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Fabrication of ZrO_2/Ceramic Nanocomposite for Water Purification

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Abstract: In this study, ZrO_2 nanoparticles were prepared by successful microwave irradiation cohesive method. Compared to conventional methods, the advantages of microwave synthesis, very short reaction time and small particle production with narrow size distribution, high purity, efficient heating, environmentally friendly, cost-effective, uniform and special heat distribution and increase the speed of the reaction. On the other hand, ZrO_2 is a highly resistant material to crack and fracture propagation, high thermal expansion, excellent conductivity and low thermal conductivity. In this type of synthesis, the aqueous solution containing $Zr(NO_3)_4.5H_2O$ and NaOH was exposed to 650 W microwave radiation. The obtained sediments were characterized by FT-IR and UV-vis analyzes. The sediments were uniformly coated on a ceramic membrane and a very thin layer formed by a wet layer on the substrate. The evaporation and drying process was performed under constant conditions. In this work, the ceramic membrane was used because of its apparent advantages, including high stability, long life, high flux and low deposition. The results showed that according to the XRD diagram based on the Shearer equation, the ZrO_2 nanoparticles had crystalline order and sharp and distinct peaks. The FE-SEM images also showed that the morphology of the tubular structure was oriented towards the tetragonal and nanoparticles with dimensions less than 100 nm on the ceramic surface.

Keywords: ZrO_2; ceramic; microwave irradiation; conventional methods; water purification

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1. Introduction

Water purification to acquire potable water is a major challenge for the present day civilization. Many water purification methods and technologies have been developed and employed over the years [1]. Many methods require a great deal of cost and energy. One way to purify water is to use ceramics. Undoubtedly, ceramic membranes can be considered as one of the most promising inorganic membranes so far and can become the new playmaker in the desalination and water treatment industry. Comprehensive research and in-depth studies on easier and cheaper synthesis and fabrication methods to reduce their price will definitely change the membrane market for water treatment applications. Overcoming challenges such as reducing the capital cost of ceramic membranes by reducing the steps in the fabrication process and lowering the sintering temperature plus understanding the formation mechanisms of ceramic membrane microstructures, the reliability and reproducibility of the fabrication process, incorporating different coatings of different nanoparticles on ceramic membranes and a good knowledge of the effects of water chemistry and its interaction with ceramic membranes can help progressing this area [2]. The market for the use of inorganic membranes and ceramics is still small and is expected to increase in the near future. However, global attention to mineral membranes and ceramics is growing rapidly. Due to their capability of higher permeability and selectivity, it has attracted much attention [3-5]. Ceramic membranes have thermal and chemical stability. And they can be easily washed and cleaned with various cleaning agents. And sterilized at high temperatures. Without affecting their performance or lifespan. Due to the high cost of production, ceramic membranes are rarely used in the production of potable water and wastewater treatment [6-9] However, ceramic membranes have already attracted more attention due to lower operating costs and synthesis coupled with improved membrane performance [10–12]. Alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2) can be used as adsorbents on ceramic surfaces. And they will be very effective in removing pollutants. Zirconia has been used as an adsorbent in the removal of contaminants such as arsenic [13], phosphate [14]. Zirconium is a non-toxic material, its oxide (ZrO_2), like many of its compounds, is white and resistant to corrosion. In recent years, there has been considerable interest in. ZrO_2 has three polymorphs: monoclinic (m), tetragonal (t) and cubic (c) phases. The monoclinic phase is thermodynamically stable up to tetragonal phase exists in the temperature range 1100-2370 °C, and the cubic phase is found above 2370 °C [15]. The existence of metastable t-ZrO_2 at low temperature has been reported, and fine powders of t-ZrO_2 at mild temperature have been prepared by many methods, including forced hydrolysis [15-16], sol-gel method [17], hydrothermal method [18], thermal decomposition [19], coprecipitation [20], surfactant templating method [21] and spray pyrolysis [22]. However, it is very useful for us to find a fast, simple, and energy efficient approach to produce fine t-ZrO_2 powders. Microwave-assisted synthesis is another way to produce inorganic compounds since 1986. Compared to conventional methods, the advantages of microwave synthesis, very short reaction time and small particle production with narrow size distribution, high purity [23], efficient heating and environmentally friendly, cost-effective, uniform and special heat distribution and increase the speed of the reaction [16]. But so far, zirconia has not been used as a ceramic adsorbent. In this work, we first immobilized zirconia on ceramics by spin-coating method. Then its activity to remove methylene blue was tested. Results of experiments were measured by UV-Vis instrument.

2. Experimental procedure

2.1. Chemicals

All of the chemicals were made by Merck and all aqueous solutions were prepared using deionized water.

2.2. Identifying techniques

Morphology and elemental composition using Fourier transform infrared (FT-IR). The FT-IR spectra were collected with a Shimadzu 8400_s Fourier transform infrared (FT-IR) spectrometer in the range of 400-4000 cm^{-1}. X-ray diffraction (XRD) measurements were performed using a Philips PW-1730 X′pert diffractometer with monochromated Cu-kα radiation (λ=1.54056Å). Microstructure of sample was measured by Scanning electron micrograph (SEM), Tescan MIRA3model. UV-Vis-DRS spectroscopy of samples was done in the range about 200-800 nm by a Shimadzu UV-2550 spectrophotometer.

2.3. Synthesis of ZrO_2

ZrO_2 nanoparticles were successfully prepared by hydrolysis of $Zr(NO_3)_4.5H_2O$ under microwave irradiation in NaOH aqueous solutions. In a typical synthesis, an aqueous solution containing 0.10 mol L^{-1} $Zr(NO_3)_4.5H_2O$ and 5 mol L^{-1} NaOH was first heated to 80 °C at 300 rpm for 45 min. The gel was exposed to microwave radiation at 650 W power. Microwave irradiation was performed in a 30- to 30-second cycle (for 10 seconds, 20 seconds off) for 6 minutes, then cooled to room temperature. The collected precipitate was washed once with water and once with ethanol. The oven was then dried for 5 h at 320 °C.

2.4. Ceramic preparation

Initially, the ceramic membrane was made of a material called mullite. The mullite was ball-milled until micro size, pressed under 400 bar in disk format. The sample was heated to 80 °C for 2 h to remove moisture. It was then placed in the furnace at 1200 °C for 2 h.

2.5. Preparation of zirconia on ceramic

The prepared ceramic sample was coated by a spin coating method with a zirconia solution layer. In the first step, the solution was transferred to a slowly spinning substrate. In the second stage, the liquid was pumped by the centrifugal force. In the third step, the excess fluid in the liquid film flowed radially to the outlet under the substrate. Finally, the rotation continued until complete evaporation

2.6. Application of adsorption

The effect of initial dye concentration on the adsorption capacity was investigated in a range from 5 to 50 mg L^{-1} of MB with ceramic composite at 25 °C. The recyclability of the sample was conducted in the 10 mL of 20 $mg.L^{-1}$ MB solution. The dye removal was determined according to the following:

$$\text{Dye removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

where C_0 and Ce ($mg.L^{-1}$) are the initial and equilibrium concentration of MB, respectively.

3. Results and discussion

Different methods were used to evaluate the crystalline structure and grain size (XRD), morphology (FE-SEM), surface binding properties (FT-IR) and wavelength (UV) of the ZrO_2 powder.

3.1. X-ray diffraction and Phase structure

XRD results show that the primary product through microwave synthesis is tetragonal ZrO_2. The X-ray diffraction pattern for zirconia is shown in Fig. 1. For pure zirconia a series of sharp and strong peaks was observed. They can be attributed to the tetragonal structure of zirconia. No additional peaks were observed in the zirconia diffraction pattern. Which shows the appropriate purity of the synthetic sample and there are crystalline phases in this sample. XRD data show that at 600 °C the ZrO_2 films were formed using tetragonal phase nanoparticles. The distinguishing characteristic peaks for tetragonal occur at 2θ= 30.2, 34.5, 50.2 and 60.2º corresponding to the (1 0 1), (1 1 0), (2 0 0) and (2 1 1) reflections.

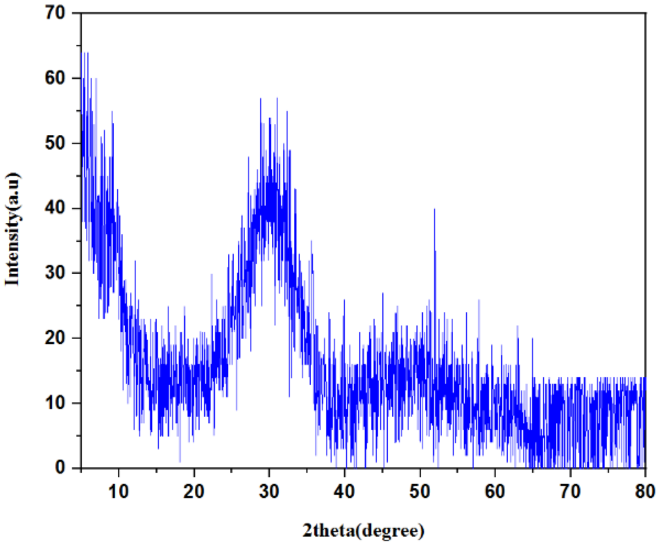

Figure 1. XRD image of ZrO_2 at 600 °C.

3.2. FT-IR analysis

Fig. 2 shows the FT-IR spectrum of ZrO_2. Bands observed at 3400 cm^{-1} and 1600 cm^{-1} are assigned to the bending and stretching vibrations of the O-H bond due to absorbed water molecules. The sharp band at 640 cm^{-1} is the characteristic of m-ZrO_2. A broad band around 1500 cm^{-1} is ascribed to Zr-O vibrations of t-ZrO_2. FT-IR spectra showed Zr-O bond formation.

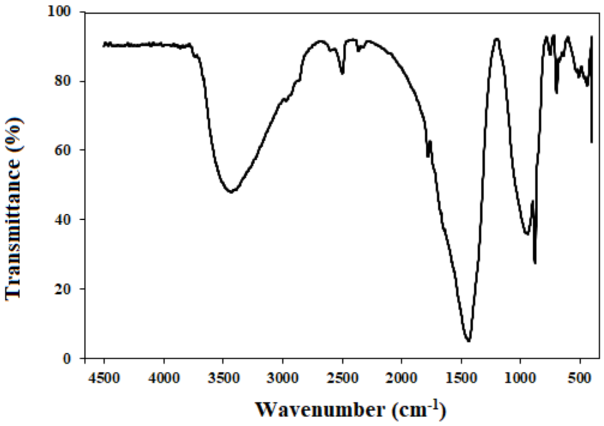

Figure 2. FT-IR spectrum of ZrO_2 in the 400–4000 cm^{-1}.

3.3. *UV-Vis DRS analysis*

The UV-Vis DRS spectrum of the synthesized zirconia is shown in Fig. 3. Zirconia absorbs a significant absorbance from about 4-5 nm to shorter wavelengths. This may be related to the electron transfer process from the capacitive band to the conduction band. Gap band analysis shows that a decrease in the size of the nanoparticles can cause cleavage and transfer of the valence bands. Important factors that can affect the optical band gap are the defects and changes in the crystallinity. In this analysis, the ZrO_2 band gap can be attributed to the defect.

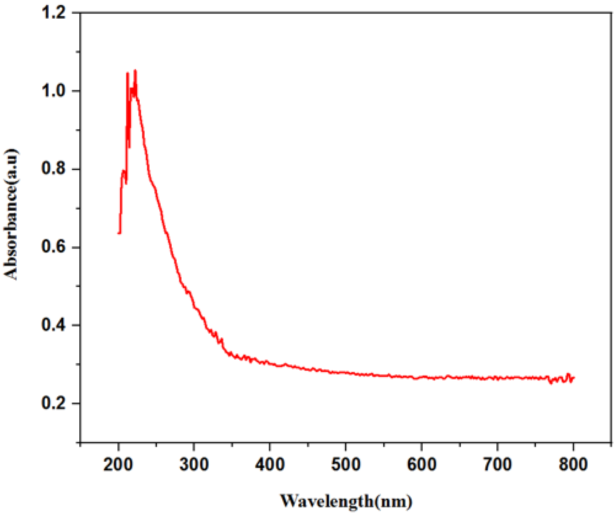

Figure 3. DRS spectrum of ZrO_2.

3.4. *FE-SEM images*

SEM method was used to study the morphology and microstructure of the sample, as shown in Fig. 4. Synthetic hollow zirconia spheres are observed. Their average diameter is about 36 micrometer. Zoom images show more areas below the cone. This fragment consists of particles about 10.5 to 24.3 nm. The FE-SEM method shows that this ceramic membrane is suitable for removing water pollutants.

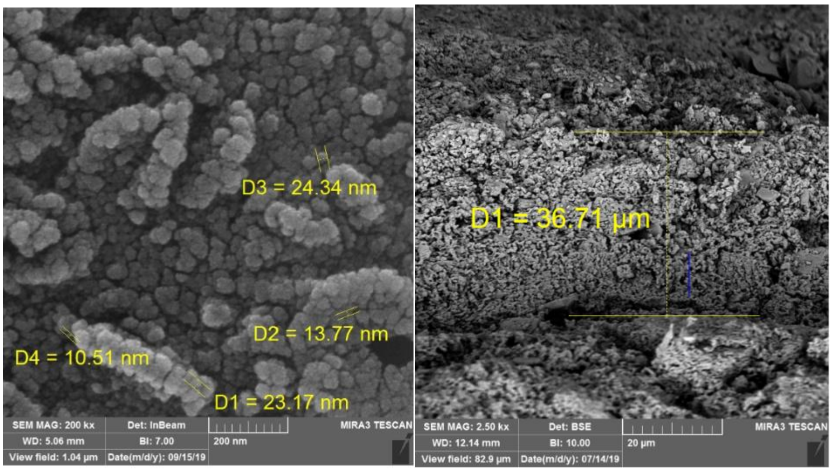

Figure 4. SEM images of ZrO_2 on ceramic.

3.5. *Adsorption study*

The standard curve of methylene blue resulted by UV-Vis spectroscopy was determined (Fig. 5).

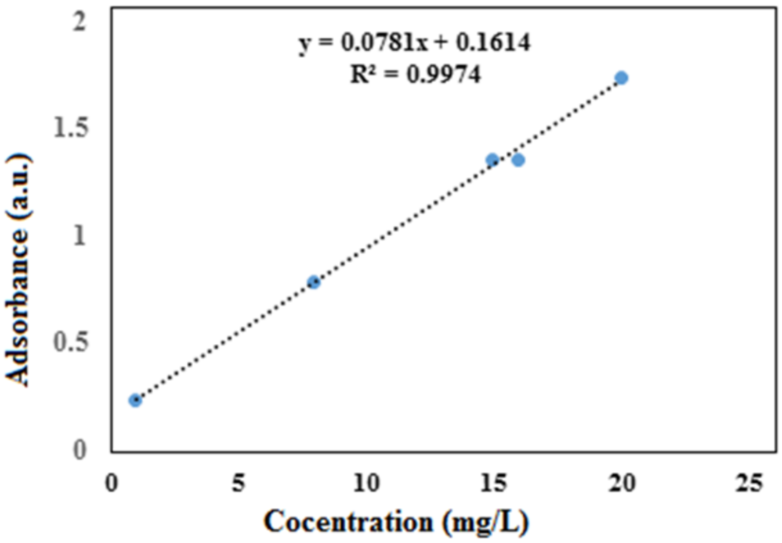

Figure 5. The standard curve of methylene blue.

The dye adsorption capacities onto ceramic composite increased with the increase of the concentration of dye solutions. The removal efficiencies for MB initially increased and then decreased which might be due to the fact that large numbers of vacant active sites were available for the adsorption at a lower initial concentration, and then saturated sites were difficult to capture the dye molecules. UV-Vis curves of MB (20 mg/L) before and after adsorption by ZrO_2/ceramic composite were shown in Fig. 6.

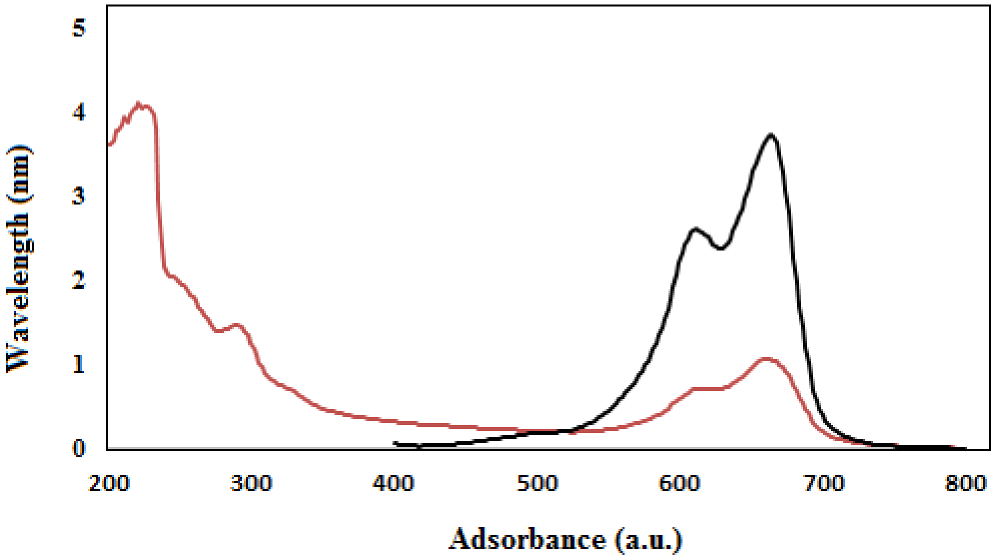

Figure 6. UV-Vis curves of MB before and after adsorption by ZrO_2/ceramic composite.

3.6. The reusability of ZrO_2/ceramic composite

The reusability of the ZrO_2/ceramic composite is important for their economic feasibility and applicability. Therefore, the desorption-adsorption cycles were performed. Desorption studies were carried out using distilled water and ethanol solution, and the dye removed for each cycle were shown in Fig. 7. It can be seen that sample still retained adsorption capacity for MB even after four cycles of reuse.

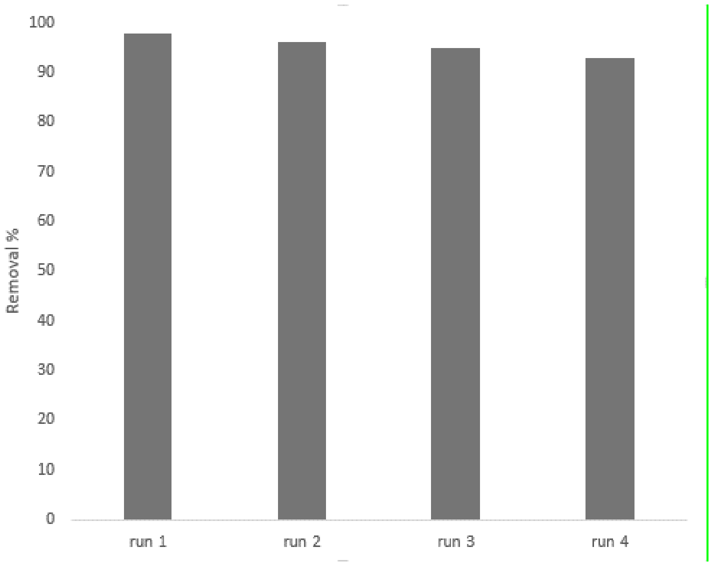

Figure 7. Reusability of ZrO_2/ceramic composite.

4. Conclusion

Removing paint from wastewater using nano-sorbents has two advantages: water purification and wastewater management. We investigated the adsorption of MB dye on ZrO_2/ceramic composite and found that the ZrO_2/ceramic composite.could be successfully used for the removal of dyes from aqueous solutions.

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