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## Photocatalytic properties of $\text{ZrO}_2$ nanoparticles in removal of nitrophenol from aquatic solution

### ABSTRACT

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$\text{ZrO}_2$  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  $\text{ZrO}_2$  was obtained 62 nm. Also, photocatalytic removal of nitrophenol from aqueous solution by using nanoscale  $\text{ZrO}_2$  under UV light irradiation was studied. The effect of initial pollution concentrations in 3, 5 and 10 ppm in presence of  $\text{ZrO}_2$  nanoparticles was studied in photocatalytic degradation process. Nitrophenol was degraded 84, 78 and 66% in the presence of 0.04 g of  $\text{ZrO}_2$  within 70 minutes.

**Keywords:** *Photocatalyst;  $\text{ZrO}_2$ ; 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.  $\text{ZrO}_2$  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 ~8–13 MPa<sup>1/2</sup>), strong (compressive strength ~1000–1800 MPa), 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.

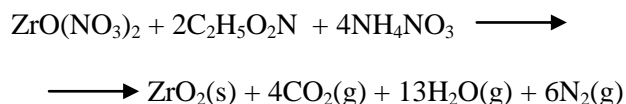
Sol-gel auto-combustion is a way with a unique combination of the chemical sol-gel process and the combustion process based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous and fluffy product with large surface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

In this paper ZrO<sub>2</sub> nano photocatalyst was synthesized by sol-gel auto-combustion method with cheap materials. Then, the structural and photocatalytic properties of synthesized ZrO<sub>2</sub> 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(NO<sub>3</sub>)<sub>4</sub>, and glycine, C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>N, 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 ZrO<sub>2</sub> 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 ZrO<sub>2</sub> 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,  $\beta$  is half-intensity width of the relevant diffraction;  $\lambda$  is X-ray wavelength and  $\theta$  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 ZrO<sub>2</sub> Nanoparticles

Photocatalytic degradation of nitrophenol was used to evaluate the photocatalytic activity of synthesized ZrO<sub>2</sub> 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  $\text{ZrO}_2$  (JCPD 01-079-1768). The average crystalline size calculated from Sherrer equation were 64 nm for  $\text{ZrO}_2$ .

#### 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  $\text{ZrO}_2$  as a major element in the final powders.

#### SEM Images of Nanoparticles

SEM images of  $\text{ZrO}_2$  nanophotocatalysts is shown in Figure 3. It is observed that  $\text{ZrO}_2$  nanopowders were shaped in cavity structures.

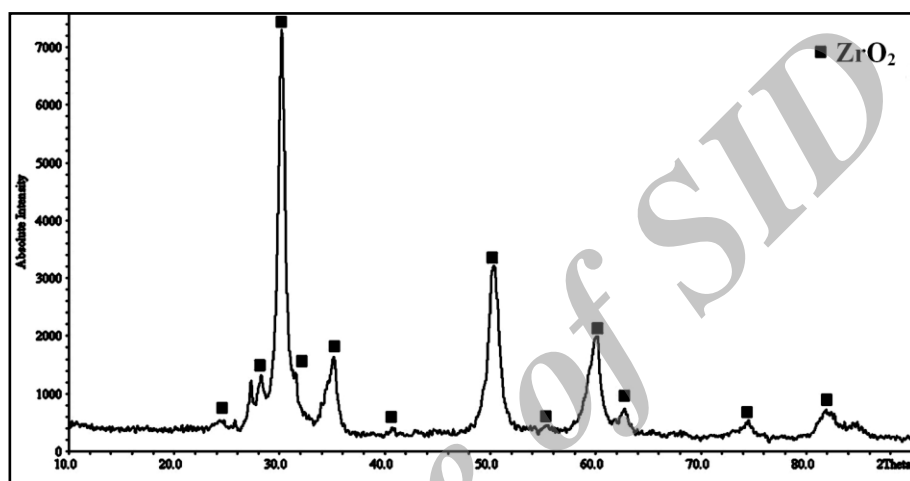


Fig. 1. XRD patterns of  $\text{ZrO}_2$  nanoparticles.

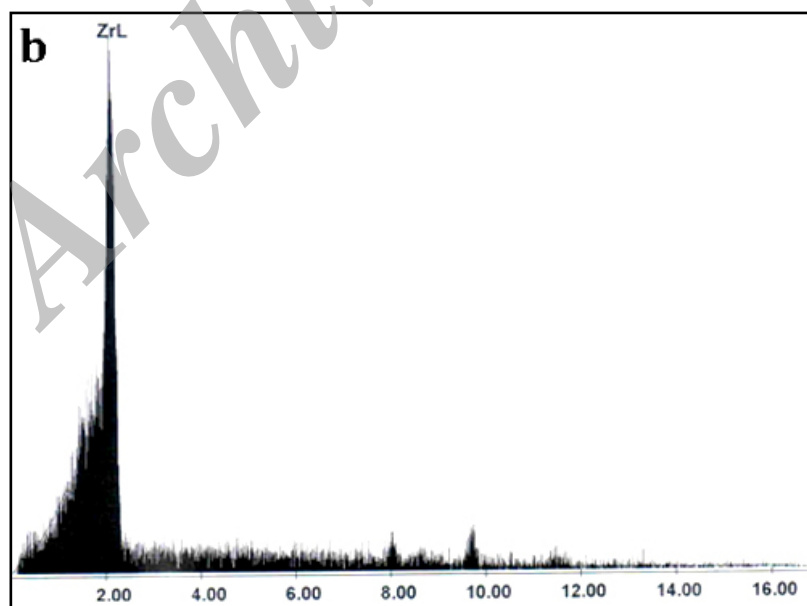


Fig. 2. EDAX analysis of nanoparticles  $\text{ZrO}_2$ .

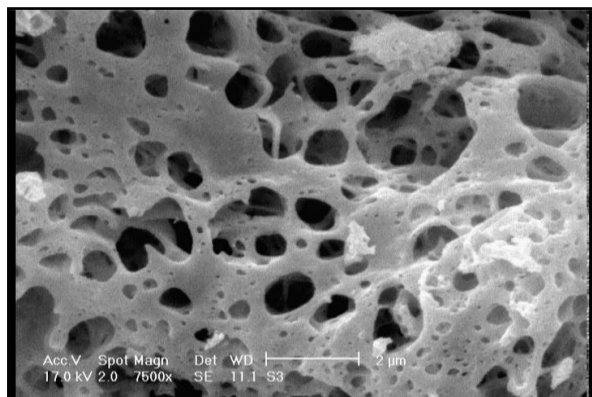


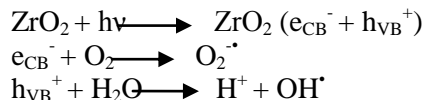
Fig. 3. SEM images of nanoparticles  $\text{ZrO}_2$

### Photocatalytic Degradation

#### • Evaluation of Photocatalytic of $\text{ZrO}_2$ 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 oxidation. 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,  $A_0$  is initial absorption of and A is absorption after several minutes.

The photo activity of  $\text{ZrO}_2$  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  $\text{ZrO}_2$ . The absorption spectrum shows in Figure 4(a-c).

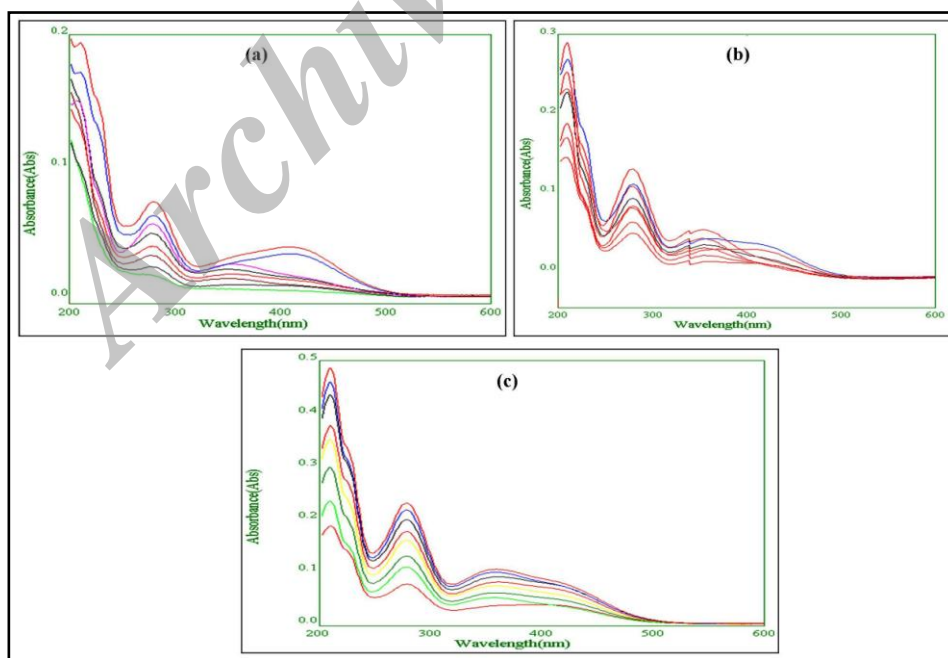


Fig. 4. Absorption spectrum of photo degradation reaction in presence of a) [NP]= 3mg/L,  $\text{ZrO}_2$  = 0.04 g, b) [NP]= 5 mg/L,  $\text{ZrO}_2$  = 0.04 g and c) [NP] = 10mg/L  $\text{ZrO}_2$  = 0.04 g.

### 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 present 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.

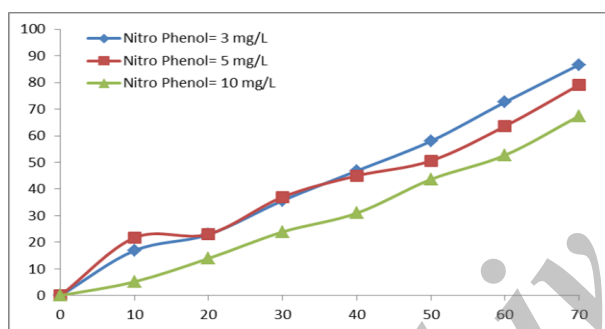


Fig. 5. Effect of Nitro Phenol concentration on the photodegradation reaction in the presence of 3, 5 and 10 mg/L.

### CONCLUSIONS

ZrO<sub>2</sub> 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<sub>c</sub>) 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 ZrO<sub>2</sub>. 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 ZrO<sub>2</sub> was summarized in Table 1.

Table 1. The effect of different concentrations of nitrophenol in presence of 0.04 g ZrO<sub>2</sub>

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

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