Mesoporous magnesia: Synthesis, characterization, adsorption behavior and cytotoxic activity

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HIGHLIGHTS

- Mesoporous MgO was prepared by one-step sol-gel synthesis procedure.
- Mesoporous MgO has a surface area of 140 m^2/g and pore size of 4.5 nm.
- The adsorption capacity of mesoporous MgO is much higher than the commercial MgO.
- Mesoporous MgO exhibited promising cytotoxicity towards hepatocellular carcinoma cells.

GRAPHICAL ABSTRACT
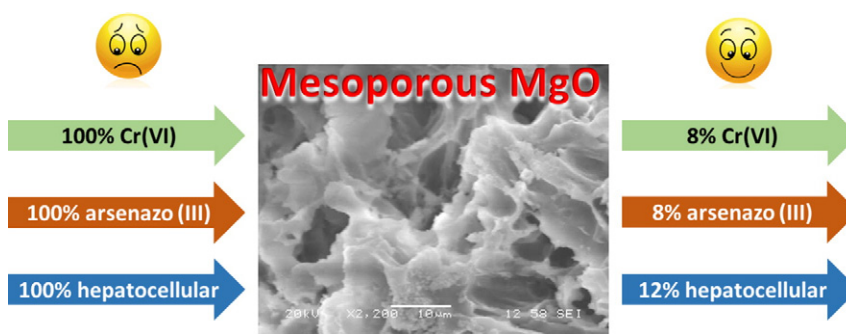
ARTICLE INFO

ABSTRACT

Mesoporous magnesia (MgO) was prepared in one-pot synthesis procedure based on sol-gel technique by using triethanol amine as a template. The characterization data confirmed the mesoporosity of the prepared material and showed that it has a high surface area compared to commercially available MgO. The adsorption behavior of mesoporous magnesia was tested in the removal of chromium (VI) ions and arsenazo (III) dye from wastewater. The adsorption capacity of mesoporous magnesia was much higher than commercial MgO. Furthermore, the cytotoxic behavior of mesoporous magnesia was evaluated against three types of cancerous cells, i.e. hepatocellular carcinoma, colon carcinoma, and breast carcinoma cells. The obtained results were promising and encouraging with respect to hepatocellular carcinoma cells, in which 88% of the 1000–2000 cancerous cells could not survive in the presence of 50 μg of mesoporous magnesia.

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1. Introduction

Magnesia or magnesium oxide (MgO) is a non-toxic, environmentally friendly and stable material, it exhibits high potential in several physical and chemical applications, and therefore, it attracted a lot of interest in the last few years [1,2]. In catalysis field, MgO has been used as a heterogeneous basic catalyst [3] in different organic reactions such as

Aldol condensation of acetone [4]. It has been reported also that MgO can perfectly supports other metal active sites such as Ni [5]. Furthermore, MgO has been applied as an adsorbent for different contaminants present in waste/surface water such as the removal of heavy metals [6] and dyes [7]. Moreover, MgO considers one of the promising metal oxides in capturing CO_2 from flue gases [8]. On industrial scale, MgO is used as an additive in paints, conductor products, and refractory materials [9–11]. The efficiency of MgO in the above mentioned applications depends on its morphological structure and texture properties. Recently, researchers directed their efforts to synthetize MgO with a high surface area and wide uniform pore system to enhance the efficiency in the

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desired application. Several methods have been reported about the synthesis of mesoporous magnesia such as sol-gel [12], hydrothermal decomposition [13], precipitation [14], chemical gas phase deposition [15], combustion aerosol synthesis [16], and hard-templating method [17].

TUD-1 mesoporous material is a three dimensional siliceous stable matrix, which can be prepared in one-pot synthesis procedure based on sol-gel technique by using triethanol amine as a template [18]. TUD-1 has been used a support for several transition elements such as Ti [19], Mo [20], Cr [21], Co [22], Fe [23] etc., and the prepared materials have been applied as catalysts in different applications. Following the success of siliceous TUD-1, Shan and coworkers [24] reported the synthesis of mesoporous alumina by the same synthesis method of siliceous TUD-1. Mesoporous alumina was reproduced by other research groups and it has been used in catalysis field [25].

The rapid increase in the industrial activates has led to a serious increase the concentrations of heavy metals (e.g. Cr, Hg, Cd, Pb, … etc) and dyes (e.g. methyl orange, methylene blue, arenazo III, … etc) in wastewater. These heave metals and dyes have a serious negative effect on human health as well as the ecological environment. Hence, the removal of these contaminates is crucial [26]. Several methods were developed to treat wastewater, notably the adsorption method. Many materials were introduced as adsorbents for Cr(VI) and arsenazo (III) dye such as polypyrrole/attapulgite core-shell nanocomposite [27] graphene oxide doped Fe_2O_3 [28], metallic iron supported on sand or MnO_2 [29] and recently, cyclophosphazene bridged mesoporous organosilicate [30]. However, a simple cost-effective, easy-synthesized material with high adsorption efficiency is highly required.

Cancer is one of the awful diseases around the world. In cancer, a group of cells in a certain origin grow abnormally, invasion and even metastasis [31]. The current therapy of cancer includes radiation, chemical and surgery [32]. Inorganic nanoparticles, including magnesium oxide, attract a lot of interest because they show a high toxicity towards the cancerous cells [33–35]. However, more investigations are needed to explore the cytotoxic activity of the modified magnesium oxide.

In the current study and for the first time, mesoporous magnesia is introduced as the third member of the mesoporous TUD-1 family. Mesoporous magnesia was prepared by the one-pot sol-gel technique. The prepared material was characterized by different characterization techniques, and it was tested as adsorbent for aresenazo (III) dye and hexavalent chromium ions in aqueous solutions. More importantly, the use of mesoporous magnesia as an anti-cancer agent was evaluated against three types of cancerous cells.

2. Experimental

2.1. Synthesis

Mesoporous magnesia was prepared according the method adapted by Shan and coworkers [18], in which the mesoporous material is obtained by aging, drying and calcining a homogeneous synthesis mixture, consisting of a solution of magnesium nitrate, triethanolamine (TEA) and tertraethyl ammonium hydroxide as a base. In a typical synthesis, 15 g of TEA was diluted by 3.6 ml of H_2O, and the resulting mixture was added dropwise to solution of magnesium nitrate 14.1 g/10 ml H_2O while stirring. After stirring for about 30 min, 19.7 ml of tetraethyl ammonium hydroxide (TEAOH, 25%, Aldrich) was added dropwise. Finally, the obtained clear solution was aged at room temperature for 24 h, dried at 100 °C for 24 h, heated in a Teflon-lined stainless steel autoclave at 180 °C for 4 h, and then calcined at 600 °C for 10 h by using a heating ramp rate of 1 degree/min under flow (30 ml/min) of 8% oxygen in nitrogen gas. For comparison, the commercially available MgO was purchased from Sigma-Aldrich and the sample was used directly without any further treatment/purification.

2.2. Characterization

The degree of crystallinity of the prepared samples was investigated by XRD measurements which was performed by using Schimadzu 6000 DX instrument diffractometer equipped with a graphite monochromator using $CuK\alpha$ radiation ($\lambda = 0.1541$ nm). The samples were scanned over a range of 5–80° 2θ with steps of 0.02 degree. The total surface area (m^2/g) and pore size distribution of the prepared samples where determined by N_2 adsorption/desorption method conducted at 77 K on NOVA 2000e adsorption apparatus (Quantachrome, USA). Usually, 0.1–0.25 g sample was packed into the sample tube and degassed at 250 °C for 2 h for the removal of adsorbed gases and impurities adsorbed on the surface of the sample. After degassing, the sample tube was allowed to cool at room temperature, and then fixed into analysis chamber containing liquid nitrogen for analysis. Finally, the total surface area of prepared materials was determined by the multi-point Brunauer–Emmett–Teller (BET) method. The pores size and pore volume were determined from desorption branch of N_2 curve by using Barrett–Joyner–Halanda (BJH) method. Scanning electron microscopy (SEM) Jeol Model 6360 LVSEM, USA, was used to observe the pore structure of the synthesized sorbent materials. The surface morphology for the samples was studied and then recorded after coating with platinum equipped with an EDX device (Jeol Model 6360 LVSEM, USA) for qualitative and semi quantitative analyses. UV–Vis spectra were collected at ambient conditions on a CaryWin 300 spectrometer using $BaSO_4$ as reference. Samples were heated overnight at 180 °C and then the diffuse reflectance spectra were recorded at ambient conditions in the wavelength range of 190–800 nm. The diffuse reflectance spectra were converted into Kubelka-Munk function F(R) by using the equation $F(R) = (1-R)^2/2R$. High-Resolution Transmission Electron Microscopy (HR-TEM) was carried out on a Philips CM30UT electron microscope with a field emission gun as the source of electrons, operated at 300 kV. The Fourier transform infrared spectroscopy (FTIR) spectra were collected at ambient conditions for the two samples by using Thermo Nicolet iS10 spectrometer. The IR spectrum of commercial MgO was measured directly without any further treatment for the sample, while the spectrum of mesoporous MgO was collected after calcination step directly. Spectra were collected by using KBr pellets in the range of 4000–400 cm^{-1}.

2.3. MgO as an adsorbent

For sorption study, two model compounds were examined, hexavalent chromium ions and arsenazo (III) dye. Batch experiments were conducted with 50 ml of ammonium dichromate standard solution (100 ppm) or arsenazo (III) (100 ppm) dye solution in 250 ml stoppered bottles containing 0.05 g of MgO solid powder at pH .5 in the case of Cr(VI) and 0.1 g of MgO in the case of dye experiments. The mixture was shaken by a mechanical water shaker thermostated at 25 ± 1 °C for 30 min. The concentration of Cr (VI) ions was determined by using atomic absorption spectrometer (VARIAN, SpectrAA 220). While the concentration of the investigated dye was measured using a Shimadzu UV/visible double-beam spectrophotometer (model UV-1800, Japan) that has a wavelength range 200–1100 nm.

In order to calculate the thermodynamic parameters; sorption enthalpy change (ΔH), entropy change (ΔS) and the free energy change (ΔG), the adsorption experiments were carried out in three different temperatures in the case of dye and five different temperatures in the case of chromium experiments.

The uptake (q_e) was calculated from the following equation

$$q_e = \frac{V}{m} \times (C_0 - C_e)$$

where C_0 is initial concentration while C_e is the concentration at equilibrium, V is the aqueous volume and m is the solid mass.