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RESEARCH PAPER

A Comparative Study of Photocatalytic Activity of ZnO/ activated Carbon Nanocomposites Prepared by Solid-state and Conventional Precipitation Methods

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ABSTRACT

ZnO/activated carbon nanocomposites (ZnO/ACns) were synthesized by applying two different solid-state and precipitation methods. Precipitation method was initiated with zinc chloride and sodium hydroxide as starting materials in the presence of activated carbon. The synthesized sample was calcined at 250 °C for 1 h. The preparation of nanocomposite by solid-state method was accomplished by heating a mixture of $ZnCl_2$ and activated carbon at 250 °C for 1 h, which led to the formation of ZnO particles on the surface. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Photocatalytic activity of these ZnO/acnes was evaluated by the degradation of methyl orange under UV-light radiation. The SEM images of samples show that the agglomerations of particles are much less in solid-state method prepared samples. The results of EDS indicate that the ratio of Zn/C in the pure activated carbon and nanocomposites prepared by solid-state and precipitation methods were 0, 1.7 and 3.7 % (W/W), respectively. The XRD of the samples clearly shows that the sample prepared by the above routes has ZnO structures. Finally, ZnO/ACn prepared by the solid-state method demonstrated better photocatalytic efficiency against methyl orange dye than composites made by precipitation method.

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INTRODUCTION

Water purification is currently popular among many scientists. Organic pollutants are known as the main contaminants of wastewater. So far, much attention has been focused on diminishing or degrading of organic pollutants in the wastewater. It has been shown that utilizing of photocatalysts is one of the most beneficial and efficient ways to remove organic pollutants from water [1-3]. Rapid growth of industry has caused different environmental problems, especially water pollution. Various synthetic dyes, which are widely used in industries, have been released into the natural environment and these pollutants are extremely hazardous to the health of human beings. Most of these dyes are not decomposed under ambient conditions and are commonly resistant to classical biological treatment [4]. Hence, the development of an efficient treatment method for dye treatment is a scientific problem of considerable interest. Recently, numerous researchers have concentrated on the photocatalytic degradation for dye removal because this approach can completely eliminate mineral dyes in wastewater [5-7].

Zinc oxide (ZnO) is one of the most popular

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photocatalysts due to its low toxicity, chemical stability, and superior photocatalytic properties [8]. Nevertheless, it is hard to recover the pure ZnO powder from the treated effluent, which restricts the virtual application of ZnO photocatalyst in the industry. Finding effective approaches to resolve the problem is real significant. So far, nanoparticles have been immobilized using various supports, which are generally porous materials. Accordingly various porous materials have been investigated, e.g. as activated carbon [4,9], clays [10,11], and silica gels [7,12]. Among these supports, activated carbon (AC) is real promising for two reasons: (1) AC is able to absorb the pollutants and then propagate them onto the surface of photocatalysts. Therefore, a higher concentration of pollutants around the photocatalysts than that of the bulk solution is created which increments the degradation rate of the pollutant and (2) the intermediates produced during degradation can be also adsorbed by AC and then further oxidized. Meanwhile, in the process of dye removal in wastewater treatment, AC supported ZnO could be separated and reused easily from suspension, thus the lifetime of photocatalyst could be lengthened [4].

Over the past decade many techniques have been developed for immobilizing nanoparticles onto a solid surface, for example sol–gel, hydrothermal, precipitation, dip coating, and hydrolysis and impregnation [13]. Xing *et al*. (2016) synthesized TiO_2/ activated carbon composite by a sol-gel method. Prepared composite had a photocatalytic activity of 93.2% for removal of Rhodamine B from the 400 mL solution at initial concentration of 2×10^{-5} mol/L under 450 mm Hg lamp irradiation [14]. In another work, Chen *et al*. (2017) synthesized ZnO nanoparticles co-doped with Ag and N supported on activated carbon through the sol-gel method. The prepared Ag-N-ZnO/ activated carbon exhibited the degradation efficiency of 98.82% within 120 min under visible light radiation for methyl orange (30 ppm) [15].

Recently, solid-state method has been applied to prepare different nanoparticles/support composites such as TiO_2/silica gel [5], TiO_2/ nanoclay [10], copper oxide/ silica gel [16] and Ag/ silica gel [19]. Solid-state production of supported catalysts offers advantages including: (1) the produced materials are mainly on the external surface of the support, (2) most of the traditional steps in catalyst preparation, such as saturation and reduction can be avoided, (3) the produced materials are pure (no chemical agents were used) and (4) this synthetic procedure is rapid and simple [6]. As far as this study is concerned, the synthesis of ZnO/activated carbon nanocomposites via molten salt method has not been available in the literatures.

This article compares photocatalytic activity of ZnO/Activate carbon nanocomposites prepared by two different conventional precipitation method and novel solid-state method. Photocatalytic activity of these ZnO/ACns was evaluated by the degradation of methyl orange under UV-light irradiation.

MATERIALS AND METHODS

Zinc chloride, activated carbon (AC), methyl orange is purchased from Merck (Tehran, Iran). All reagents were used without further refining.

Preparation of ZnO/ACns

Solid-state method

ZnO/ACns were prepared by a modified synthetic procedure of lotfiman and Ghorbanpour [12]. Activated carbon was exposed to the heated salt of $ZnCl_2$ at 250 °C for 60 min. This procedure was conducted using 10 g of activated carbon and 0.2 g of salt. Then, the samples were washed adequately with distilled water. After dissolution, the nanocomposites were dried in an oven at 25 °C.

Precipitation method

Solution of 0.2 g of zinc chloride dissolved in 100 mL distilled water was prepared. Accordingly, under magnetic stirring, 10 g activated carbon and sodium hydroxide was added to complete the precipitation, leading to the formation of a white gel. The prepared sample was then washed with distilled water. Then, the powder was dried at room temperature for 24 h and heated at 250 °C for 60 minutes.

Characterizations

The microstructure and chemical composition of the samples were observed by a scanning electron microscope conjugated with energy dispersive X-ray (EDX) (LEO 1430VP, Germany). X-ray diffraction (XRD) patterns of the samples were characterized using an X-ray diffractometer (Philips PW 1050, The Netherlands) with CuKα radiation (λ = 1.5418 Å, 40 kV, 30 mA, 2θ = 0–80° and 0.05° step).

Photocatalytic activity

The photocatalytic activity of the composites was studied by the degradation of methyl orange under UVA-light radiation (Philips, Netherlands) in a photocatalytic reactor at room temperature. In each experiment, 0.1 g photocatalyst was added into a 250 mL vessel containing 200 mL methyl orange (1000 ml, 25 ppm) solution under magnetic stirring (100 rpm) and maintained in the dark for 15 min in order to allow for adsorption equilibrium, and then the suspension was irradiated under UV light. The power of UV lamp was kept at 4W and an average irradiation intensity of 1206 W/m^2 was maintained throughout the experiments. The distance between the reactor and lamp housing is 5 cm. Then, about 2 mL of the suspension sample was collected at certain times during the irradiation period, which was centrifuged at 12000 rpm for 10 min to remove the photocatalyst. The remaining methyl orange in the solution was measured at 465 nm using a spectrophotometer (Nanospec 2UV-A, made in Germany). The photocatalytic degradation efficiency was estimated according to the following equation:

$$\text{Degradation (\%)} = \left(\frac{A_0 - A}{A_0}\right) \times 100 \quad (1)$$

Where represents the initial absorbance of the dye solution and A represents the initial absorbance after irradiation.

RESULTS AND DISCUSSIONS

Characterizations

The following reaction is supposed to take place in the preparation of nanoparticles of zinc oxide by the solid-state method:

$$ZnCl_2 + 2\,H_2O \Rightarrow Zn(OH)_2 + 2\,HCl \quad (2)$$

$$Zn(OH)_2 \Rightarrow ZnO + H_2O \quad (3)$$

The high temperature prompted the chemical reaction between $ZnCl_2$ and water (atmospheric water vapor or surface water). In step (2), zinc chloride yields zinc hydroxide and HCl. Then, calcinations of zinc hydroxide resulted in the formation of the ZnO particles. During the calcinations process, OH of hydroxide is removed in the form of H_2O. In the participation method, the following reaction is supposed to take place:

$$ZnCl_2 + NaOH \Rightarrow Zn(OH)_2 + NaCl \quad (4)$$

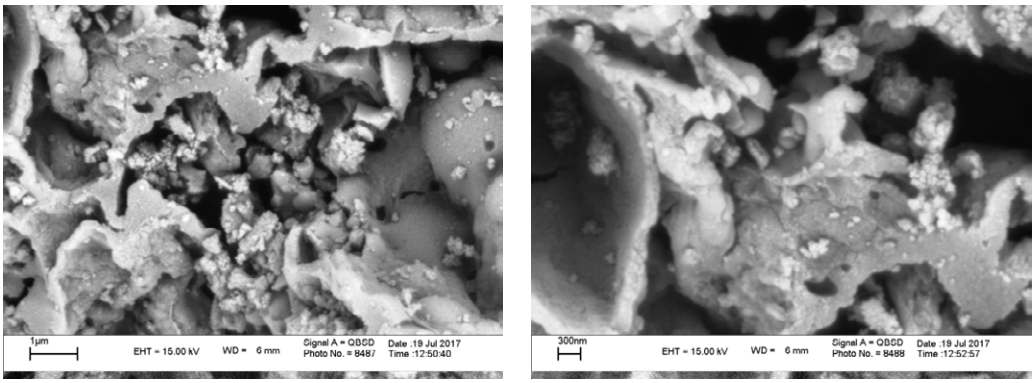
$$Zn(OH)_2 \Rightarrow ZnO + H_2O \quad (5)$$

In step 4, zinc chloride gives a precipitate of zinc hydroxide with sodium chloride. Then, after calcination of dried precipitate of zinc hydroxide, the nanoparticles of zinc oxide are obtained.

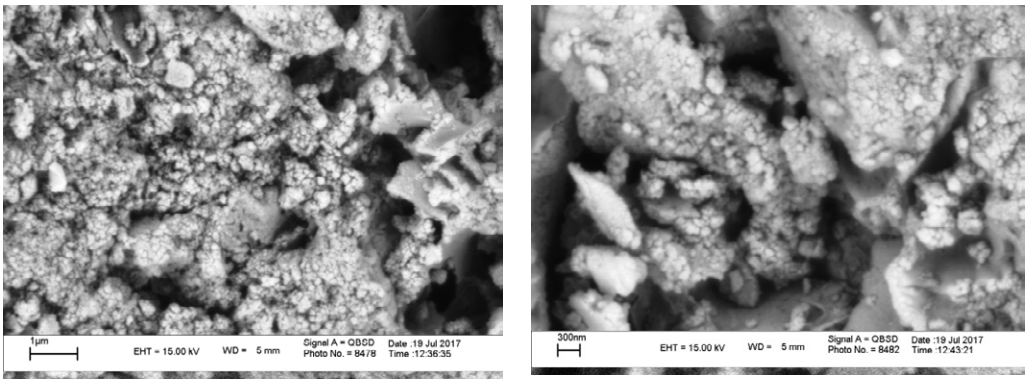
The SEM micrographs of the pure activated carbon and ZnO/ACn were shown in Fig. 1. SEM micrographs of the pure AC exhibit its porous nature (Fig. 1.a). SEM images of the carbon/ZnO composites prepared by each method are shown in the presence of spherical shape ZnO particles on the surface of activated carbon (Fig. 1.b-c). Moreover, SEM micrographs of composite clearly reveal the surface texture and porosity nature. The immobilization of ZnO in the carbon matrix partially blocked the porosity of the carbon surface, even though the composite still displays a porous character with a relatively large pore volume and surface area. This suggests that the ZnO did not enter the inner micro porosity of the carbon during the immobilization and remained on the outer surface and most accessible (large) pores.

The main difference between composites prepared by solid-state and precipitation method is the agglomeration and distribution of ZnO nanoparticles on the activated carbon support. Higher magnification image indicate a large agglomeration of nanoparticles presence in the prepared composite by precipitation method. This agglomeration results in non-homogenous distribution of nanoparticles on the support. In the prepared samples by solid-state methods, nanoparticles were spread homogeneously on the support while low surface exists without coating. One of the main applications of support is to prevent of nanoparticles agglomeration. Thus, the solid-state method has good agreement with this aim.

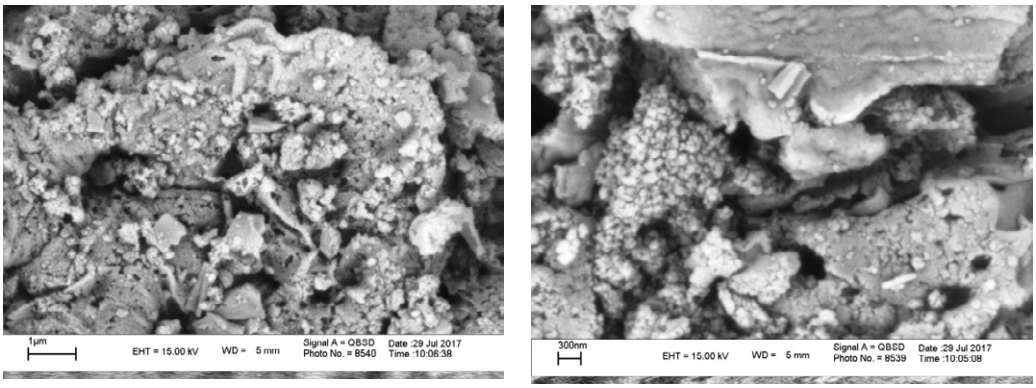
The presence of ZnO on the activated carbon surface was determined using the EDX analysis presented in Table 1. Some amount of Zn has been detected at the surface of the composite material sample. This analysis of the composites further confirmed the successful immobilization of the ZnO particles by the presence of the Zn in the composites. The results indicate that the ratio of Zn/C in the pure activated carbon was 0%. This ratio increased to 1.7 and 3.7 % for samples prepared by solid-state and precipitation method, respectively. Thus, the amount of Zn ions in the composites depends on the synthesis method.



(a)



(b)



(c)

Fig. 1. The SEM micrographs of (a) activated carbon and ZnO/ACn prepared by (b) solid-state and (c) precipitation method.

This finding is in agreement with SEM results (Fig. 1).

Fig. 2 shows the activated carbon and ZnO/Acn XRD patterns. After the synthesis step, new diffraction peaks appeared which can be indexed to crystalline phase of formed ZnO nanoparticles. The strong and narrow diffraction peaks in the pattern of solid state prepared composites compared to composites prepared by precipitation method indicate that the product has better crystallinity. Thus, while the precipitation method results in higher loading of

Table 1. Chemical composition of the activated carbon and ZnO/ Activated Carbon

Element	Concentration (wt%)		
	Activated carbon	Solid-state method	Precipitation method
Carbon	77.7	86.1	82.3
Oxygen	20.5	11.0	13.2
Magnesium	0.3	0.2	0.2
Potassium	0.2	0.2	0.2
Calcium	1.1	0.8	0.8
Iron	0.2	0.3	0.3
Zinc	0	1.4	3.0

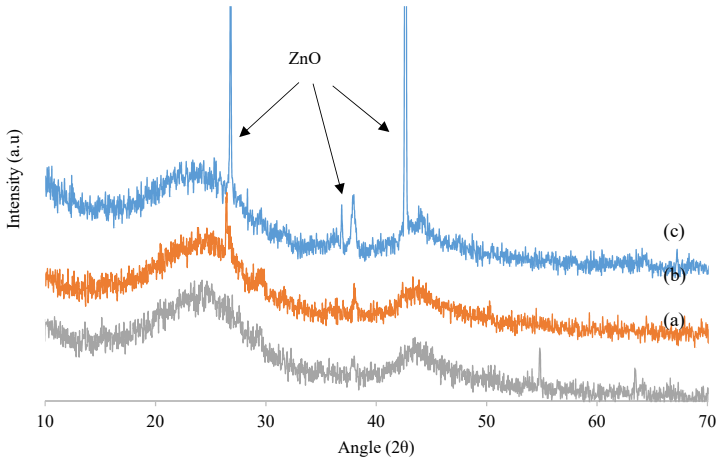


Fig. 2. The XRD patterns of (a) activated carbon and ZnO/ACn prepared by (b) solid-state and (c) precipitation method.

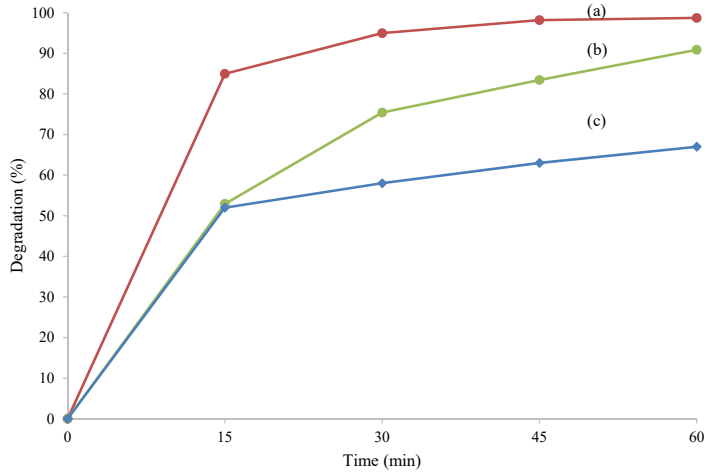


Fig. 3. The degradation of the dyes by the ZnO/ACn prepared by (a) solid-state, (b) precipitation method and commotional Degusa TiO_2 against methyl orange

Zn ions on the activated carbon (Table 1), they were amorphous and did not crystallize. In other hand, the increase in the diffraction intensity in solid state produced composite can be attributed to nanoparticles preferentially formed outside the pores of activated carbon.

Photocatalytic activity

The application of the prepared nanocomposites as a photocatalyst was investigated for the dye removal of MO. The degradation of the dyes by the ZnO/ACn is shown in Fig. 3. Both composites showed high degradation performances at short

Table 2. Summary of photocatalytic activity of nanoparticles

Type of catalyst	Type of pollutant	pollutant concentration (ppm)	Degradation (%)	References
ZnO/montmorillonite	Methylen blue	10	97	[6]
ZnO	Methyl orange	15	92	[18]
ZnO	Methyl orange	10	95.4	[19]
ZnO/bentonite	Acid red 35	20	84.9	[20]
ZnO/montmorillonite	phenol	10	88.5	[21]

reaction times and after only 1 h the catalysts were able to completely degrade the dyes. However, it can be seen that the composite prepared by solid-state method shows higher yield in the photocatalytic decomposition of methyl orange dye in water than prepared composite by precipitation method. The possible reason for the better dye removal efficiency of these composites could be attributed to higher crystallinity and lower agglomeration of ZnO nanoparticles on the activated carbon substrate, which increases the surface area and available average active sites as a result. The photocatalytic materials prepared by solid-state method are very promising due to their ease of production and low cost.

The catalytic activity of the commercial titanium oxide nanoparticles of DEGUSSA Co. is investigated under the test conditions to perform better comparison. According to Fig. 3 the activity of both composites is better than TiO2. The reason for this might be the presence of active carbon base in the composite structure. As indicated in the introduction, the presence of activated carbon has increased the photocatalytic activity of the composites through the adsorption of contaminants and the production of intermediates due to its decomposition. This is also observed in previous works. For example, the results of some previous work are briefly presented in Table 2. Fatimah *et al*. (2011) investigated the photocatalytic activity of ZnO/montmorillonite for methylene blue degradation. This test is carried out with10 ppm concentration of the desired contaminant and catalyst dosage of 2 g/lit and after150 minutes the rate of degradation reached 97%. Here the concentration of contaminant is higher (25 ppm), the optimum catalyst is 0.5 g / lit, and also the duration of the radiation is less (60 minutes). In another work, Kumar *et al*. (2013) [18] synthesized zinc oxide nanoparticles using the synthesis of ZnO nano-mushrooms (ZNM) by the solution combustion method to degrade methyl orange. After the 210 minutes the removal percentage was 92% under optimal conditions.

CONCLUSIONS

ZnO/activated carbon nanocomposite (ZnO/ACn) were synthesized by solid-state method and precipitation method. The SEM images of samples show that the agglomerations of particles are much less in solid-state method. The results of EDS indicate that the ratio of Zn/C in the pure activated carbon and nanocomposites prepared by solid-state and precipitation method was 0, 1.7 and 3.7 %, respectively. The XRD of the samples clearly shows that the sample prepared by the above route has pure ZnO. Both ZnO/ACn showed high degradation performances at short reaction intervals.

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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