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Photocatalytic properties of ZrO_2 nanoparticles in removal of nitrophenol from aquatic solution

ABSTRACT

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ZrO_2 nanopowder was prepared by the sol-gel auto-combustion method. The product was characterized by X-ray diffraction (XRD), energy dispersive analysis of X-ray (EDX) and scanning electron microscopy (SEM). The average crystalline size of ZrO_2 was obtained 62 nm. Also, photocatalytic removal of nitrophenol from aqueous solution by using nanoscale ZrO_2 under UV light irradiation was studied. The effect of initial pollution concentrations in 3, 5 and 10 ppm in presence of ZrO_2 nanoparticles was studied in photocatalytic degradation process. Nitrophenol was degraded 84, 78 and 66% in the presence of 0.04 g of ZrO_2 within 70 minutes.

Keywords: *Photocatalyst; ZrO_2 ; Degradation; Sol-gel auto-combustion method.*

INTRODUCTION

Nitrophenol is one of the important contaminating materials that have high toxicity level receiving in water resources. Its high toxicity, even at low concentrations, has motivated the search and improvement of many treatment techniques. In this sense, photocatalysis can yield feasible, convenient methods for the treatment of phenolic wastewaters [1-3]. Photocatalytic degradation process is one of the developing technologies in treatment of wastes containing persistent organic materials. The photocatalysis system using semiconductive particles is a very promising technique and has attracted extensive attention in recent years [4]. Semiconductor nanoparticles have attracted interests of many academic and industrial researchers because of their properties based on quantum size effects and high surface area [5, 6]. Among these materials, zirconia attracts attention due to its application as an engineering ceramic for both mechanical and electrical purposes. ZrO_2 is a wide bandgap semiconductor (~5.0 eV) and has been proven to have the photocatalytic performance.

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Zirconia as an oxide material is hard (Vickers hardness ~13–24 GPa), tough (fracture toughness ~8–13MPam^{1/2}), strong (compressive strength ~1000–1800MPa), thermally stable (m.p. 2680°C), and chemically inert [7].

Photocatalyst was synthesized with different process such as co-precipitation [8, 9], sol-gel [10-12] and chemical vapour deposition (CVD) [13]. It is well recognized that sol-gel autocombustion is an effective method for synthesis of semiconductor nanoparticles for different advanced applications such as photocatalysis.

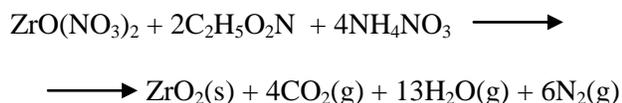
Sol-gel auto-combustion is a way with a unique combination of the chemical sol-gel process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous and fluffy product with large surface area. This process is less complicated than the others [14, 15].

In this paper ZrO₂ nano photocatalyst was synthesized by sol-gel auto-combustion method with cheap materials. Then, the structural and photocatalytic properties of synthesized ZrO₂ nanoparticles in removal of nitrophenol from aquatic solution were investigated.

EXPERIMENTAL

Synthesis of Nanophotocatalysts

Tetragonal, zirconia powders were synthesized by sol-gel auto-combustion of an aqueous solution containing zirconium nitrate, Zr(NO₃)₄, and glycine, C₂H₅O₂N, in the required molar ratio of 1:2.5. All the reagents used in the experiments were analytically pure and used without further purification and treatment. The theoretical equation for the formation of ZrO₂ from reaction mixture used for the combustion is given below:



Ammonia solution was slowly added to adjust pH to 7. The solution was allowed to evaporate on a hot plate and maintained at 70°C under continuous stirring. After the evaporation of

water, the resulting gel was ignited to form a loose powder. Finally the precursor was calcined at 600°C for 2 hours to obtain ZrO₂ nanoparticles.

Materials Characterization

The phase identification of the nanopowders was recorded by X-ray diffraction with *Cu-Kα* radiation. The crystallite powders size was also measured by X-ray line broadening technique using the Scherrer formula indicated in equation (1):

$$D = (0.9)\lambda / \beta \cos\theta \quad (1)$$

Where *D* is the grain diameter, *β* is half-intensity width of the relevant diffraction; *λ* is X-ray wavelength and *θ* the diffraction angle.

A Philips XL-30 scanning electron microscope was used to characterization the morphologies and microstructure of the samples.

Assessment of the Photocatalytic Degradation of Nitrophenol in Presence of ZrO₂ Nanoparticles

Photocatalytic degradation of nitrophenol was used to evaluate the photocatalytic activity of synthesized ZrO₂ nanopowders. First the solution of 3,5 and 10 mg/L of dye were prepared in deionized water, then 100 ml of prepared solution are transferred in three purely clean containers. An amount of 0.04 g of nano photocatalyst was added to containers. Solutions were set height of 30 cm from UV lamp with power of 30 W for a time interval of 70 minutes. The solutions were continuously stirred during the mentioned time interval. Samples were taken from containers solution and were filtered, centrifuged for 20 minutes to ensure that nanoparticles were removed completely from samples, and clear transparent solution were obtained. Finally, samples are taken from obtained solutions and put in the double beam spectrophotometry to investigate the absorption of samples.

RESULTS AND DISCUSSION

X-Ray Diffraction of Nanoparticles

The phase and purity of nanopowders were determined from the XRD pattern is shown in Figure 1. Well-defined sharp peaks indicate the

good crystalline quality and confirm the formation of single-phase zirconia dioxide nano photocatalyst. The diffraction peaks appeared in the XRD patterns can be indexed with the standard patterns for ZrO_2 (JCPD 01-079-1768). The average crystalline size calculated from Sherrer equation were 64 nm for ZrO_2 .

EDAX Analysis

The elemental composition of nanopowders is determined from the EDX

spectrum over a selected zone. The representative spectrum of sample is shown in Figure 2. The spectrum of obtained precursor indicated the presence of ZrO_2 as a major element in the final powders.

SEM Images of Nanoparticles

SEM images of ZrO_2 nanophotocatalysts is shown in Figure 3. It is observed that ZrO_2 nanopowders were shaped in cavity structures.

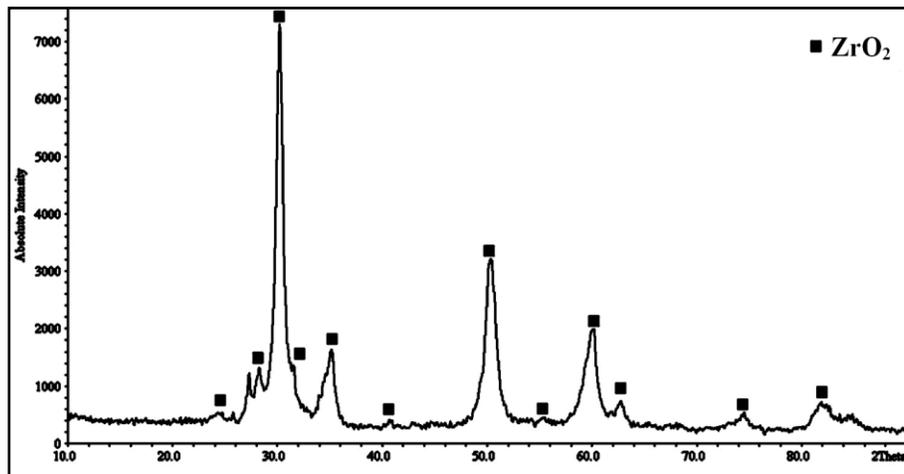


Fig. 1. XRD patterns of ZrO_2 nanoparticles.

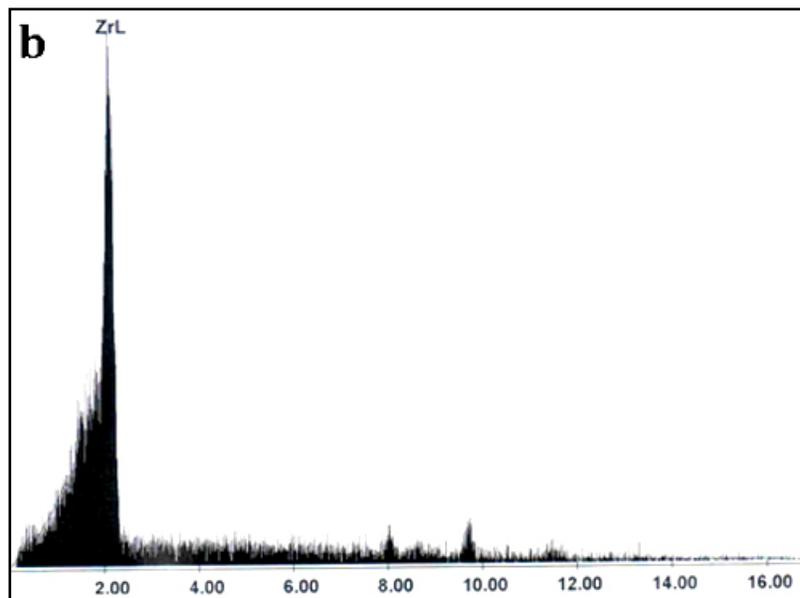


Fig. 2. EDAX analysis of nanoparticles ZrO_2 .

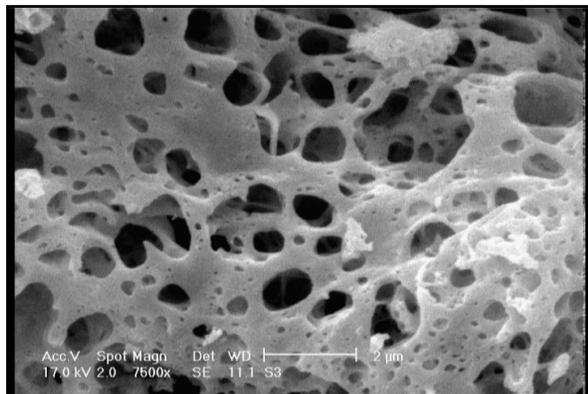


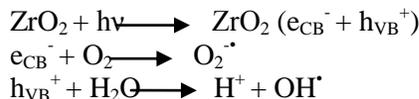
Fig. 3. SEM images of nanoparticles ZrO₂

Photocatalytic Degradation

• **Evaluation of Photocatalytic of ZrO₂ Nanoparticles**

In a photocatalytic system, photo-induced molecular transformation or reaction takes place at the surface of catalyst. A basic mechanism of photocatalytic reaction on the generation of electron-hole and its destination is as follows: when a photocatalyst is illuminated by the light stronger than its band gap energy, electron-hole pairs diffuses out to the surface of photocatalyst and participates in the chemical reaction with electron donor and acceptor. Those free electrons and holes

transform the surrounding oxygen or water molecules into OH free radicals with super strong oxidization. It can oxygenolyse various kinds of organic compounds and some parts of minerals. Reactions can be shown as follows [14]:



Degradation of dye calculated from equation (2):

$$X = \frac{A_0 - A}{A_0} \quad (2)$$

Where X is degradation percentage, A₀ is initial absorption of and A is absorption after several minutes.

The photo activity of ZrO₂ was carried by using UV light irradiation. Degradation can be monitored by optical absorption spectrophotometer (UNICO double beam spectrophotometer). Photodegradation of nitrophenol in concentration of 3, 5 and 10 mg/L was carried with 0.04 g ZrO₂. The absorption spectrum shows in Figure 4(a-c).

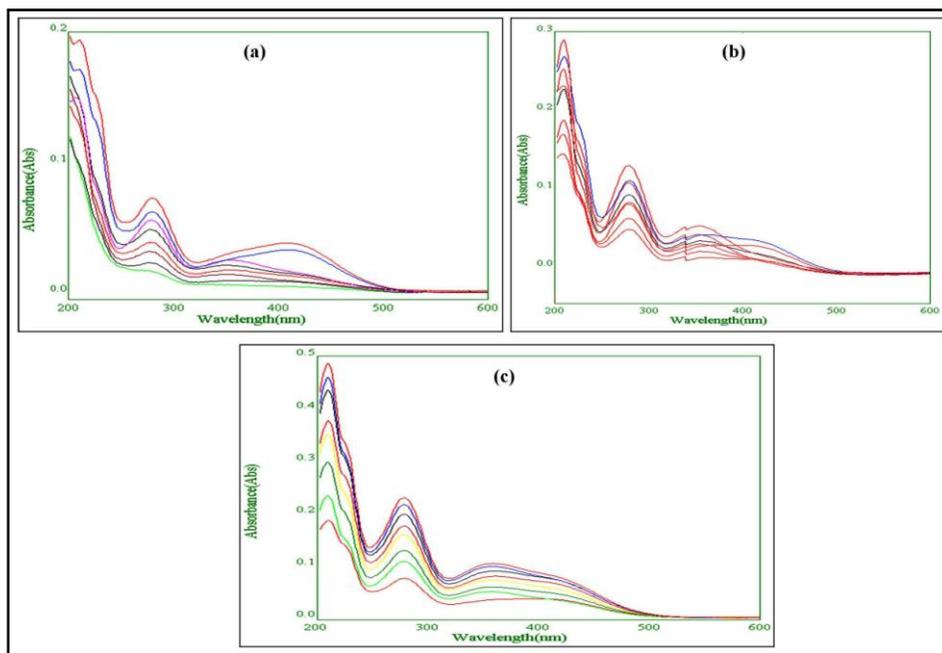


Fig. 4. Absorption spectrum of photo degradation reaction in presence of a) [NP]= 3mg/L, ZrO₂ = 0.04 g, b) [NP]= 5 mg/L, ZrO₂ = 0.04 g and c) [NP]= 10mg/L ZrO₂ = 0.04 g.

The Effect of Pollution Concentration

The initial concentration of nitrophenol solution on its removal was illustrated in Figures 5 with pollution concentration of 3, 5 and 10 mg/L in presence of 0.04 mg nano photocatalysis.

The effect of initial concentration of nitrophenol solution on the photocatalytic degradation is an important aspect of the study. The results showed that the removal rate decreased with increasing initial dye concentration. It can be seen that as initial dye concentration increases, more dye substances are adsorbed on the surface of nanocatalysts. Therefore, the generation of hydroxyl radicals will be reduced, because of fewer active sites for adsorption of hydroxyl ions and generation of hydroxyl radicals [15]. Furthermore, with increasing dye concentration, the adsorption of photons are decreased by the catalyst, as a result, the removal percent is reduced.

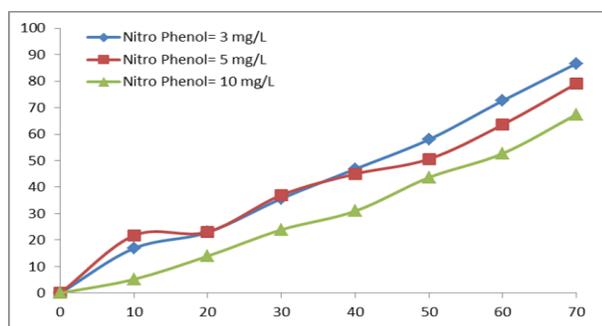


Fig. 5. Effect of Nitro Phenol concentration on the photodegradation reaction in the presence of 3, 5 and 10 mg/L.

CONCLUSIONS

ZrO₂ nanopowders were synthesized by sol-gel auto-combustion method. This technically, simple cost effective and high time and energy efficient process.

The following features of sol-gel auto-combustion method contribute to the unique properties of the synthesized products. First, the initial reaction media being in the liquid state (e.g. aqueous solution) allows mixing the reactants on the molecular level, thus permitting precise and uniform formulation of the desired composition on the nanoscale. Second, the high reaction temperature (T_c) ensures high product purity and crystallinity.

The average particles size was determined with sheerer formula by X-ray

spectrum data and estimated about 64 nm for ZrO₂. These nanoparticles were employed to photocatalytic destruction of nitrophenol in presence of UV light irradiation. The effect of different concentration of nitrophenol on the degradation percentage in presence of 0.04 g ZrO₂ was summarized in Table 1.

Table 1. The effect of different concentrations of nitrophenol in presence of 0.04 g ZrO₂

Dye concentration (mg/L)	Photocatalytic degradation (%)
3	84
5	77
10	66

REFERENCES

- [1] Araña, J., Pulido Melián, E., Peña Alonso, A., *et.al*, 2007, Photocatalytic degradation of phenol and phenolic compounds Part I. Adsorption and FTIR study, *J. Hazard. Mater.*, 146: 520–528.
- [2] Meshram, S., 2011, Continuous flow photocatalytic reactor using ZnO–bentonite nanocomposite for degradation of phenol, *Chem. Eng. J.*, 172: 1008-1015.
- [3] Zhao, B., 2010, Degradation of 4-nitrophenol (4-NP) using Fe–TiO₂ as a heterogeneous Photo-Fenton catalyst, *J. Hazard. Mater.*, 176: 569-574.
- [4] Zheng, W., Bingru, Z., Fengting, L., 2007, A simple and cheap method for preparation of coupled ZrO₂/ZnO with high photocatalytic activities, *Environ. Sci. Engin. China*, 1(4): 454–458.
- [5] Hosono, E., Shinobu, F., Toshio, K., Hiroaki, H., 2004, Non-Basic solution routes to prepare ZnO nanoparticles. *J Sol-Gel Sci. Techn.*, 29:71–79.
- [6] Marto, J., 2009, Photocatalytic decolouration of Orange II by ZnO active layers screen-printed on ceramic tiles. *J. Hazard. Mater.*, 163: 36.

- [7] Epstein, P., Dinka, P., Alexander, S., 2007, Solution combustion synthesis of nanomaterials, *Proceedings of the Combustion Institute* 31: 1789–1795.
- [8] Chu, X., 2011, Aqueous-phase reforming of ethylene glycol on Co-ZnO catalysts prepared by the co-precipitation method, *J. Mol. Catal. A- Chemical.*, 335: 129-135.
- [9] Chen, C., 2008, Synthesis and characterization of nano-sized ZnO powders by direct precipitation method, *Chem. Eng. J.*, 144: 509-513.
- [10] Liu, Y., 2009, Effects of Cr-doping on the optical and magnetic properties in ZnO nanoparticles prepared by sol-gel method, *J. Alloys Compd.*, 486: 835-838.
- [11] Khorsand Zak, A., 2011, Effects of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified sol-gel combustion method, *Ceram. International*, 37: 393-398.
- [12] Lee, J., 2009, Evolution of ZnO nanostructures in sol-gel synthesis, *Current Appl. Phys.*, 9: 792-796.
- [13] Wang, S. L., 2010, Large-scale preparation of chestnut-like ZnO and Zn-ZnO hollow nanostructures by chemical vapor deposition, *J. Alloys Compd.*, 502: 118-122.
- [14] Comparelli, R., Faanizza, E., Curri, L., 2008, Photo-degradation of methylene blue using Ta-doped ZnO nanoparticles, *Appl. Catal. B: Environ.*, 60: 1-11.
- [15] Modirshahla, N., Behnajady, M. A., Jangi Oskui, M. R., 2009, Investigation of the efficiency of ZnO photocatalyst in the removal of p-nitrophenol from contaminated water. *Iran. J. Chem. Chem. Eng.*, 28: 49-55.

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