

ZnO/bentonite Nanocomposites Prepared with Solid-state Ion Exchange as Photocatalysts

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ABSTRACT

Photocatalyst nanocomposites of ZnO/bentonite clay are synthesized by Solid-state ion exchange method. The ion exchange intercalation process of clays is used to incorporate the catalyst into the basal space of the layered structure of clays. The purpose of this study is to find a new method focused on simplifying and saving time to prepare ZnO/bentonite composite with photocatalyst property. The ZnO doped bentonite nanocomposite synthesizes accomplished by placing bentonite in a melting bath of ZnSO₄ for 10, 20, 40, 60 and 90 min. Morphological (SEM), optical (UV/vis reflection) and analytical (EDX) techniques characterize the nanocomposites. According to SEM results, after ion exchanging, the parent structure of bentonite remains, and only the distance between flakes increases significantly. EDX analysis clearly suggests the success of ion exchange of the expense of Ca²⁺, Na⁺ and Mg²⁺ cations with Zn²⁺. The calculated band gaps for the composites were 3.14 eV (10 min), 2.64 eV (20 min) and 2.54 eV at longer periods, respectively. All prepared composites showed acceptable degradation performances. The greatest photocatalytic activity is detected in ZnO/bentonite composite solid-state ion exchanges, which lasts 60, and 90 min.

Keywords: ZnO/bentonite, Nanocomposites, Solid-state ion exchange, Photocatalysts.

1. Introduction

Dye removal from effluents is environmentally important because sometimes even insignificant and invisible amounts of dyes might be extremely toxic. Thus, dye removal is an environmental challenge and a public health matter. Azo dyes such as Methyl Orange are the largest type of textile dyes used in industrial applications. These reactive azo dyes are not easily removable by conventional treatment methods due to their stability and non-biodegradable nature [1]. The dye-contaminated wastewaters released by textile industrial wastewaters cause potential environmental hazards against the ecosystem and they must be treated before being discharged into the natural water bodies.

One of the most promising techniques employed to remove organic pollutants is mainly focused on their oxidative mineralization by heterogeneous photocatalysis including Advanced Oxidation Processes [2]. These processes induce the oxidation of various complex organic compounds and turn them into products that are more easily degradable by biological methods. Generally, these processes are involved with (i) photogeneration of electrons in the conduction band trapped by a recipient (such as superoxide/hydroxyl radicals) and (ii) photogenerated holes in the valence band consumed by the donors, i.e. organic pollutants [3,4]. Among various photocatalysts such as TiO₂ and ZnO has been used extensively due to its various applications in degradation of various

environmental pollutants [1,2,5]. Zinc Oxide enjoys unique electrical and optical properties that have many important applications, such as transparent conducting films, solar cells and photocatalyst and antibacterial materials [6-8]. A great deal of research conducted so far has used the slurry systems, in which the suspensions with minutely powdered photocatalysts are used [3]. However, the main problem with this separation method is the later removal of photocatalyst particles from the slurry, which requires costly stages such as filtration. Obviously removing photocatalysts is a long and expensive procedure. Moreover, ZnO is unstable in acid conditions and shows rapid deactivation in large volumes due to aggregation [9]. The solution is used to immobilize the photocatalyst on an inert support. Therefore immobilizing helps to eliminate the expensive phase separation procedures, inhibits pollution caused by runoff of the photocatalysts removal process and thus, extends life and reusability of the photocatalyst. An improvement in ZnO photocatalytic activity due to quantum size can also lead to effective absorption of photons [9-10]. So far, several researchers have attempted to prepare ZnO composite by attaching or impregnating ZnO into a stable inorganic support such as activated carbon [11,12], clay [1,2] and silica gel [7]. Among these supports, clays are considered as an appealing substrate for immobilization of a variety of nanoparticles because of being inexpensive and widely available [1,6]. Clays are natural minerals with hydrous aluminum silicates and a layered structure composed of silicate sheets bonded to aluminum oxide/hydroxide. Various strategies have been recently developed to achieve ZnO/supported materials [1-3,6]. The preparation methodologies of ZnO/layered clay based materials mainly include the in situ formation of ZnO nanoparticles in the presence of the clays or organo-clays in aqueous media followed by diverse Zn salt precursors and experimental conditions [3]. The ion exchange intercalation process of clays is also used to incorporate the catalyst into the basal space of the layered structure of clays [13]. The purpose of this study is to find a new method known as solid-state ion exchange, which is focused on simplifying and saving time to prepare ZnO/bentonite composite with photocatalyst property. Solid-state ion exchange is an attractive alternative to promote reactions and reduce processing time due to direct heating of the reaction [6,13,15,16]. The Solid-

state ion exchange operation is accomplished by immersing bentonite in a molten salt bath containing the dopant ions, which replaces alkali ions in the clay matrix. Here, some experimental results of photocatalytic activity of ZnO/bentonite nanocomposites prepared by solid-state ion exchange method are presented.

2. Experimental

Bentonite clay (K-montmorillonite), used as a solid support for photocatalyst, is provided by the Kansas Jam Company (Rasht, Iran). Methyl Orange and $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$ are purchased from Merck. All reagents had analytical grade and used without further refinement. All aqueous solutions are prepared using distilled water. Bentonite is submitted to a solid-state ion-exchange process by immersion into $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$ at 550–560 °C for 10, 20, 40, 60 and 90 minutes. The process is conducted using 2 g of bentonite and 2 g of $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$. After the ion exchange process, the bentonite is washed carefully through sonication with distilled water. The main purpose of this step is to dissolve any compounds that are not contained in the bentonite. After dissolution, the bentonite is dried in an oven at 25 °C.

The microstructure and chemical composition of the samples are observed by scanning electron microscopy along with energy dispersive X-ray (EDX) (LEO 1430VP, Germany). Absorption spectra of bentonite and ZnO/bentonite nanocomposites are measured by a UV–vis diffusive reflectance spectrophotometer (DRS), within the wavelength range of 200–1000 nm (Sinco S4100, Korea).

Photocatalytic activities of the composites are evaluated by the photo degradation of methyl orange (100 ml, 25 ppm) under 4 W UVA-light radiations (Philips, Netherlands). Weighed amount of photocatalyst (0.05 g) is first dispersed in 50 ml of methyl orange solution. The result is then irradiated with UV illumination in a photo reactor. After the reaction, the solution is immediately centrifuged and its absorbance is measured to calculate the percentage of degradation using the UV–visible spectrophotometer. The photocatalytic degradation efficiency is calculated according to the following equation 1:

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

Where, A_0 represents the initial absorption of the dye solution and A denotes the initial absorption after irradiation.

3. Results and discussion

The SEM images of bentonite and Zn ion exchanged bentonite are presented in Figure 1. The scanning electron micrograph of bentonite (figure 1a) shows the typical layered structure with numerous nanosized flakes of clay particles with a sheet-like morphology. After ion exchanging, the parent structure of bentonite remains and only the distance between flakes increased significantly. This is due to the presence of heat and zinc penetration into the bentonite structure during the ion exchange process [6].

However, even at composite prepared in 90 min, the presence of ZnO particles is not clearly identified on the surface. In the ion exchange process, the nanoparticle is added to the bentonite structure and zinc is replaced by calcium bentonite and converted into zinc oxide nanoparticles by heating. In this case, no particles can be observed with SEM.

Thus, zinc in the bentonite intermediate layer is “composed of silicate sheets bonded to aluminum

oxide/hydroxide”. In other words, the ion exchange between interchangeable ions of bentonite in this medium and zinc in molten salt has taken place. These results are consistent with previous research findings [6,13-16].

The Energy Dispersive X-ray (EDX) analysis is carried out to differentiate between the parent and modified Solid-state ion exchange bentonite by identifying the elemental composition of each sample. The chemical composition data are summarized in Table 1. The semi quantitative elemental analysis provided by EDX detected several elements involved in creating the structure of bentonite that are Si, Al, O, C, Mg, Ca, Na and K as shown in Table 1. After modification with zinc ions, the Si, O and Al content of the nanocomposites are practically unchanged. According to the table most of Ca^+ has been removed after modification. Furthermore, the weight percent of Na^+ and Mg also slowly reduced after modification. Moreover, the weight percent of Zn^{2+} is increased from 0.01 to more than 1.69 because of performing the cation

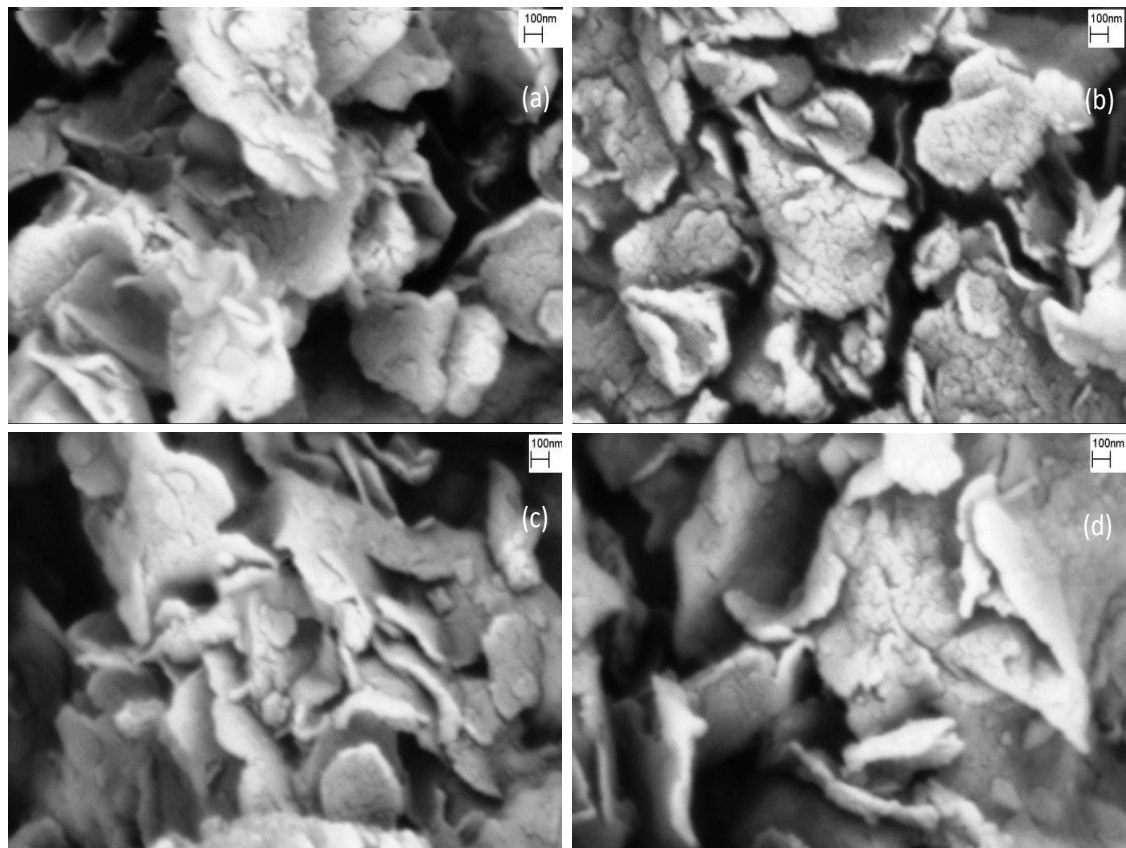
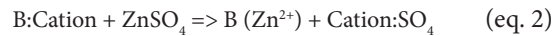


Fig. 1- SEM images of the parent bentonite (a), ion exchanged bentonite for 10 (b), 60 (c) and 90 (d) min.

exchange method. These clearly suggest the success of ion exchange of the expense of Ca^{2+} , Na^+ and Mg^{2+} cations with Zn^{2+} . On the other hand, the greatest decrease in the amount of cations in the structure of bentonite and vice versa cause the increase in the amount of alternative zinc (from 0.01 to 1.69), during the first 20 minutes. By increasing the process time to 40 minutes, the amount of zinc replaced will be increased to 2.17. At higher periods, changes in zinc content are very low. The reason for this is the high speed of mass transfer due to the process at high temperature. That is, the main ion exchange is carried out during the first 20 minutes, and the ion exchange will continue at a lower rate at the second 20 minutes. Then, the ion exchange speed is very slow. On the other hand, the distance traveled for ion exchange is short during the initial period due to the presence of cations at the general surface. Therefore, the process of mass transfer and ion exchange occurs at a higher speed.

UV/vis reflectance spectra of bentonite and Zn ion exchanged bentonite are illustrated in Figure 2. It is observed that the absorption of ZnSO_4 or Zn^{+2} is at 310 nm. This peak is weekend and shifted to higher wavelength at around 320 nm after solid-state ion exchange method, which is associated with the formation of nanocomposites. Within 10 to 20 min of the process, the intensity of this peak is rapidly decreased. During the next

40 min, this reduction continued slowly. Finally, after 60 min, the intensity remained relatively constant. In addition, after solid-state ion exchange of bentonite clay by ZnSO_4 a new adsorption peak is appeared at 380 nm that corresponded to the ZnO nanoparticles [3]. Thus, it can conclude that solid-state ion exchange of bentonite clay for 10 min is due to the replacement of calcium in clay by Zn^{2+} ions and most of zinc, which is introduced to bentonite, is in the ionic form according to the following equation 2:



At longer periods, the Zn^{2+} ions oxidized into ZnO particles in the presence of atmospheric O_2 and thermal energy while it seems that after 60 min the oxidation of zinc to ZnO is almost complete. This process was shown in Figure 3 schematically.



According to previous reports, the calculated Band gap energy (E_g) value for the ZnO nanoparticles is 3.2 eV, which corresponds to the near-UV region emission [9]. The corresponding E_g values calculated for the composites are 3.14 eV (10 min), 2.64 eV (20 min) and 2.54 eV at longer periods, respectively (Table 2). This observation

Table 1- Weight percentages of the existing elements in bentonite before and after modification

Ion exchanged time(min)	Weight percentages of occurrence elements				
	0	20	40	60	90
Oxygen	52.70	53.68	53.70	53.65	53.58
Sodium	0.89	0.47	0.45	0.47	0.37
Magnesium	1.10	1.08	1.05	0.86	0.78
Aluminium	6.21	6.62	7.21	7.06	7.12
Silicon	35.33	35.25	34.34	34.67	34.88
Potassium	0.89	0.78	0.72	0.73	0.75
Calcium	2.85	0.42	0.36	0.31	0.24
Zinc	0.01	1.69	2.17	2.25	2.27

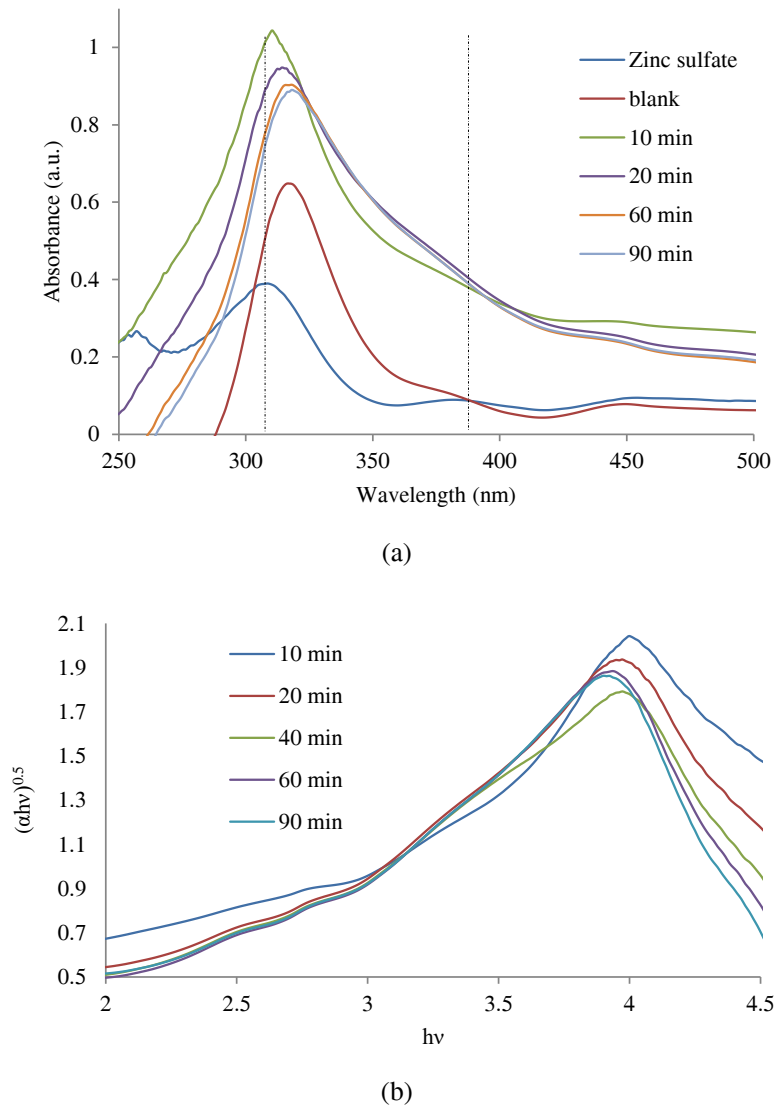


Fig. 2- Diffusive reflectance spectra (a) and band gap (b) of prepared ZnO/bentonite nanocomposites.

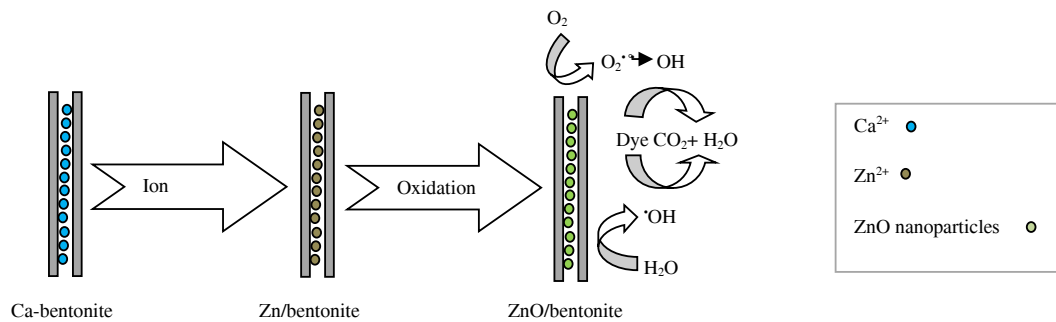


Fig. 3- A schematic of preparation steps of ZnO/bentonite nanocomposites.

was attributed to the formation of ZnO/bentonite composites. The substrate presence seems to have lowered the band gap, which is observed in some previous investigations as well [17]. It is worth noting that the decrease in the band gap value is more important than the one observed previously for ZnO/clay composite catalysts [9,18,19].

The dye removal by the composites is shown in Figure 4. First, mechanism of degradation activity of a photocatalyst is described. The Photocatalyst particles' band structure is composed of a low energy valence band filled with electrons and an empty high-energy conduction band, which are separated by forbidden band. When applying an energy bigger than the width of the forbidden band to illuminate the catalyst, the valence band electrons on the surface may absorb the light energy to move to the conduction band. Then the conduction band gets reducible electrons, yet the valence

band produces holes possessing oxidizability. These electrons and holes can move to the surface

Table 2- Band-gap energy value for prepared composites

Ion exchanged time (min)	band gap (eV)
10	3.14
20	2.64
40	2.54
60	2.54
90	2.54

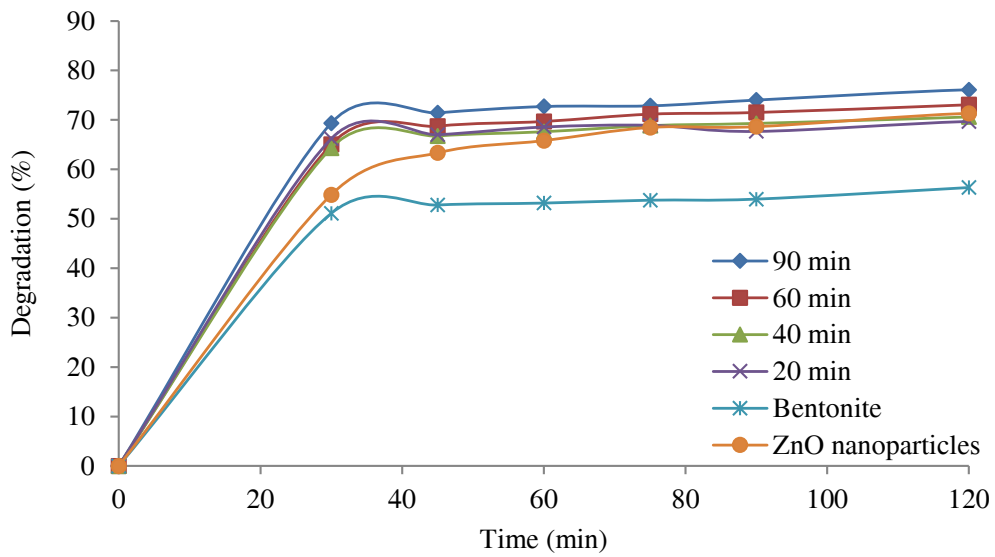


Fig. 4- Dye removal by prepared ZnO/bentonite nanocomposites.

Table 3- Zinc concentration in water at different contact periods between Zn-bentonite and aqueous media

		Zinc concentration in water (ppm)					
Ion exchange time (min)		MML	10	20	40	60	90
Contact time (h)	3 h	0	0.79	0.39	2.39	2.49	3.29
	6 h	0	1.74	1.62	3.39	3.79	2.71

of the catalyst by light energy, and can react with other substances. In addition, they can react with deliquescent oxygen and water in suspended liquid and produce hydroxyls with high chemical activity [20]. Interestingly, all of the prepared composites showed acceptable degradation performances. Among different composites, all of them showed similar behavior against MO, while parent bentonite showed the lowest activity. Preparation at longer periods increased the photocatalytic activity significantly, which is compatible with the effects observed in DRS and EDX results of these composites. Composites prepared at longer periods contain more zinc in the form of ZnO, thus their photocatalytic activity is enhanced. It is observed that the adsorption capacity of ZnO/bentonite nanocomposite is significantly high due to bi-functional nature of the catalyst where ZnO can form complex with MO while the acidic character of bentonite clay is responsible for binding and subsequent decomposition under UV irradiation. In addition, ZnO can easily release or store oxygen under different conditions to form large amounts of oxygen vacancies on the surface. These two reasons probably account for the superior adsorption capacity of ZnO-clay nanocomposite [2].

Garbanpour et al. (2017) achieved methyl orange rate of 51% using TiO₂/SG nanocomposite after 300 minutes [2]. Ye et al. (2015) synthesized zinc oxide/ montmorillonite nanocomposite by the alkaline hydrolysis method. The phenol

degradation efficiency in 10 ppm, pH=7, and the 1 g/lit catalyst dosage in 240 minutes was equal to 88.5% [21]. In another study, Xu et al. (2014) prepared ZnO/bentonite nanoparticles by the sol-gel method. In this research, the degradation of yellow acid 11 by ZnO/bentonite nanoparticles under UV irradiation was 90% after 90 minutes [22]. Therefore, the results of this research are acceptable compared to previous works with the difference that in this study the nanocomposite synthesis method is much simpler.

Photocatalyst recycling is of great importance for the development of heterogeneous photocatalytic processes in wastewater treatment and can be used to reduce the operating costs significantly. Accordingly, optimal photocatalyst recycling was investigated using methyl orange photocatalytic degradation for 3 consecutive periods. The reduction in the degradation rate is attributed to the presence of the residual intermediate particles in degradation of the methyl orange molecules on the photocatalyst surface that prevents the photon to reach the photocatalyst surface. On the other hand, this decrease depends on the amount of residual nanoparticles on the catalyst surface. According to Figure 5, photocatalytic activity during these three periods has relatively small difference and the results show that it is possible to reuse the photocatalyst, which is important for practical applications.

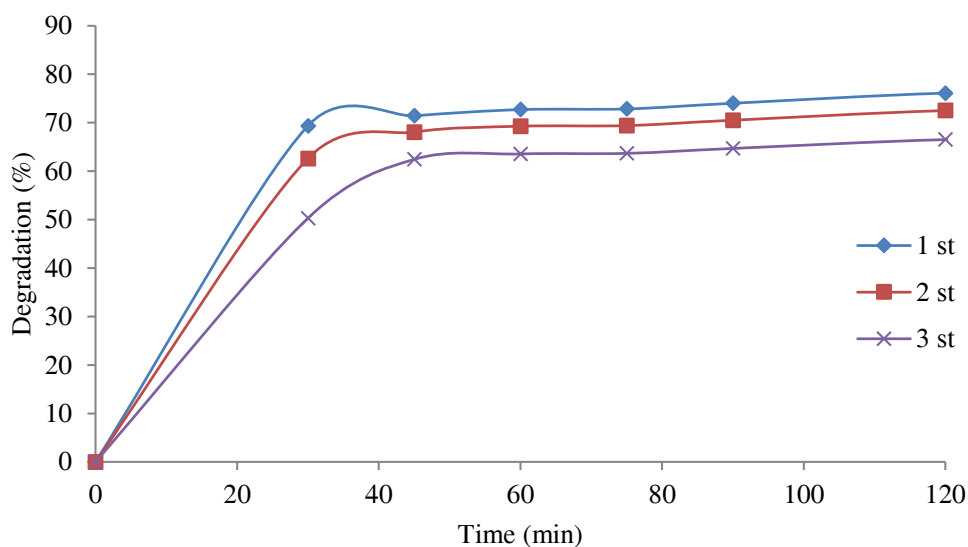


Fig. 5- Reuse of the ion exchanged bentonite for 90 min after 3 recycles.

4. Conclusions

ZnO/bentonite nanocomposites are synthesized to be used as a photocatalyst substance by the rapid and simple solid-state ion exchange method. According to SEM results, after ion exchanging, the parent structure of bentonite remains and only the distance between flakes increases significantly. EDX analysis clearly suggests the success of ion exchange of the expense of Ca^{2+} , Na^+ and Mg^{2+} cations with Zn^{2+} . The calculated band gaps for the composites were 3.14 eV (10 min), 2.64 eV (20 min) and 2.54 eV at longer periods, respectively. All prepared composites showed acceptable degradation performances. The greatest photocatalytic activity is detected in ZnO/bentonite composite solid-state ion exchanges, which lasts 60, and 90 min.

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