

Synthesis of Fe₃O₄@SiO₂@CS magnetic bionanocomposite by silica extracted from wheat straw for removal of Basic Red 46 dye from aqueous solutions

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Abstract

In the present study, amorphous silica was successfully extracted from wheat straw by acid leaching technique using various acids including HCl, HNO₃, H₂SO₄ and H₃PO₄ and was used in the synthesis of Fe₃O₄@SiO₂ nanocomposite. Then, the synthesized nanocomposite were functionalized by chitosan functional group (CS) to obtain Fe₃O₄@SiO₂@CS bionanocomposite. The percentages of the constituents, the crystallization state, the identification of the functional groups and the surface morphology of the produced materials were investigated using XRF, XRD, FT-IR, VSM, BET, SEM and zeta potential analyzes. Finally, the synthesized Fe₃O₄@SiO₂@CS bionanocomposite was used for removal of Basic Red 46 dye from aqueous solutions as an efficient and effective adsorbent. The results showed that pure and active silica with purity of 96.52% was extracted from wheat straw using acid leaching with HNO₃ acid. Also, the results of VSM analysis showed the superparamagnetic properties of Fe₃O₄@SiO₂@CS bionanocomposite with magnetic properties of 17.55 emu g⁻¹. In addition, the results of dye removal showed that the Basic Red 46 dye removal efficiency using synthesized Fe₃O₄@SiO₂@CS bionanocomposite was 97% and adsorption capacity of it was 1700 mg g⁻¹, which is much higher and desirable than many other adsorbents.

Keywords: Agricultural waste; wheat straw; Fe₃O₄@SiO₂@CS bionanocomposite; adsorption; Basic Red 46

1. Introduction

Silica (SiO₂) is a raw material that due to its unique physical and chemical properties has many technological applications such as thermal insulation, filler composite materials, thixotropic agents and so on [1]. Examples of silica use include glass, ceramics, cement, pharmaceuticals, cosmetics and silica-based materials in general [2, 3]. Silica is the second most abundant element in the Earth's crust, accounting for about 32% of its weight [2]. The crystalline silica is inactive and cannot be used in chemical reactions. To convert crystalline silica to amorphous silica that can be used in chemical reactions, very high temperatures (ca. 2000 °C), various chemicals and complex equipment are required. Therefore, the process will be very costly and highly contaminating for the environment. Plants rooted in the soil adsorb the silica in the form of silicic acid during their growth process [4]. Some plants, such as the *Equisetum*, *Cyperaceae* and *Poaceae* families are rich in amorphous silica that accumulate the amorphous silica in hydrated form (SiO₂.nH₂O) in their tissues [5]. Plant species that accumulate large amounts of silica in their aerial parts are called silica super accumulator plants. In these plants the accumulated silica is in the range of 5 to 30% of the dry weight of the plant [6]. Many studies have been performed on the distribution, deposition, physiology and extraction of silica from plants such as rice, wheat, barley and bamboo

[7, 8]. These plants are largely produced by waste in the agricultural sector. According to FAO statistics, in developing countries about 40% of agricultural products become waste. Since wheat is an important crop and accounts for the largest production in the world, most of the waste produced in the agricultural sector is related to this crop. Around 54 million tons of wheat straw is produced annually worldwide [9]. Wheat straw is often burned in the fields after harvesting the wheat crop. Burning wheat straw in the fields will reduce soil organic matter and greatly reduce soil fertility in the long run. In addition, it destroys soil microorganisms and disrupts the natural process of agricultural ecosystems. Besides, it also affects the environment and causes air and surface and groundwater pollution [10]. Wheat straw is recognized as a valuable agricultural waste from the harvesting and processing of wheat from fields that is rich in amorphous silica, easy to extract and require no complex chemicals and equipment. Therefore, it can be used as a cheap, readily available raw material for the production of silica-based materials. On the other hand, iron oxide magnetic nanoparticles (Fe_3O_4 MNPs) coated with silica have recently received special attention due to its many environmental applications. Silica coating can also prevent the aggregation and agglomeration of Fe_3O_4 MNPs and improve their dispersion in aqueous solutions.

2. Materials and methods

In this study, first, silica extraction from wheat straw was optimized by different methods of simple combustion and acid leaching using different hydrochloric, nitric, sulfuric and phosphoric acids. Then, iron oxide magnetic nanoparticles (Fe_3O_4 MNPs) were synthesized by co-precipitation method and using it and silica extracted from wheat straw the $\text{Fe}_3\text{O}_4@SiO_2$ magnetic nanocomposite was synthesized. Finally, the synthesized nanocomposite was functionalized using chitosan functional group to obtain $\text{Fe}_3\text{O}_4@SiO_2@CS$ bionanocomposite and was used as an efficient adsorbent for removal of Basic Red 46 dye from aqueous solutions.

3. Results and discussion

The results showed that pure and active silica with purity of 96.52% was extracted from wheat straw using acid leaching with HNO_3 acid. Also, the results of VSM analysis showed the superparamagnetic properties of $\text{Fe}_3\text{O}_4@SiO_2@CS$ bionanocomposite with magnetic properties of 17.55 emu g^{-1} . In addition, the results of dye removal showed that the Basic Red 46 dye removal efficiency using synthesized $\text{Fe}_3\text{O}_4@SiO_2@CS$ bionanocomposite was 97% and adsorption capacity of it was 1700 mg g^{-1} , which is much higher and desirable than many other adsorbents.

4. Conclusions

In the present study, wheat straw agricultural waste was selected to produce amorphous silica and it was used in the synthesis of $\text{Fe}_3\text{O}_4@SiO_2$ magnetic nanocomposite and then the nanocomposite was functionalized using chitosan functional group to obtain $\text{Fe}_3\text{O}_4@SiO_2@CS$ bionanocomposite. For the extraction of silica, wheat straw agricultural waste was investigated by two methods of conventional combustion and acid leaching using HCl , HNO_3 , H_2SO_4 and H_3PO_4 acids. The results of XRF analysis showed that the active silica was successfully extracted by acid leaching using HNO_3 with 96.52% purity. The results of XRD analysis showed that the crystalline structure of $\text{Fe}_3\text{O}_4@SiO_2$ nanocomposite remained stable after being chitosan functionalized. The results of adsorption experiments showed that this bionanocomposite had a removal efficiency of 97% and an adsorption capacity of 1700 mg g^{-1} which showed high potential for removal of dye pollutants from aqueous solutions.

References

- [1] T.-H. Liou, Preparation and characterization of nano-structured silica from rice husk, *Materials Science and Engineering: A*, 364(1) (2004) 313-323.
- [2] S. Kamari, F. Ghorbani, A.M. Sanati, Adsorptive removal of lead from aqueous solutions by amine-functionalized magMCM-41 as a low-cost nanocomposite prepared from rice husk: Modeling and optimization by response surface methodology, *Sustainable Chemistry and Pharmacy*, 13 (2019) 100153.
- [3] S. Kamari, F. Ghorbani, Synthesis of magMCM-41 with rice husk silica as cadmium sorbent from aqueous solutions: parameters' optimization by response surface methodology, *Environmental Technology*, 38(12) (2017) 1562-1579.
- [4] H. Motomura, T. Fujii, M. Suzuki, Distribution of silicified cells in the leaf blades of *pleioblastus chino* (Franchet et Savatier) Makino (Bambusoideae), *Annals of Botany*, 85(6) (2000) 751-757.
- [5] P.B. KAUFMAN, P. DAYANANDAN, C.I. FRANKLIN, Y. TAKEOKA, Structure and function of silica bodies in the epidermal system of grass shoots, *Annals of Botany*, 55(4) (1985) 487-507.
- [6] S. Agarie, W. Agata, H. Uchida, F. Kubota, P.B. Kaufman, Function of silica bodies in the epidermal system of rice (*Oryza sativa* L.): testing the window hypothesis, *Journal of Experimental Botany*, 47(5) (1996) 655-660.
- [7] D. An, Y. Guo, Y. Zhu, Z. Wang, A green route to preparation of silica powders with rice husk ash and waste gas, *Chemical Engineering Journal*, 162(2) (2010) 509-514.
- [8] M. Madani Hosseini, Y. Shao, J.K. Whalen, Biocement production from silicon-rich plant residues: perspectives and future potential in Canada, *Biosystems Engineering*, 110(4) (2011) 351-362.
- [9] T. Robinson, B. Chandran, P. Nigam, Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw, *Water Research*, 36(11) (2002) 2824-2830.
- [10] F. Ghorbani, S. Kamari, Application of response surface methodology for optimization of methyl orange adsorption by Fe-grafting sugar beet bagasse, *Adsorption Science & Technology*, 35(3-4) (2017) 317-338.