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Magnesium Aluminate nano-particles: preparation, characterization and investigation of their potential for dye removal from wastewaters

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ABSTRACT
Magnesium aluminate ($MgAl_2O_4$) nanopowders were prepared *via* a novel and inexpensive method for the preparation using aminoethanol as percipitating agent. The as prepared powders were characterized by using XRD, FE-SEM and DLS techniques. $MgAl_2O_4$ nanoparticles as a catalyst was examined on the photo degradation removal of Reactive Red 195A dye from wastewaters.
Keywords: *$MgAl_2O_4$ nanoparticles, Photo degradation, Reactive Red 195A, wastewaters*.

1. INTRODUCTION
Pollution treating from the aqua environment is not only an essential indispensability but also requires management to reduce costs and provide appropriate solutions to avoid any additional contamination. For example, many drugs used in pharmaceutical therapies when released into water resources from sanitary sewers causes synergistic effects on humans [1-4]. The conventional water treatment methods cannot effectively remove pollutants from wastewaters. Thus finding new ways which are inexpensive and efficient is in demands. Photocatalytic removal of wastes such as heavy metals, drugs, and organic dyes has been proven to be a useful technique in the purification processes of wastewaters. However, different heterogeneous photocatalysts are investigated, but metal oxides semiconductors have received much attention. From the litrature viwe, metal oxides have been widly used as photocatalysts for the efficient degradation of pollutants and amongest spinel structures are of great interest [5-7].

In general, some of these methods are multi-step, high cost, are not environmentally friendly, and require minimizing their cost and hazards. Our search is to find new photocatalysts that decrease the cost and risks of the prepared strategy and decreasing adverse effects on human kinds or the environment.

As continuing of our studies [8-21], the present work focus on the synthesis and characterization of $MgAl_2O_4$ nanoparticles and investigation of their potential for Reactive Red 195A removal an industrial dye from wastewaters.

2. EXPERIMENTAL
All reagents were purchased from Merck and Aldrich and used without further purification. Field Emission Scanning Electron Microscope (FE-SEM) images were obtained on HITACHI S-4160. Dynamic light scattering (DLS) measurement was done using a Malvern Zetasizer Nano ZS (ZEN 3600) instrument. The powder X-Ray diffraction patterns were measured with D_8, Advance, Bruker, axs, diffractometer using Cu-Kα irradiation.

2.1. Preparation of $MgAl_2O_4$ nanoparticles. Two different solutions were prepared. A solution of $MgCl_2$ (20 mmol) and $Al(NO_3)_3$ (40 mmol) in 200 ml of water (solution A). Solution B was prepared by dissolving of 2-aminoethanol (180 mmol) in 100 ml water. Solution (B) was slowly added dropwise to the solution (A) under vigorous magnetic stirring. The mixture was continuously stirred for another 60 min. The resulting gel was filtered, washed with water several times, dried in an oven at 100°C for one hour, and finally calcined at 700 °C for two hours.

2.2. Dye solution preparation. A mother solution of 200 mg/L Reactive Red 195A was prepared by dissolving an accurate amount of dye in a liter of pure water. The lower concentration of dye solutions was prepared by diluting the mother solution. The pH of each solution was adjusted in acidic and basic media *via* HCl or NaOH (1 M) solutions.

2.3. Photocatalytic degradation experiments. Typical procedure: 10 mL of dye solution (30 mg/L) was inserted into 100 mL glass beaker. 25 mg of $MgAl_2O_4$ nanoparticles was added to the beaker. The pH of the solution was adjusted to 7. The mixture was stirred at dark for 30 min for the adsorption of dye on the surface of $MgAl_2O_4$ nanoparticles. The solution was then exposed to UV light (365 nm wavelength) from a xenon lamp for variable time intervals, and then the sample was quickly subjected to concentration measurement using GC analysis instrument. The degradation yield was calculated from the following equation:

$$\text{Degradation Yield (\%)} = \frac{C_0 - C_t}{C_0} * 100 \quad (1)$$

3. RESULTS AND DISCUSSION
$MgAl_2O_4$ nanoparticles were prepared by a simple sol-gel method using a $MgCl_2$ and $Al(NO_3)_3$ precursors with ethanolamine as precipitant agent at room temperature followed by calcination at 700 °C.

The X-ray powder diffraction (XRD) analysis of $MgAl_2O_4$ nanoparticles shows a cubic spinel structure (space group Fd-3m, Reference code: 01-073-2210) with pronounced diffraction peaks presented in 19.0, 31.2, 36.8, 44.8, 59.3 and 65.2 [2 theta degree]. The average grain size of $MgAl_2O_4$ nanoparticles is estimated by Scherrer formula using the values of full width at half maximum (FWHM) of the most intensive XRD diffraction peaks and was found to be 92 nm (Figure 1).

Figure 2 shows FE-SEM image of $MgAl_2O_4$ nanoparticles. Figure 2 shows that the sample consisted of uniform particle in shape and size but the size of the particles is less than 100 nm. The surface rough of the sample is relatively homogeneous.

The particle size distribution of $MgAl_2O_4$ nanoparticles was determined by DLS techniqe and the results are shown in Figure 3. Before DLS analysis, 0.01 g of sample dispersed in 25 mL of deionized water, stirred for 30 minutes and ultrasonicated for 60 minutes. The average diameter of the sample was determined to be about 58 nm.

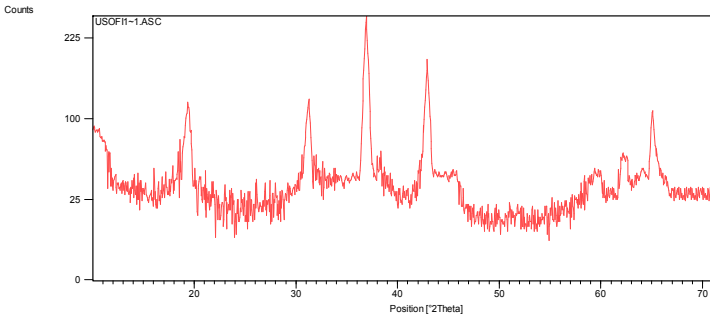


Figure 1. XRD pattern of $MgAl_2O_4$ nanoparticles calcined at 700 °C.

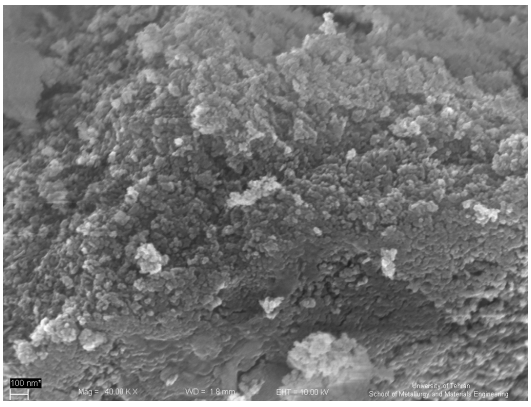


Figure 2. FE-SEM photograph of $MgAl_2O_4$ nanoparticles calcined at 700 °C.

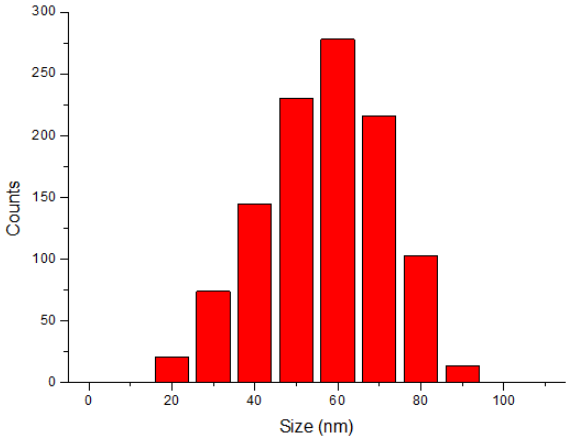
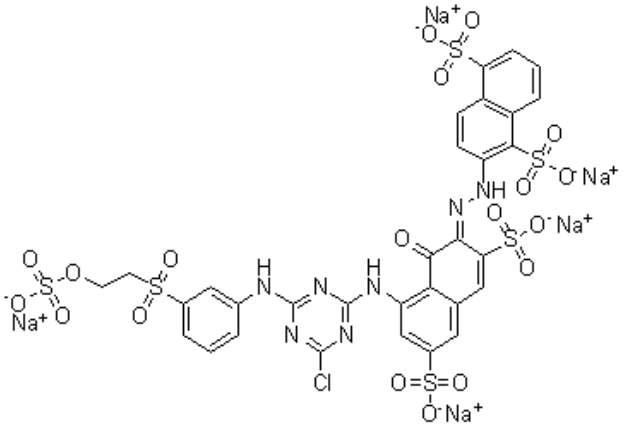


Figure 3. Particle size distribution of $MgAl_2O_4$ nanoparticles determined by DLS analysis.

Catalytic activity. The potential of $MgAl_2O_4$ nanoparticles as a catalyst was examined on the degradation removal of Reactive Red 195A dye from wastewaters. The chemical structure of Reactive Red 195A is illustrated in Scheme 1.



Scheme 1. Molecular Structure of Reactive Red 195A (CAS Registry Number: 77365-64-1)

3.1. Effect of pH and irradiation time. At first, the degradation behavior of selected drugs with the concentration of 100 mg/L were conducted during 0-8h times at pH = 7 using $MgAl_2O_4$ nanoparticles (100 mg/L). The obtained result summarized in Figure 4 shows degradation of dye is higher than 80%.

Next, the effect of different acidic and basic conditions was examined by varying pH from 4-11 values. Under acidic condition (pH = 4) only a maximum of 20% of dye was degraded. While at pH = 11 degradation yield is near zero (Figure 4). This result is due to the like charges of dye and catalyst in acidic and basic conditions that have a repulsive effect. At nutral condition, dye has positive charge while catalyst has negative charge, thus the cohesion effects are dominant.

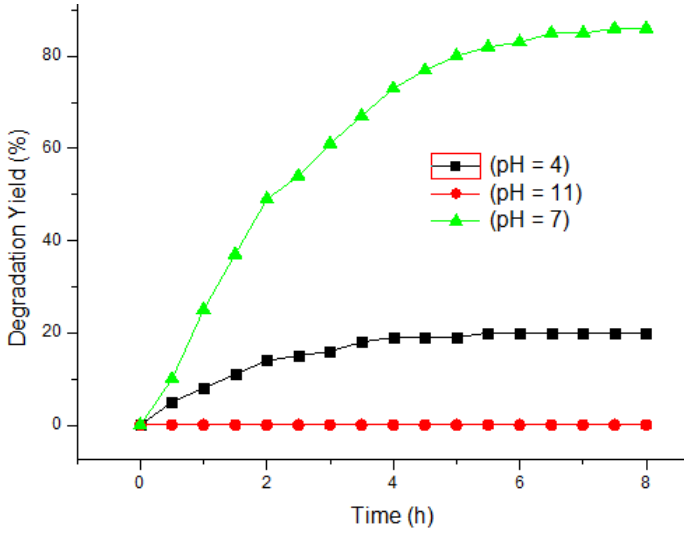


Figure 4. photocatalytic degradation of Reactive Red 195A: effect of reaction time and pH (catalyst: 0.02g, dye concentration: 30 mg/L.)

3.2. Effect of initial dye concentration. Next, the effect of initial dye concentration on the degradation yield was investigated. At the same condition as 0.025g of catalyst and pH = 7, various concentration of drugs (10, 20, 30, 40, 50, and 60 mg/L) were subject to the study. The obtained results are depicted in Figure 5. As revealed from Figure 5, with an increasing on the drug concentration, the degradation efficiency increases. However, at more than 30 mg/L degradation rate seem to be decreased which may be due to the saturation of the active sites on the adsorbent. Additionally, at higher concentration the light penetration into the

suspension reduced, thus a decreasing in the drug degradation occurred.

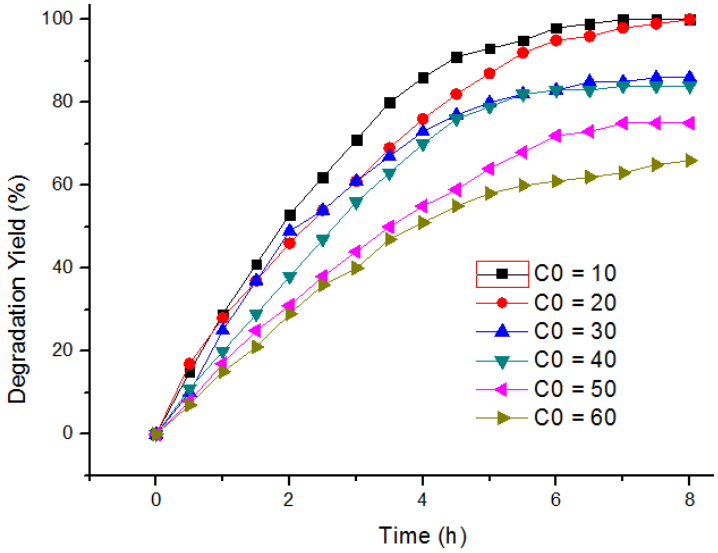


Figure 5. photocatalytic degradation of Reactive Red 195A: effect of initial dye concentration (pH = 7, catalyst: 0.025 g).

3.3. Effect of catalyst dosage. At next step, the effect of various catalyst dosages including 0.01, 0.025, 0.05 and 0.1g was followed for determination of dye degradation efficiency (Figure 6). The results revealed that the drug removal percentage is increased with rising the catalyst amount at a range of 0.01-0.05 mg/L. The more increasing of catalyst amount to 0.1g causes a decreasing on the degradation yield (Figure 6). This behavior is because active sites increased with increasing on the catalyst dosages. The latest decreasing on the dye degradation efficiency is because of the particles agglomeration and reducing the specific surface area as well as active sites.

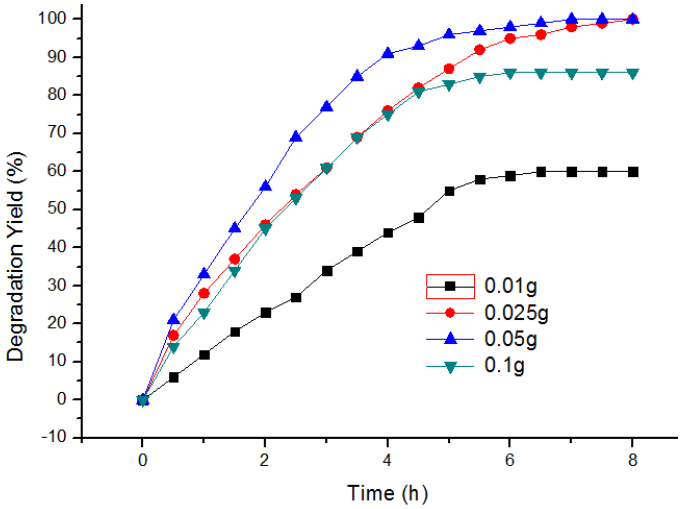


Figure 6. photocatalytic degradation of Reactive Red 195A: effect of catalyst dosage (pH = 7, dye concentration: 20 mg/L).

4. CONCLUSIONS

We found that $MgAl_2O_4$ nanoparticles have a real potential for the photocatalytic degradation of Reactive Red 195A an industrial synthesized dye in aqueous media. $MgAl_2O_4$ nanoparticles were synthesized by a facile sol-gel route, and were characterized by using XRD, FE-SEM and DLS techniques. Experimental obtained results demonstrated that the dye removal efficiency increased from 0 to 100% by modifying the influential parameters, including pH, initial dye concentration, and catalysis dosage. The optimum conditions are founded to be 0.025g of catalyst, pH = 7, and concentration of dye (20 mg/L).

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