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Nano-silica and Zeolite-Y: Synthesis, Characterization and Application in the Photocatalytic Degradation of Azo Dyes

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ABSTRACT

In this study a novel approach for the synthesis of nano-Silica and Zeolite-Y is described. Nano-Silica was effectively prepared from bamboo (*Bambusa Vulgaris*) leaves ash. Zeolites are Sodium Aluminosilicates. The synthesized nano-silica was employed in the preparation of zeolite-Y which showed better results in the photo catalytic degradation of azo dyes: Methyl orange and Methylene blue. The following characterisations were performed: UV-VIS, FT-IR, SEM, TG-DTA and XRD. The photocatalytic degradation was carried out by varying contact time, pH, initial dye concentration and the percentage efficiency was calculated. Thus this work is a clear enclosure of the synthesis, characterisation and applications of both nano-silica and zeolite-Y.

Keywords: Nano-Silica, Zeolite-Y, Photo catalytic degradation, Percentage efficiency, Azo dyes, contact time.

Introduction

Nanoparticles have attracted much attention due to their unique properties such as low size, large surface area, and good activity (P. Dileep and Sunil k. Narayanankutty, 2020). Many researches include the production of Nano-Silica from other agro wastes like rice husk ash (Olawale et al., 2012), maize husk (Olawale et al., 2019), corn cob (Mohanraj et al., 2012), bagasse (Affandi et al., 2009) and bamboo culm (Tarek et al., 2021). Bamboo leaves give rise to a serious management problem, due to its large volume at the time of disposal, for which the most common and easy solution is land filling or incineration in an open field; This is of no use but of a nuisance to the environment, creating massive pollution and could be overcome by collecting the bamboo leaves and subjecting it to the treatment and production of nano-silica which is of a greater use today (Benlin Giftna and Begila David, 2022). Nano-silica may be prepared by following a very simple process of alkali treatment followed by acid precipitation at desired concentrations (Subitha and Prabha Littis Malar, 2020). Zeolite-Y can be effectively prepared using Nano-Silica. They were dealuminated by steaming and were introduced as fluid-cracking catalysts in the year 1970 (Wolfgang Lutz, 2014). It can be also used in the ion-exchange process in the decontamination of radioactive waste solutions (Ramsharan Singh and Prabir K. Dutta, 1999). In this work Zeolite Y is used in the Photo degradation of Azo dyes.

MATERIALS AND METHODS

Bamboo leaves ash, Sodium hydroxide (3M), Buffer (CH_3COONa-CH_3COOH), dilute hydrochloric acid, Con. Sulphuric acid, Aluminium hydroxide and Double deionised water were used.

Synthesis of Nano-Silica

The cleaned and dried bamboo leaves were burned in a muffle furnace (model: STXMF112) for 5 hours at 800°C and then left to cool down for a day. The ash obtained was ground into fine powder of uniform size. 5 grams of the prepared bamboo leaf ash was treated with 3M NaOH solution. The solution was covered well with thin foil sheet and heated using a hot plate with magnetic stirrer (model: LMMS-5LC) by constant stirring for 6 hours. It was allowed to settle for a day and the filtrate was isolated. Dilute HCl at 2M concentration was added to the filtrate under constant stirring. The pH was checked using a digital pH sensor (model: SSI-303) and found out to be 2. A buffer solution consisting of sodium acetate and acetic acid was used to maintain the pH level around 8 especially for high purity of the silica. Then the contents were allowed to stand for a day at room temperature. The precipitate obtained was washed several times with water and dried well in a drying oven (model: LDO-A13) for 15 hours to obtain pure Nano-Silica.

$$\text{Ash} + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$Na_2SiO_3 + 2HCl \longrightarrow SiO_2 + 2NaCl + H_2O$$

Synthesis of Zeolite Y

6g NaOH, 4g Al $(OH)_3$ and 45ml distilled water was heated at 70ºC for 2 hours to obtain sodium aluminate. Now colloidal silica (30%) was added to the solution and heated for 2 hours. Meanwhile, con.H_2SO_4 is added to the mixture as a catalyst. The container is perfectly sealed and heated at 100 ºC for 24 hours until Zeolite Y is formed as a precipitate. The precipitate is washed, filtered and dried. The prepared Zeolite Y had the ratio of Si: Al> 1.5.

$$Al(OH)_3 + NaOH + H_2O \xrightarrow{\triangle} NaAlO_2 + 3\,H_2O$$

$$NaAlO_2 + \text{colloidal Si} \xrightarrow[H_2SO_4]{\triangle} Na_2O.Al_2O_3.4\text{-}8\,SiO_2.8\text{-}9\,H_2O$$

RESULTS AND DISCUSSION

Characterization of Nano-silica

UV- VIS Spectral Analysis

The UV- Vis spectral analysis of Nano-Silica was obtained in the range of 200-800 nm. The UV spectrum was recorded by the UV-1700 series spectrophotometer from Shimadzu, Europe. The UV-VIS analysis was carried out using 16 ml of TEOS precursor at 650°C and the absorption peak was obtained around 235nm.This confirms the formation of amorphous silica nano particles. The optical band gap, as calculated using the Tauc's equation, was found to be zero by plotting $(\alpha h\upsilon)^2$ against hυ. Here, n= 1/2 for direct allowed transitions that take place during absorption of UV-Vis light. The zero band gap in nano-silica shows that there is no difference in energy between the valence electron band and the conduction band, so the electrons can move from occupied states in valence band to empty states in the conduction band without any threshold energy.

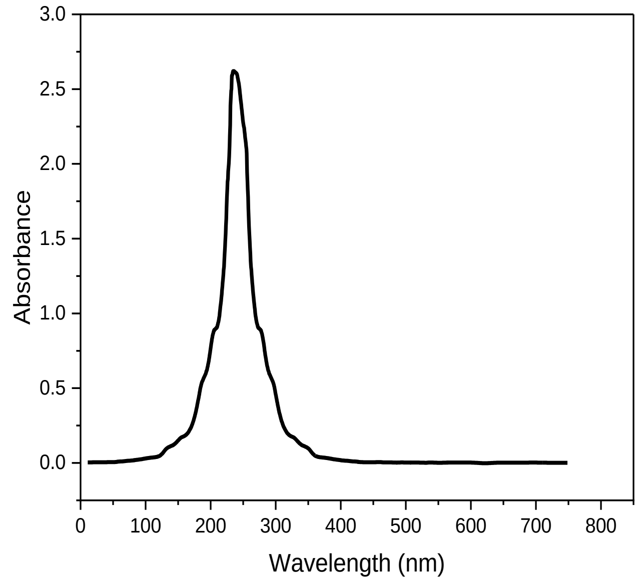

Fig.1. UV-VIS absorption spectrum of nano-silica.

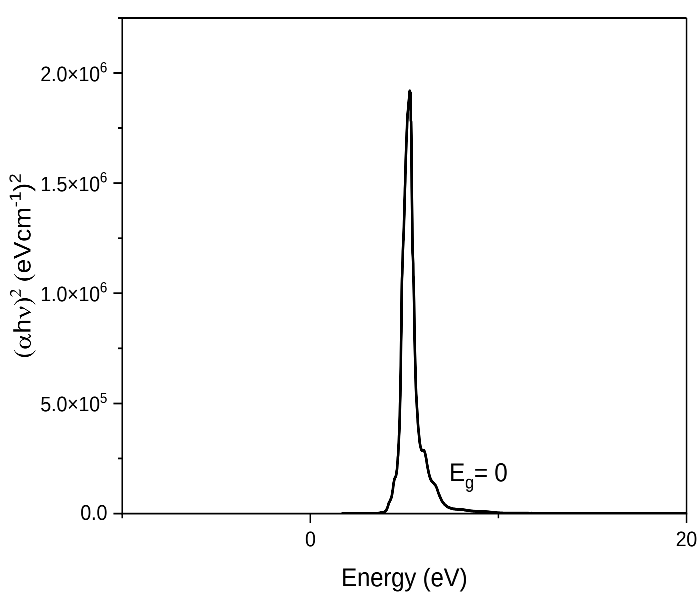

Fig.2. Band-gap energy of nano-silica

FT-IR spectral analysis

The FT-IR spectral analysis was obtained in the range 450-4000 cm^{-1}. The analysis was done by the FTIR- 8400S series spectrometer from Shimadzu, Europe.

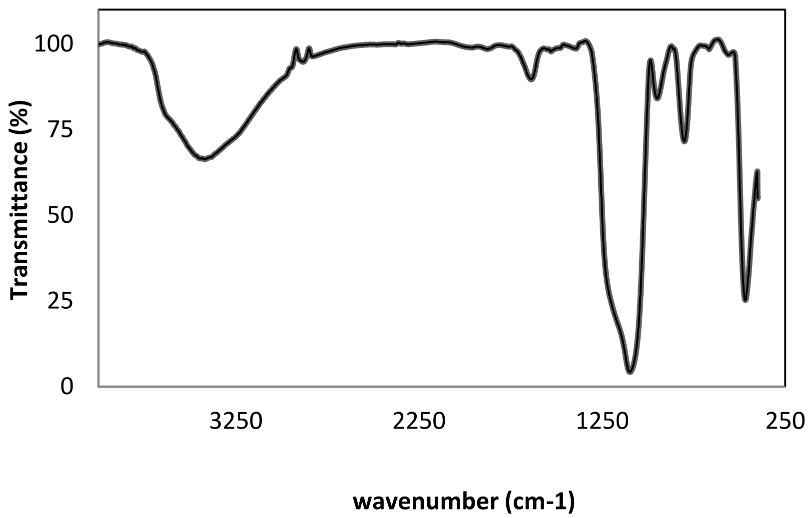

Fig.3.Fourier Transform- Infra Red spectrum of nano-silica.

In the above spectrum, the strong broad band at 3444.63 cm^{-1} is due to the O-H stretching vibrations owing to the presence of silanol (Si-O—H) by adsorption of a water (H-O-H) molecule. The peak at 2882.42 cm^{-1} is also due to the O-H stretching due to the intra molecular bond. The bending vibrations of water molecules trapped in the silica matrix produces a peak at 1637.45 cm^{-1}. The Si-O-Si siloxane band stretching accounts for the sharp peak at 1098.39 cm^{-1}.

X-Ray Diffraction Analysis

XRD is used to study the crystal structure, composition and physical properties of materials. The XRD analysis of Nano-Silica below 600°C for 2 hrs showed a broad peak at 2θ= 22.68°. The broad peak confirms the amorphous nature of nano-silica. Using Bragg’s formula, the particle size of nano-silica was found to be 19 nm.

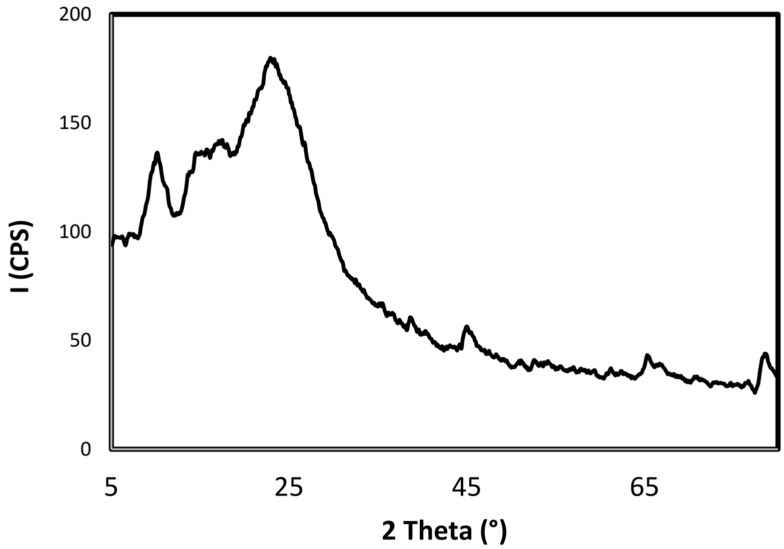

Fig.4. X-Ray Diffraction pattern of nano-silica.

Scanning Electron Microscopy (SEM)

SEM provides the microscopic image of the sample by scanning the surface of the sample with a beam of electrons. The SEM images of Nano-Silica showed the adsorption of spherical shaped silica Nano particles there by confirming the amorphous nature of nano-silica.

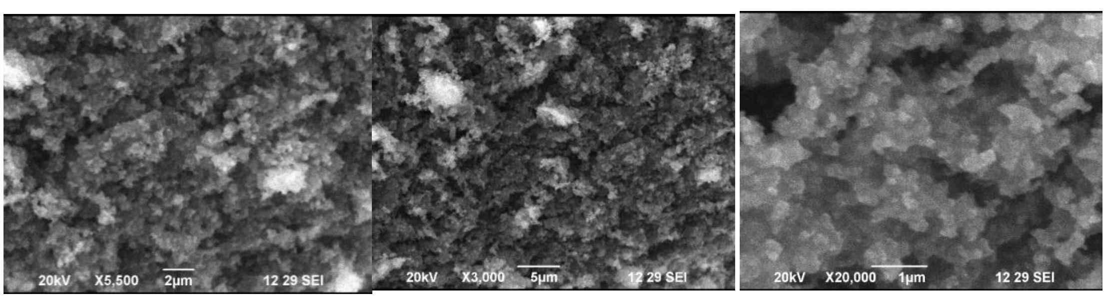

Fig.5. SEM images of nano-silica obtained from the bamboo leaves ash

Thermo Gravimetric Analysis (TG-DTA)

TG-DTA measures multiple thermal properties of a sample at once. The TG component measures the temperatures at which the sample decomposes, reduces or oxidizes and also the weight changes that occur. The DTA component measures the melting, glass transition temperature and dehydration parameters. The temperature range was 0ºC to 1000ºC.

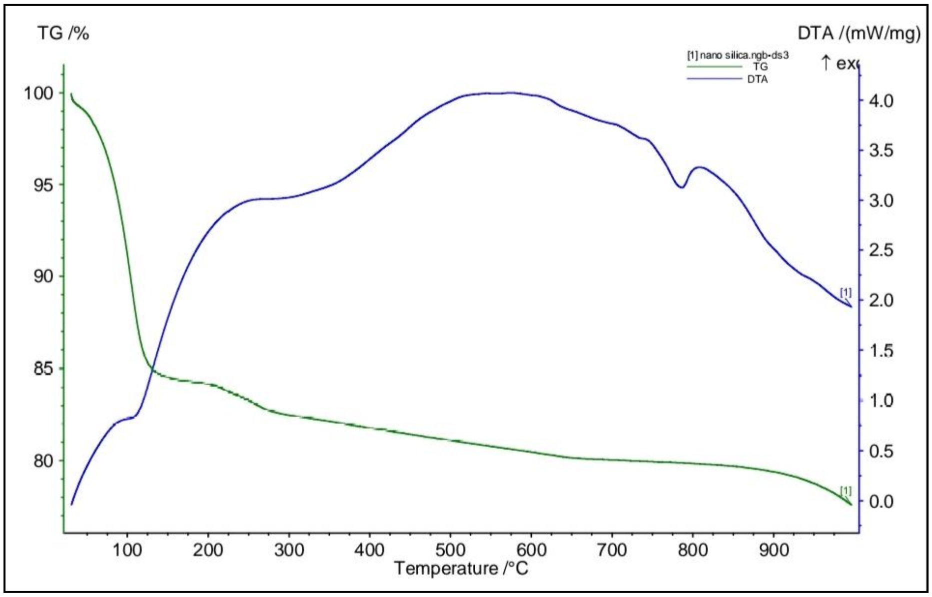

Fig.6. TG-DTA plot of nano-silica.

The final mass percentage was observed to be 77.6% at 1000ºC. DTA curve shows that the process is exothermic because of the depression in the DTA curve. Hence, heat is released. The glass transition temperature is observed to be 100ºC. The thermal stability of nano-silica as per the TG curve was found good.

Characterisation of Zeolite-Y

UV- VIS Spectral Analysis

The UV- VIS spectral analysis of zeolite-Y was obtained in the range of 200-800 nm. The UV spectrum was recorded by the UV-1700 series spectrophotometer from Shimadzu, Europe. The maximum absorption peak is at 242 nm. The optical band gap, as calculated using the Tauc's equation, was found to be 0eV by plotting $(\alpha h\upsilon)^2$ against $h\upsilon$. Here, n = 1/2 for direct allowed transition that takes place during absorption of UV-Vis radiation. Here, the energy gap between the valence band and conduction band is approximately zero, and so the compound was characterized for its electrical properties.

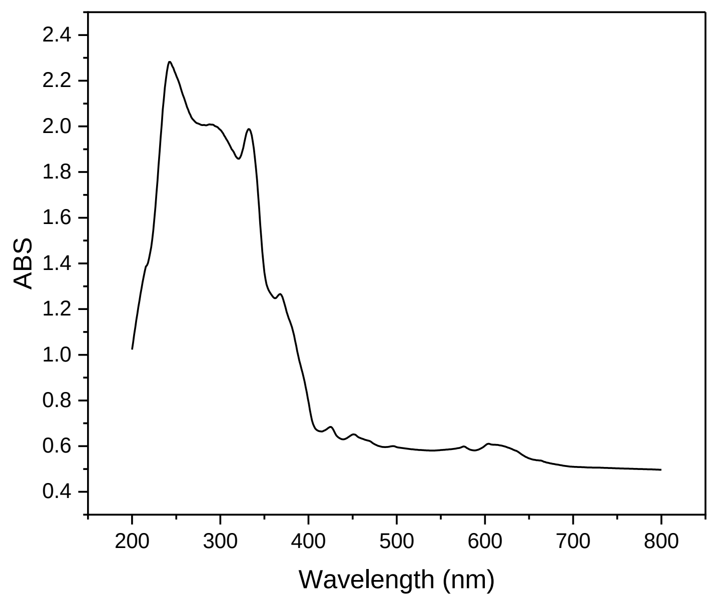

Fig.7. UV- VIS of zeolite-Y

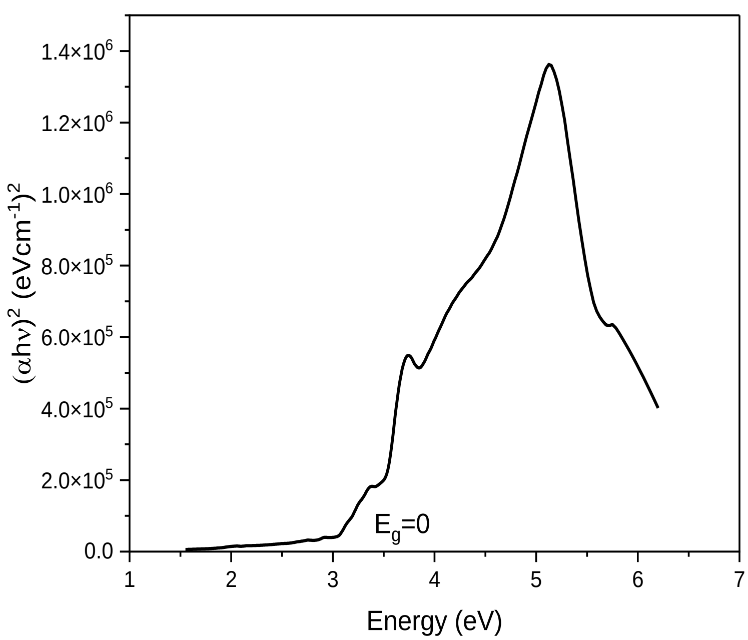

Fig.8. Band-gap energy plot of zeolite-Y

FT-IR spectral analysis

The FT-IR spectral analysis was obtained in the range 450-4000 cm^{-1}. The analysis was done by the FTIR- 8400S series spectrometer from Shimadzu, Europe. The three prominent peaks found at 400 cm^{-1}, 2350 cm^{-1}, 2400 cm^{-1} and 3400 cm^{-1}were due to the alkene sp^2 C-H bend, C=O group disappearance, asymmetric CH_2 stretching and O-H bending vibrations respectively.

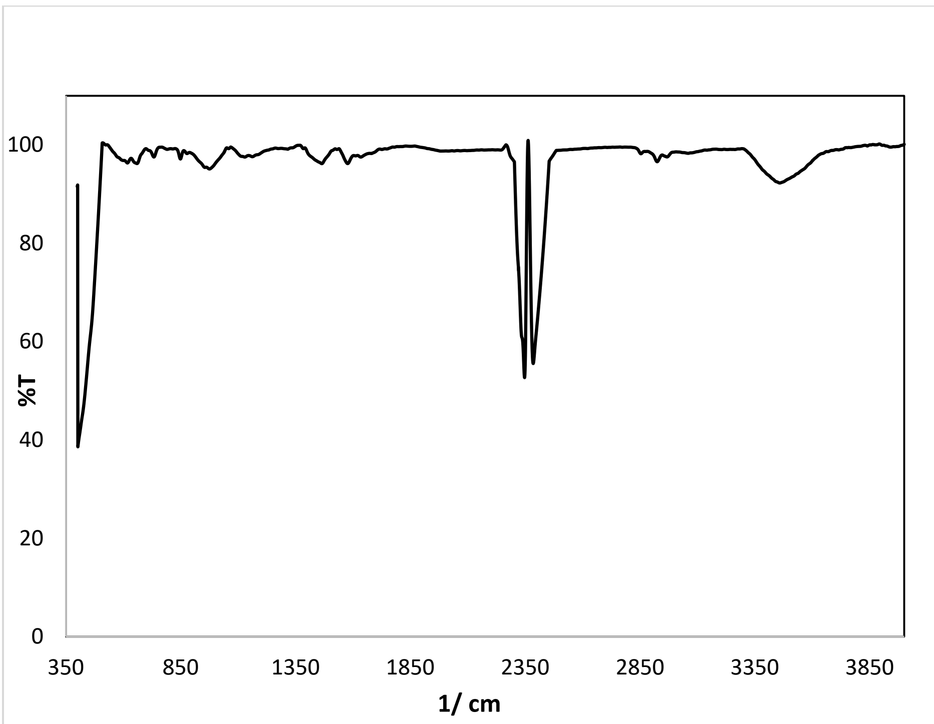

Fig.9. FT-IR of Zeolite-Y

X-Ray Diffraction Analysis

XRD is used to study the crystal structure, composition and physical properties of materials. The diffraction peak is at 28.87º. The particle size as per Bragg's equation is 12.71 nm.

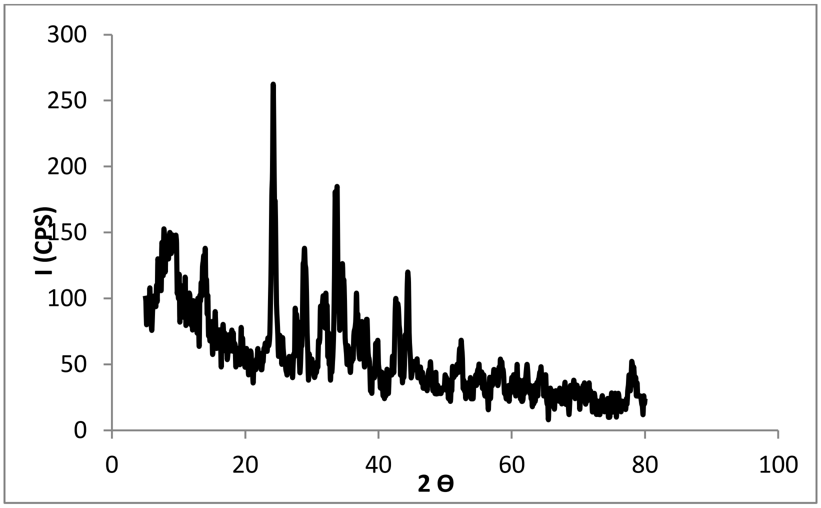

Fig. 10. XRD pattern of zeolite-Y

Scanning Electron Microscopy (SEM)

SEM provides the microscopic image of the sample by scanning the surface of the sample with a beam of electrons. The images show flaky appearance which are agglomerate indicating the amorphous nature of zeolite-Y.

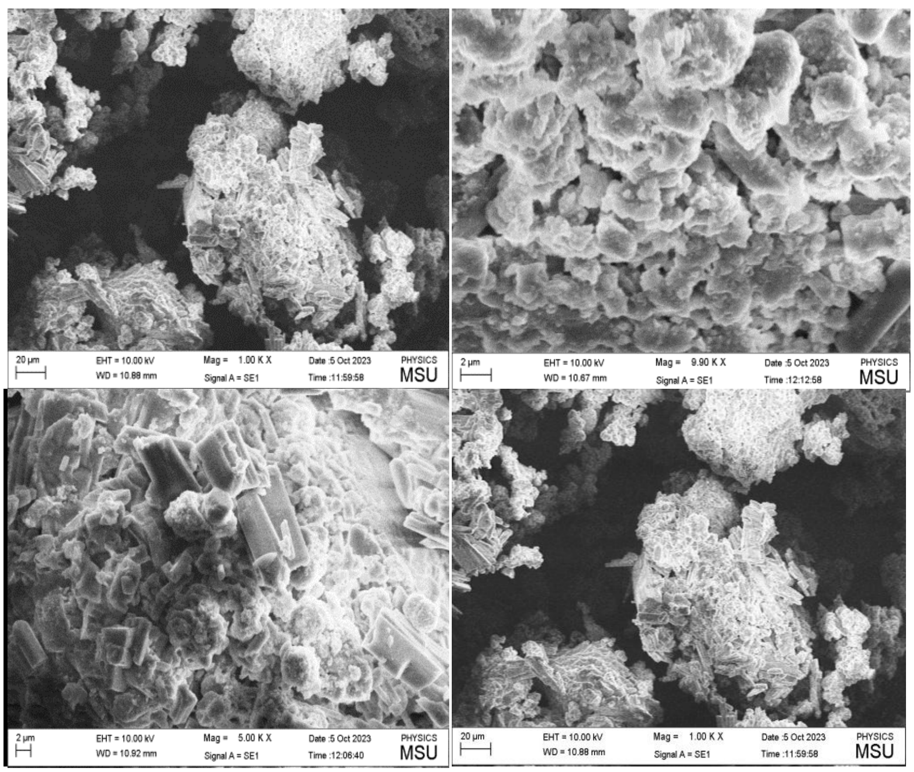

Fig.11. SEM images of Zeolite

Thermo Gravimetric Analysis (TG-DTA)

The final mass percentage was observed to be 64.38% at 1000ºC. DTA curve shows that the process is endothermic because of the rise in the DTA curve. Hence, heat is absorbed during the process. The glass transition temperature is observed to be 95ºC. The thermal stability of zeolite-Y as per the TG curve was found good.

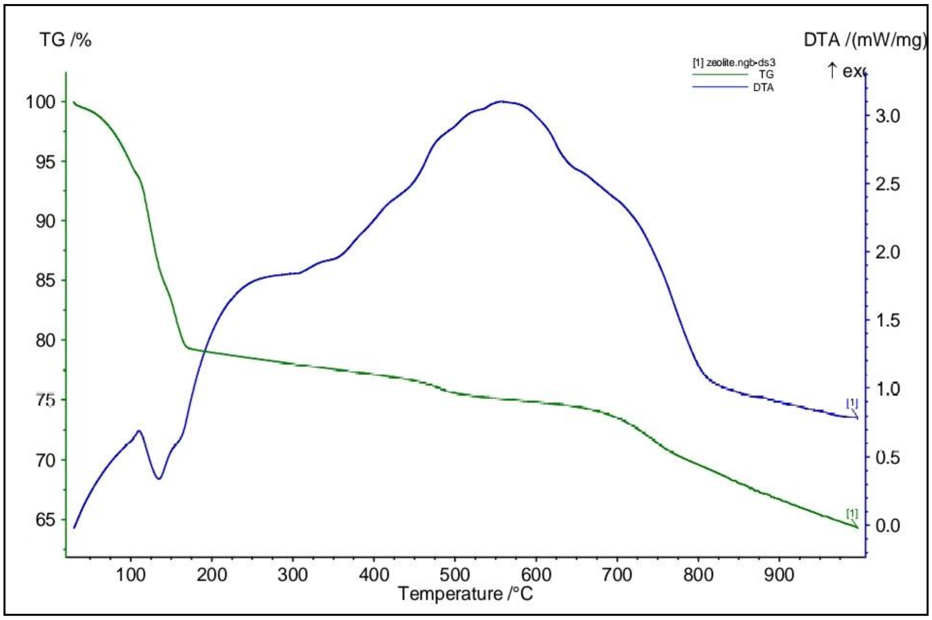

Fig.11. TG-DTA plot of Zeolite-Y

Photo catalytic degradation of Methyl Orange and Methylene Blue by Nano-silica and Zeolite-Y

Photocatalyic degradation happens with the attack of organic pollutants by the hydroxyl radical generated on the surface of nano-silica / zeolite-Y during the process. A large variety of organic pollutants can be broken down by this method. The detailed method of photocatalytic degradation of azo dyes(methyl orange, methylene blue) by nano-silica and zeolite-Y prepared from nano-silica, is enclosed. Nano-silica and zeolite-Y are good photocatalysts and showed better degradation properties subjective to their zero band gap energy as studied by their tauc plots.

Photo catalytic degradation was carried out using ultrasonic bath sonicator (ATS - 1). The factors under variation were contact time, pH and initial concentration of the dye. Using these, the graphs were plotted and the dye degradation values were noted.

Photocatalytic reactions of nano-silica:

$$SiO_2 + h\upsilon \longrightarrow SiO_2\,(h^+_{(VB)} + e^-_{(CB)})$$

$$SiO_2\,(h^+_{(VB)}) + H_2O \longrightarrow SiO_2 + H^+ + HO^\bullet$$

$$SiO_2(e^-_{(CB)}) + O_2 \longrightarrow SiO_2 + O_2^{\bullet -}$$

Photocatalytic reactions of Zeolite-Y:

$$\text{Zeolite} + h\upsilon \longrightarrow \text{Zeolite}\,(h^+_{(VB)} + e^-_{(CB)})$$

$$\text{Zeolite}\,(h^+_{(VB)}) + H_2O \longrightarrow \text{Zeolite} + H^+ + HO^\bullet$$

$$\text{Zeolite}\,(e^-_{(CB)}) + O_2 \longrightarrow \text{Zeolite} + O_2^{\bullet -}$$

Degradation of Dyes:

$$\text{Dye} + HO^\bullet \longrightarrow \text{Degradationproducts}$$

$$\text{Dye} + (h^+_{(VB)}) \longrightarrow \text{Oxidation products}$$

$$\text{Dye} + (e^-_{(CB)}) \longrightarrow \text{Reduction products}$$

Photo degradation graphs of Methyl Orange and Methylene Blue by Nano-silica and Zeolite-Y

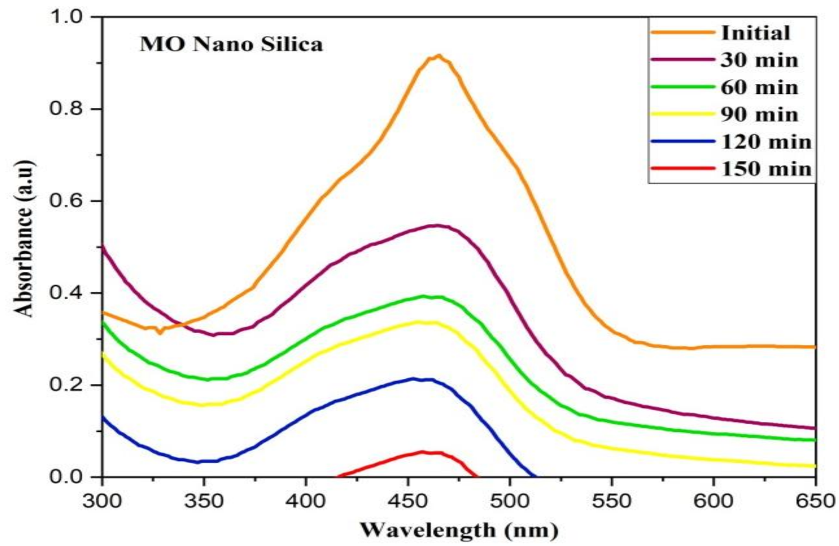

Fig.12. Photo degradation of Methyl orange dye by Nano-silica

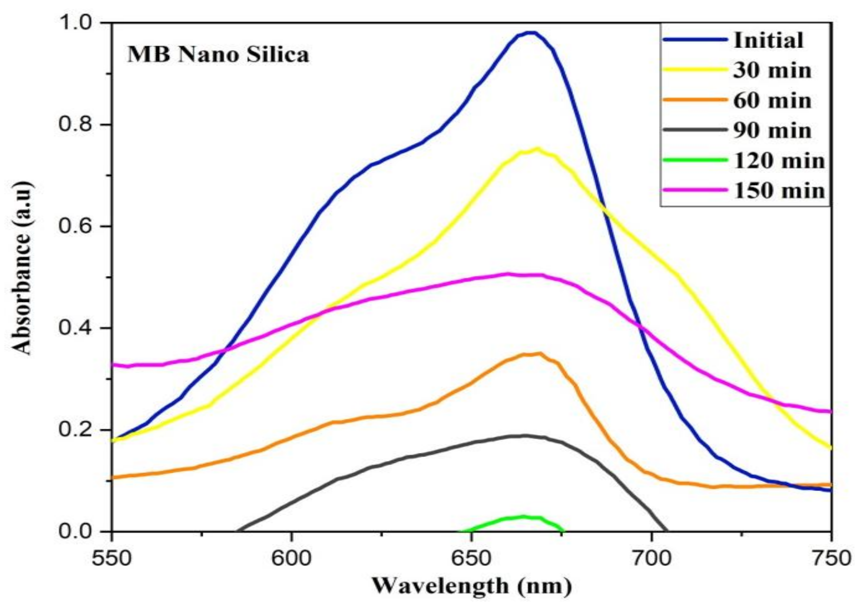

Fig.13. Photo degradation of Methylene Blue by Nano-silica

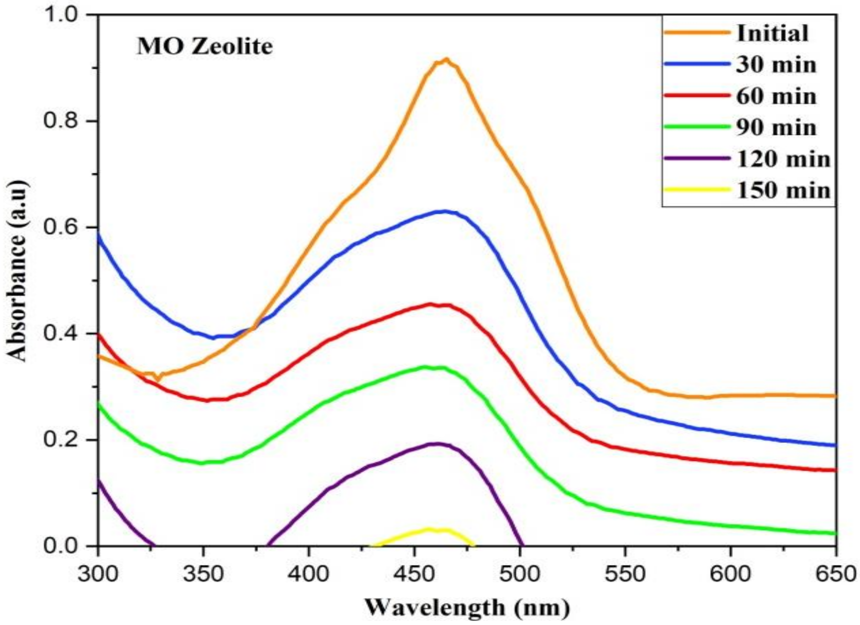

Fig.14. Photo degradation of Methyl Orange by Zeolite-Y

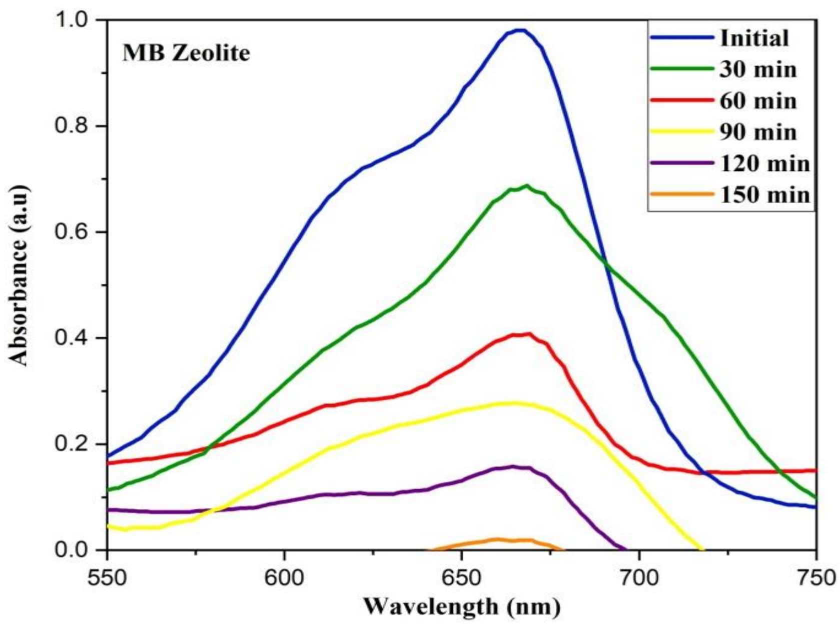

Fig.15. Photo degradation of Methylene Blue by Zeolite-Y

The percentage degradation of Methylene blue dye by Nano-Silica and Zeolite-Y were 97.2% and 98.2% respectively. The percentage degradation of Methyl orange dye by Nano-Silica and Zeolite-Y were 94.3% and 96.8% respectively.

Conclusion

The study encloses the importance of using biodegradable substances for environmental purposes. Azo dyes are mainly textile industrial effluents. They are harmful to the environment. The prepared Nano-Silica and Zeolite were able to almost completely degrade those harmful industrial effluents.

Declaration of competing interest

None

Acknowledgement

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