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Preparation and characterization of Montmorillonite/ZrO_2 nanocomposite and its application for removal of Congo red

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ABSTRACT: Montmorillonite/ZrO_2 nanocomposites were prepared by the sol-gel method under ultrasonic irradiation. The montmorillonite was incorporated into Zirconium gel. After stirring for 24 hr, the mixture was irradiated for 30 min under ultrasonic irradiation. The filtrated composite gel was calcinated at 400°C for 3h in furnace. The morphology of prepared catalysts was characterized by field emission scanning electronic microscopy (FESEM). Energy Dispersive X-ray Spectroscopy (EDS) determined the elemental analysis. Fourier transform infrared (FT-IR) was specified the vibration modes. Moreover, the crystallite size and crystalline structure were characterized by X-ray diffraction (XRD). The photodegradation properties of MMT, ZrO_2 and MMT/ZrO_2 nanocomposites were compared for removal of Congo red. The results indicated that the photodegradation property of the MMT/ZrO_2 nanocomposites was higher than of bare nano ZrO_2.

Keywords: *Montmorillonite, Nanocomposite, Nano ZrO_2, Photocatalyst.*

INTRODUCTION

Congo red (CR) is a well-known dye in textile and paper industry wastewaters. It has very acute toxicity and bio-recalcitrant nature. For almost two decades, the wastewater problem has become a controversially crucial issue [1, 2]. There are many methods to treat industrial wastewater. Photocatalytic processes are one of the treatment technologies developed economically and technically [3]. ZrO_2 is a chemically inert inorganic metal oxide with high stability toward acids, alkalis, oxidant and reductants [4]. Zirconia has been proposed as an important photocatalyst for the decomposition of organic compounds in the aqueous system. The expectation is that its physical strength and chemical inertness will increase the properties of Montmorillonite (MMT) upon the formation of the MMT/ZrO_2 nanocomposite. MMT is a kind of natural 2 : 1 type layered clay mineral with high exchange capacity, swelling ability and high surface area [5-9]. In an aqueous solution, the photogenerated electrons (e^-) and holes (h^+) can react with the dissolved O_2, surface hydroxyl groups and adsorbed water molecules to form hydroxyl radicals (OH^0) and superoxide (O_2^-) ions. The present research aimed at the preparation of MMT/ZrO_2 nanocomposite by sol-gel method under ultrasonic irradiation, then, the photo-catalytic activities of the synthesized

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nano-composites were investigated for degradation of Congo Red (CR) in water under UV irradiation.

EXPERIMENTAL

Materials

All the chemical reagents used in this research were analytical grade and without further purification. De-ionized water (DI) was used in all experiments.

Synthesis of MMT/ZrO_2 nanocomposite

For preparation of ZrO_2 gel, 0.01 mol (2.3 g) $ZrCl_4$ was firstly dissolved in 100 mL DI water and stirred to get a precursor solution, then ammonia solution was added slowly into the precursor solution until pH of mixture was adjusted 9 during stirred solution, and the white suspension of $Zr(OH)_4$ appeared.

$$ZrCl_4 + 2NH_{3(aq)} \rightarrow Zr(OH)_4 + 2NH_4Cl$$

The MMT was directly incorporated into the ZrO_2 gel to get the MMT/ZrO_2 composite gel. As aging time, the mixture of reaction was continuously stirred for two days. The solution was sonicated by an ultrasound horn at 85% amplitude delivering power of 200W by the titanium flat tip of probe for 30 min to achieve an MMT/ZrO_2 homogenous gel. After filtering, the prepared white powder of MMT/ZrO_2 composite was calcinated in furnace at 400°C for 3h [10, 11].

Photodegradation process

In order to test the photocatalytic activity of the MMT/ZrO_2 nanocomposite, Congo red (CR) was chosen as a model of water pollution to evaluate the catalytic behavior of the samples Photodegradation of 10 ppm CR solution was used to evaluate the performance of nano ZrO_2 and MMT/ZrO_2 nanocomposite photocatalysts. For each condition, 0.05 g of photocatalyst was dispersed into 100 ml of 10 ppm CR solution. The photocatalytic reaction was conducted at room temperature under UV light from a single 8W UV tube at 254 nm positioned horizontally above the liquid surface. The distance between the lamp and the base of the beaker was 20 cm. Each experiment was conducted for 30 min with 5ml sample aliquots extracted every 5 min. The decomposition of CR was monitored by measuring the absorbance of the solution at 502 nm (λ max of CR) using the UV–Vis spectrophotometer [7]. The photocatalytic degradation (%PD) was calculated by the following formula:

$$PD(\%) = \frac{A_o - A_t}{A_o} \times 100$$

where A_0 is the initial absorbance of CR solution, and A_t is the absorbance of the CR solution after irradiation time (t).

RESULTS AND DISCUSSION

FT-IR Analysis

The FT-IR spectra of nano ZrO_2 and MMT/ZrO_2 nanocomposite are showed in the range, 400–4000 cm^{-1} in Fig. 1. The bands at 1636 and 1429 cm^{-1} are attributed to the bending vibrational modes of the H_2O and M-O-H respectively. Additionally, the broad bond about 3407 cm^{-1} is assigned to the symmetry and asymmetry stretching vibration of the hydroxyl group of water and M-O-H. The FT-IR spectrum of ZrO_2 showed in Fig. 1a. The important bands at 470 and 542 cm^{-1} are attributed to the vibration of the Zr–O –Zr and O-Zr-O bonds. The FT-IR spectrum of MMT/ZrO_2 nanocomposite as shown in Fig. 1b the significant band at 1060 cm^{-1} is assigned to the Si–O bond. The band around 912 cm^{-1} is attributed to the stretching vibration of tetrahedral Al^{3+} [4, 12].

Surface morphology

FESEM was used to study the morphology of the

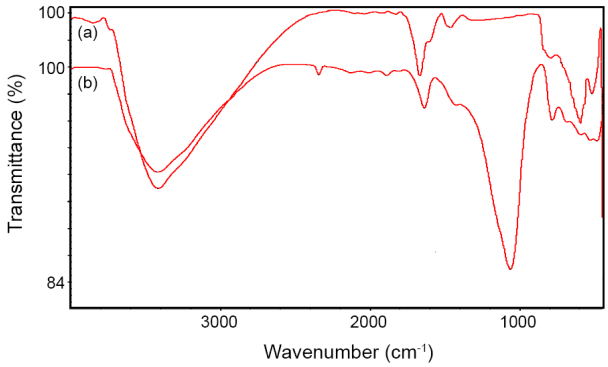

Fig. 1. FT-IR spectra of the (a) nano ZrO_2 ; (b) MMT/ZrO_2 nanocomposite.

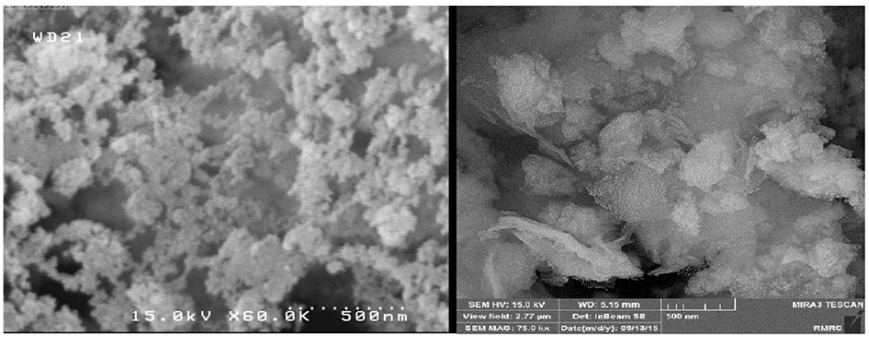

Fig. 2. FESEM images of (a) nano ZrO_2; (b) MMT/ZrO_2 nanocomposite.

surface. Fig. 2 shows the FESEM images of (a) nano ZrO_2 and (b), ZrO_2/MMT nanocomposite. MMT can act as a bed/support for nanoZrO_2 particles. In Fig. 2 (b), ZrO_2 can be seen to be scattered on the surface of MMT. The FESEM images show that the ZrO_2/MMT nanocomposite was formed successful and confirm the FT-IR, EDS and XRD analysis results. The mean particle size of nanoZrO_2 and ZrO_2/MMT nanocomposite are 43 and 32 nm respectively.

EDS Spectroscopy

Fig. 3 shows the EDS spectra of nano ZrO_2 and MMT/ZrO_2 nanocomposite. The presence of ZrO_2 on MMT can be proved by energy-dispersed X-ray spectra (EDX) in Fig. 3b. EDS data was shown the nano ZrO_2 is 20% of MMT/ZrO_2 nanocomposite.

XRD Analysis

X-ray diffraction (XRD) patterns of the catalysts were obtained using Cu Kα radiation (λ=1.541 Å). The XRD patterns of the nano ZrO_2 and ZrO_2/MMT nanocomposite are shown in Fig. 4. In Fig. 4a the peaks indicate the respective reference code 01-081-1546 for the tetragonal structure of ZrO_2 with space group P42/nmc. The diffraction peaks of crystal planes are shown for the tetragonal zirconium dioxide. Fig. 4b, the overall crystalline structure shows the tetragonal of zirconium dioxide. The diffraction peaks appear at 2θ, 6.390, 8.585, 19.810, 20.845, 22.535, 26.625, 28.825, and 32.560 are related to the montmorillonite clay. These values of 2θ are observed that have a good agreement with the data of the montmorillonite in the library of the instrument [4, 12]. The average crystallite size of samples D_v was calculated based upon the XRD pattern for quantitative purpose using the Debye- Scherer equation: The crystallite size of catalysts was determined from the average of three peak of maximum intensity by using Scherrer formula:

$$D_v = \frac{K\lambda}{B\cos\theta}$$

where K is the "Scherer constant" (around 0.9), λ=1.541 Å is the wavelength of the X-rays, θ is the Bragg angle for the peak at 2 θ, β is the "integral breadth" of the peak at 2θ. The average crystallite size of nano ZrO_2 and ZrO_2/MMT nanocomposite are 28

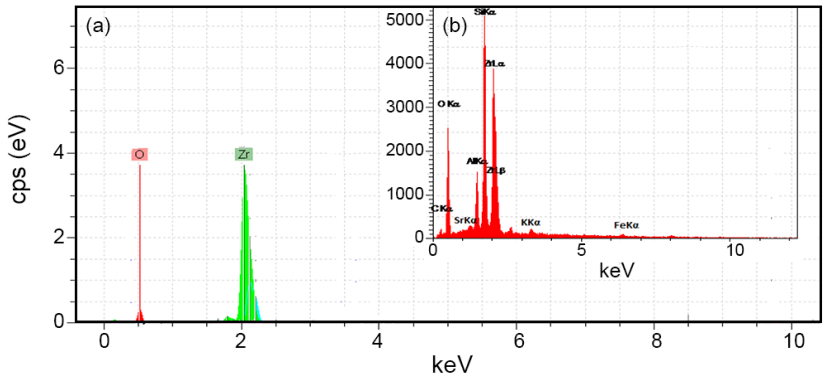

Fig. 3. EDS spectra of (a) nano ZrO_2; (b) MMT/ZrO_2 nanocomposite.

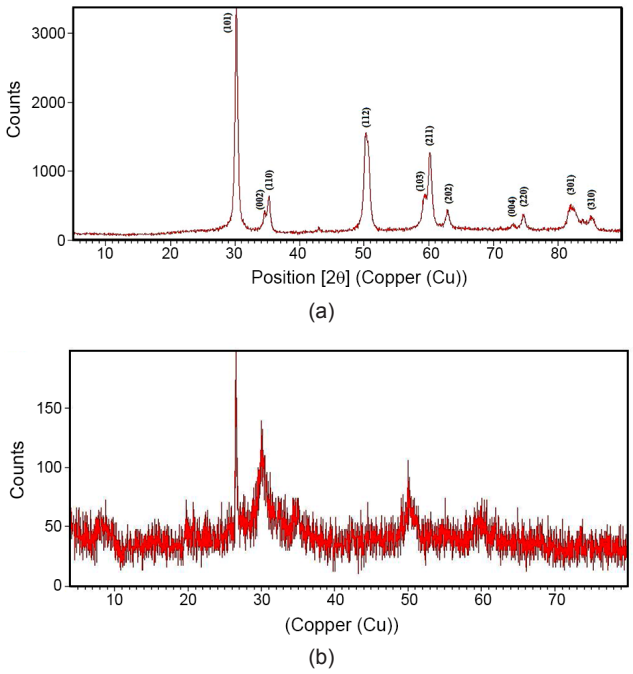

Fig. 4. XRD patterns of (a) nano ZrO_2 ; (b) MMT/ZrO_2 nanocomposite

and 23 nm respectively.

Photodegradation

The results of the photodegradation of Congo red are shown in Fig. 5, where the photodegradation percent is plotted against the UV irradiation time. The blank experiment without any catalyst under UV irradiation was rarely decomposited 3% degradation of CR. Nano ZrO_2 was photo-degradated 11% of CR after 30 min. The most efficiency of CR degradation has seen on the MMT/ZrO_2 nanocomposite 69% after 30 min under UV irradiation. The decomposition of CR was due adsorption of dye molecules on the surface of MMT and the photodegradation ability of ZrO_2 under UV irradiation. Furthermore, the strong electrostatic field present in the MMT framework can effectively

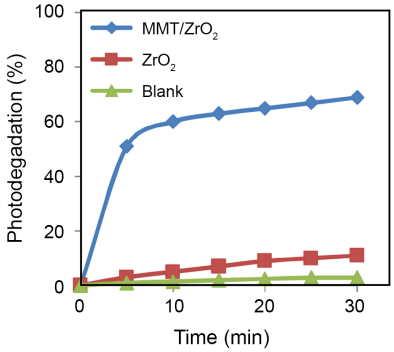

Fig. 5. The results of the photodegradation of Congo red

separate the electrons and holes produced during photo-excitation of nano ZrO_2 and so resulted in lower recombination of them and higher photodegradation efficiency [13]. The MMT/ZrO_2 nanocomposite catalyst is shown the best results in photodegradation processes as compared with bare nano ZrO_2.

CONCLUSIONS

MMT/ ZrO_2 nanocomposites were synthesized via a facile sol-gel method using ultrasonic irradiation. This research shows that nano ZrO_2 particles were, on the surface of the montmorillonite. The average crystal size of ZrO_2 on the MMT/ZrO_2 nanocomposites was smaller than that in pure ZrO_2 at the same annealing temperature. The comparison of the FT-IR spectra, XRD patterns, EDS spectra and FESEM images of MMT/ZrO_2 nanocomposite with the pure ZrO_2 NPs, have been showed formation of MMT/ZrO_2 nanocomposite. The results of this investigation indicate that the adsorption property of this composite increases the photocatalytic degradation efficiency of the dye. The structure of the MMT with its channels and pores creates an extended area for dispersing nano ZrO_2 and this prevents the aggregation of the particles. Therefore, a large number of the dye molecules can absorb on the MMT/ZrO_2 nanocomposite. So, the rate and efficiency of degradation of Congo red become much higher as compared with the bare nano ZrO_2.

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