Study on photocatalytic-adsorption properties of hollow $ZrFe_2O_4$ cauliflowers for removal of organic pollutants

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Abstract

Hollow zirconium ferrite cauliflowers were synthesized by a facile solvothermal method using ultrasonic waves. The prepared nanoparticles were employed for the removal of methylene blue (MB) in the wastewater treatment. X-ray diffraction (XRD) pattern of the ferrite sample is well in agreement with the standard pattern of the $ZrFe_2O_4$ structure. Scanning electron microscopy (SEM) image reveals that the resultant ferrite is nanoporous structurally and the average sizes of cauliflowers and holes diameter were measured at 150 and 20 nm, respectively. UV-visible absorption spectroscopy was used to record the adsorption and photocatalytic behaviors of prepared ferrite.

1- Introduction

Extensive literature is available on the suitability of magnetic nanoparticles (MNPs) for various bioapplications [1-4]. Magnetic materials like zirconium ferrite has exhibited unique magnetic properties because of its low toxicity, good biocompatibility and tunable magnetic properties ferrite have received considerable attention in various areas such as catalysis magnetic refrigeration systems, drug delivery and targeting, heat transfer applications, cancer therapy, enzyme immobilization and magnetic cell separation [5].

Various methods to eliminate pollutants compounds from wastewater have been reported in the previous published articles among them, the advanced oxidation processes, in which the photo-degradation processes are included. These processes consist in the decomposition of organic molecules interacting with both, an UV or visible light as well as the interaction with a photo-catalyst material [6]. Methylene Blue (MB), which is commonly applied to cotton, wood, and silk [7], can cause various symptoms including difficulty in breathing, nausea, and vomiting [8,9], and can impair photosynthetic processes in aquatic ecosystems [10-12]. Furthermore, dye substances typically exhibit long term chemical stability [13-15], and their complex aromatic structure is not conducive to biological degradation [16-17]. Therefore, it is of environmental importance to develop efficient methods to remove MB from wastewater effluents [18].

Utilization of a combination with magnetite is more economical, due to the ease of separation and recovery of the catalyst after the elimination of the pollutant Naturally a catalyst that has the ability to remove contaminants in visible light is more desired [19].

In this work, for the first time, synthesis of $ZrFe_2O_4$ cauliflowers with nanopores, the catalyst was used for photocatalytic degradation of methylene blue under visible light LED lamp. The nanoscale pores in addition to the photocatalytic degradation process, causing part of the contaminants to be removed from the environment by adsorption.

2- Experimental

2-1- Materials

In this study, iron (III) chloride ($FeCl_3$), zirconium chloride ($ZrCl_4$), ammonium acetate, ethylene glycol ($C_2H_6O_2$) and ethanol were used to prepare the samples.

2-2- Preparation of $ZrFe_2O_4$ cauliflowers

A mixture of 70 mL ethylene glycol, iron (III) chloride and zinc chloride was stirred in a mechanic stirrer to achieve a clean solution. Then, the above solution was added during stirring 2.312 g NH_4Ac. With continued practice of mixing, the color turns to dark yellow and palms appeared. This solution for 40 min was sonicated. The solution is then placed in an oven at 215 ºC for 24 h to obtain a black precipitate.

2-3- Characterization of $ZrFe_2O_4$ cauliflowers

The particle morphologies of the $ZrFe_2O_4$ powder were observed by an AIS2100 (Seron Technology) scanning electron microscopy (SEM) and a JEOL 2010F transmission electron spectrophotometer using a KBr pellet for sample preparation. Furthermore, the structure of particles was analyzed by powder X-ray diffractometer (XRD).

2-4- Photocatalytic experiments

Photocatalytic activity studies of the $ZrFe_2O_4$ were evaluated by the degradation MB solution. In a typical process, the catalytic reaction was carried out in a 100 mL photoreactor, which contains 50 mL of MB dye (10 mgL^{-1}) solution and 0.05 g of catalyst. Before irradiation, the solution was stirred in the dark (15 min) for obtaining an equilibrium point of initial physical adsorption of MB over the surface of samples. Irradiation was carried out using a 5 W LED visible light (with emission wavelength about 460-490 nm). All photocatalytic experiments were accomplished at the same conditions. For determination of MB decolorization at specified periods, the lamps were turned off and 3 mL of each sample was collected and indirectly monitored by relating the optical absorbance to the MB degradation amount using a double beam UV–Vis spectrophotometer at a wavelength of 664 nm.

3. Results and discussion

3.1. Characterization of $ZrFe_2O_4$ cauliflowers

FT-IR spectra of $ZrFe_2O_4$ indicated in Fig. 1 in the range 400–4000 cm^{-1}. In the spectrum of $ZrFe_2O_4$, in the lower frequency regions (at around 545-560 cm−1), typical of ferrite materials and ascribable to the vibration of Fe–O in the spinel lattice.

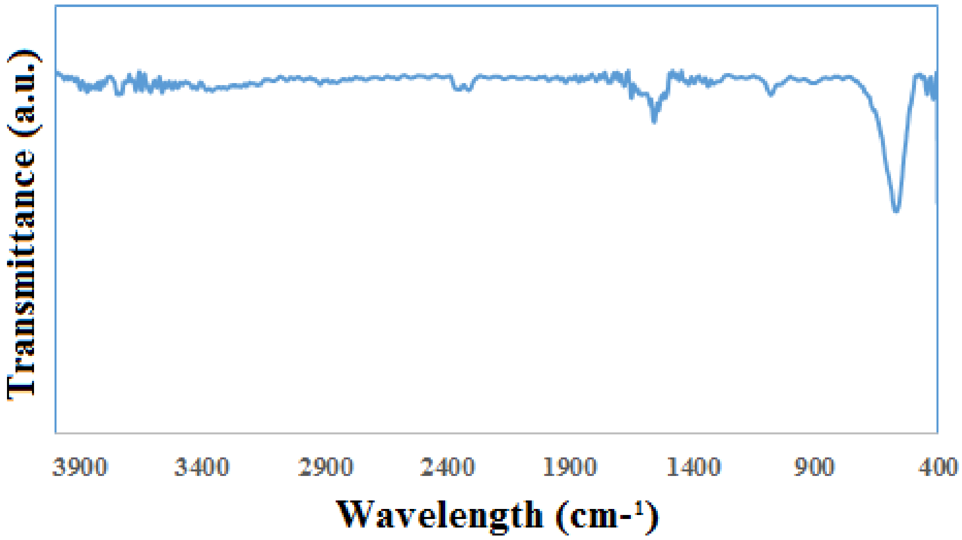


Fig. 1. IR Spectrum of $ZrFe_2O_4$.

The phase structure of the prepared $ZrFe_2O_4$ was characterized by XRD (Fig. 2). All the characteristic reflection peaks at 2θ = 29.86°, 35.15°, 36.77°, 42.72°, 52.98°, 56.47°, 62.25° can be ascribed to the diffraction of cubic ZrFe2O4 crystal with the (220), (311), (222), (400), (422), (511), and (440) planes, respectively, indicating the successful preparation of the sample using the solvothermal method.

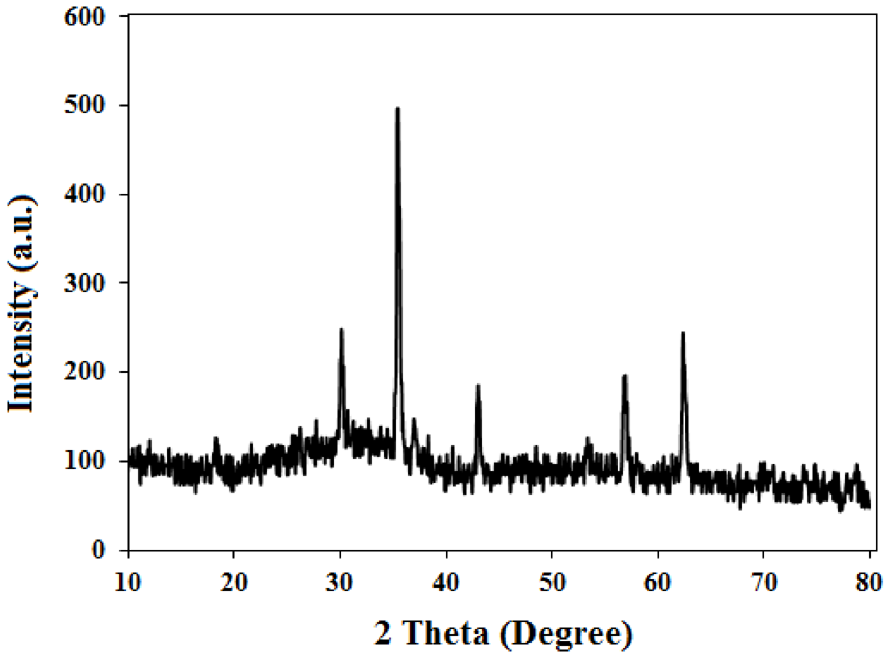


Fig. 2. SEM image and XRD pattern of $ZrFe_2O_4$

The EDX analysis and SEM image of $ZrFe_2O_4$ are shown in Fig. 3. EDX analysis show the presence of Zr in prepared ferrite. The SEM image shows that the morphology of prepared ferrite is clearly similar with spheres and cauliflowers.

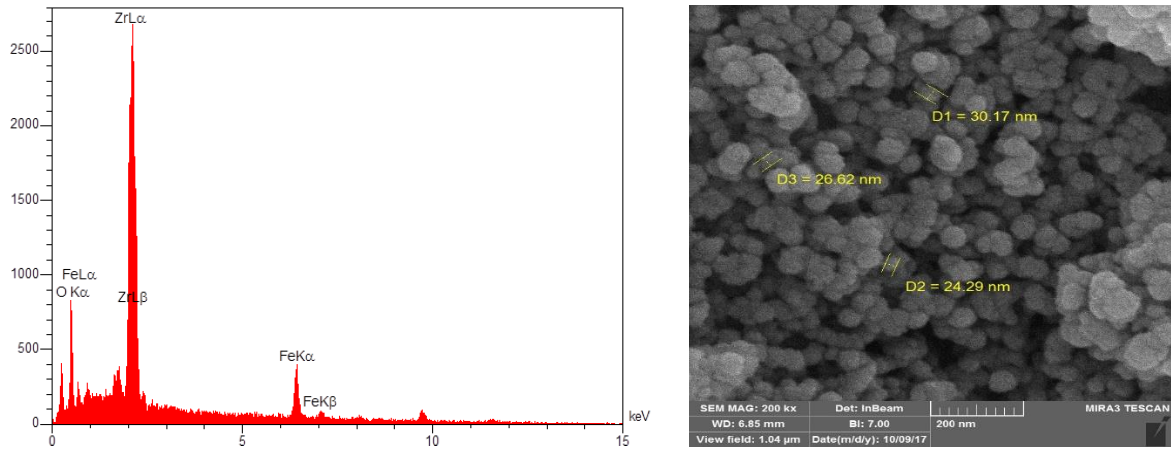


Fig. 3. EDX analysis and SEM image of $ZrFe_2O_4$.

3-3- Photocatalytic degradation of methylene blue

The photocatalytic activities of pure $ZrFe_2O_4$ cauliflowers catalysts were evaluated by the degradation of MB in aqueous solution under LED visible light irradiation. The photocalytic activity and adsorption property of $ZrFe_2O_4$ was compared in Fig. 4A. Removal of MB was carried out about 50% by adsorption on $ZrFe_2O_4$, but MB was degraded in the presence of $ZrFe_2O_4$ under LED light irradiation about 78%. This figure show that photolysis degraded only 12% of MB. Concerning the initial MB concentration, it can be concluded that there was a decrease in the photodegradation of MB with increasing initial MB concentration (Fig. 4B). Fig. 4C show the images of MB solution before and after photocatalytic degradation process.

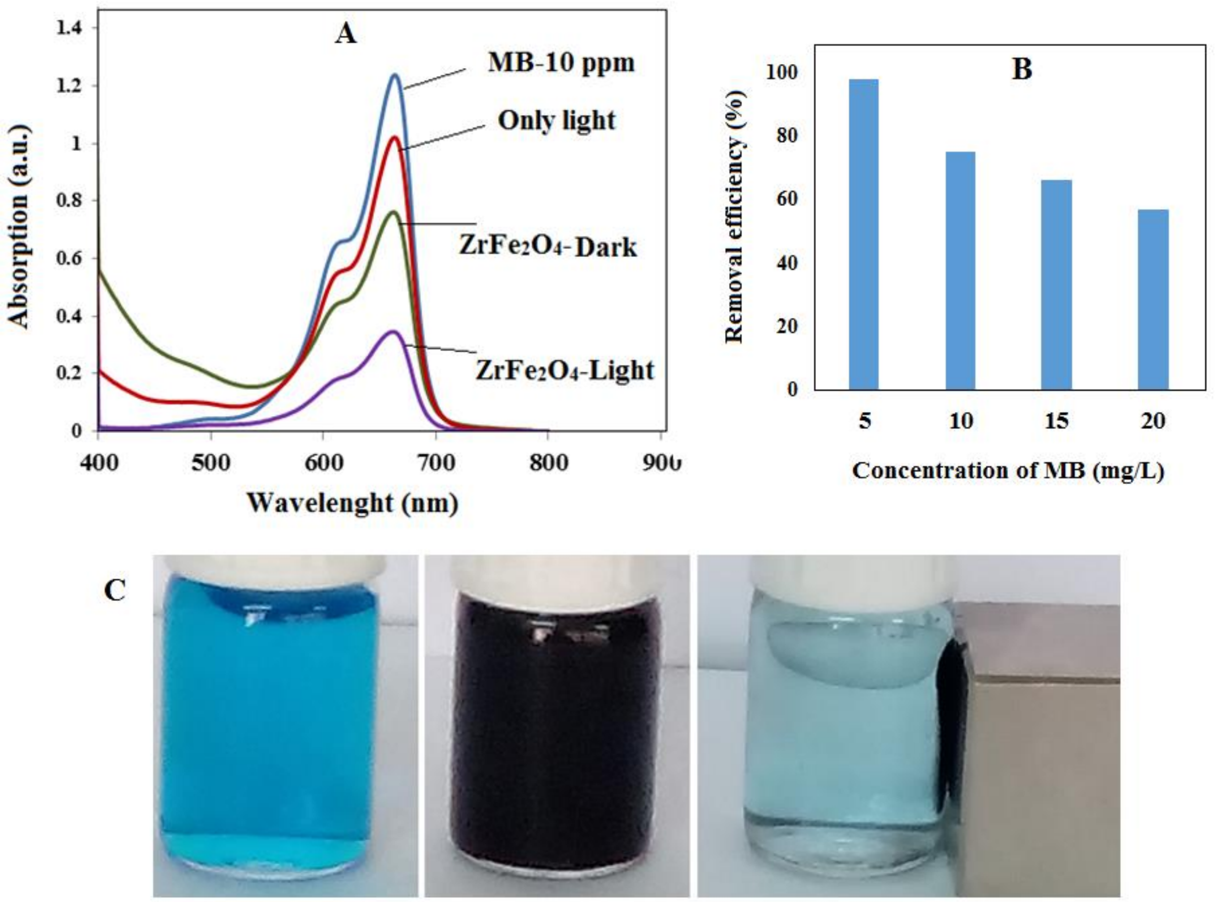
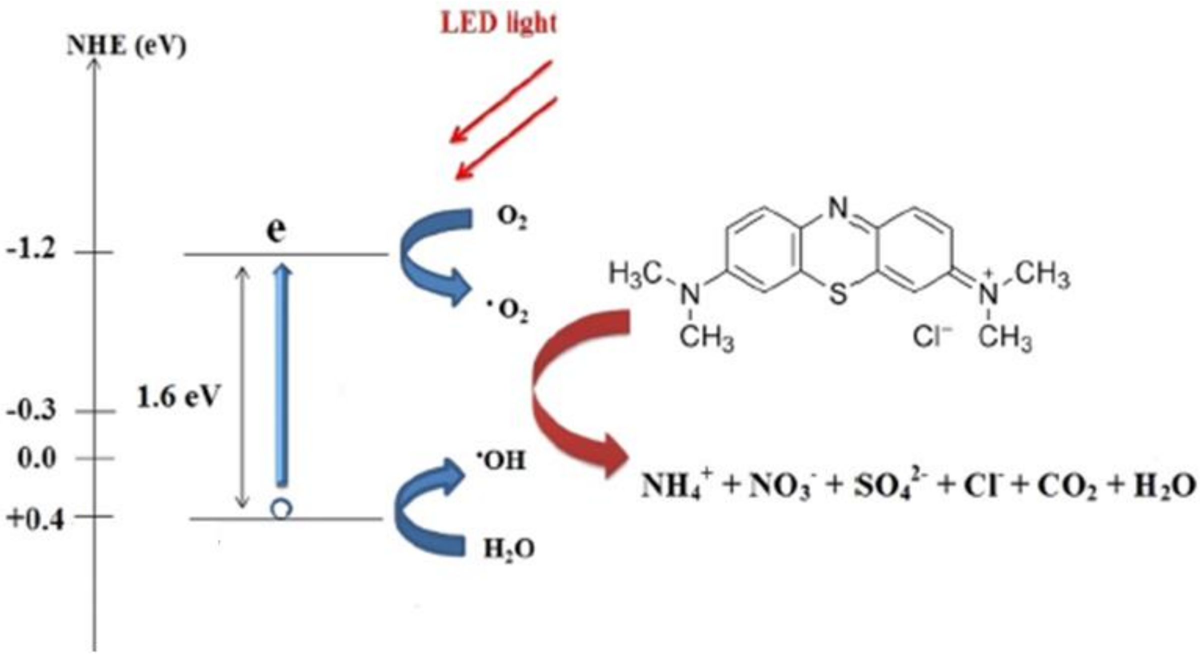


Fig. 4. UV-Vis spectra of MB (10 mg/L) in the presence of $ZrFe_2O_4$ at different conditions. (B) Effect of concentration of MB and (C) The photograph of the MB solution (concentration: 10 mgL^{-1}), before and after light irradiation.

A possible mechanism has been shown in Scheme 1. It is well known that $ZrFe_2O_4$ has a low band gap of approximately 2 eV or lower can effectively absorb visible range of sunlight. The electrons in the valence band (VB) of $ZrFe_2O_4$ are preferentially excited to its conduction band

(CB) under visible light irradiation and therefore generate an equal amount of holes in its VB. The photoexcited electrons reduce molecular oxygen to the superoxide radicals. On the other hand, in aqueous medium, the holes in the valence band of $ZrFe_2O_4$ oxidize the water molecules to generate hydroxyl radicals. The hydroxyl radicals can convert to H_2O_2 and superoxide radical anion to regenerate hydroxyl radicals. Finally, derived hydroxyl radicals decompose MB to carbon dioxides and water.



Scheme 1. The mechanism of MB photodegradation by $ZrFe_2O_4$.

4- Conclusions

Magnetically $ZrFe_2O_4$ nanohallow cauliflowers as visible-light-driven photocatalysts was prepared by hydrothermal method. Visible light photocatalytic activity of the nanohallow cauliflowers was investigated by degradation of MB. After visible light irradiation for 3 h, about 78% of MB molecules were degraded on $ZrFe_2O_4$.

References

[1] Jordan, A., R. Scholz, R., Wust, P., Schirra, H., Schiestel, T., Faehling, H., Felix, R., J. Magn. Magn. Mater, (1999) 194, 185-196.

[2] H.Lu, A. H., Salabas, E. L., Schüth, F., Angew. Chem., Angew.,Int.Ed. Engl., (2007)46, 1222-1244.

[3] Hafeli, U., Andra, W., Nowak, H., Wiley-VCH, Weinheim, 9, 3745–3754(1998).

[4] Prasad, N.K., Bahadur, D., Vasseur, S., Duguet, E., *UK: John Wiley & Sons, Ltd*, 15-30(2008).

[5] Gangwar A., All S.K., Srivastava M., Meen S.S., Prasadrao E.V., Mandal R.K. Yusuf S.M., Prasa N.K. A.Gangwaretal. (2016)401, 559–566.

[6] Saffari, J., Mir, N., Ghanbari, D., Khandan-Barani, K., Hassanabadi, A. and Hosseini-Tabatabaei, M.R., Sonochemical synthesis of Fe3O4/ZnO magnetic nanocomposites and their application in photo-catalytic degradation of various organic dyes. *Journal of Materials Science: Materials in Electronics, (*2015), *26*(12),.9591-9599.

[7] S.C. Nunez, T.M. Yoshimura, M.S. Ribeiro, H.C. Junqueira, C. Maciel, M.D. Coutinho-Neto, M.S. Baptista, Urea enhances the photodynamic efficiency of methylene blue, J Photochem Photobiol B 150 (2015) 31-7. 21

[8] H.C. Junqueira, D. Severino, L.G. Dias, M.S. Gugliotti, M.S. Baptista, Modulation of methylene blue photochemical properties based on adsorption at aqueous micelle interfaces, Physical Chemistry Chemical Physics (2002) 4(11) 2320-2328.

[9] H.C.J. Divinomar Severino, Marcos Gugliotti, Dino S. Gabrielli and Mauricio S. Baptista, Influence of Negatively Charged Interfaces on the Ground and Excited State Properties of Methylene Blue, Photochemistry and Photobiology 77(5) (2003) 459–468.

[10] W. Stawinski, A. Wegrzyn, T. Danko, O. Freitas, S. Figueiredo, L. Chmielarz, Acid-base treated vermiculite as high performance adsorbent: Insights into the mechanism of cationic dyes adsorption, regeneration, recyclability and stability studies, Chemosphere 173 (2017) 107-115.

[11] J. Xu, P. Xin, Y. Gao, B. Hong, H. Jin, D. Jin, X. Peng, J. Li, J. Gong, H. Ge, X. Wang, Magnetic properties and methylene blue adsorptive performance of CoFe2O4/activated carbon nanocomposites, Materials Chemistry and Physics 147(3) (2014) 915-919.

[12] J. Fu, Z. Chen, M. Wang, S. Liu, J. Zhang, J. Zhang, R. Han, Q. Xu, Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): Kinetics, isotherm, thermodynamics and mechanism analysis, Chemical Engineering Journal 259 (2015) 53-61. 22

[13] A. Paz, J. Carballo, M.J. Pérez, J.M. Domínguez, Biological treatment of model dyes and textile wastewaters, Chemosphere (2017).

[14] A. Ayati, M.N. Shahrak, B. Tanhaei, M. Sillanpaa, Emerging adsorptive removal of azo dye by metal-organic frameworks, Chemosphere 160 (2016) 30-44.

[15] W. Stawinski, O. Freitas, L. Chmielarz, A. Wegrzyn, K. Komedera, A. Blachowski, S. Figueiredo, The influence of acid treatments over vermiculite based material as adsorbent for cationic textile dyestuffs, Chemosphere 153 (2016) 115-29.

[16] S. Zhu, S. Jiao, Z. Liu, G. Pang, S. Feng, High adsorption capacity for dye removal by CuZn hydroxyl double salts, Environmental Science: Nano 1(2) (2014) 172.

[18] Zhang, P., Lo, I., O'Connor, D., Pehkonen, S., Cheng, H. and Hou, D., 2017. High efficiency removal of methylene blue using SDS surface-modified ZnFe2O4 nanoparticles. *Journal of Colloid and Interface Science*, *508*, pp.39-48.

[19] Rahimi, R., Heidari-Golafzani, M. and Rabbani, M., 2015. Preparation and photocatalytic application of Zn Fe 2 O 4@ ZnO core–shell nanostructures. *Superlattices and Microstructures*, *85*, pp.497-503.