The Influence of Stabilizing Agents on Adsorption and Photodegradation Properties of Synthesized ZnO Nanoparticles

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ABSTRACT

The utilization of ZnO nanoparticles in photo catalytic removal of environmental pollutants from waste waters especially organic dyes and heavy metals has been explored extensively. The outstanding challenge in this new promising field has been the augmentation of the extent of removal of the pollutant by the nanoparticles. Several tactics have been employed in the endeavour of increasing the efficiency of the nanoparticles in removal of the pollutants but most of them have proved ineffective. Thus, the core intent of this study was to assess the influence of stabilizing agents on adsorption and photodegradation properties of synthesized ZnO nanoparticles. Methyl orange was used as a model dye since it’s an organic dye similar to that used in the textile and paper industries. Precipitation technique was used to synthesize ZnO nanoparticles. Two samples L₁ and L₂ were synthesized, L₂ with a stabilizer (Oxalic acid) and L₁ without. They were characterized using scanning electron microscopy (SEM), Fourier transform infra-Red (FTIR), and energy dispersive X-ray spectroscopy (EDX), methods of analysis. The EDX results showed elemental composition of ZnO nanoparticles which indicated 54% Zn, 44.07% O and 1.93% Mn impurities for L₁ and 55.34% Zn, 42.3% O and 2.37%Mn impurities for L₂. The findings clearly showed increased adsorption power evidenced when the photocatalyst was enhanced using a stabilizer. Although the difference in adsorption was minor, it was appreciable. In future, researchers should focus on the development of novel stabilizers for nanomaterials/nanocomposites with a high efficiency for the removal of different heavy metal ions and organic dyes. Considering the economics of adsorbents, it is necessary to synthesize low-cost effective and recyclable stabilizers for their extensive application in our daily life.

Key Words: Stabilizers, ZnO nanoparticles, photodegradation

INTRODUCTION

Zinc oxide nanoparticles have been used to remove of heavy metals and organic dyes from water (Hua et al., 2012; Bystrzejewska et al., 2009). Both powder and thin film forms of nano ZnO have been explored to date for environmental applications. Powder-form nano ZnO photo-catalysts normally show higher photo-efficiency due to the increased active surface area. However, this form of photo-catalysts when used in suspension state in water has certain limitations due to particle aggregation and technical challenges in separation and recovery. In comparison, thin film ZnO can be easily recovered, yet its surface area is low leading to poor overall efficiency (Gupta & Tripathi, 2012). However, both form of the photocatalyst have limited efficiency in removal of pollutants from waste waters. This research therefore explored a different method of improving their efficiency by utilizing stabilizers which tend to inhibit the reaction between two or more other chemicals. A stabilizer also refers to a chemical that inhibit separation of suspensions, emulsions, and foams (Schwarzenbach et al., 2005).

Most stabilizers for semiconductor nanoparticles include organic thiols, oleic acids, urea, oxalic acids and others are water soluble. ZnO nanoparticles give significant stability under any type of stabilizer (Herrmann & Helmoltz, 2010). Oxalic acid is the most common organic stabilizer used during synthesis of ZnO nanoparticles. It is used as a chemical capping in which it passivizes the surface of particles so that they do not agglomerate or ripen to form larger particles. This ensures that the nanoparticles synthesized yield stable products with uniform size distribution (Zaidi & Pant, 2008).

The capping agent further provides protective organic shell to particles to prevent the nanoparticles from aggregating in solution. It also promotes formation of fewer, larger nuclei and thus nanocrystal particle sizes (Gnanasangeetha and Sarala Thambavani, 2013). Stabilizers enable the nanoparticles to be resistant...
to deactivation and thus its performance which depends on the nature and concentration of the stabilizing agent used. The difference in performance is due to electrical conductivity of stabilizers, the morphology and interface roughness and stabilizer particle interaction (Hu et al., 2003).

The crystal structure of nano ZnO is vital because without it, oxalic acid has no effect on wurtzite structure as revealed by X-ray diffraction (Kanade et al., 2006).

This study assessed the influence of stabilizing agents on adsorption and photodegradation properties of synthesized ZnO nanoparticles. Methyl orange was used as a model dye since it’s an organic dye similar to that used in the textile and paper industries. Methyl orange (MeO) is an organic dye with a chemical formula of C_{14}H_{14}N_{2}SO_{3}Na and characterized by sulphonic groups, which are responsible for high solubility of these dyes in water (Guettai & Amar, 2005).

MATERIALS AND METHODS

ZnO nanoparticles were synthesized using precipitation method. In this method, ZnO nanoparticles were prepared in two ways. In the first set, 100ml of 1M ZnSO\(_4\) solution was added to 100ml of 2M NaOH solution in drops. When the addition was complete, the mixture was kept at room temperature under constant stirring using magnetic stirrer for a period of 2-4 hours. The constant stirring makes the precipitation homogeneous and minimal particles which reduce the specific surface free energy of crystal nucleus which inhibit agglomeration and growth of the crystal nucleus so the particle size of the product is reduced (Zhang et al., 2008).

The resultant precipitate obtained was filtered then rinsed with distilled water. The formed white precipitate of Zn(OH)_2 was allowed to settle, filtered using filter paper of pore size 0.4µm in a suction pump, washed with distilled water several times and dried in hot oven at 150°C for 45 minutes. The synthesized ZnO nanoparticles were further irradiated at 180 W with microwave radiation in a microwave oven for 30 minutes. This was named as sample L_1. The above procedure was followed to synthesize ZnO nanoparticles in different experimental conditions. ZnSO\(_4\), NaOH and oxalic acid were used as stabilizing agents. Thus one more sample was obtained and referred to as L_2.

The precipitation reaction was represented as:

\[
\text{ZnSO}_4(aq) + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2(s) + \text{Na}_2\text{SO}_4(aq)
\]

\[
\text{Zn(OH)}_2(s) \text{Heat} \rightarrow \text{ZnO(s) + H}_2\text{O(l)}
\]

The resultant ZnO nanoparticles particles after irradiation were collected and stored in brown bottles.

The synthesized ZnO nanoparticles were subjected to SEM, PXRD, FTIR and EDX to confirm the nanostructure.

Influence of Stabilizer on the effectiveness of the Nano ZnO: Factors that govern degradation process:

The effect of stabilizers on degradation of MeO dye in the aqueous suspension by ZnO nanoparticles was studied by varying the experimental conditions. In this case, a stabilizer (oxalic acid) was added to one sample (L_2) during the synthesis and another sample (L_1) synthesized without the stabilizer.

Preparation of Dye Solution

The stock solution (1000ppm) was prepared and stored in brown bottles. The stock solution was diluted to get different required initial concentrations of the dye used. Dye concentration was determined by using absorbance measured before and after the treatment using UV-Vis spectrometer.

The stock solution was diluted to different initial concentrations10, 20, 30, 40 and 50 ppm for methyl orange in standard measuring flasks by making necessary dilutions with required volume of distilled water. The optical density of each dye solution was measured using UV-Vis spectrophotometer (model – No-SL-150 Elico) at maximum wavelength value for MeO dye. A plot of optical density versus initial concentration was drawn. This plot was used as standard graph for estimation of dye by interpolation technique. The values of optical density for dye solutions before and after removal of dye were obtained by using UV-Vis spectrophotometer. Using these optical densities the corresponding dye concentration was obtained from the graph.

Stock solution of MeO dye (1000ppm) was suitably diluted to get the required initial concentration from 15 – 45ppm. A 10ml of the dye solution of known initial concentration (C_1) was transferred to 50ml beaker. Required amount of the photo-catalysts (L_1 and L_2) were exactly weighed and then transferred to the dye solutions. The beakers were then exposed to fluorescent light and direct sunlight for a fixed period of contact time.
After bleaching, the optical density (OD) values of these solutions were measured using UV-Vis spectrophotometer and the final concentrations ($C_2$) obtained from the standard graph. The extent of removal of the dye for $L_1$ and $L_2$ in terms of percentage removal was calculated using the following relationship:

$$\text{Percentage removal} = \frac{100(C_1 - C_2)}{C_1}$$

Where
- $C_1$ = initial concentration of dye (ppm)
- $C_2$ = final concentration of dye (ppm)

**RESULTS AND DISCUSSION**

**Powder X-Ray Diffraction (PXRD)**

The X-ray diffraction pattern of ZnO nano photocatalysts was recorded at 2θ angle. Figure 1 shows the XRD patterns of the synthesized ZnO nanoparticles.

![Figure 1: XRD patterns of the synthesized ZnO nanoparticles](image)

The diffraction peaks at 31.7, 34.4, 36.2, 47.4, 56.4, 62.5, 67.6, and 68.7 can be indexed to ZnO as per the standard JCPDS file 80-0075. Powder diffraction patterns are characteristic of a particular substance: it is its “fingerprint” and can be used to identify a compound. Powder diffraction data from known compounds have been compiled into a database by the JCPDS. The synthesized sample can be confirmed to be ZnO nanoparticle. Clear crystallinity of the ZnO nanoparticles was observed and samples had similar patterns. This suggests that the oxalic acid added as stabilizing agent had no effect on the Wurtzite structure of ZnO (Herrmann et al., 2010). Similar results were obtained by Gu et al. (2004) who characterized synthesized nano-ZnO using PXRD. For their three samples prepared. The sizes obtained were about 26 nm.

The average crystallite size of synthesized ZnO nanoparticles was found to be around 26 nm.

![Figure 1](image)

FTIR of the ZnO nanocatalyst indicates the presence of water molecule adsorbed on the surface due to bands at around 3400 cm$^{-1}$ which may be assigned to OH stretching vibration of adsorbed H$_2$O or due to residual Zn(OH)$_2$ present in the powder. The absorption band at 430 cm$^{-1}$ correlated to metal oxide bond (Zn-O).

![Figure 2: Observed FTIR pattern](image)

FTIR spectra of ZnO obtained showed absorption band at 432.0 cm$^{-1}$ which they attributed to (Zn-O) stretching frequency. Likewise peaks at 3401.3 cm$^{-1}$ represent (OH) stretching mode. Shanthi and Muthuselvi (2012) also carried out a similar study and their analysis showed a broad band between 419-430 cm$^{-1}$. The spectra showed
bands at (3250 and 3500 cm\(^{-1}\)) which was assigned to OH stretching vibrations.

**SEM Analysis**

Figures 3 and 4 show the SEM diagrams for sample L\(_1\) and L\(_2\) at high magnification, respectively.

These images showed that the ZnO nanoparticles obtained formed rod shaped clusters distributed within the range of 100nm. The diagrams also show that the surface was not uniform but porous in nature. It shows that the nanocatalyst has considerable number of pores where there is a good possibility for the heavy metals to be trapped and adsorbed onto these pores and it is a good sign for effective adsorption of heavy metals (Joshi and Shrivastava, 2012). The photographs also showed different surfaces for L\(_1\) and L\(_2\). The L\(_1\)_\(_\)showed round ended while L\(_2\)_\(_\)showed sharp ended nanoclustures. This showed that the stabilizing agent had an influence on the morphology of the samples.

Similar studies were made by Soltaninezhad and Amrnifar (2011) who studied surface morphology of ZnO nanoparticles produced by Spray Pyrolysis. The pictures observed showed particles that were spherical in shape. However, Joshi and Shrivastava (2012) determined the surface texture which was found to be rough and porous in nature.

Due to these close similarities, the ZnO nanoparticles were confirmed. The difference in distribution range is attributed to the level of accuracy during synthesis and also method of synthesis (Joshi and Shrivastava, 2012).

**EDX Analysis**

Figures 5 and 6 shows the EDX spectra and reveal that the samples were made up of Zn, O and traces of Mn impurities. The peak at the intense peak is assigned to the bulk ZnO and the less intense on to the surface ZnO. The peak at 0.5 KeV can only be attributed to O and not Mn due to overall position of the peaks. The elemental composition of the nanomaterial was found to be 55.34% Zn, 42.3% O and 2.37% Mn for L\(_1\) and 54% Zn, 44.0% O and 1.93% Mn for L\(_2\).

Similar work has been done by (Joshi and Shrivastava, 2012) who characterized nano ZnO synthesized by precipitation technique. Their EDX spectra showed a peak at 0.5 KeV for oxygen 1 KeV for ZnL\(_\alpha\), 8.6 for ZnK\(_\alpha\) and 9.6 KeV for ZnK\(_\beta\). The elemental composition was found to be 71% Zn, 18.5% CO and 10% C with carbon as the impurity.
**Photodegradation Studies**

The optical density of each dye was measured using UV-Vis spectrophotometer at maximum wavelength of 480 nm. A plot of optical density versus initial concentration is shown in Figure 5. This plot was used as standard graph for estimation of dye concentration by interpolation technique.

![Figure 5: Standard curve for methyl orange dye](image)

**Effect of variation of initial concentration of dye on photo degradation of methyl orange dye**

Table 1 show the effect of variation of initial concentration of methyl orange dye on photodegradation.

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Sample</th>
<th>Concentration of dye</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunlight</td>
<td>L₁</td>
<td>15 mgL⁻¹, 30 mgL⁻¹, 45 mgL⁻¹</td>
<td>98.4%, 96.1%, 94.7%</td>
</tr>
<tr>
<td></td>
<td>L₂</td>
<td>2.49, 6.83, 20.89</td>
<td>97.4%, 97.2%, 93.6%</td>
</tr>
<tr>
<td>Fluorescent</td>
<td>L₁</td>
<td>14.23, 26.40, 41.31</td>
<td>92.0%, 89.0%, 88.2%</td>
</tr>
<tr>
<td></td>
<td>L₂</td>
<td>14.04, 29.81, 38.03</td>
<td>91.8%, 88.9%, 88.0%</td>
</tr>
</tbody>
</table>

Effect of variation of dose of photo catalyst (L₁ and L₂) on photo degradation of MeO dye

The initial concentration 30 mgL⁻¹ of the dye and pH in all beakers were kept constant at pH 7.0 and the dose of photo-catalyst was varied from 200 mg to 400 mg with a contact time of four hours and the results are shown in Table 2.

![Table 2: Effect of variation of dose of photo catalyst (L₁ and L₂) on photo degradation of MeO dye](image)

Photo catalytic degradation of the dye was found to decrease with increase in initial concentration of methyl orange. This could be due to more dye molecules than ZnO nanoparticles; in this case the photo-catalyst became the limiting factor. It was noted that degradation rate decreased with increase in dye concentration. The decrease in dye degradation could be attributed to reduction of OH⁻ radicals on the catalyst surface when covered by dye ions (Poulis & Tsachpinis, 1999).

The results are similar to those reported by Li et al. (2005) when methyl orange was irradiated with sunlight source, the degradation of the dye decreased as the dye concentration increased. This could be due to the fact that the generation of OH radicals on the catalyst surface is reduced since the active sites are covered by dye ions. Also Kansal et al. (2006) concluded that photocatalytic degradation of methyl orange decreased as the dye concentration increased.

This decrease is as a result of increasing the number of photons absorbed by catalyst lower concentration (Davis, 2006). According to Shanthi and Muthuselvi (2012), the decrease in photo degradation is as a result of dye molecules imparting darker colour to the solution which acts as a filter to the incident light reaching the photo catalyst surface. Sampa and Biney (2004) further explained that the increase in the concentration of a dye solution result in the photons getting intercepted before they can reach the catalyst surface, thus decreasing the absorption of photons.
Photo catalytic degradation of methyl orange dye increased with an increase in concentration of ZnO particles. This is due to increase in photo-catalyst molecules available to degrade the dye. Further increase of ZnO concentration increases turbidity of the solution and decreases light penetration into the solution and therefore, removal efficiency decreases (Kartal et al., 2001).

Oxalic acid used is a capping agent provided protective organic shell to particles to prevent the nanoparticles from aggregating in solution. It also promotes formation of fewer, larger nuclei and thus nanocrystal particle sizes. Stabilizers enable the nanoparticles to be resistant to deactivation and thus its performance which depends on the nature and concentration of the stabilizing agent used (Prach et al., 2013).

The results of this study are similar to those of Joshi and Shrivastava (2012) who studied removal of methylene blue using ZnO nano particles, by varying the dose of photo catalyst from 2.0 g/l to 5.0 g/l and degradation increased from 86.0% to 92.8%. The increase in the amount of catalysts increased the number of active sites of the photo catalyst surface, which in turn increased the number of hydroxyl and superoxide radicals (Sampa & Biney, 2004).

**Effect of variation of contact time on photo degradation of MeO dye**

The results are presented in Table 3.

Table 3: Effect of variation of contact time on photo degradation of MeO dye

<table>
<thead>
<tr>
<th>Radiations</th>
<th>Sample</th>
<th>Contact time in hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 2 3 4 5</td>
</tr>
<tr>
<td>Sunlight</td>
<td>L₁</td>
<td>11.8 6.8 5.9 1.4 0.5</td>
</tr>
<tr>
<td></td>
<td>L₂</td>
<td>4 3 9 5 8</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>60.5 77. 80. 95. 98.</td>
</tr>
<tr>
<td></td>
<td>removal</td>
<td>2 0 2 0</td>
</tr>
<tr>
<td>Fluorescent</td>
<td>L₁</td>
<td>9.12 4.2 2.6 0.9 0.5</td>
</tr>
<tr>
<td></td>
<td>L₂</td>
<td>3 8 7 3</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>69.6 85. 91. 96. 98.</td>
</tr>
<tr>
<td></td>
<td>removal</td>
<td>9 1 8 2</td>
</tr>
</tbody>
</table>

The results indicate that, the percentage removal of dye increase with increase in contact time. This is in agreement with the results reported by Shanthi and Muthuselvi (2012), who studied the effects of contact time on removal of malachite green using ZnO nano particles. The increased contact time causes the photo-generated OH radicals and other peroxide radicals all being highly oxidant species decompose the dyes completely to mineral end products (Hofman, 1995).

**CONCLUSION**

The findings clearly showed that increased adsorption power was evidenced when the photocatalyst was enhanced using a stabilizer. The difference in adsorption was minor but appreciable. Table 2 shows % removal of 94.2 and 97.2 for L₁ and L₂, respectively using 300mg of ZnO nano particles under sunlight radiation. The crystal structure of nano ZnO without as well as with oxalic acid has no effect on Wurtzite structure as revealed by X-ray diffraction. SEM reveals different nature of surfaces and microstructures for nano ZnO obtained with and without stabilizers (Rajesh and Raychaudhuri, 2013).

**Recommendations**

In future, researchers should focus on the development of novel stabilizers for nanomaterials/nanocomposites with a high efficiency for the removal of different heavy metal ions and organic dyes. Considering the economics of adsorbents, it is necessary to synthesize low-cost effective and recyclable stabilizers for their extensive application in our daily life.

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