

Proceeding Paper

# Anion Removal by Magnetic Carbon Xerogel Nanocomposite: The Role of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles, Catalyst, Carbonization, and H<sub>2</sub>O<sub>2</sub> Surface Modification <sup>†</sup>

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**Abstract:** Magnetic carbon xerogel composites with Fe<sub>3</sub>O<sub>4</sub> nanoparticles (MNPs) prepared via co-precipitation can effectively remove arsenic (As(V) and As(III)) and fluoride ions from groundwater. The optimum conditions for the synthesis of these materials were studied, including the molar ratios of MNPs and catalyst. Carbonization and post-synthesis treatment with H<sub>2</sub>O<sub>2</sub>-induced surface modification were applied. SEM and Fe analysis revealed the presence of Fe in the materials. This study provides a promising new method for the removal of arsenic and fluoride from groundwater, with the feasibility of reusing adsorbent and magnetic separation, which could have a significant impact on public health.

**Keywords:** arsenic; fluoride; carbon xerogels; kinetic model; magnetic nanoparticles; surface modification

## 1. Introduction

The high concentration of arsenic and fluoride in groundwater is a major issue in Mexico and other parts of the world [1]. These pollutants can have adverse health effects [2]. The maximum permissible limit of the World Health Organization (WHO) for arsenic and fluoride in drinking water is less than 10 µg/L and 1.5 mg/L, respectively.

The application of nanoadsorbents cannot easily increase the adsorption efficiency of various contaminants due to the nano size of the adsorbent, high surface area, high reactivity, and large number of active sites [3]. Iron oxide-based adsorbents with magnetic properties have been shown to be effective for the removal of different anionic and cationic species in water and wastewater treatment, and they can be separated using external magnetic fields [4]. Macroporous xerogel carbon with a 3D interconnected structure based on the polycondensation of resorcinol (R), formaldehyde (F), and catalyst solutions (C) is interesting due to its nanostructures and can be applied to various applications [5].

This research focuses on the generation of magnetic materials that can be easily recovered from the aqueous medium. Modified RF organic carbons were synthesized by doping iron oxide nanoparticles into the carbonaceous structures of xerogel to remove anions from water. The performance of As(V), As(III), and  $F^-$  adsorption on magnetic carbon xerogels with varying molar ratios of  $Fe_3O_4$  nanoparticles (MNPs) prepared using different methods, alkaline catalysts, and surface modification was investigated. The kinetic adsorption of anions was conducted in a batch system using synthetic aqueous solutions and groundwater.

## 2. Materials and Methods

### 2.1. Preparation of $Fe_3O_4$ Nanoparticles and Magnetic Carbon Xerogel Nanocomposites

In this study, MNP materials were synthesized via three modified methods, as described in a previous investigation [6]: conventional co-precipitation (MC), conventional oxidation (MO), and solvothermal (MS). Magnetic carbon xerogel composites with  $Fe_3O_4$  nanoparticles were prepared through direct sonication with a molar ratio of  $R/F = 0.5$  and water content of  $R/W = 0.06$ , and they were synthesized by loading different MNPs (MO, MC, and MS), with  $M/R$  molar ratios of 0.01 and referred to as XMO, XMC, and XMS, respectively.  $Na_2CO_3$  was used as alkaline catalyst in the polycondensation of RF and was considered to compare the molar ratios of  $R/C$  between 100 and 200 with MC only with  $M/R = 0.1$ ; finally, they were obtained and named as XMC1 and XMC2, respectively.

After carbonization, the following conditions were applied to obtain magnetic carbon xerogels: pyrolysis temperature of 600 °C, heating ramp of 2 °C/min for 6 h, and nitrogen flow of 100 mL/min. Post-synthesis treatment by  $H_2O_2$ -induced surface modification was applied to enhance the binding of metal on the surface of xerogels [5]. The final materials were denoted as XMC1-600M and XMC2-600M.

### 2.2. Characterization

The morphology of the materials was analyzed using an FEI-FIB Dual Beam (Helios Nanolab 600, FEI Company, Hillsboro, OR, USA) with electron beams accelerated by a low-voltage power supply (5 kV). The Fe content in the magnetic carbon xerogel nanocomposites was analyzed using an atomic absorption spectrometer (AAS) (Analyst 400, Perkin Elmer, Waltham, MA, USA).

### 2.3. Adsorption of Anions and Determination of Arsenic and Fluoride

For the preliminary study, fluoride adsorption was conducted on magnetic carbon xerogels at pH 3 and 5, for contact times of 4 h and 24 h, with dosages of 1 g/L and initial concentrations of 7.55 mg/L.

Adsorption of As(V) and As(III) was conducted at pH 3, with dosages of 2 g/L and initial concentrations of 0.1 and 0.75 mg/L, respectively. The adsorption kinetic study was performed for  $F^-$ , As(III), and As(V) at pH 3, with a dosage of 2 g/L and initial concentration of 5.23, 1.0, and 0.5 mg/L, respectively. The adsorption was performed for 10–480 min.

Finally, ternary adsorption of anions on magnetic carbon xerogels from aqueous solution and groundwater was performed at pH 3, with a dosage of 2 g/L and initial concentrations of 0.5, 0.5, and 5.24 mg/L, respectively. Groundwater from the state of Durango, Mexico (coordinates 24°04'65.5" N 104°58'89.8" W), was used in the adsorption experiments. The physicochemical properties of the groundwater were analyzed for  $Cl^-$ ,  $F^-$ , As, Fe, Mn,  $NO_3^-$ ,  $SO_4^{2-}$ , and  $PO_4^{3-}$ , which were 2.9, 4.24, 0.06, 0.02, 0.009, 1.55, 6.5, and 0.5 mg/L at pH 6. Due to the low concentration of arsenic, As(III) and As(V) were added to the groundwater.

After the batch adsorption experiment, the residual concentrations of arsenic samples were determined using a fast sequential flame atomic absorption spectrometer (AAS), SpectrAA-220 (Varian, Inc., Mulgrave, VIC, Australia). Fluoride was determined potenti-

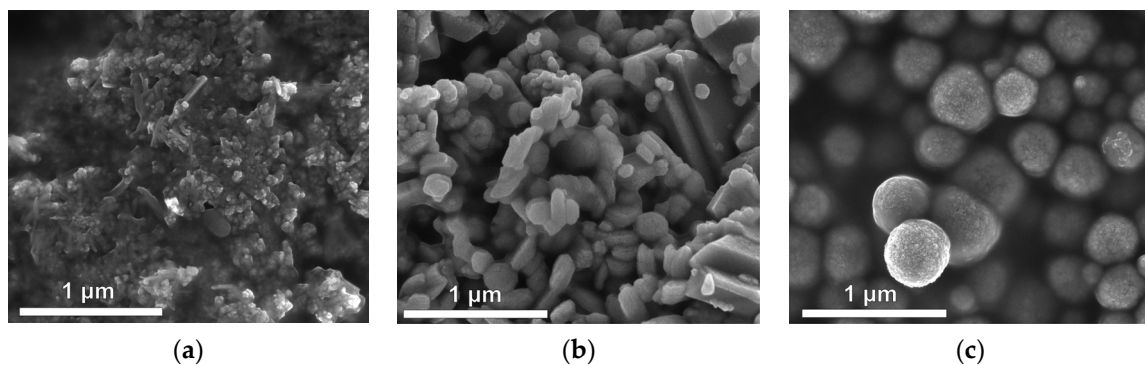
metrically using a fluoride ion-selective electrode (ISE), 9609BNW (Thermo Scientific™, Waltham, MA, USA).

### 3. Results

#### 3.1. Characterization of Magnetic Carbon Xerogel Nanocomposites

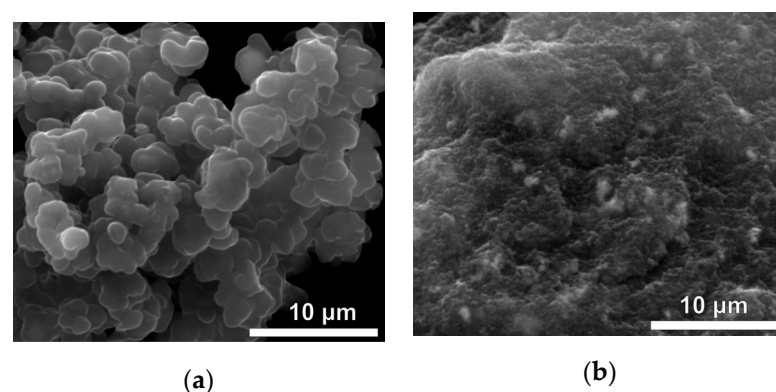
Magnetic xerogels were synthesized by loading different MNPs, MO, MC, and MS, with M/R molar ratios of 0.01 and 0.1. The Fe contents by weight in the synthesized magnetic xerogels XMC, XMC1-600M, and XMC2-600M were 0.59%, 3.9%, and 4.42%, respectively, as determined via AAS.

Figure 1 shows the morphological study of  $\text{Fe}_3\text{O}_4$  nanoparticles. Figure 1a, SEM images of MNPs prepared via conventional co-precipitation (MC), shows small, quasi-spherical particles, with a diameter of about 9.1–27.9 nm [7]. This is relatively smaller than MNPs synthesized via conventional oxidation (MO) and solvothermal (MS) methods. MO shows  $\text{Fe}_3\text{O}_4$  nanoparticles of various dimensions and irregular shapes (Figure 1b), while MS shows uniformly sized microspheres with a diameter of approximately 300 nm (Figure 1c), which is larger than the reported value of 180 nm [8].



**Figure 1.** SEM images of  $\text{Fe}_3\text{O}_4$  nanoparticles via (a) conventional co-precipitation (MC), (b) conventional oxidation (MO), and (c) solvothermal method (MS).

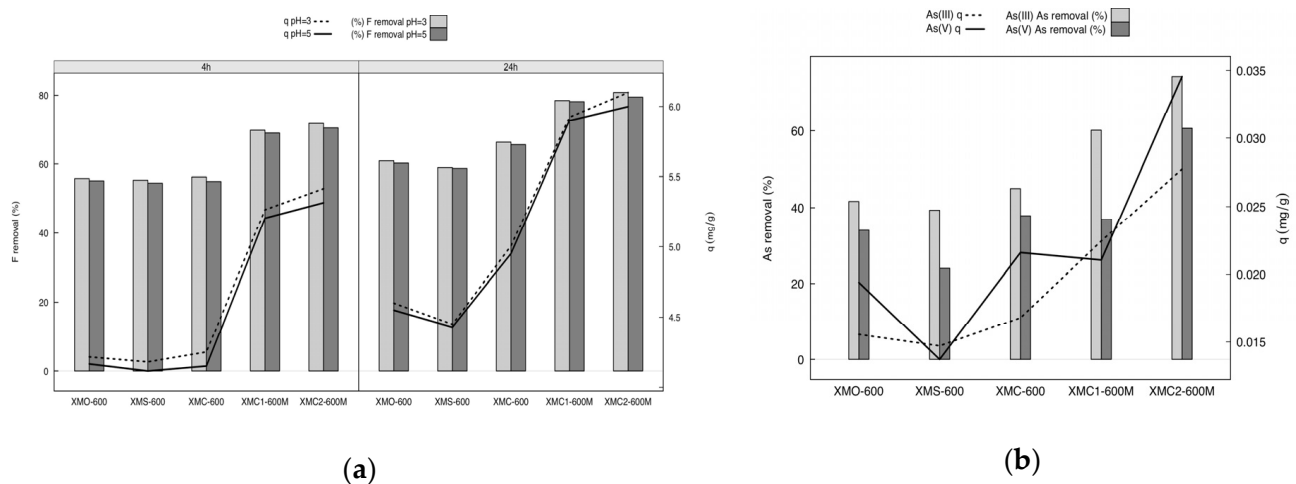
XMC2-600M has smaller polymer particles and more compact microclusters than XMC1-600M because of the reduced R/C ratios (Figure 2).



**Figure 2.** SEM images of magnetic carbon xerogel nanocomposites with R/W = 0.06, M/R = 0.1, and R/C ratios of 200 and 100 for (a) XMC1-600M and (b) XMC2-600M, respectively.

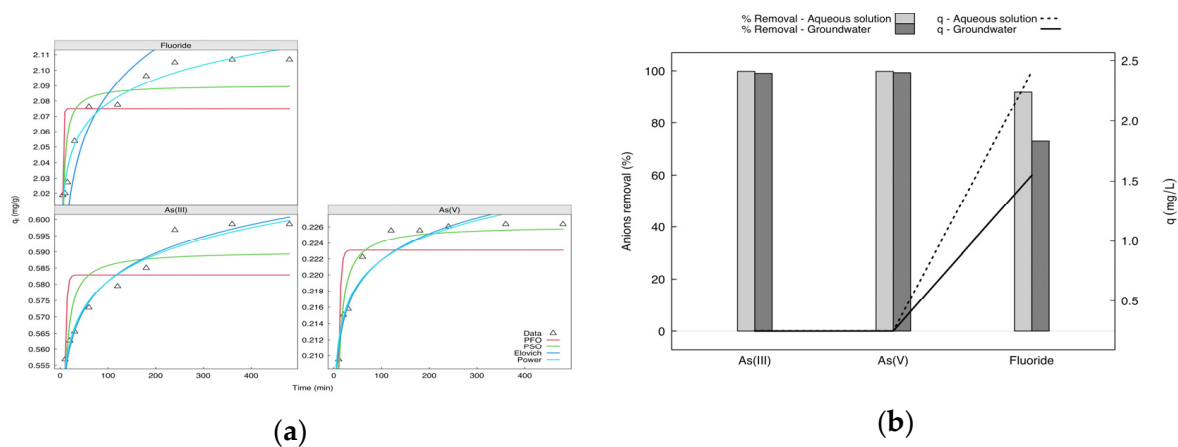
#### 3.2. Batch Adsorption Experiments for Anions

Preliminary studies with variations in the molar ratios of M/R (0.01 and 0.1) and R/C (100 and 200) of magnetic carbon xerogels showed that the addition of  $\text{Fe}_3\text{O}_4$  nanoparticles to XMC2-600M can significantly improve the removal of fluoride and arsenic, as shown in Figures 3a and 3b, respectively.



**Figure 3.** Preliminary study of adsorption of (a) fluoride and (b) arsenic (As(III) and As(V)) onto magnetic carbon xerogel nanocomposites with variation in M/R and R/C.

The adsorption kinetics experimental data were analyzed with non-linear regression using four kinetic models: the pseudo-first-order model (PFO), the pseudo-second-order model (PSO), the Elovich equation, and the power function equation. Figure 4a shows the adsorption kinetic curves of As(III), As(V), and  $F^-$  from the aqueous solution. The anion adsorption was initially rapid in the first 10 min, followed by a slower and decreasing phase with time until it gradually approached equilibrium at 240 min.



**Figure 4.** (a) Kinetic adsorption and (b) ternary adsorption from aqueous solution and groundwater of As(III), As(V), and  $F^-$  on magnetic carbon xerogel nanocomposites.

The adsorption of anions in ternary systems of aqueous solutions and groundwater was studied in a batch system (Figure 4b). The results showed that XMC2-600M ( $R/C = 100$ ,  $R/W = 0.06$ ,  $M/R = 0.1$ ) had the highest removal of As(V), As(III), and  $F^-$  from aqueous solution, approximately 99.58%, 99.58%, and 91.99%, respectively. When applied to groundwater, the removal of As(V), As(III), and  $F^-$  on XMC2-600M was 99.28%, 99.0%, and 73%, respectively.

#### 4. Discussion

The Fe content of the magnetic xerogels increased with increasing M/R molar ratios by approximately six-times from 0.01 to 0.1. The decrease in the R/C molar ratio significantly changed the morphology of the final material, leading to an increase in the relative density and a decrease in the void space. This is because the increased mass per unit volume led to a more compact structure [9].

The co-precipitation method is a simple and effective way to synthesize MNPs that have good removal and adsorption capacity for arsenic and fluoride. This is because it uses a stoichiometric ratio of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  as an iron source [10]. Increasing the molar ratios of M/R can further improve the adsorption capacity.

The kinetic study found that the PSO model is the best fit for the As(V) adsorption process, and the power function model is the best fit for the adsorption of all three anions. The results also suggest that the adsorption process is chemisorption and that the rate of adsorption of As(V) is higher than As(III).

The presence of  $\text{F}^-$  in the mixed solution had an insignificant influence on the adsorption of As(III) and As(V) in both types of solutions. However, the amount of  $\text{F}^-$  adsorbed on magnetic carbon xerogel in the ternary system of groundwater was less than in the aqueous solution. This was attributed to the competition of  $\text{F}^-$  with other ions for active sites on the surface of the adsorbent. Specifically, arsenate and sulfate ions bound  $\text{F}^-$  on the surface of the adsorbent, reducing the availability of active sites for  $\text{F}^-$  adsorption [11].

## 5. Conclusions

The molar ratios of resorcinol, MNPs, and catalyst were varied to investigate the anion adsorption capacity by designing materials with different structures. Magnetic carbon xerogel composites with MNPs prepared via co-precipitation had a greater effect on the adsorption of arsenic (As(V), As(III)), and fluoride than other methods. The carbonization process and the post-treatment with  $\text{H}_2\text{O}_2$  play a role in increasing the adsorption capacity. These materials can be tailored to effectively adsorb anions from aqueous solution and groundwater, and they can be easily recovered from the aqueous phase for reuse using an external magnet.

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