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Tailoring Magnetite Nanocrystal Morphology via Solvothermal Method for Enhanced Heavy Metal and Fluoride Adsorption.

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INTRODUCTION & AIM

Contamination by heavy metals is a pressing issue due to its numerous hazardous effects on human health. One of the main challenges associated with this type of contamination is the resistance of heavy metals to degradation and their accumulation in living organisms. Fluoride contamination through natural occurrence is prevalent in many regions worldwide, including Mexico. To achieve efficient removal of heavy metals from water, a high surface area absorbent is necessary. This enhances contact and interaction with heavy metal ions, and the use of nanoparticles significantly improves this aspect. This study investigates the preparation of Fe_3O_4 nanoparticles using a solvothermal method. This method allows for the production of ultrafine magnetite powders with homogeneous particles, a narrow size distribution, and consistent morphology, free from other crystalline phases that could hinder heavy metal ion absorption.

METHOD

The synthesis of magnetite nanoparticles (MS) was carried out in a 100-mL Teflon-lined stainless-steel autoclave with a solvent containing Ethylene glycol, $FeCl_3 \cdot 6H_2O$, trisodium citrate dihydrate, and Urea. In this investigation, reaction times between 6 and 12 h were studied to find optimum conditions for enhancing the removal of fluoride. Finally, the particles precipitated after the solvothermal treatments were magnetically separated from the hydrothermal solution at 6 h, 8 h, 10 h, and 12 h, respectively. The samples were named MS1, MS2, MS3, and MS4. Fluoride kinetic adsorption experiments were conducted with different initial pH values (3 and 5), dosages of 0.1–1.0 g/L, and contact times (60–180 min). The initial concentrations of fluoride was 5 mg/L. Fluoride levels were measured using a fluoride ion-selective electrode (Orion 9609BNWP, Thermo Scientific, USA, by adding 1 mL of TISABIII to the samples before determination.

RESULTS & DISCUSSION

XRD analysis of MSs (Figure 1) was carried out using an XRD Xpert-Philips PW3040 diffractometer. The XRD results confirmed the crystalline structure for all four samples and corresponded to the standard peaks of Fe_3O_4 (the Joint Committee on Powder Diffraction Standards (JCPDS):19-0629). Relative crystallinity of MSs by hydrothermal method with varying reaction times of 6 h, 8 h, 10 h, and 12 h was 22.41%, 22.47%, 23.39%, and 24.08%, respectively.

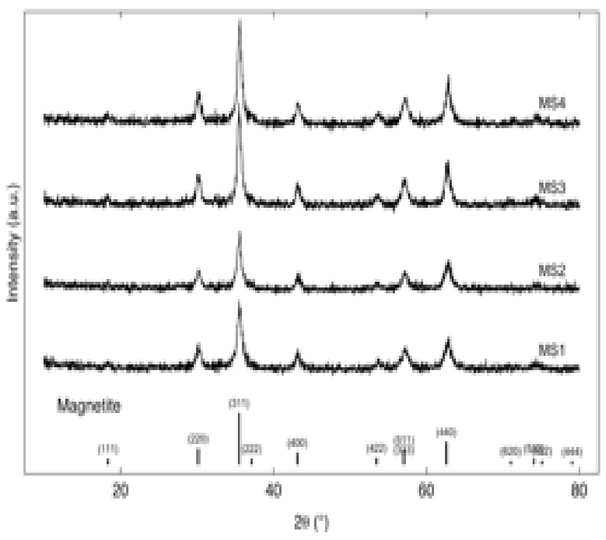

Figure 1. XRD patterns of MSs with varying reaction times of 6-10 h.

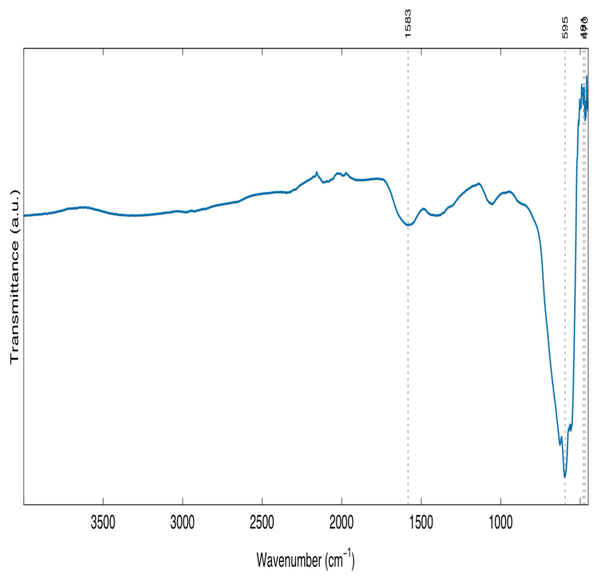

Figure 2. FTIR spectra of magnetite nanoparticle (MS3).

FTIR spectroscopy was carried out with a Frontier FT-IR/NIR spectrometer. FTIR spectra of magnetite nanoparticles (MS3) are shown in Figure 2. The absorption bands at 1577 cm^{-1}, 598.86 cm^{-1}, and 464.74 cm^{-1} correspond to H-O-H bending vibrations and Fe-O bonds (Silva C. et al., 2020).

The morphology of MSs, using scanning electron microscope with focused ion beam (SEM/FIB) FEI brand, Scios model. SEM images (Figure 3) confirmed that the obtained particles were magnetite in the form of homogeneous spherical particles, offering controlled particle sizes ranging from 13.49 nm to 61.64 nm.

RESULTS & DISCUSSION

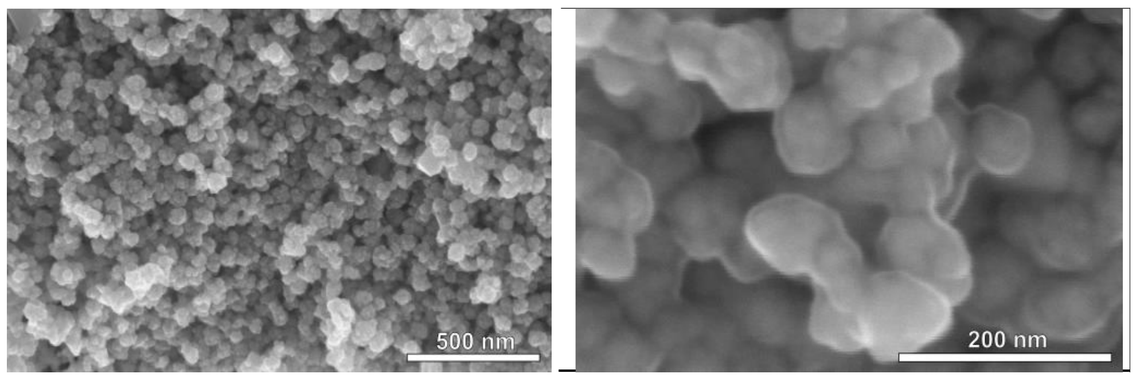

Figure 3. SEM images of magnetite nanoparticle (MS3).

Transmission electron micrographs were obtained using a transmission electron microscope (TEM), FEI Talos F200S G2, operating at 200 kV. TEM images showed an agglomeration of spherical iron nanoparticles. Selected area electron diffraction (SAED) patterns confirmed the crystallinity of magnetite. The elemental composition of magnetite nanoparticles was analyzed by energy-dispersive X-ray spectroscopy (EDS) and found to consist of 43.36% oxygen and 56.63% iron.

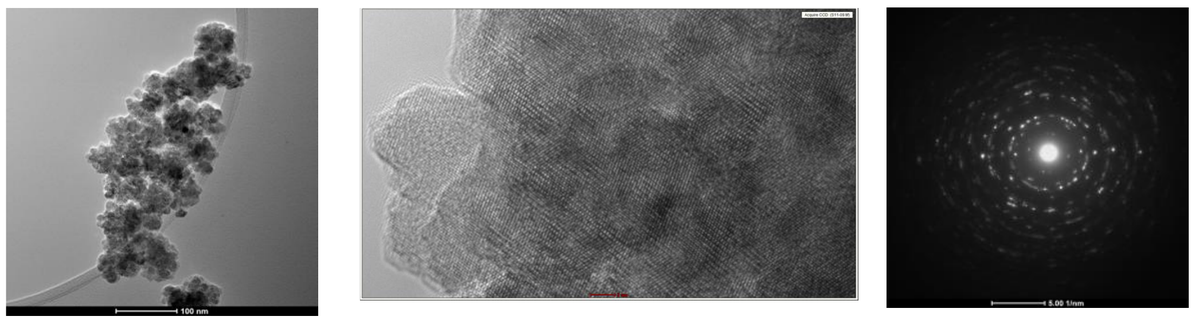

Figure 4. (a) TEM images (b) High-resolution TEM (HRTEM) micrographs (a) and Selected Area Electron Diffraction (SAED) diffractogram of MS3

MS3, synthesized with a reaction time of 10 hours, was found to be optimal for fluoride removal efficiency, which was approximately 44.89% higher than that of the other MSs. Adsorption kinetics were studied with varying pH (3 and 5) and dosage (0.1 and 1.0 g/L) to investigate fluoride removal. The parameters and error indices of various kinetic models, including the Power equation, Elovich, PSO, and PFO models, were analyzed using MS3. The Power equation outperformed the other models in fitting the experimental data of MS3 with pH 5 and dosage of 1 g/L, as it obtained higher R^2 values (0.9899) and lower RMSE values (0.0215). The synthesized MS exhibited excellent fluoride adsorption capacities, even at low dosages and short contact times within 3 h. The nanoparticles' performance was influenced by pH, with a slightly higher adsorption efficiency observed at pH 5 compared to pH 3.

CONCLUSION

This study successfully synthesized magnetite nanoparticles using a solvothermal method. The solvothermal method proved effective in producing magnetite nanoparticles with a controlled size distribution and desired morphology. The synthesized MS with a reaction time of 10 h demonstrated efficient fluoride removal capabilities, with optimal performance observed under specific conditions.

FUTURE WORK / REFERENCES

Future research could explore scaling up the synthesis process and evaluating the long-term stability and reusability of these nanoparticles.

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