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BaO-ZnO nano-composite efficient catalyst for the photo-catalytic degradation of 4-chlorophenol

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ABSTRACT
A flower like nano-composite of BaO and ZnO was synthesized through a one-pot precipitation method using 2-aminoethanol as precipitating agent. X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) were employed to clarify the structure and morphology of the BaO-ZnO nano-composite. The photocatalytic behavior of BaO-ZnO nano-composite was evaluated in the photo-catalytic degradation of 4-chlorophenol under UV irradiation technique. The effect of various parameters including catalyst dosage, 4-chlorophenol concentration, pH and temperature on the degradation of 4-chlorophenol was investigated. The complete photocatalytic degradation of 4-chlorophenol was achieved in acidic condition.
Keywords: *BaO-ZnO nano-composite, BaO, ZnO, nano-composite, photocatalytic degradation, 4-chlorophenol.*

1. INTRODUCTION
The widespread occurrence of toxic organic compounds in wastewater increased concern over public health. Among of the toxic organic compounds phenols are well-known for their bio-recalcitrant and acute toxicity. These compounds defile the aquatic environment through various outputs of industrial and non-industrial activities. Therefore, the purge of the industrial effluents from the phenolic compounds is an imperative requirement to ensure the human health [1-4].Traditional methods of wastewater treatment, combined with some limitations and disadvantages, are unable to decompose all of the phenolic compounds. Thus, the using of catalytic systems which can eliminate these compounds by decomposing them into non-hazardous species is a demanding area of research. Recently, photocatalytic degradation of phenolic compounds with or without ultraviolet light has been reported to be a useful method for the removing of these compounds from wastewaters [5-11]. This method has the advantages as it is cost-effective, environmentally friendly and is able to destroy a wide range of phenolic compounds without generation of harmful byproducts. Some of the photo-catalysts shown a good choice to achieve an effective elimination of phenolic compounds are TiO_2, ZnO, CuO, CeO_2, V_2O_5 ant etc. [5-11].

Herein, a novel nano-composite BaO and ZnO with a nano-flower like morphology being pre-pared by homogeneous precipitation methods. The as-prepared nano-composite was found to be enabling the photo-catalytic degradation of 4-chlorophenol under UV radiation.

2. EXPERIMENTAL SECTION
2.1. Material and instrumentation.
All reagents were purchased from Merck and Aldrich and used without further purification. XRD data were collected from the synthesized powders for phase identification and determination of crystallite size by Philips TW3710 X'Pert diffractometers using Cu-Kα radiation. FE-SEM was taken by a Hitachi S-4160 photograph to examine the shape of the samples. TEM image was taken by a PHILIPS CM20 microscope to examine the shape and size of nano-composite.

2.2. Synthesis procedure.
A solution of barium chloride (100 mmol) and zinc nitrate (30 mmol) was prepared by dissolving of zinc nitrate and barium chloride in 250 ml of water (solution A). The 2-aminoethanol solution was prepared by dissolving the 2-aminoethanol (200 mmol) in 50 ml of water (solution B). Solution (B) was slowly added drop-wise to solution (A) under vigorous magnetic stirring. The mixture was aged for 1h at room temperature. The resulting precipitate was filtered, washed with water several times and dried in an oven at 80 °C for 5 h and finally calcined at 500 °C for 2 h.

2.3 Photocatalytic degradation procedure.
The photocatalytic degradation of the 4-chlorophenol solution was performed using a solution of the 4-chlorophenol substrate in water and BaO-ZnO nano-composite as catalyst. The solution was stirred under UV irradiation (273 nm) with three 8 W ultraviolet lamp as a source in Pyrex flasks at room temperature. The absorption spectrum of the suspension mixture was measured periodically using a GC spectrophotometer (Shimadzu, UV-2450, Japan) after centrifugation to ensure the degradation of 4-chlorophenol solution.

3. RESULTS SECTION

3.1. Characterization of the BaO-ZnO nano-composite.

Figure 1 shows the powder XRD patterns of the BaO-ZnO nano-composite calcined at 500 °C.

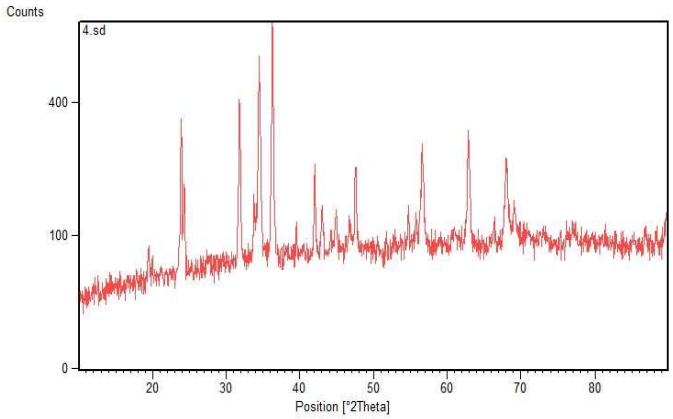

Figure 1. XRD pattern of BaO-ZnO nano-composite calcined at 500 °C.

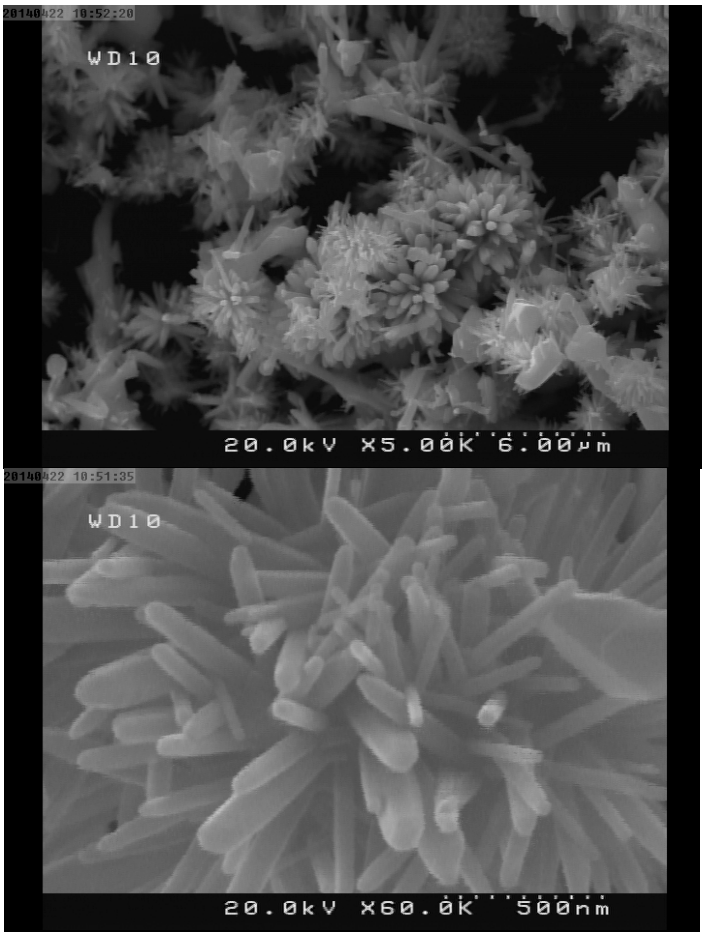

Figure 2. FE-SEM photograph of BaO-ZnO nano-composite.

The XRD pattern was obtained using an advance diffractometer (for 2θ range from 0° to 80° with a step size of 0.01° (2θ)) with monochromatic Cu-Kα radiation to identify the crystalline nature of the composite. The XRD peaks were appeared in 31.8, 34.4, 36.2, 47.5, 56.6, 62.8, 67.9 and 69.1 can be indexed to a hexagonal structure of ZnO. The diffraction peaks observed at 23.9, 24.3, 33.7, 34.1, 34.6, 42.0, 44.9 and 46.8 (2θ degrees) are assigned to the orthorhombic structured BaO.

The average crystal size of the nanoparticles was calculated by the Debye–Scherer formula (1), and found to be 64 and 102 nm for ZnO and BaO phases, respectively.

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (1)$$

Where, k is the shape factor, D is the crystalline size, θ is the diffraction angle, β is the full width half maximum of diffraction angles in radians.

Figure 2 shows the FE-SEM images of the as-prepared BaO-ZnO nano-composite which shows that the composite consist of nanoflowers generated from the ZnO and BaO nano-rods with a diameter of less than 100 nm.

3.2. Photocatalytic degradation of phenol.

Initially, the effect of different ZnO catalysts, including commercial ZnO, nano-ZnO (25 nm), and BaO-ZnO nano-composite on the photocatalytic degradation of 4-chlorophenol was examined by UV irradiation technique. It was inferred from control experiments that the presence of both nano-composite and UV light is necessary for photo-degradation. From the Figure 3, it is observed that BaO-ZnO nano-composite exhibits significantly greater efficiency than commercial ZnO and nano-ZnO with 60% of degradation. This may be due to increase in the adsorption strengths of phenol into the surface of the catalyst as well as producing of reactive intermediates which consequently contributes to the improvement of the photocatalytic activity of BaO-ZnO nano-composite.

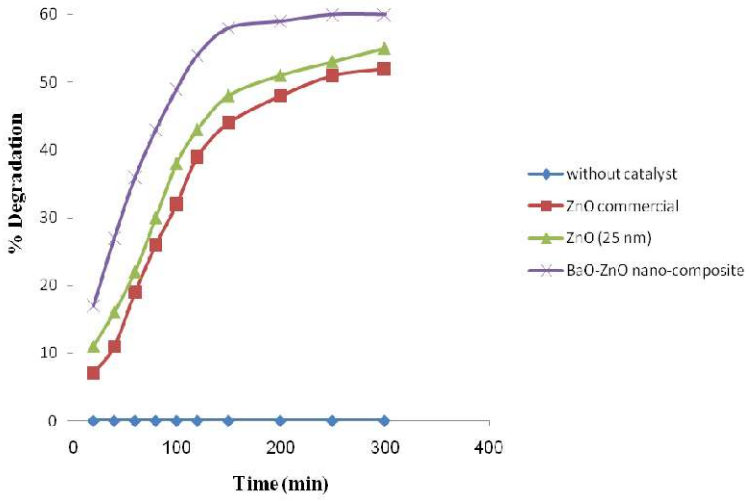

Figure 3. Photo-catalytic degradation of 4-chlorophenol: effect of different catalysts.

It is well known that with the absorption of UV photons in the aqueous solutions, a cascade of reactive species including superoxide anion ($O_2^{\bullet-}$) and hydroxyl radicals ($HO^{\bullet}$) is generated. The abundance of these species in the system is dependent on various factors, including pH, electrochemical potential of the media and the structure of photocatalyst [12, 13].

Figure 4 shows the effect of catalyst concentration on the photodegradation activity of 4-chlorophenol under UV irradiation. The decrease of 4-chlorophenol concentration can be improved up

to 0.1 g of the catalyst and the higher amount of the catalyst has a lower percent of degradation.

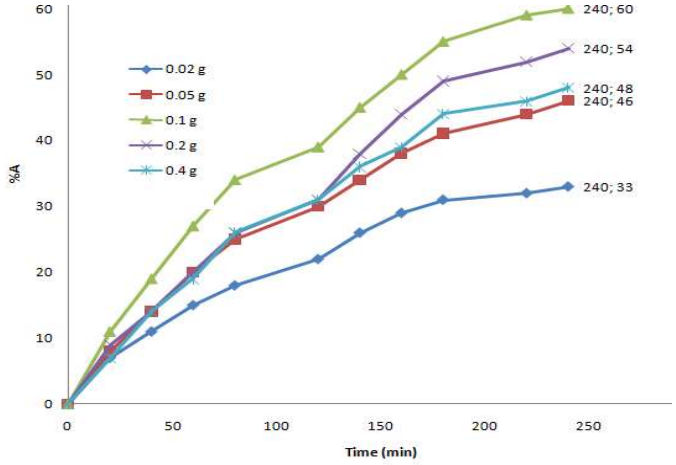

Figure 4. Photo-catalytic degradation of 4-chlorophenol: effect of catalyst dosage.

The influence of 4-chlorophenol concentration on degradation rate was studied from 0.5 to 8 g/L at a constant catalyst loading of 0.1 g and a solution pH of 5. The volume of 4-chlorophenol solution was 10 ml. It is observed that the degradation rate increases with an increase in concentration of 4-chlorophenol up to 2 g/L and then decreases (Figure 5). The UV λmax value of 4-chlorophenol is 280 nm. Further experiments were made to study the effect of temperature on the photocatalytic degradation of 4-chlorophenol. It was observed that with an increasing on the reaction temperature, the yield of the degradation reaction was increased (Figure 6).

Next, the effect of solution pH was examined in the range of 3−10, as shown in Figure 7. Increasing and decreasing of pH was done by the using of NaOH and HCl for basic and acidic condition, respectively. It was found that in acidic media (pH= 3) complete conversion of 4-chlorophenol was observed, however, it was declined in basic condition (pH= 9). On the other hand,using H_2O_2 in pH = 5 show a complete degradation of 4-chlorophenol.

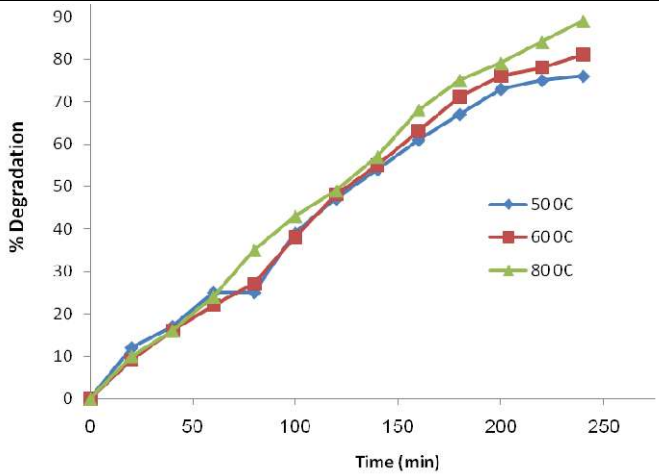

Figure 6. Photo-catalytic degradation of 4-chlorophenol: effect of temperature.

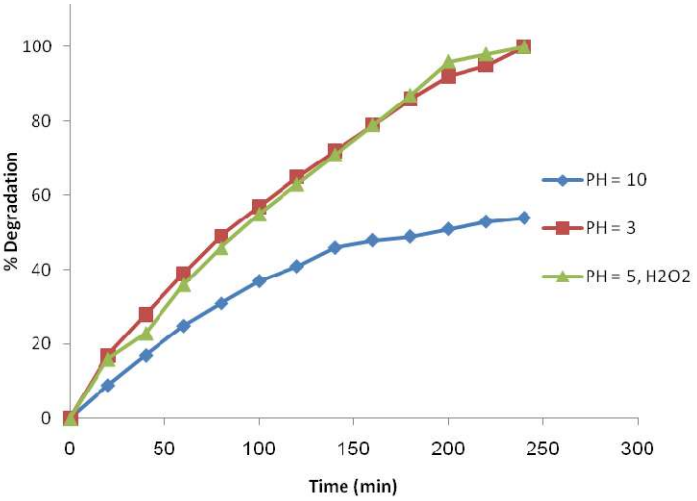

Figure 7. Photo-catalytic degradation of 4-chlorophenol: effect of initial pH solution.

4. CONCLUSIONS

In conclusion, a simple preparation method of BaO-ZnO nano-composite was reported. The photocatalytic behavior of the as-prepared BaO-ZnO nano-composite was evaluated by 4-chlorophenol degradation experiments. Nearly complete degradation of 4-chlorophenol under the exposure of UV was achieved in acidic condition. Moreover the effects of catalyst loading, 4-chlorophenol solution concentration, temperature and pH were investigated. In comparison with ZnO, BaO-ZnO nano-composite is more effective for the photocatalytic degradation of 4-chlorophenol.

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6. ACKNOWLEDGEMENTS

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