visible spectroscopy, X-ray diffraction (XRD), energy dispersive X-ray (EDX), Field Emission Scanning electron microscopy (FE-SEM).

2. Materials and Methods

2.1. Chemicals

All chemicals used were of analytical grade. Tin chloride ($SnCl_2$), Hydrochloride (HCl), and oxalic acid were purchased from Sigma-Aldrich and used without further purification. All the experiments and preparation were performed using Double Distilled Water (DD).

2.2. Extraction of amorphous silica from Rice Husk

About 80 g of rice husk was washed with DD water and filtered, and then rice husk was treated with 0.001 HCl in 1:3 (rice husk : acid) ratio for approximately 24 Hours. After that rice husk was filtered and washed with DD water to a pH of 7. The filtered rice husk (RH) was ashed in a muffle furnace at 500 °C to get 16 g of white powder. Then 16 g of RH ash was treated with 500 ml of 10 % HCl and refluxed for about 4 hours. The refluxed solution filtered and the obtained reside was washed many time with DD water until the residue is free of acid. The white residue dried at 90 °C for about 5 hours, then it calcinated in a furnace for about 6 hours at 700 °C.

2.3. Synthesis of tin oxide silica nanocomposite

Tin oxide was synthesized using the sol-gel method. 50 mL of 0.1 M tin chloride, and 50 mL of 0.1 M of oxalic acid, were heated individually to 80 °C and then hot solutions were mixed together, a white precipitate was formed. The resulting solution was cooled. The residue was filtered, washed with DD water till no Cl^- ions was detected and then the precipitate was dried 90 °C. Tin (II) oxalate formed was loaded in a muffle furnace and calcinated at 800 °C for about 1hour.

The overall reaction of tin (II) oxalate decomposition (eq.1) is given by

$$SnC_2O_4 \longrightarrow SnO_2 + 2CO \quad (1)$$

The obtained tin oxide was used to prepared tin oxide- silica nanocomposite. About 1 gm of tin oxide and 5g of amorphous silica were added in 100 ml of DD water in 250 ml of the beaker. It is stirred at a constant rate at 100 °C, and then completely water evaporated. The solid mass transferred in silica crucible was calcinated at 700 °C for about 4 hours.

2.4. Characterization

The absorption spectra of synthesized silica and tin silica nanocomposite were done using UV-Visible Spectrometer. X-ray diffraction measurements were done by X-ray diffractometer using Cu Kα radiation (λ= 1.54056A˚) to conform the crystalline nature and phase conformation. Morphology and surface were investigated by the field emission scanning electron microscopy TESCAN VEGA3. The chemical composition of the prepared nanocomposite was measured by EDX performed in FE-SEM.

2.4. Catalytic reduction of dyes

The reduction of rhodamine B (RhB) and crystal violet (CV) using sodium borohydride in the presence of TOS nanocomposite was carried out to demonstrate the catalytic activity. 1 mL of 0.1 mM of sodium borohydride solution was mixed with 10 mL of 100 ppm of RB and CV solution in a beaker, respectively. Both solutions were continuously stirred at 500 rpm; subsequently, 0.03 g of TOS nanocomposite was added in RhB and CV solutions. UV-Vis spectra were recorded at regular intervals of time for RhB and CV solution.

3. Result and discussion

UV - visible spectrum of amorphous silica did not show any absorption in the range of 200 to 800 nm,[12] but in the case of TOS nanocomposite an absorption peak was seen at Δλ 342 to 370nm (fig 1).

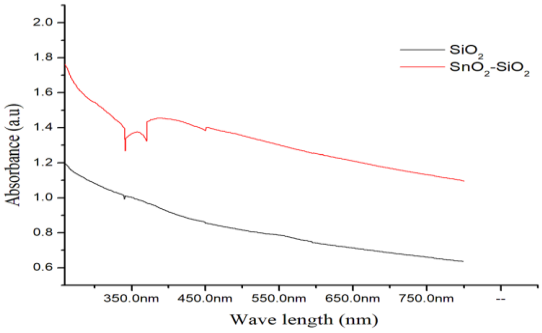

Fig. - 1 UV - visible spectrum of amorphous silica and TOS nanocomposite

The amorphous and crystalline nature of SiO_2 and TOS nanocomposite was confirmed by XRD analysis. The XRD diffractogram of biogenic silica showed (fig 2 a) a broad peak at 2 ɵ = 22.5,[13] which suggested rice husk derived SiO_2 has an amorphous nature.[14]

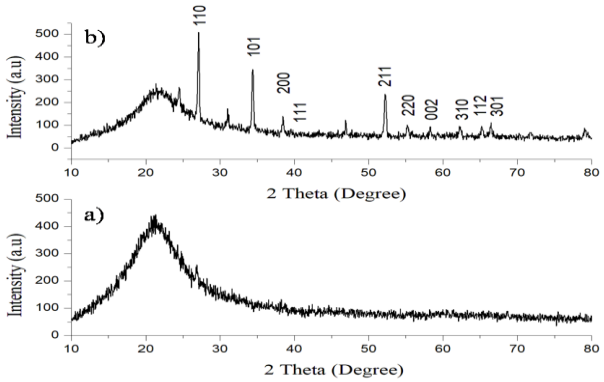

Fig. - 2 XRD diffractogram a) amorphous silica b) TOS nanocomposite

XRD diffractogram of TOS nanocomposite is showed (fig 2 b) smaller broad curve-shaped peak at 2 ɵ = 21.7 to contribute to amorphous silica and other peaks formed were due to crystallinity of SnO_2 at approximately 2ɵ = 27.1°, 34.2° and 52.1°.[14]

The surface morphology and shape of the prepared SiO_2 and TOS nanocomposite were examined by using FE-SEM. The amorphous silica scanned different magnifications were collected and analyzed (Fig 3). The images illustrated that the non-uniform fish scale shapes like particle and some needle shape particles were formed. The particle size came under micro size with larger agglomerates.

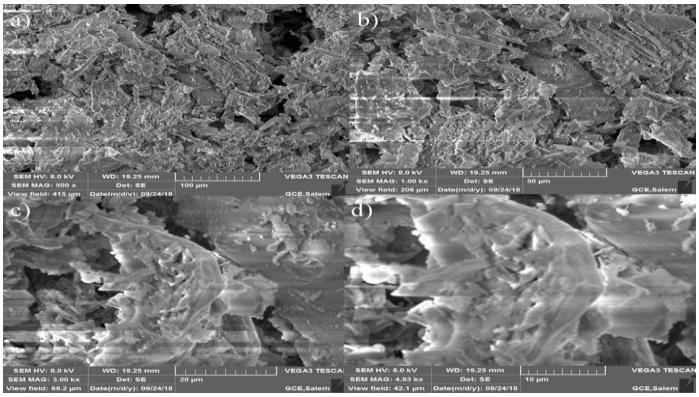

Fig. - 3 SEM image of amorphous silica at different magnification

The synthesized TOS nanocomposite surface morphology and shape were shown in fig (4). FE-SEM image of TOS nanocomposite scanned at the different magnification like 3000, 10000, 20000X. The TOS nanocomposite shape was mixture of irregular shapes with agglomerate particle with surface porous in nature at 1000 nm.

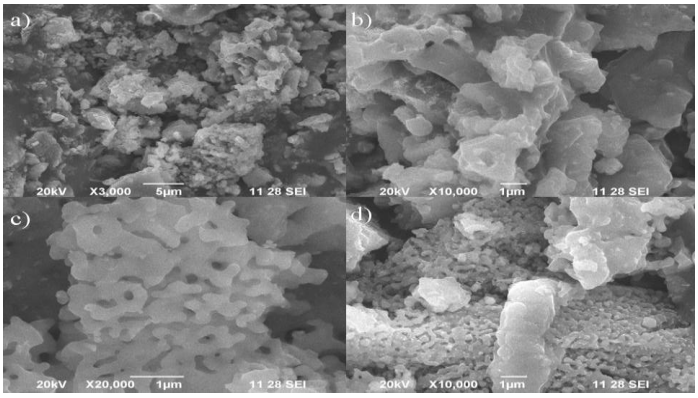

Fig. - 4 SEM image of TOS nanocomposite at different magnification

The resulting amorphous silica and TOS nanocomposite's chemical composition has been analyzed by EDX analysis shown in fig 5 a, b. The EDX analysis of amorphous silica (fig 5 a) shows a significant amount of oxygen, silicon, and other impurities (51.59 % and 10.98%, respectively). On the other hand, TOS nanocomposite was confirmed by EDX analysis and showed (fig 5 b) O, Si, Sn, C, Na, and Cl, of 63.31 %.

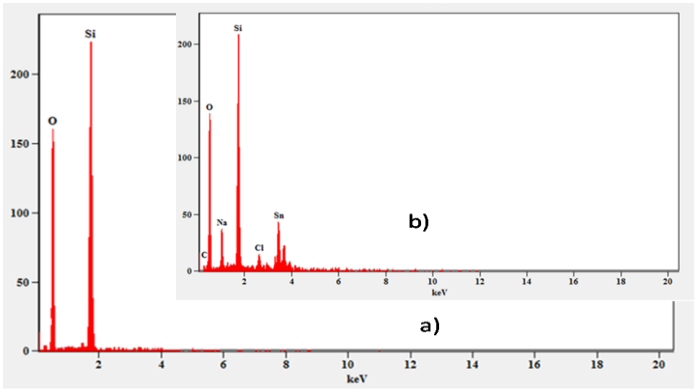

Fig - 5 EDX analysis a). Amorphous silica; b) TOS nanocomposite

Synthesized TOS nanocomposite catalytic activity was determined by reduction of aqueous Rhodamine (RhB) and CV in the presence of $NaBH_4$. The reaction was monitored by UV-Vis spectrometer in the range between 400 to 800 nm at room temperature. For the comparison control experiments were carried out under different conditions like (i) without catalyst (ii) with catalyst and $NaBH_4$. The fig 6 shows the reduction of RhB with and without catalyst. The presence of TOS nanocomposite and $NaBH_4$ could result in a more effective reduction of RhB (fig 6). The absorption peak of RhB decreased quickly after the addition of TOS nanocomposite with $NaBH_4$. The catalytic reaction was completed within 30 min, indicating the efficient catalytic performance of the TOS nanocomposite.

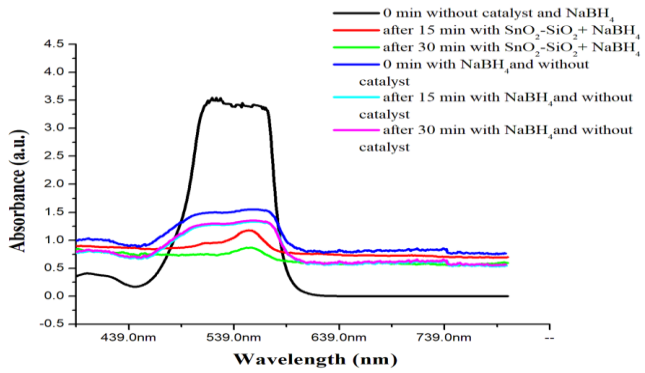

Fig - 6 UV-Vis spectra of catalytic reduction of RhB

TOS nanocomposite catalytic activity was examined for reduction of aqueous CV also. When the reduction process was carried out in the presence of TOS nanocomposite with $NaBH_4$, a rapid decreased in intensity of peak at 570 nm (fig 7) was seen. The reduction process required about 5 min for completion in presence of catalyst compared to 30 min without catalyst.

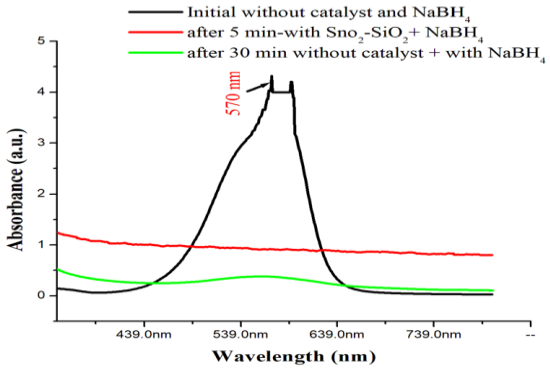

Fig - 7 UV-Vis spectra of catalytic reduction of CV

3. Conclusion

This method reports preparation of facile, cost-effective method for synthesis of rice husk derived silica and tin oxide – silica oxide nanocomposite. The silica and nanocomposite were characterized by UV, XRD, SEM which confirm the amorphous nature of silica and crystallinity of tin oxide – silica oxide nanocomposite. The SEM image revealed that the average size of the synthesized tin oxide – silica oxide nanocomposite size is below 1000 nm. The synthesized tin oxide – silica oxide nanocomposite showed high catalytic activity reduction of rhodamine B and crystal violet with $NaBH_4$ with less time.

REFERENCES

1) Banazadeh A, Salimi H, Khaleghi M, Shafiei-Haghighi S. Highly efficient decolorization of hazardous dyes in aqueous phase by supported palladium nanocatalyst - A green approach. J. Environ. Chem. Eng. Published online 2016:2178–2186.

https://doi.org/10.1016/j.jece.2015.09.007

2) Ameen S, Park D.R, Shin H.S. Silicon nanowires arrays for visible light driven photocatalytic decolorization of rose bengal dye. J. Mater. Sci. Mater. Electron. Published online 2016:10460–10467.

https://doi.org/10.1007/s10854-016-5135-8

3) Dai J, Chen J, Lin S, Xia S, Chen S, Deng Y. Reduction of nitro phenols using nitroreductase from E. coli in the presence of NADH J. Hazard. Mater. Published online2009:141-143.
https://doi.org/10.1016/j.jhazmat.2009.04.122

4) Atarod M, Nasrollahzadeh M, Sajadi S.M. Euphorbia heterophylla leaf extract mediated green synthesis of Ag/TiO2 nanocomposite and investigation of its excellent catalytic activity for reduction of variety of dyes in water J. Colloid Interface Sci. Published online 2016: 272 - 279.

https://doi.org/10.1016/j.jcis.2015.09.073

5) Manjula P, Satyanarayana L, Swarnalatha Y, Manorama SV. Raman MASNMR studies to support the mechanism of low temperature hydrogen sensing by Pd doped mesoporous SnO_2. Sensors and Actuators. B, Chemical. Published online 2009: 28-34.
http://dx.doi.org/10.1016/j.snb.2009.02.051.

6) Feng YS, Zhou SM, Li Y and Zhang LD. Preparation of the SnO_2/SiO_2 xerogel with a large specific surface area. Materials letters. Published online 2003: 2409-2412.

https://doi.org/10.1016/S0167-577X(02)01245-4

7) Lorenzi R, Lauria A, Mochenova N, Chiodini N and Paleari A. Study of the absorption edge of SnO2 nanoparticles embedded in silica films. Journal of Non-Crystalline Solids. Published online 2011: 1888-1891.
http://dx.doi.org/10.1016/j.jnoncrysol.2010.12.045.

8) Adam F, Appaturi JN, Thankappan R and Nawi MAM. Silica–tin nanotubes prepared from rice husk ash by sol–gel method: characterization and its photocatalytic activity. Aplied Surface Science. Published online 2010: 811-816.

http://dx.doi.org/10.1016/j.apsusc.2010.07.070.

9) Grieken RV, Martos C, Sánchez MS, Serrano DP, Melero JA, Iglesias J. Synthesis of Sn–silicalite from hydrothermal conversion of SiO_2–SnO_2 xerogels. Microporous and mesoporous materials. Published online 2009: 176-185.

https://doi.org/10.1016/j.micromeso.2008.10.020

10) Wei TY, Kuo CY, Hsu YJ, Lu SY and Chang YC. Tin oxide nanocrystals embedded in silica aerogel: Photoluminescence and photocatalysis. Microporous and mesoporous materials. published online 2008: 580-588.

https://doi.org/10.1016/j.micromeso.2007.10.040

11) Wu Z.G, Jia Y.R, Wang J, Guo Y, Gao J.F. Core-shell SiO2/Ag composite spheres: synthesis, characterization and photocatalytic properties. Materials Science-Poland. Published online 2016:806-810. https://doi.org/10.1515/msp-2016-0121

12) Liou T.H, Chang F.W, Lo J.J. Pyrolysis kinetics of acid-leached rice husk. Industrial & engineering chemistry research, Published online 1997: 568-573. https://doi.org/10.1021/ie9604536

13) Zhang Q, Ye J, Tian P, Lu X, Lin Y, Zhao Q, Ning G. Ag/TiO_2 and Ag/SiO_2 composite spheres: Synthesis, characterization and antibacterial properties. RSC advances published online 2013: 9739-9744. **https://doi.org/10.1039/C3RA40596F**

14) Ferreira CS, Santos PL, Bonacin JA, Passos RR, Pocrifka LA. Rice Husk Reuse in the Preparation of SnO_2/SiO_2 Nanocomposite. Materials Research. Published online:2015 639-43. https://doi.org/10.1590/1516-1439.009015