

A Comparative Study between Photocatalytic activity of ZnO/bentonite Composites Prepared by Precipitation, Liquid-state Ion Exchange and Solid-state Ion Exchange Methods

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ABSTRACT

The purpose of this research is to produce ZnO/bentonite nanocomposites with precipitation, liquid-state ion exchange (LSIE) and solid-state ion exchange (SSIE) methods and compare their photocatalytic activity. The physicochemical properties of the prepared photocatalysts were determined by scanning electron microscope (SEM), energy dispersive X-ray (EDX) and diffusive reflective spectroscopy (DRS) analysis. The Photocatalytic activity was evaluated by degradation of methyl orange (MO) with prepared photocatalysts. SEM images showed that the ZnO particles were successfully distributed on the bentonite in the samples prepared by precipitation method. Nevertheless, after ion exchange-based methods, no particles were formed on the bentonite surface. The EDX analysis showed that the Zn contents in the ZnO/bentonite were 0.39, 0.44 and 0.66% prepared with LSIE, SSIE and precipitation methods, respectively. Based on changes in the UV-vis spectrum of Parent zinc chloride and bentonite, the DRS analysis confirmed the formation of ZnO/bentonite composites. The photo-degradations of MO were 85, 87 and 84% for the composites prepared by LSIE, SSIE and precipitation methods, respectively. Finally, the photocatalytic composites prepared by the solid-state method were very bright due to their simple production, low price and short time due through direct heating of the reaction.

Keywords: Liquid-state Ion Exchange, Photocatalytic activity, Precipitation Method, Solid-state Ion Exchange, ZnO/bentonite Composites

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INTRODUCTION

Among various photocatalysts, Zinc oxide (ZnO) is one of the most popular photocatalysts due to its low toxicity, chemical stability, and superior photocatalytic properties [1,2]. Unfortunately, the use of this nanoparticle in pure form leads to its agglomeration. On the other hand, their subsequent isolation from the outflow is difficult and requires filtering operation, which is time-consuming

and leads to increased costs. To overcome these problems, nanoparticle stabilization on the base has recently been used [3-6].

Interestingly, ZnO attachment on a support can extend life and reusability of the photocatalyst [3]. Furthermore, the surface of the support can be used to prevent the guest particles from aggregation [11]. Besides, these composites may provide a combination of properties of both species

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and have advanced functions depending on the compositions [5]. So far, several researchers have attempted to prepare these composites, by attaching or impregnating nanoparticles onto a stable support such as activated carbon [2,8], clays [9-11] and silica [7,12]. Among different types of supports, bentonite exhibits beneficial properties, such as large surface area, swelling behavior, adsorption and ion exchange properties [9,13]. Previous investigations suggested that the porous structure and high specific surface area of this clay were beneficial to photoactivity via enhancing adsorption, which is determining critical step in the heterogeneous photocatalytic reaction. Therefore, a combination of adsorption and heterogeneous photocatalyst makes photo-oxidation more effective for dye removal from wastewater [10].

Using clay in nanoparticle preparation and immobilization, various preparation techniques including precipitation [14], liquid phase ion exchange (LSIE) [15] and solid-state ion exchange (SSIE) [3,5,15,16] have been applied. In the liquid phase ion exchange method, cations in the interlayer space of clay minerals such as Na^+ or Ca^{2+} can be converted into various inorganic or organic cations such as Zn^{2+} via an ion-exchange reaction. Therefore, ion-exchanged cations occupy the interlayer space in natural clays. Finally, by applying heat treatment, the ion-exchanged cations undergo dehydration reaction and are converted to metal oxide clusters in the interlamellar space of clay particles [17,18]. In the precipitation method, the precipitate can be formed as nuclei and then nuclei grow to become particles. Nuclei formation and growth depend on the concentration of precursor solution and reaction time. The synthesis of ZnO nanoparticles by the precipitation method involves the reaction of zinc salts such as ZnCl_2 with basic solutions containing NaOH [19,20]. In most studies done so far, LSIE and precipitation method have been used to prepare composites. The solid method has been recently used in a number of studies to prepare various antimicrobial composites [3,5]. In this method, a zinc salt such as ZnCl_2 is mixed with bentonite and heated at around the melting point of a zinc salt. Synchronized application of heat and ion exchange creates a fast process [3,5]. SSIE is simpler and faster than the other two methods. So far, no studies are conducted to compare the photocatalytic activity of the nanocomposites produced by each of these methods. The purpose

of this research is to produce nanocomposites with each of these methods and compare their photocatalytic activity.

MATERIALS AND METHODS

Preparation of ZnO/bentonite composites

Solid-state ion exchange

Bentonite (Kansas Jam Company, Rasht, Iran) was exposed to the heated salt of ZnCl_2 (Merck) at 250 °C for 60 min. This operation was conducted using 2 g of bentonite and 2 g of salt. Then, the samples were adequately washed out by distilled water. After dissolution, the nanocomposites were dried in an oven at 25 °C.

Liquid-state ion exchange

Bentonite (2 g) was exposed to the aqueous of ZnCl_2 (2% W/V) at 25 °C for 240 min. Then, the samples were adequately washed out by distilled water. The prepared sample was then collected and washed with distilled water. Then, the powder was dried at room temperature for 24 h and heated at 250 °C for 60 min.

Precipitation method

A solution of 2 g zinc chloride dissolved in 100 mL of distilled water was prepared. To this, under magnetic stirring, 2 g bentonite and sodium hydroxide (Merck) was added to complete the precipitation, leading to the formation of a white gel. The prepared sample was then collected and washed with distilled water. Then, the powder was dried at room temperature for 24 h and heated at 250 °C for 60 min.

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). Diffuse Reflectance UV-vis Spectroscopy (DR UV-Vis) of the powder samples was conducted within the wavelength range of 200–800 nm using a spectrophotometer (Scinco S4100, S. Korea).

Photocatalytic activity

Photocatalytic activities of the composites were evaluated by the photodegradation of methyl orange (100 ml, 25 ppm) under 4 W UVA-light radiations (Philips, Netherlands). A weighed amount of photocatalyst was first dispersed in 50 ml of methyl orange solution. The result was then irradiated with UV illumination in a photoreactor.

After the reaction, the solution was immediately centrifuged and its absorbance was measured to calculate the degradation percentage using the UV-visible spectrophotometer. The photocatalytic degradation efficiency was calculated according to the following equation:

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

Where A_0 is the initial absorbance of the dye solution and A represents the initial absorbance after irradiation.

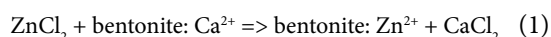
RESULTS AND DISCUSSION

Characterization

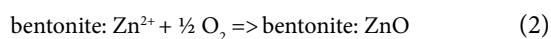
The surface morphology of the parent bentonite and prepared ZnO/bentonite composites were detected by SEM. The crude bentonite has a layered structure with numerous nano-sized flakes, which provides a suitable surface area to immobilize ZnO (Fig. 1a). As observed in Fig. 1, after ion exchange and solid-state ion exchange, the parent structure of bentonite remains, only the introducing of zinc

ions provided more porous composite texture (Fig. 1b,c).

The expected chemical reaction occurred when the molten solution of ZnCl_2 reached bentonite. The high temperature prompted the ion exchange reaction by diffusion of present zinc in the molten salt or aqueous solution of zinc chloride and calcium of bentonite matrix. The chemical reaction is as follows:



Further, calcinations of obtained bentonite: Zn^{2+} resulted in the formation of the ZnO particles.



Interestingly, after these ion exchange based methods, no particles can reach the bentonite surface. This is because of the very small size of ZnO particles (smaller than 2 nm) which in the interlayer space of bentonite (Fig. 2b). These are consistent with previous reports [3,5].

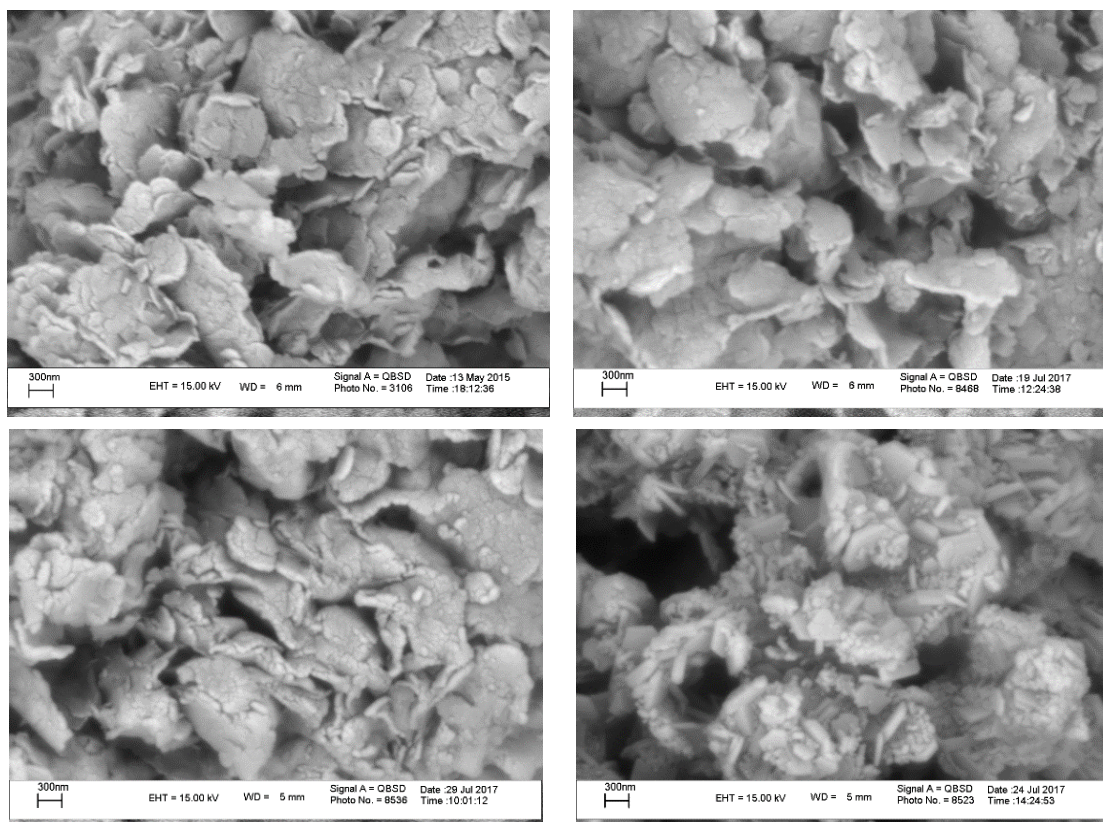


Fig. 1. Typical SEM images of parent bentonite (a) and ZnO/bentonite photocatalyst prepared using LSIE (b) and SSIE (c) and precipitation method (d)

The following reaction is supposed to take place in the participation method:



In step 3, zinc chloride gives a precipitate of zinc hydroxide and sodium chloride. Moreover, the nanoparticles of zinc oxide are obtained after calcination of dried precipitate of zinc hydroxide. Nevertheless, the prepared ZnO/bentonite composite by precipitation method contains heterogeneous particles on its surface. On the other hand, ZnO nano-sheets typically cover the surface of bentonite (Fig. 2b).

The presence of zinc in the prepared ZnO/bentonite material was checked by EDX analysis (Table 1). Raw bentonite contained Oxygen, Magnesium, Aluminum, Silicon, Sulfur, Potassium, Calcium, and Iron. The domination of calcium content as an exchangeable cation indicates a

calcium type of bentonite. After modification, the Zn contents in the ZnO/bentonite were 0.39, 0.44 and 0.66% prepared using LSIE, SSIE and precipitation methods, respectively. Therefore, in the composites prepared by methods based on ion exchange, the amount of loaded zinc is less than that of the precipitation method. This can be achieved by limiting the exchange of ion exchange capacity of bentonite.

The diffuse reflectance absorption spectra of parent bentonite and ZnO/bentonite photocatalysts were obtained. The UV-visible spectrum of bentonite showed an absorption onset at 312 nm (Fig. 3). Pure zinc chloride also has a strong absorption peak at 306 nm and a weak peak at 250 nm. In the nanocomposites prepared by each of the used methods, the peaks around 306 nm have red-shifted to around 317 nm and the peak disappeared around 250 nm. Therefore, these changes in the UV-vis spectrum of Parent zinc chloride and bentonite were attributed to the formation of ZnO/bentonite composites.

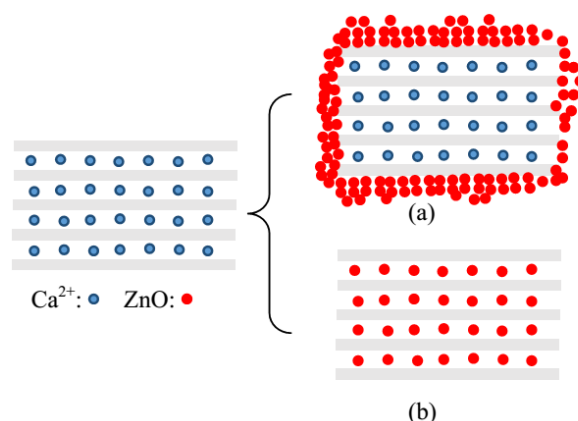


Fig. 2. The Schematic illustration of the composites prepared by using precipitation method (a) and ion exchange method (b)

Table 1. Composition (% w/w) of parent bentonite and ZnO/bentonite photocatalysts

	bentonite	SSIE	Ion LSIX	Precipitation method
Oxygen	56.31	51.98	51.53	51.46
Magnesium	1.45	1.53	1.14	1.48
Aluminum	8.18	8.68	8.84	8.53
Silicon	29.39	34.82	35.55	35
Sulfur	1.51	0	0	0
Potassium	1.11	1.39	1.01	1.12
Calcium	1.01	0	0.32	0.42
Iron	1.04	1.16	1.21	1.33
Zinc	0	0.44	0.39	0.66
Sum	100	100	100	100

In another hand, the amount of light absorption by the composite prepared by the chemical precipitation method is greater than the composites prepared by ion exchange methods. Based on the SEM images and the schematic illustrated in Fig. 2, in the precipitation method, nanoparticles are set on the surface, which allows more light absorption. In the ion exchange method, particles are formed inside the bentonite structure, which causes less adsorption of light. In addition, in the precipitation method, more amount of zinc is introduced to the composite structure, which results in a higher amount of light absorption.

Photodegradation

To evaluate the effect of various production methods on the degradation of MO, the efficiencies of parent bentonite and prepared ZnO/bentonite were separately evaluated in terms of the photocatalyst dosage of 1 g/L and initial MO concentration of 25 mg/L (Fig. 4).

As this figure shows, bentonite only decreases MO concentration only during the first 15 minutes, and the dye concentration remains constant. This behavior is due to dye absorption by bentonite. Interestingly, the behavior of composites undergoes a different process. That is, in these composites, adsorption was performed over the first 15 minutes, and the dye concentration continued to decrease after it. This secondary reduction is the result of photocatalytic activity, which is absent in the bentonite sample. On another hand, the efficiencies of ZnO/bentonite were significantly higher than parent bentonite. The photodegradation of MO were 85, 87 and 84% for the composites prepared by LSIE, SSIE and precipitation methods, respectively. The SSIE prepared composite behavior is comparable to other composite materials prepared by alternative procedures. Finally, the photocatalytic materials prepared by the solid-state method are very promising due to their ease of production and low cost.

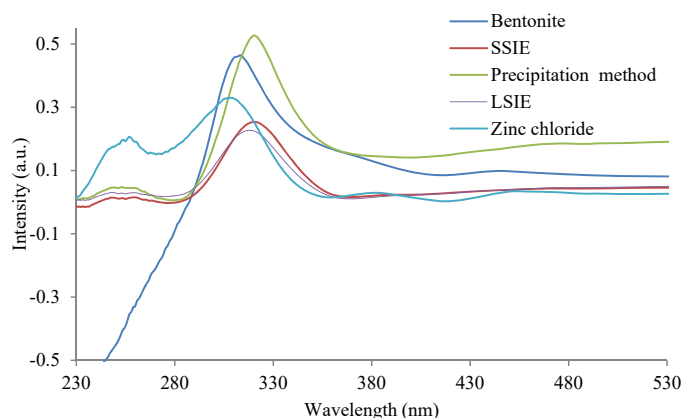


Fig. 3. UV/vis reflectance spectra of pure zinc chloride, bentonite and ZnO/bentonite photocatalysts

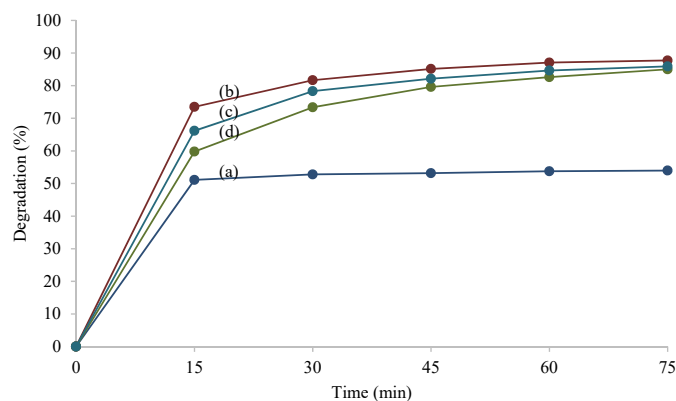


Fig. 4. The degradation of the methyl orange by the bentonite (a) and ZnO/bentonite composites prepared by SSIE (b), LSIE (c) and precipitation method (d)

CONCLUSIONS

ZnO/bentonite composites were prepared by three different synthetic methods. The EDX powder confirmed the formation of composites. The photodegradation of MO were 85, 87 and 84% for the composites prepared by LSIE, SSIE and precipitation methods, respectively. Thus, the photocatalytic materials prepared by the solid-state method are very bright due to their simple production and low price.

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest.

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