RESEARCH ARTICLE

Removal of Pollutants from Aqueous Solutions by using Zinc oxide Nanoparticles

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ABSTRACT

This work presents a low-cost method to produce Zinc oxide (ZnO) nanostructured materials for the treatment of water polluted with model organic pollutants (e.g., brilliant green dye). Zinc oxide was prepared using the thermal solvent technique at a temperature of 37°C, at pH 6, and the samples were incinerated for one hour at a temperature of (500°C). Also, silver doped ZnO (Ag-ZnO) was prepared by photo deposition using ultraviolet rays. The photodissociation of Brilliant green dye was studied using ultraviolet rays under different conditions in the presence of Ag-ZnO, studying the effect of some factors, such as the effect of dye concentration and intensity of incident light. The results showed that the smashing efficiency of the zinc oxide surface increased by 92.8% after adding silver. It also showed that the photocatalytic breakdown rate increases with decreasing concentration of Brilliant green dye. Increasing the intensity of the light led to an increase in the rate of photocatalytic breakdown.

Keywords: Water treatment, Brilliant green dye, Nanocomposites, Zinc Oxide, Photocatalytic, Degradation

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INTRODUCTION

Toxic organic chemicals contained as pollutants in industrial wastewater should be destroyed or converted into harmless chemical substances before being disposed of in the environment.[1,2]

The photocatalytic degradation of pollutants using semiconductors as photocatalysts is a green approach and plays a vital role in chemical transformation and environmental rehabilitation. Certain metal oxides (e.g., TiO_2, ZnO, SnO_2), which can collect maximum light energy from solar radiation, are used as photocatalysts.[3] The photocatalytic method is inspired by photosynthesis in nature, using light as the most abundant renewable energy. Photocatalysis converts light into chemical energy, such as the H_2 production via the photo electron chemical water separation or the radical production of hydroxyl and peroxide for the photodegradation of pollutants.[4] However, most photocatalysts of semiconductor metal oxides have low efficiency due to their large band gap and the high recombination rate of pairs of photosensitive electron holes (excitons).[5] Therefore, selecting a suitable photocatalyst material with a suitable band gap and a low rate of recombination of electron holes is necessary for the photocatalytic process. There are various approaches to improve the catalytic activity of a photocatalytic surface.

The surface morphology plays an important role in modifying the electronic and optical properties of a semiconductor with the enhancement of its harvesting capacity.[6] A variety of morphologies, such as nanoparticles,[7] nanotubes,[8] nanowires,[9] nanostructures,[10] and nonporous structures[11] have been reported to improve the photocatalytic activity of semiconductors. Among the semiconductors and metal oxides, ZnO has been selected for the ease of forming various types of nanostructured morphologies. In addition, it was chosen due to its unique properties such as biocompatibility, photosensitivity, high electron mobility, low cost, and morphological flexibility.[12,13]

ZnO nanomaterials can play an essential role in the photocatalytic degradation of organic pollutants due to their high photosensitivity, stability, broadband gap (3.37 eV), and high photocatalytic efficiency.

In particular, transition metals such as silver, platinum, and iron might improve the charge transfer by trapping the photochemical load carriers and by enhancing the performance of the photochemical degradation process,[14,15] caused by the recombination of electrons and holes before the peroxide activation process.

Experimental Materials

All the chemical reagents used in the synthesis procedure: Zinc acetate ($Zn(CH_3COO)_2.2H_2O$, Purity > 99.999%, Sigma-Aldrich), Oxalic acid($H_2C_2O_4$, Purity > 99.8%, India

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Production), Silver nitrate($AgNO_3$, Purity > 99%, Sigma-Aldrich), Methanol(CH_3 OH, Purity >99.5 % , Scharlau) , Brilliant green $C_{27}H_{33}N_2.HO_4S$, Purity >99.5 %, Sigma-Aldrich).

Preparation of Zinc Oxide Nanoparticles

The solvothermal method was used to prepare ZnO nanoparticles. Firstly, in a beaker, we dissolve 5 gm of zinc acetate in 150 mL of distilled water; in another beaker, we dissolve 8 gm of Oxalic acid in 150 mL of distilled water.

Then mix the two chemical compounds above and the series of chemical reactions that takes place. The complete hydrolysis of zinc acetate with the aid of $H_2C_2O_4$ in water should result in forming a ZnO colloid. The resulting solution was transferred into the rotary (flask). Afterward, the (Rotary flask) was in contact with the sealing ring made of (Teflon + Viton) materials of the rotary evaporation device, as shown in Figure 1. Then we turn on the device and regulate the temperature of the heater (stainless water bath) at different temperatures (30–50°C) and the water cooling temperature (refrigerant) at (27–15°C) to distill a solvent into the solution. Finally, the mixture is dried inside the flask.

The final product was obtained from the equilibrium between hydrolysis and the condensation reaction. Due to heating, zinc acetate inside the solution undergoes hydrolysis forming acetate ions and zinc ions.

The resulting residues are washed several times with distilled water until pH is equal to 7 and placed for drying in the oven at a temperature of about 60°C overnight, then ground in a mortar and turned into a fine powder. The white powder is calcinated at (500°C) for one hour.

Preparation of Metal doped ZnO Nanocomposites

Metal-doped ZnO was prepared by suspending 1 gm of ZnO powder in 100 mL of distilled water and 3 mL of $AgNo_3$ (0.01) M by sonication for three minutes, followed by exposing the surface of the mixture to nitrogen gas for ten minutes under continuous magnetic stirring. Then (1 mL of methanol) was added, after which the mixture was irradiated with light intensity (1.71) mW.cm^{-2} (LED lamp) overnight, as shown in **Figure 2**. After irradiation, the resulting powder was washed with distilled water several times and dried overnight in an oven at 60°C. The same previous work steps are repeated by taking 2 mL of $AgNo_3$ and 0.5 mL of methanol. We take 2 mL of $AgNo_3$ and 1 mL of methanol.

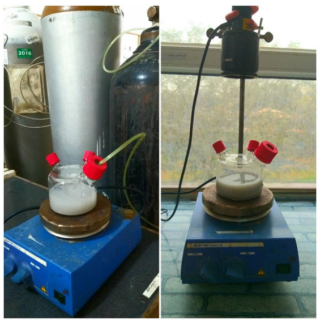

Figure 2: Image for the photodeposition of silver doped ZnO (a) Exposes the mixed surface to nitrogen gas (b) Irradiate the mixture with a lamp LED.

RESULT AND DISCUSSION

Concentration Effect of Dye

To evaluate the application of the solution-grown silver doped ZnO (Ag-ZnO) nanocomposite as a catalyst for the photodegradation of the textile pollutant, Brilliant green dye, The initial concentration of dye solution plays a pivotal role in deciding the rate of dye degradation. We have carried out their photocatalytic degradation kinetics at room temperature in the presence of UVA light using a wavelength of 365 nm (3.39 eV).[16]

Figure 3 shows that with an increase in the dye concentration, the photocatalytic degradation efficiency increased and reached a maximum at the dye concentration of 5 ppm. Beyond this optimum dye concentration, a further increase in dye concentration decreased the photocatalytic Degradation Efficiency. At relatively high concentrations of dye beyond the optimum point, although the active surface sites remain constant for a fixed catalyst concentration, the number of adsorbed dye molecules accommodated on the photocatalyst surface increases.[17]

Because the generation of valence band holes on the surface of the photocatalyst required for reacting with dye molecules does not increase as the intensity of light and the amount of catalyst are unchanged, there was an observed decrease in the photocatalytic degradation efficiency, probably due to

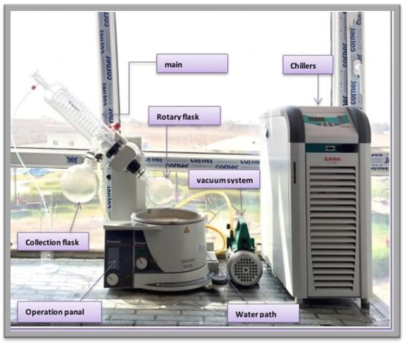

Figure 1: The rotary evaporation device, College of Science for Women University of Babylon.

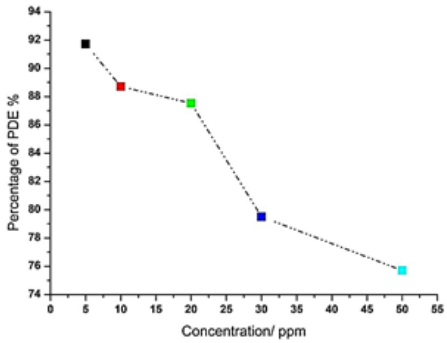

Figure 3: Effect of brilliant green dye concentration PDE% of Ag-ZnO nanocomposite

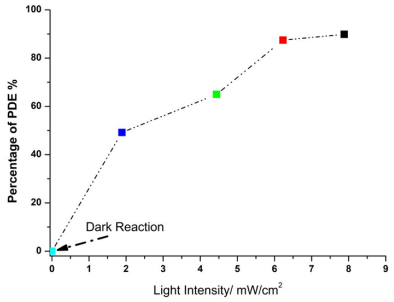

Figure 4: Effect of light intensity on PDE % of brilliant green dye

the blockage of the adsorption of hydronium cations at active surface sites, to be reduced to produce hydrogen. At a low dye concentration, the photocatalytic reaction rate is limited by the mass transfer of dye from the solution to the Ag/ZnO surface. However, at a middle dye concentration, due to the gradual adsorption saturation of dye on the Ag/ZnO surface, the interfacial reactions govern the overall process. Furthermore, at a high dye concentration, the active sites on the Ag/ZnO surface may be covered by excessive dye adsorption, and thus the hydroxyl radicals in dye hydrolysis decrease resulting in a lower dye degradation rate.[18]

Light Intensity Effect on Photodegradation of the Dye

Light intensity determines the extent of light absorption by the semiconductor catalyst at a given wavelength. The rate of initiation of photocatalysis, electron-hole (e^-/h^+), and formation in the photochemical reaction strongly depend on light intensity.[16]

Light intensity distribution within the reactor invariably determines the overall pollutant conversion and degradation efficiency. Consequently, the dependency of pollutant degradation rate on light intensity has been studied in numerous investigations of various organic pollutants.[19]

Figure 4. shows that a linear relationship is observed between light power and photocatalytic degradation efficiency. The photocatalytic degradation efficiency rate increases with the UV light's intensity as more radiation falls on the catalyst and, therefore, more hydroxide radicals.[20]

They are produced, resulting in a high rate of photocatalytic degradation efficiency.

It has been shown from Figure 4. that at low light intensity (0–4.5 $mW.cm^{-2}$), the rate will increase linearly with increasing light intensity (first-order), while at intermediate light intensity (6.5 $mW.cm^{-2}$) the rate will depend on the square root of light intensity, in high light, and rate independent of light intensity. Low intensity reactions involving electron-hole formation (e^-) is predominant and electron-hole recombination (e^-) non-significant.[21] In the lower light intensity range, the higher the incident light intensity led to a greater increase in the absorption potential between photons and active sites on the ZnO surface. On the other hand, when the light intensity increases, the separation between electrons and holes competes with recombination, causing the reaction rate to decrease.[7,22,23]

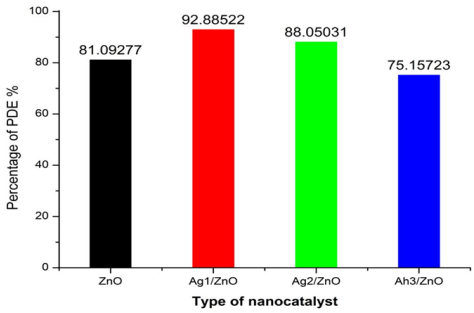

Figure 5: Selectivity of the best photocatalyst surface PDE % with a type of nanocatalyst

Selectivity of the Best Photocatalyst Surface

The Ag content plays an important role in increasing optical efficiency and preventing electron-hole pair recombination. It is known that noble metal nanoparticles deposited on the surface of ZnO act as effective traps for photogenerated electrons due to forming a Schottky barrier upon contact with metallic semiconductors. These electrons improve the rate of oxygen reduction and prevent electron-hole recombination.[24]

Under illumination, when ZnO and Ag nanoparticles come into contact, the photogenerated electrons are distributed between both types of particles, resulting in electron transfer from excited ZnO to Ag, until the two systems achieve equilibrium. The electron accumulation of the Ag particles increases the Fermi level to a more negative potential, which also causes a shift in the Fermi level of the compound closer to the conduction band of the composite.[25]

Figure 5 shows a significant and noticeable increase in the photocatalytic degradation efficiency of Ag1/ZnO. In contrast, the photolysis efficiency of the remaining types of nanocatalysts decreased. A similar dependence of photolysis efficiency on the amount of Ag loading has been documented previously.[26]

The photolysis efficiency of Ag/ZnO undergoes the smaller amount of Ag on the ZnO surface. Because of the less accumulation of some small particles, the dispersion of Ag usually decreases with the increase in load. Decreased quantity results in low efficiency of Ag and weak photoactivity of Ag/ZnO. In addition to Ag scattering, the photocatalytic degradation efficiency of Ag/ZnO is also affected by Schottky barriers between the surface of Ag and ZnO.[27]

When the Ag content is in the right amount, the number of Schottky barriers at the Ag/ZnO interface is enhanced by increasing Ag loading, which increases the photocatalytic degradation efficiency.[28]

However, when the Ag loading is less than the amount in type Ag1/ZnO, the active sites on the ZnO surface that are available for light absorbers and electron donors are covered with excess Ag particles. Moreover, some Ag particles may act as recombination centers for photogenerated electrons and holes.[29]

CONCLUSIONS

This article prepared the zinc oxide/silver nanocomposite using the photo-deposition method. The photolysis processes of the brilliant green dye depend on the amount of "catalyst dose" and the optimum value equal to 0.2 g Ag-ZnO of the nanocomposite. The effect of dye concentration on the optimum value of bright green 5 ppm and light intensity of 8 mW/cm^2 was studied. Photolysis "decreases" with "increasing" the concentration of brilliant green due to a decrease in the concentration of OH-adsorbed on the catalyst's surface. The photolysis of brilliant green light increases with increasing light intensity.

Photocatalytic Decomposition: Brilliant green is equal to 92.8%, with an increasing amount of silver loaded on the surface of zinc oxide

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