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Low temperature Synthesis, Characterization of spherical ZnO and study its photocatalytic activity

M. Velu[1], G. Gurumoorthy[1*]
[1]Department of Chemistry,
Faculty of Arts & Science,
Bharath Institute of Higher Education & Research, Selaiyur,
Chennai-73, Tamilnadu, India.
Email-gurumoorthychemistry.cbcs@bharathuniv.ac,in

Address for Correspondence

M. Velu[1], G. Gurumoorthy[1*]
[1]Department of Chemistry,
Faculty of Arts & Science,
Bharath Institute of Higher Education & Research, Selaiyur,
Chennai-73, Tamilnadu, India.
Email-gurumoorthychemistry.cbcs@bharathuniv.ac,in

ABSTRACT

Synthesis of ZnO nanospheres (ZnONS) using solution deposition method at low temperature which is most effective technique for the synthesis of nanostructure and commercially accepted, higher deposition rate and easily can collect from glass substrate. Hexamethylenetetramine (HMT) play a duel role as surface modifying agent and as surfactant for ZnONS stability. The ZnONS was deposited on glass substrate when immersed in the precursor solution at optimum conditions. The prepared ZnONS were analyzed using UV-visible, FT-IR, XRD, FE-SEM, and EDX. In this present investigation, ZnONS used as a catalyst for the photodegradation of organic pollutant like Rhodamine B and performed well with degrading ability nearly 97% at 120 mins of exposure.

Key words: Zno nanospheres, hexamethylenetetramine, Photodegradation, Rhodamine B

1. Introduction

The rapid increases of the human population as well as higher number industries and its effluent has directly affect our environment, resulting in the depletion of natural resources, particularly

freshwater resources [1, 2]. Dyes are organic compounds which are predominantly used in various industries like textile, printing, plastics, paper, food and leather industries and these industries consume huge amount of water, as a result significant amount of dye containing effluent were dumped in water bodies disposal of residual dyes and dye wastewater into water bodies in recent years. Some of these dyes are carcinogenic, mutagenic and poisonous and some of them present remain in long time. To avoid the toxicity of effluent, it needs different methods to removal dyes [3-5]. Physical and biological treatments, on the other hand, do not remove contaminants; they just change their phase. Chemical treatments have the disadvantage of requiring the use of powerful oxidants such as ozone and chlorine, both of which are pollutants. So the photocatalysis is the most efficient techniques because dyes can be destroyed when bombarded by UV irradiation in the presence of photocatalyst due to their absorption in the visible region [6-11]. Rhodamine B is xanthenes organic dye which dissolves easily in water and this is well recognized water tracer fluorescent materials and also it's a highly allergic to the eyes, skin and our respiratory system. As a result, preventing dye wastewater pollution is a critical issue that must be addressed globally [12-21].

Heterogeneous photodegradation acquired higher interest in the last decades for the removal of organic pollutants by metal oxides. The various metal oxides have wide range of application in different fields like sensors, electric, electronics, fuel cells, coating, corrosion, organic synthesis, photodegradation and etc. Among them, zinc oxide (ZnO) and titanium dioxide (TiO_2) has been widely studied as a photocatalyst due to their non toxic and chemically stability. When compare with TiO_2, ZnO possessed strong photocatalytic activity due to large excitation binding energy (60 meV) and a broad direct band gap (3.37 eV) because TiO_2 has low quantum efficiency and larger forbidden band gap (3.2 eV) [21-30]. So the ZnO is used as a best alternative for TiO_2. In this present investigation, the synthesized ZnONS used as a photocatalyst for the removal of RhB form the water pollutants by UV irradiation method and is given in scheme 1 [31-36].

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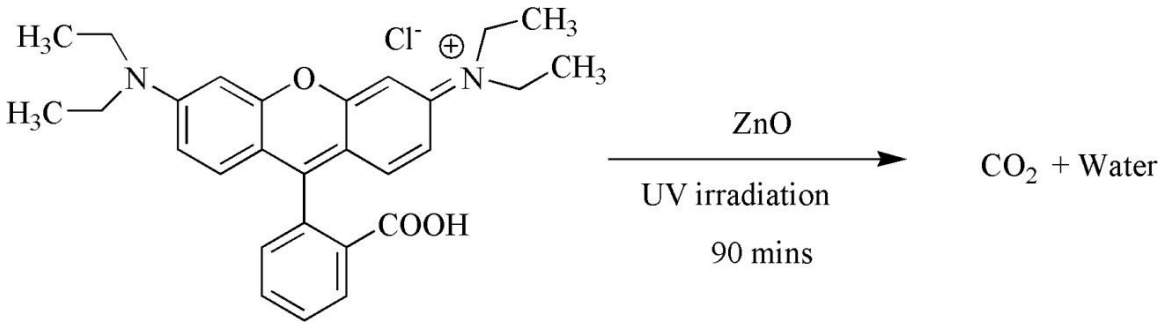

Scheme 1: The degradation pathway of the RhB in presence of UV irradiation

2. Experimental Section

Chemicals and Reagents

The metal precursor such as $Zn(NO_3).6H_2O$, HMT, NaOH Conc. H_2SO_4, Conc. HNO_3 are received from Merck and RhB form sigma aldrich. The other reagents like ethanol, methanol, Na_2HPO_4, NaH_2PO_4, KCl and NaCl were receive from SRL chemicals, Pvt. Ltd., India and the double distilled water is used for preparation of all stock solutions for the experiments.

Synthesis of ZnONSs

Synthesis of ZnO nanospheres (ZnONS) using solution deposition method at low temperature. Here hexamethylenetetramine (HMT) used as surfactant and surface modifying agent. First, the glass substrate was washed with Piranha Solution and immersed in to the (1:1 M) aqueous $Zn(NO_3)_2.6H_2O$:HMT solution and 2.0 M of aqueous NaOH was added drop wise and stirred with glass rod for homogeneity this solution kept in a thermostatically heated water bath at 60 °C for about half an hour. The white colour deposition of ZnONS was washed with copious amount of double distilled water and dried at 60 °C for 3h in vacuum air oven and then collected from glass substrate and confirmed by further analysis.

Instrumentations

For the characterization of synthesized ZnONS was dispersed in water by ultra-sonicator to obtain the electronic spectra using SHIMADZU-1800 (UV-Vis. Spectrophotometer) Japan and FT-IR spectra from Perkin Elmer Y-40, USA. XRD pattern was analyzed using Philips, JSO debye Flex 2002 Seifert with 10°/min scanning speed. The morphology, size and shapes of the

nanoparticles were confirmed by HITACHI, SU6600 with voltage 0 kV (FE-SEM), Japan and JEOL-3010 instrument was used for HR-TEM images.

3. RESULTS AND DISCUSSION

In recent years, numerous researches focused on the synthesis and application of ZnONS. The UV-vis absorbance spectra of ZnONS observed at 368 nm, which corresponds to the formation of ZnO nanostructures (Fig.1). Generally, when the nanostructures were stabilized with capping agent, a broadening and blue shift of the band would occur. In the present result 350 nm presents of HMT and the spectra shows slight blue shift compared to that of without stabilizer [22].

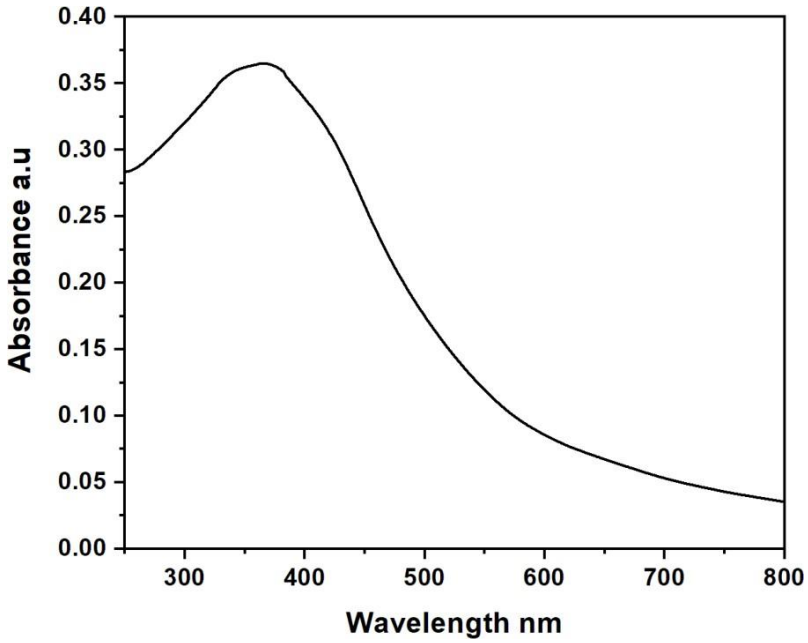

Fig 1. UV-vis. spectrum of ZnONS

Figure 2 shows the FTIR spectrum of the synthesized ZnONP, which observed the band at the rang 509 cm^{-1} attributed to the ZnO stretching and there is peak observed at the region at 3417cm^{-1} due to the trace amount of water molecule are present prepared compound [12, 22].

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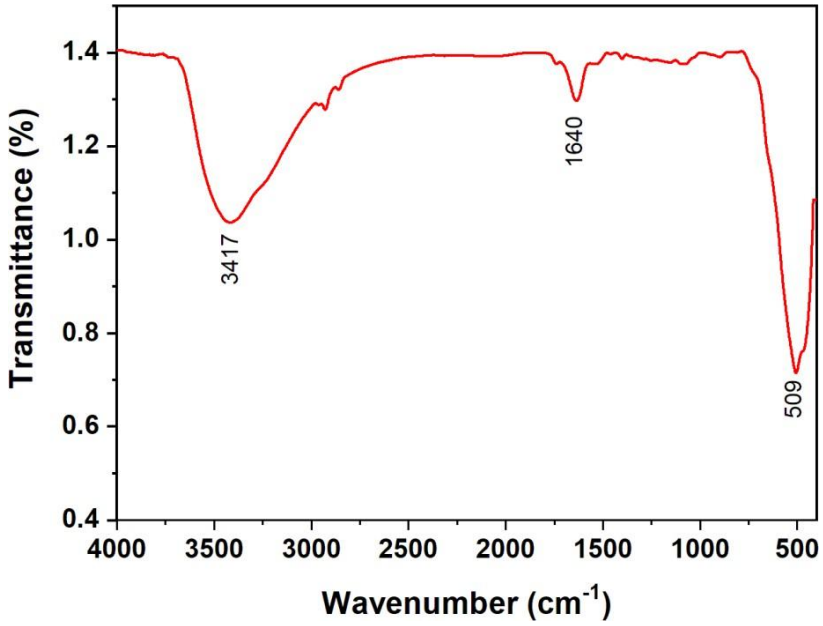

Fig 2.FTIR spectrum of ZnONS

Figure 3 show the XRD patterns of the ZnONS synthesized with capping agent HMT. The Braggs angle are observed at 31.87°, 34.48°,36.04°, 47.66°, 56.63°, 63.00°, and 68.02° which are well indexed to the crystal plane (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2) which shows the presence of hexagonal ZnO (wurtzite). The relatively broadening of the peak observed in the XRD reveal that the ZnO in nm range (JCPDS No. 36-1451). The average size evaluated from the major diffraction peak using the well-known Debye-Scherrer's formula (Eq. (1)):

$$D = 0.94\,\lambda / B\cos\theta \quad \ldots\ldots (1)$$

whereλ is the wavelength, B the full-width at half maximum of the peak in radions and θ the Bragg's angle of the XRD peak. The average size of nanocrystalline ZnO was found to be about 65.02 nm [12, 14, 27].

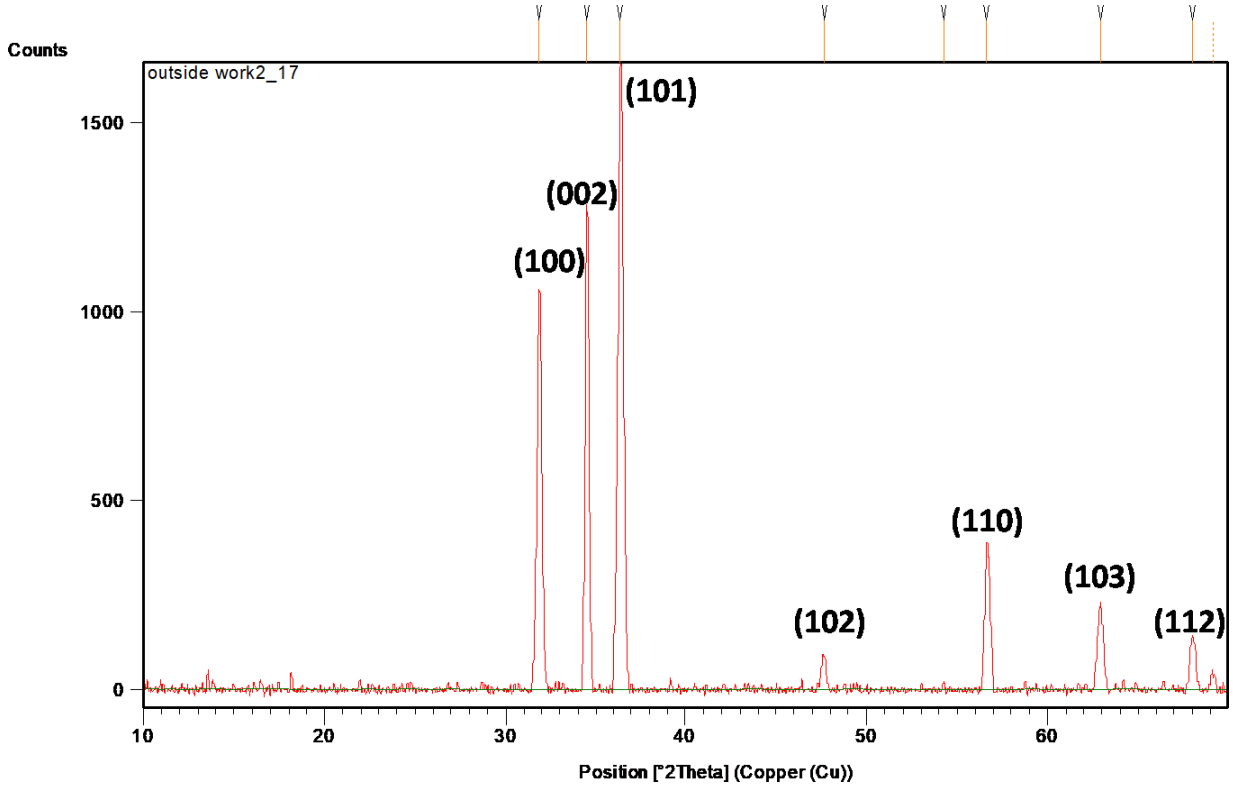

Fig 3. Powder XRD patterns of the ZnONS.

Figure 4 shows FE-SEM images of the ZnONS synthesized with HMT as a capping ligand. It can be seen that the powders were made up of particles with the shapes were spherical like NPs. The FE-SEM image was taken by mounting on the conducting copper with carbon tape and coated on carbon to avoid charging while analysis [12, 27]. . The selected area of EDAX analysis shows clearly the both elements Zn and O are present in equal proportion and any other elements are not present in our prepared compounds is confirmed from the percentile table, which is strongly indicates its purity of ZnO NPs.

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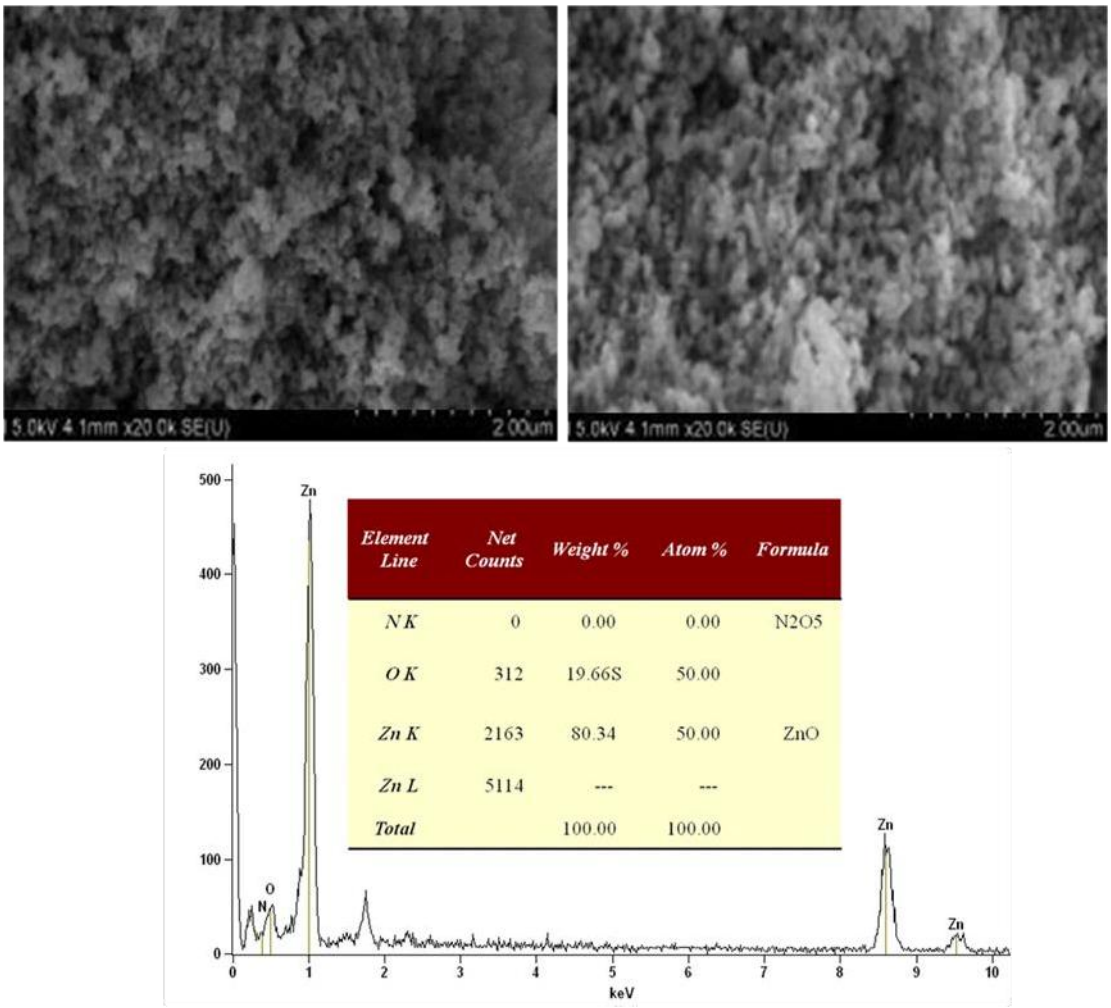

Fig.4. FE-SEM and EDX with percentile table images of ZnO NPs.

The photocatalytic activity of the ZnO nanospheres was evaluated using photo degradation of an aqueous RhB textile dye is shown in Fig.5a. The experiment carried out in a cylindrical double-walled hollow photo reactor with water circulation facility. A 20 W UV lamp (wavelength of 352 nm) was place inside the reactor. The catalytic experiments carried out with 100 mL solution of 1.0 X 10^{-5} M concentration of RhB dye and 100 mg of the ZnO nanospheres catalyst under constant stirring. About 3 mL of the aliquot solution withdrawn at predetermined time intervals (15 mins) from the reaction mixture, centrifuged and the decrease in absorbance values monitored [37-41-43]. The pseudo first order rate constants (1) were calculated from the slopes of the plots of ln C_0/C vs time. The percentage reduction of dye were calculated using the following expressions (2).

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$$k = \frac{2.303}{t} \ln \frac{C_0}{C} \quad \text{... (1)}$$

$$\text{Percentage reduction} = \frac{\text{O.D. at initial time } (C_0) - \text{O.D. at time t}(C_t)}{\text{O.D. at initial time } (C_0)} \times 100 \quad \text{... (2)}$$

where, C_o = initial concentration of the dye solution, C_t = concentration remaining after irradiation at time t.

and the relationship between $\ln(C_0/C_t)$ and degradation time shows a linear relationship which suggest that the degradation of RhB is a first-order reaction in Fig.5b. The apparent rate constants obtained as 7.7 $x10^{-4}$ min-1 for absence of catalyst and presence of ZnONS from the slope of ln (C0/Ct) versus degradation time.

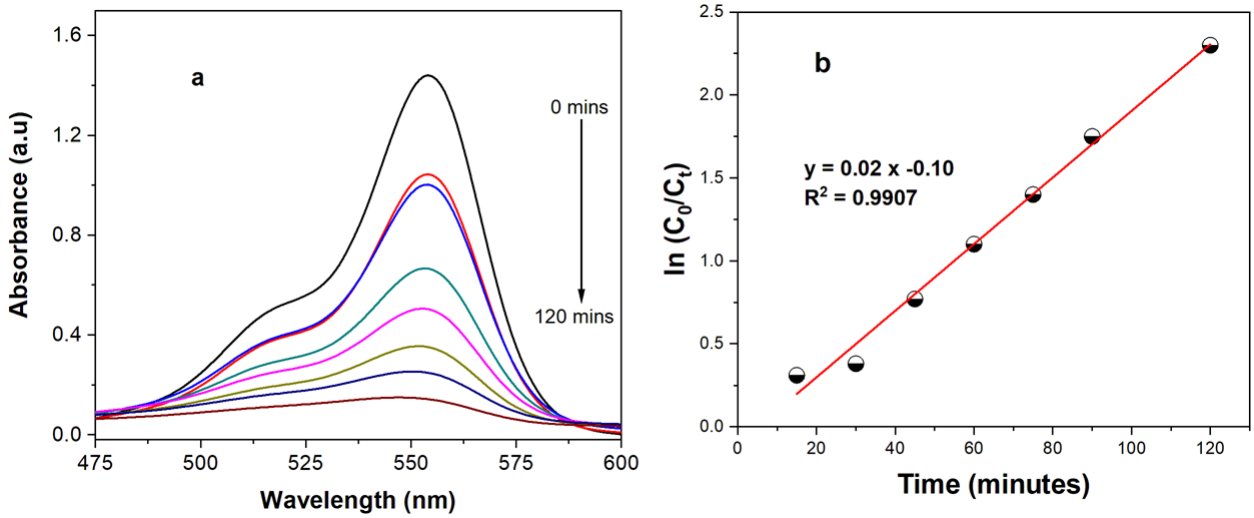

Fig. 5: UV-visible spectra for the photocatalytic degradation of RhB (a) and its calibration plot (b).

The reduction efficiency in reuseability of ZnO nanospheres (Fig.6) has confirmed by doing for 5 cycles the degradation of RhB without change of the catalyst. This process continued five times without any evident loss of its catalytic activity. The catalytic efficiency of the heterogeneous catalyst is found to be maintained without any loss in each cycle due to the inherent stabilization of ZnO nanospheres.

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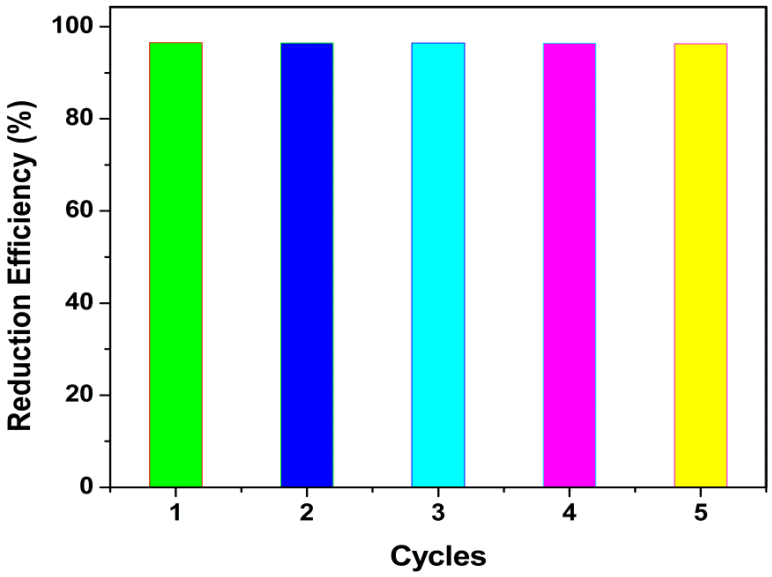

Figure 9: Reusability of ZnO nanospheres.

Conclusion

Synthesis of ZnO nanospheres (ZnONS) using solution deposition method at low temperature which is most effective technique for the synthesis of nanostructure and commercially accepted, higher deposition rate and easily can collect from glass substrate. Hexamethylenetetramine (HMT) play a duel role as surface modifying agent and as surfactant for ZnONS stability. The ZnONS was deposited on glass substrate when immersed in the precursor solution at optimum conditions. The prepared ZnONS were analyzed using different analytical techniques and which are confirmed ZnO formed like sphere which has nearly 65 nm in size with high purity and which has high surface area to subject as catalyst for the degradation of organic pollutant. ZnONS used as a heterogeneous catalyst for the photo degradation of Rhodamine B and performed well with degrading ability nearly 97% at 120 mins of exposure. The apparent rate constants obtained as $7.7x10^{-4}$ min-1 for absence of catalyst and presence of ZnO nanocatalysts, respectively.Based on the above considerations, we developed a cost effective photocatalyst for degradation of different organic dye contaminants.

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