Development of alumina/iron oxide nanocomposites as adsorbents for arsenic and fluoride removal from aqueous solutions: Process Optimization

T.C. Prathna[*], S.K. Sharma[*] and M. Kennedy[1*]

[*]Environmental Engineering and Water Technology, UNESCO-IHE Institute for Water Education, 2601 DA, Delft, The Netherlands, p.thanjavur@unesco-ihe.org; s.sharma@unesco-ihe.org
[1]Faculty of Civil Engineering, Delft University of Technology, Stevinweg 1, 2628 CN, Delft, The Netherlands, m.kennedy@unesco-ihe.org

ABSTRACT

The study was designed to optimize the process for the synthesis of alumina/ iron oxide nanocomposites and to investigate their potential as a sorbent to remove fluoride and arsenic from contaminated water. The nanocomposites had a size range between ~250-500 nm. Process variables such as the weight of iron oxide nanoparticles added during the course of synthesis of the nanocomposites and the duration of calcination were studied as a function of particle size and As and F removal potential. Increase in the weight of iron oxide nanoparticles (from 0.05 g to 0.1 g) added during the course of synthesis did not lead to a significant change in the particle size measurements nor did it increase the As and F removal capacity. Increase in the duration of calcination at 550 ºC led to a corresponding increase in the particle size from 219 ± 13.31 nm to 273 ± 19.49 nm. The sorption data for As (III), As (V) fitted best to Freundlich isotherm while for F it fitted the Langmuir isotherm. Increase in the duration of calcination from 1h to 3h showed increased q_m values for As (V) and F. The results demonstrated that 0.05 g of iron oxide nanoparticles added during synthesis and calcination of the composites at 550 ºC/3h was sufficient for optimum As and F removal.

Keywords: iron oxide, alumina, nanoparticles, arsenic, fluoride

1 INTRODUCTION

Contamination of drinking water sources continues to pose a challenge in almost all parts of the world and thus one of the Sustainable Development Goals (SDG 6) of the United Nations is to ensure universal access of safe drinking water to all by 2030 [1]. Among the various inorganic contaminants in water, arsenic (As) and fluoride (F) have been determined to be the contaminants most detrimental to human health. Hence treating drinking water for both arsenic and fluoride assumes utmost importance.

Studies have indicated the co-existence of both arsenic and fluoride in many aquifers and hence there is an urgent need to develop techniques to simultaneously remove both arsenic and fluoride [2,3]. The major challenge is to design and optimize a material which is safe and easy to use at both household and small community levels which would go a long way in reducing treatment cost.

Our previous study investigated the fluoride and arsenic removal potential of iron oxide nanoparticles and observed significant adsorption towards arsenic. However, the fluoride removal potential was insignificant as compared to other adsorbents. Since alumina is known for its affinity towards fluoride and iron oxide based materials towards arsenic [4], the objectives of the present study were to optimize the process for the synthesis of alumina/iron oxide nanocomposites towards effective arsenic and fluoride removal. The effect of process variables were determined as a function of particle size and arsenic and fluoride removal potential.

2 METHODOLOGY

2.1. Synthesis of nanocomposites

The method of Amirsalari et al [5] was followed with modifications. Briefly, 3.75 g of Al $(NO_3)_3.9H_2O$ was dissolved in 100 ml of deionized water and the solution was heated to 60 ºC. The solution was then precipitated by the addition of 2 mol/L NH_3 solution at the rate of 2 ml/min. To the obtained aluminium hydroxide gel, different amounts of prepared iron oxide nanoparticles [6] were added and stirring was continued at room temperature for 12 h. The resultant solution was then centrifuged and the pellet further calcined at 550 ºC for different duration of time.

2.1.1. Effect of process parameters

2.1.1.1. Effect of iron oxide nanoparticles

To determine the effect of iron oxide nanoparticles in the final nanocomposite on arsenic and fluoride removal, different weights of iron oxide nanoparticles, namely, 0.05 g and 0.1 g were added during the course of synthesis.

2.1.1.2. Effect of calcination

To determine the effect of the duration of calcination on fluoride and arsenic removal, the synthesized nanocomposite was calcined under different conditions namely, without calcination, calcination at 550 ºC/1 h and 550 ºC/3 h.

2.2. Physico-chemical characterization

The particle size and morphology of the nanocomposites was measured using a Particle size analyzer and Scanning Electron Microscopy.

2.3. Batch Adsorption studies

Effect of As(III) and As(V) concentration on adsorption by synthesized nanocomposite was determined by adding 0.05 g of nanocomposite in 50 mL of 500 µg/L As(III) and As(V) respectively. Studies were carried out at pH 7. Similarly effect of F concenration on adsorption by the nanocomposite was determined by adding 0.05 g of nanocomposite in 10 mg/L of F.

3   RESULTS AND DISCUSSION

3.1.   Synthesis   of   alumina/iron   oxide nanocomposites

In the current study, iron oxide nanoparticles of ~130 nm (as observed by SEM analysis) were synthesized and added to the aluminium hydroxide gel for the synthesis of iron oxide/alumina nanocomposites. A change in colour from white to brown was observed upon the addition of iron oxide nanoparticles. The dried particles obtained were characterized further using particle size and zeta potential analysis. We observed that the particles had a zeta potential of -21.23 ± 0.50 at pH 8 while the average particle size was 219 ± 13.31 nm with a polydispersity of 0.345 when 0.05 g of iron oxide nanoparticles were added to the aluminium hydroxide gel and later calcined at 550 ºC/1h. Zeta potential data is often used to predict the colloidal stability of a solution and based on literature, the zeta potential results obtained in the current study indicate that the nanocomposites are moderately stable at pH 8 [7]. According to the DLVO theory on colloidal stability, the solution stability depends on the sum of the van der Waal`s attractive forces and the electrostatic repulsive forces due to the double layer [8]. However, zeta potential results only provide information on the electrostatic repulsive forces as they measure the potential difference between the electric double layer surrounding the particle and the layer of dispersant around the double layer at the slipping plane [9]. Hence, zeta potential studies though may reflect on the surface potential of the particles, they may not paint a complete picture as regard to stability of a solution.

The morphology and elemental composition of the particles was confirmed using SEM-EDAX analysis. It was observed that the particles were polydisperse with nearly spherical particles in the range between ~250 nm to ~550 nm further forming larger agglomerates (Figure 1). Through SEM analysis, we attempted to determine whether iron oxide nanoparticles served as a template for the further growth   of   the   alumina   nanomaterials.   However, observation, at the magnification studied, did not present a clear picture. EDAX analysis confirmed the presence of Fe and Al peaks in addition to O peaks.
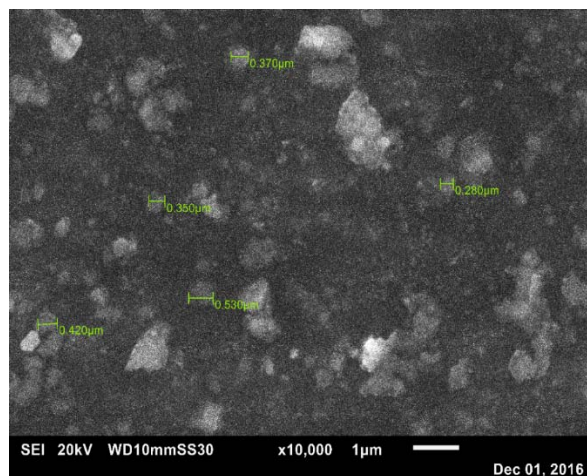

Figure 1: SEM micrograph of alumina iron oxide nanocomposites

3.1.1. Effect of iron oxide nanoparticles

Experiments were performed to optimize the weight of iron oxide nanoparticles added during the course of synthesis. The weight of iron oxide nanoparticles were increased from 0.05 g to 0.1 g.

3.1.1.1. On particle size

The particle size decreased from 219 ± 13.31 nm to 208.1 ± 19.32 nm when the weight of iron oxide nanoparticles increased from 0.05 to 0.1 g. To summarize, increase in the weight of iron oxide nanoparticles in the sample did not lead to a significant change in the size of the nanocomposites obtained.

3.1.1.2. On adsorption

3.1.1.2.1. Fluoride

The adsorption capacity of the nanocomposites towards fluoride were tested at a fixed initial concentration of fluoride of 10 mg/L. Increase in the weight of iron oxide nanoparticles led to a slight decrease in the adsorption capacity though no trend was observed. The adsorption capacity of the nanocomposites was 3.6 mg/g and slightly decreased to 1.72 mg/g when the iron oxide nanoparticle content increased from 0.05 g to 0.1 g of respectively. The decrease in the adsorption capacity could possibly be due to the decrease in alumina content in the nanocomposites with increasing concentration of iron oxide nanoparticles. The results of the study made it clear that 0.05 g of iron oxide nanoparticles were sufficient enough for efficient fluoride removal.

3.1.1.2.2. Arsenic

Similarly, the adsorption capacity of the nanocomposites towards As(III) and As(V) were tested at a fixed initial concentration of 500 µg/L. It was significant to note that increase in the weight of the iron oxide nanoparticles did not significantly affect the adsorption capacity of both As (III) and As(V).

The studies on As (III), As (V) and F made it clear that an optimum concentration of 0.05 g of iron oxide nanoparticles added to the nanocomposites during the synthesis was enough to generate efficient arsenic and fluoride adsorption. The results are tabulated in table 1.

Adsorbent	Mass of IONP (g)	Adsorption Capacity		
		As (III) (µg/g)	As (V) (µg/g)	F (mg/g)
Nanocomposites	0.05	331.25	418.05	3.60
	0.1	240.75	438.19	1.72

Table 1: Effect of iron oxide nanoparticles (IONP) on As and F adsorption

3.1.2. Effect of calcination

The next part of the study determined the effect of calcination conditions on the particle size and ultimately the arsenic and fluoride removal efficiency. In the current study, the duration of calcination was varied from 550 ºC/1 h to 550 ºC/2 h and 550 ºC/3 h.

3.1.2.1. On particle size

There was a slight inrease in the particle size on increasing the duration of calcination. We observed that on increasing the duration of calcination from 1h to 3h there was a small corresponding increase in the particle size from 219.63 ± 13.31 nm to 236.00 ± 8.88 nm. Increase in calcination treatment has been observed to cause an increase in the crystallinity and particle size of cerium oxide nanoparticles [10].

3.1.2.2. On adsorption

3.1.2.2.1. Fluoride

Effect of duration of calcination of nanocomposites on F removal was analysed by applying batch adsorption isotherm experiments at different initial concentrations of F. Table 2 shows the result of batch adsorption isotherm and the R^2 values indicated that the sorption data fit with

Langmuir isotherm and an increase in q_m values was observed with increase in calcination duration.

Calcination	Freundlich			Langmuir	
	k (mg/g)	1/n	R^2	q_m (mg/g)	R^2
1 h	1.35	0.41	0.98	2.95	0.99
3 h	1.86	0.41	0.97	4.00	0.98

Table 2: Freundlich and Langmuir isotherm values for F sorption under varied calcination conditions

3.1.2.2.2. Arsenic

Increase in the duration of calcination (from 1 h to 3 h) led to an increase in the k values (13.32 µg/g to 18 µg/g) for As (III) sorption and the data fit with the Freundlich model isotherm. However, in case of As (V), there was a decrease in k values with increase in duration of calcination. Moreover, As (V) was adsorbed more efficiently by nanocomposites when compared to As (III). The Freundlich isotherm for As (V) sorption is shown in Figure 2.
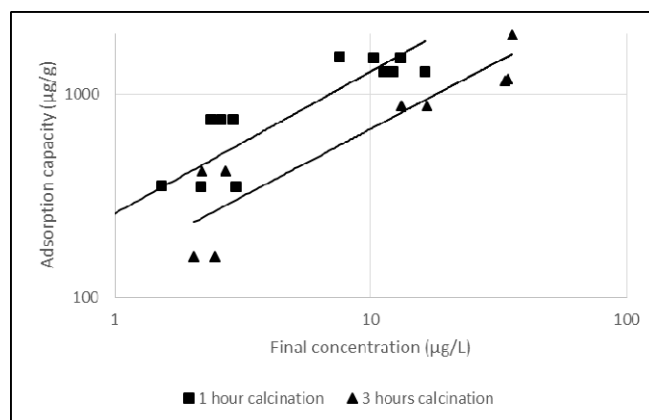

Figure 2: Freundlich isotherm for As (V) sorption under varied calcination condition

Since nanocomposites prepared with 3 h calcination showed enhanced adsorption of As (III) and F, for further studies calcination of the nanocomposites at 550ºC/3h has been carried out.

4 CONCLUSION

1. The present study focussed on the optimization of the process for the synthesis of iron oxide alumina nanocomposites for effective removal of arsenic and fluoride from aqueous solutions.
2. Process parameters like the weight of iron oxide nanoparticles added during the course of synthesis and the duration of calcination were studied in detail as a function of particle size and As and F removal capacity.
3. Increase in the weight of iron oxide nanoparticles from 0.05 g to 0.1 g did not lead to a significant change in

the particle size. Results indicated that 0.05 g of iron oxide nanoparticles was sufficient to significantly adsorb both As and F.

4. Increase in the duration of calcination from 1h to 3h at 550 ºC led to a slight increase in the particle size and also a decrease in the As (V) removal capacity. It however, enhanced the F and As (III) removal capacity. Results indicated that calcination at 550 ºC/3 h was required to significantly adsorb As and F at the concentration studied.

5. Detailed studies are currently being carried out to provide insight into the various factors affecting the adsorption of F and As(III) and As(V) by synthesized nanocomposites.

ACKNOWLEDGEMENTS

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