RESEARCH PAPER

Facile Synthesis of Nanosized MgO as Adsorbent for Removal of Congored Dye from Wastewate

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ABSTRACT

Nanostructures of magnesium oxide is one of the most attractive materials which have shown various applications in many aspects of industries. So, finding a controllable and inexpensive technique to produce desirable nanostructures of MgO is valuable. In this work, magnesium oxide (MgO) with different morphologies was successfully prepared via a simple solid-state method. The molar ratio of sodium hydroxide to magnesium salt precursor was obtained 1 to 8. Furthermore, the effect of different magnesium precursors (magnesium chloride and magnesium acetate) on the morphology of MgO was investigated. It was shown that adding halide salts (NaX) to the solid-state reaction media, in spite of the noteworthy influence on the product morphology, facilitate the formation of MgO phase from $Mg(OH)_2$. The synthesized magnesium oxide particles were characterized by Fourier transform infrared (FTIR) spectrometer, scanning electron microscope (SEM) and X-ray diffraction (XRD). Synthesized magnesium oxide particles were used to remove congored dye from waste water.

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INTRODUCTION

Magnesium oxide has a simple sodium chloride structure. It has been reported that nanostructures of MgO have various applications in a variety of aspects, for instance in catalysis [1-4], toxic waste remediation [5-8], textile improvement [9], nanocomposite membranes [10], as template for synthesis desirable structures of other nanomaterials [11] and as an effective support for immobilization of other catalytic species [12]. Such a wide applicability has motivated researchers to develop more facile and inexpensive techniques to produce magnesium oxide nanostructures. Many synthesis routes like sol–gel [13], hydrothermal [14], aqueous wet chemical [15], sonochemical [16], flame spray pyrolysis [17], and microwave [18] methods provide nano-sized MgO material, in which, the morphology and properties of the resulting MgO differs and largely depend on the applied synthesis method and processing conditions. All mentioned techniques apply environmentally malignant chemicals and organic solvents which are toxic and are not easily degraded in the environment. Furthermore, these methods are technically complex, require expensive experimental set up, and complicated control processes. So, achieving an economical, fast, efficient, and environmentally benign method to produce MgO nanostructures is very valuable. Solid-state synthesis technique, also called a dry media or a solventless reaction, is economical, fast, efficient, environmentally benign and simple method which can be used to produce different metal oxides. However, lack of control on the morphology of produced metal oxides is one of

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the main challenges of using this green technique.

Using various nanomaterials as catalysts or adsorbents for wastewater treatment is one of the most important fields of research. Among various pollutants, dye molecules have been considered as the most studied polluting agent in the field of wastewater treatment because of their toxicity for living organisms [19]. The effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution. Therefore, removing of dyes is one of the most important aspects of wastewater treatment for the mentioned industries [20]. For address this issue, nano-sized metal oxides, due to their high surface reactivity and adsorption capacity compared to their commercial analogues, and also the simplicity of their production from abundant natural minerals are very promising dye adsorbents. In this context, magnesium oxide with the pH of zero point charge (zpc) of 12.4 can be regarded as a suitable adsorbent for removal of anionic dye molecules via favorable electrostatic attraction mechanism [21]

In this work, a facile solid-state reaction procedure is used to synthesize magnesium oxide nanostructures. The role of different magnesium salts as precursors and sodium halide salts (NaCl and NaBr) as morphology modifiers in the synthesis of MgO are investigated. Finally, obtained magnesium oxide materials with different morphologies are investigated as efficient adsorbents for removal of congored dye from wastewater.

EXPERIMENTALS

Preparation of MgO structures

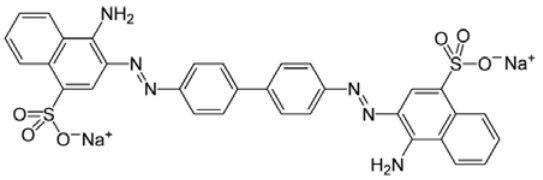
All materials including magnesium Chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), magnesium acetate tetrahydrate ($Mg(Ac)_2.4H_2O$), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium bromide (NaBr), acetone (CH_3COCH_3), and congored dye ($C_{32}H_{22}N_6Na_2O_6S_2$) were of analytical reagent grade and purchased from Merck company.

For synthesis of magnesium oxide nanostructure, $MgCl_2 \cdot 6H_2O$, NaOH, and NaX (X=Cl and Br) precursors, with a molar ratio of 1: 8: 2, were first crushed together by using mortar and pestle just for 30 seconds. The reaction started immediately during the mixing process. Then, the produced paste was heated in a closed furnace at 500 °C for 1 hour. The obtained powder was washed by distilled water and acetone for several times to removal extra ions. To investigate the magnesium salt effect as precursor, $Mg(Ac)_2.4H_2O$ was used instead of $MgCl_2 \cdot 6H_2O$ salt in the reaction. Various applied experimental conditions for the preparation of MgO nanostructures are shown in Table 1.

The morphology of the powders were examined by scanning electron microscopy (SEM) (Philips XL 30). The crystal structure of the samples were characterized by X-ray diffraction (XRD) using an X'pert diffractometer of Philips company with monochromatized Co radiation (λ=1.7889Å). The products were also characterized by Nicolet IR 100 Fourier transform infrared (FTIR) spectrometer.

Dye removal experiment

To investigate the adsorption ability of synthesized MgO structures, dye removal experiments were carried out as batch tests in 100 ml beaker. In each experiment, constant amount of magnesium oxide material (1 g/L) was added to congored dye (Scheme 1) solution (5ppm) and stirred for 5 minutes at room temperature. During all experiments the pH of solution was 10. UV-visible spectrophotometer (Shimadzu 2100)



Scheme 1. Congored molecular structure.

Table 1. Experimental condition applied for the preparation of MgO structures.

sample	Magnesium precursor salt	Sodium halide salt (NaX)	Molar ratio Mg salt: NaOH: NaX
MC8	$MgCl_2.6H_2O$	-----	1: 8: 0
MC-8-Cl	$MgCl_2.6H_2O$	NaCl	1: 8: 2
MC8-Br	$MgCl_2.6H_2O$	NaBr	1: 8: 2
MC-3-Br	$MgCl_2.6H_2O$	NaBr	1: 3: 2
MA-8-Cl	$Mg(CH_3COO)_2.6H_2O$	NaCl	1: 8: 2
MA-3-Cl	$Mg(CH_3COO)_2.6H_2O$	NaCl	1: 3: 2

was used to observe dye concentration changes. Dye removal efficiency was determined using the following equation:

$$\text{Dye removal efficiency (\%)} = (C_0 - C_f)/C_0) \times 100$$

where C_0 and C_f represent the initial and final dye concentrations, respectively.

RESULT AND DISCUSSION

Magnesium oxide characterization

Fig. 1 shows FT-IR spectra for samples MC8, MC8-Cl, MC8-Br, MC3-Br, MA8-Cl, and MA3-Cl produced by solid-state method. The strong peak at around 440 cm^{-1} was assigned to the Mg–O stretching vibration. Peaks around 3400cm^{-1} and 1600 cm^{-1} are attributed to the stretching and bending modes of the H_2O, respectively. The broadness in the spectra confirms a high degree of hydrogen bonding of water molecules among themselves and with the crystallite surface. The smaller crystallite show higher physiosorption. For sample MC8, sharp peak around 3700 cm^{-1} is due to the presence of hydroxyl ions indicating formation of $Mg(OH)_2$ phase beside MgO. The peaks centered around 1400 cm^{-1} and 1000 cm^{-1} are due to vibration of the H^-species bonded to one, two or three Mg^{2+} ions of magnesium oxide surface. The source of hydrogen is the moisture retained by MgO powder which on heterolytic dissociation leads to formation of hydroxyl and surface hydride groups as [20]:

$$Mg^{2+}{}_{LC} - O^{2-}{}_{LC} + H^+ + H^- \rightarrow Mg^{2+}{}_{LC}(H^-) - O^{2-}{}_{LC}(H^+)$$

For indication of the magnesium oxide phase formation through applied solid-state method, samples MC8, MC8-Br, and MA8-Cl were selected and analyzed by XRD. As shown in Fig. 2, sample MC8 is made of MgO and $Mg(OH)_2$ phases which confirms FTIR data. XRD patterns of two other samples (MC8-Br and MA8-Cl) show only the presence of MgO phase. The crystal grain sizes were calculated for MC8-Br and MA8-Cl samples from the FWHM of XRD pattern using the Debye–Scherrer's equation:

$$D = 0.891k/\beta\cos\theta$$

where D is the average crystallite size, k is the X-ray wavelength (0.17889 nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively. Accordingly, the crystal average size of samples MC8-Br and MA8-Cl are about 54 and 51 nm, respectively.

Scanning electron microscopy was employed to study the morphologies of prepared samples. Fig. 3 shows different morphologies of magnesium oxide formed when solid-state synthesis method was used. In the absence of NaX salts, when magnesium chloride to sodium hydroxide molar ratio was 1 to 8, an agglomerated structure was appeared (sample

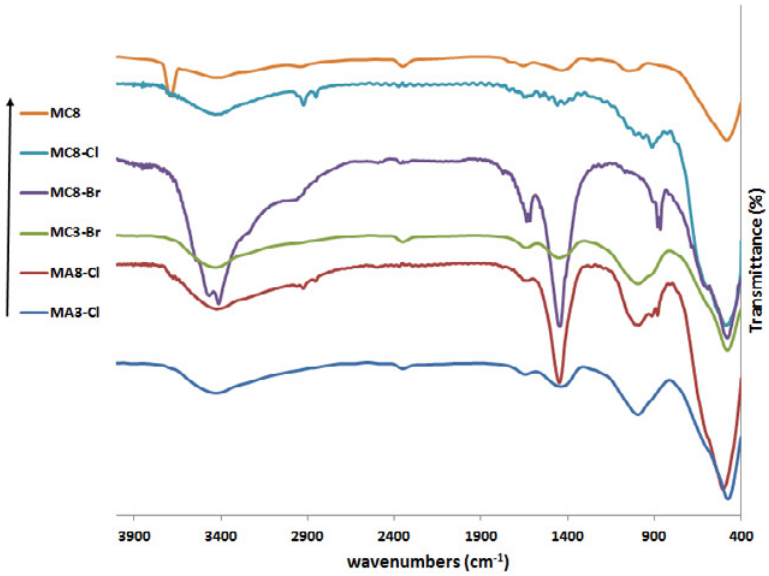


Fig. 1. Fourier transform infrared (FTIR) spectra of samples obtained via solid-state reaction.

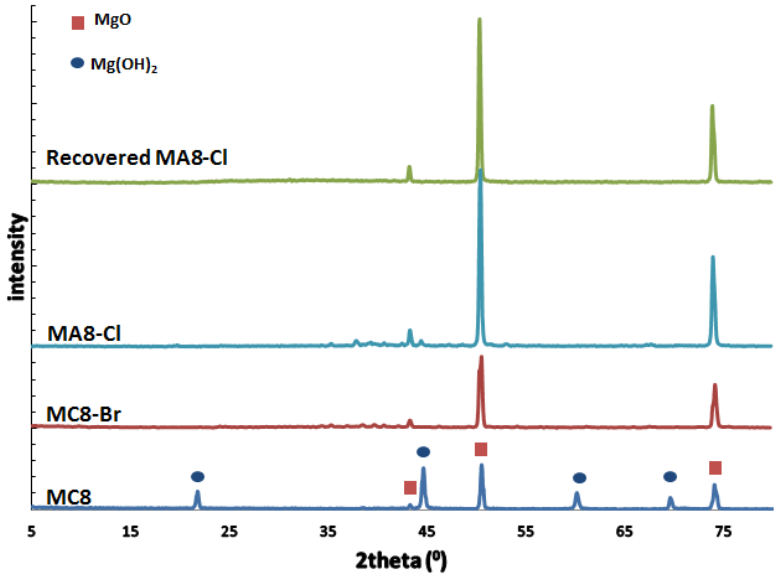


Fig. 2. The XRD patterns of MgO nanoparticles synthesized by using solid-state method.

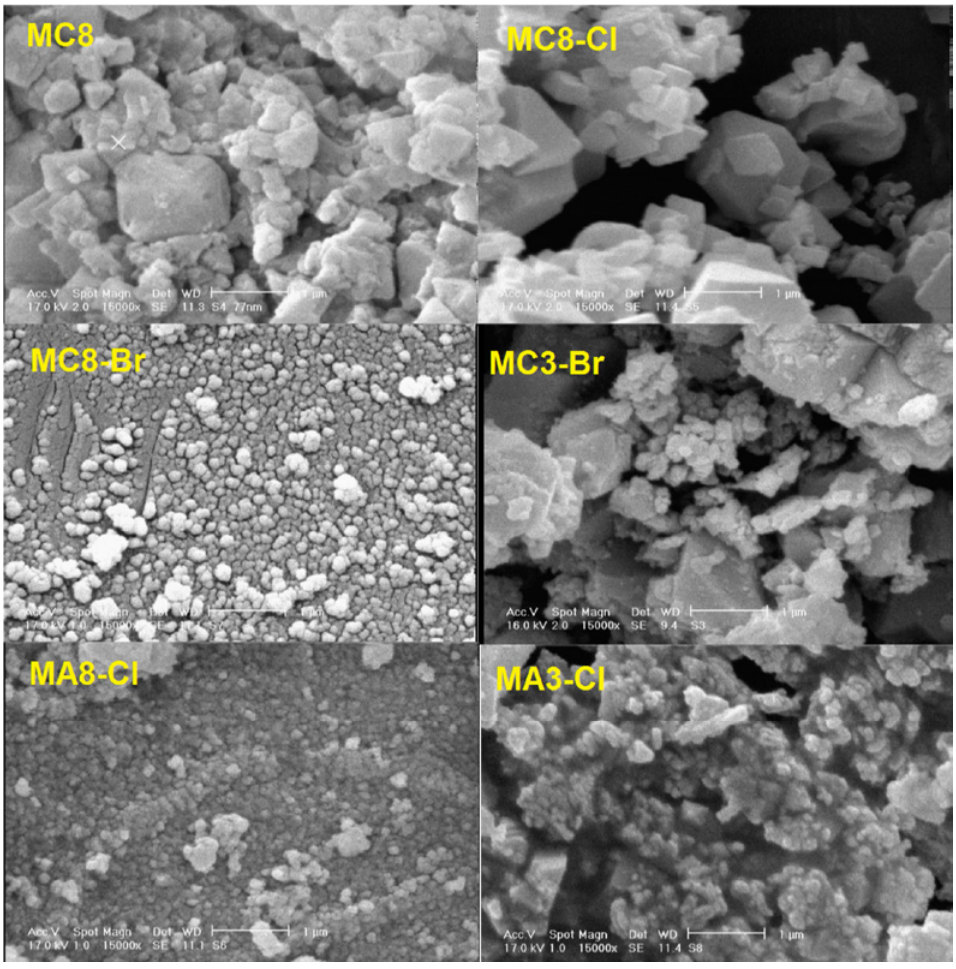


Fig. 3. The SEM images of samples obtained via solid-state reaction.

MC8) while by adding NaCl to the reaction precursor mixture no noteworthy morphological changes was observed (sample MC8-Cl). By using NaBr salt instead of NaCl, nanoparticles of MgO were formed. The role of NaOH amount on the morphology of final MgO can be perceived from SEM image of sample MC8-Br. As seen, in the presence of NaBr salt, while the ratio of $MgCl_2$: NaOH was 1:3, an agglomerated structure of sample MC3-Br was obtained. Magnesium salt precursor effect on the morphology of magnesium oxide product also was investigated by using $[Mg(CH_3COO)_2].2H_2O$ salt instead of $MgCl_2.6H_2O$ in presence of NaCl. SEM image of sample MA8-Cl shows that by using magnesium acetate salt, nanoparticle of MgO is obtained while by decreasing the amount of NaOH (changing the molar ratio of Mg:NaOH:NaCl from 1:8:2 to 1:3:2) the agglomerated nanoparticle structure (sample MA3-Cl) is achieved .

Growth mechanism of MgO nanostructures

The overall reaction of formation of MgO via solid-state reactions can be shown as follows:

$$MgCl_2 \cdot 6H_2O(s) + 2NaOH(s) \rightarrow 2NaCl\ (s) + Mg(OH)_2\ (s) + 6H_2O(l+g) \quad \text{(step1)}$$

$$Mg(OH)_2\ (s) \rightarrow MgO\ (s) + H_2O\ (g) \quad \text{(step2)}$$

At the first step of the reaction, by grinding of magnesium chloride salt with sodium hydroxide, $Mg(OH)_2$ phase is formed. The reaction is often self-initiated and self-sustained with H_2O vapor releasing after grinding of the mixture. After the calcination at 500 °C (step 2), the formed $Mg(OH)_2$ is completely converted to MgO material. It is well known that the structure of products via a solid-state reaction strongly depends on the rate of nucleation and growth of particles. It can be assumed that excess amount of NaOH, adding

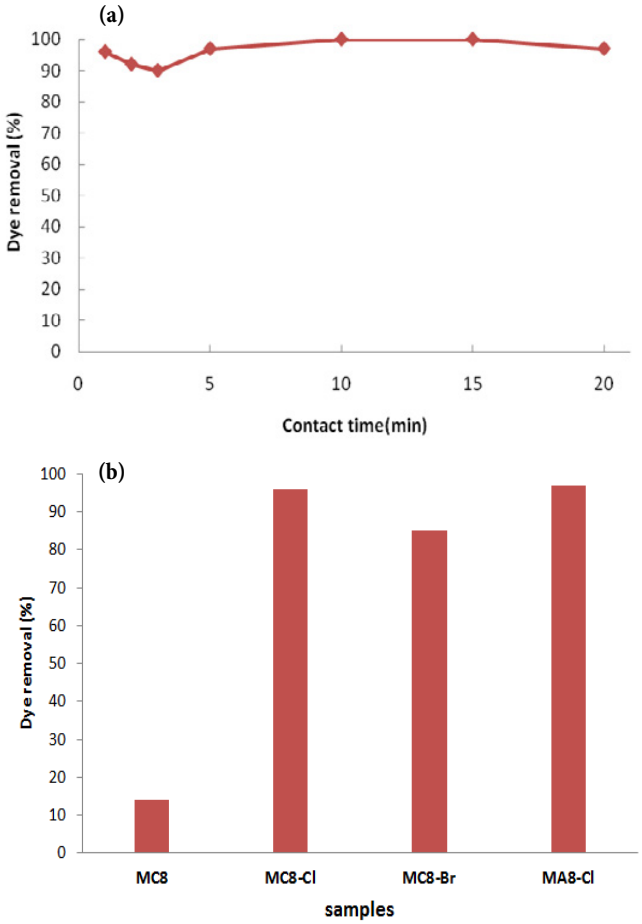


Fig. 4. (a) The congored removal efficiency of sample in different times, (b) the removal of congored dye by applying samples MC8, MC8-Na, MC8-Br, and MA8-Cl within 5 minutes.

sodium bromide salt to the reaction mixture, may increase the nucleation rate. Furthermore, adding NaBr as salt-assisted additive is expected to cause cage-like shells that surround the $Mg(OH)_2$ and MgO particles and reduce the growth rate of particles [17]. As a result, the added NaBr promotes the formation of nanoparticles of MgO. XRD pattern of MC8 sample indicates the formation of MgO and $Mg(OH)_2$ phases. By adding sodium halide salts (NaCl or NaBr) to the reaction mixture, the only crystal phase obtained is MgO. So, it is concluded that the presence of NaX salts facilitate the conversion of $Mg(OH)_2$ to MgO (step 2).

Dye removal study

The ability of MgO with different morpgologies in congored dye adsorption was investigated by using samples MC8, MC8-Cl, MC8-Br, and MA8-Cl as dye adsorbents. As seen in Fig. 4a, sample MA8-Cl removed 97% of congored dye from water within only 5 minutes that is shorter than the reported values for dye removal by using many other adsorbents [22]. Fig. 4b shows congored removal efficiency for MC8, MC8-Cl, MC8-Br, and MA8-Cl samples after 5 minutes. For agglomerated structures, compared to MC8-Cl, MC8, which is formed of mixed phases of MgO and $Mg(OH)_2$, shows the lower dye removal efficiency. So, it can be concluded that the presence of magnesium hydioxide beside magnesium oxide phase decreases the interaction of anionic congored dye with MgO surface. Sample MA8-Cl shows the most efficiency of dye removal due to its nano-sized structural properties. The decrease of particle size leads to creation of large specific surface area, thus a large fraction of MgO atoms are available on the surface to interact with congored dye molecules. To investigate the stability of the adsorbent, after finishing the adsorption test, MA8-Cl sample was separated and washed several times by hot water and ethanol and dried at 100 ° C for overnight. XRD analysis of the recovered MA8-Cl (Fig. 2) showed that the structure of MgO is retained after recovery.

CONCLUSION

Various morphologies of MgO was prepared by using an easy green solid-state reaction method. It was shown that the presence of halide salts in the solid-state reaction mixture facilitates the formation of magnesium oxide phase from magnesium hydroxide, and also has effect on the final product morphology. The role of the type of magnesium salt precursor and amount of NaOH on the MgO morphology was discussed. Dye adsorption study showed that the sample with lower agglomeration prepared from magnesium acetate precursor has the best efficiency in removal of congored from wastewater.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

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