



# Magnetic Core Nanoparticles Coated by Titania and Alumina for Water and Wastewater Remediation from Metal Contaminants

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Nanomaterials have been widely used for remediation of contaminated streams. However, using nanomaterials within water and wastewater might be dangerous since fate and health impact of nanoparticles is still unknown. Therefore, it is mandatory to avoid contamination by removing all the nanoparticles from the treated stream. This can be performed by immobilizing the nanoparticles on supports, although this approach leads to lower efficiency values. Another possibility is to use suspended nanoparticles: in this case, efficiency of the treatment process is enhanced. If nanomaterials have a magnetic core-shell, then suspended nanoparticles can be removed in a safe and easy way by using magnetic traps.

In the present study, new nanomaterials based on magnetic core-shell structure were developed: the magnetic core guarantees a complete removal from the treated water and wastewater streams, whereas the shell (coating) is functionalized to eliminate specific classes of pollutants.

A first experimental step allowed to produce the magnetic nanoparticles and perform a coating with SiO<sub>2</sub> in order to electrically isolate the core from the ambient and to avoid degradation. This procedure is well established and the production of SiO<sub>2</sub> coated magnetic nanoparticles are nowadays a validated procedure by using a spinning disk reactor. In a successive step, the silica shell magnetic cores were coated by titania and/or activated alumina particles with the aim of removing metals by adsorption.

In the present study, the arsenic adsorption capacity of silica shell magnetic cores nanoparticles coated by titania and/or activated alumina was investigated through kinetic experiments.

All the tested adsorbents performed very well showing very rapid rates of the adsorption process. Among them, the best performing media were found to be those with titania coating. The best fitting kinetic model was found to be the pseudo-second order one for all of the adsorbents.

## 1. Introduction

Nanomaterials have been widely used for remediation of contaminated streams. However, fate and health impact of nanoparticles added to water and wastewater is still unknown. Therefore, it is mandatory removing all the nanoparticles after treatment in order to avoid any possible contamination. If nanoparticles are being immobilized on fixed supports, then their migration is prevented; however, the use of a fixed bed can reduce removal efficiency of contaminants due to their slow diffusion rate within the fixed porous bed.

Another possibility is to use suspended nanoparticles: in this case, efficiency of the treatment process is enhanced due to the higher rate of the mass transfer process. If nanomaterials have a magnetic core-shell, then suspended nanoparticles can be removed in a safe and easy way by using magnetic traps.

More recently nanomaterials have been successfully applied for the removal of arsenic among other contaminants from aqueous solution (EPA 2003a; EPA2003b). Nanoscale zerovalent iron (nZVI) demonstrated to be effective for the removal of arsenic through reduction mechanism to elemental arsenic which in turn immobilizes the arsenic anions onto the iron for easy removal (Ramos et al., 2009). Nanoparticles

can also be surfacemodified for environmental applications (Luther et al., 2012), e.g. by coating with activated alumina or titania oxide to enhance their reactivity to arsenic (Chiavola et al., 2016a).

The present study shows the results of an experimental activity aimed at investigating the arsenic adsorption capacity of silica shell magnetic cores nanoparticles coated by titania and/or activated alumina.

Magnetite nanoparticles were chosen since have large specific surface area with a strong tunneling effect and a small size of the border effect which might be useful for the adsorption process; furthermore, they possess the general properties of ordinary iron and therefore potentially a high affinity to arsenic. Magnetite is a naturally occurring mineral, but can be also easily prepared in the laboratory from solutions containing ferric and ferrous ions. The iron nanoparticles have a uniform particle size, high purity and low contents of carbon, nitrogen, oxygen, sulfur, phosphorus and other harmful elements. Previous studies showed the ability of iron-based magnetic nanoparticles to reduce very rapidly arsenic concentration below the limit concentration set for drinking water (i.e. 10  $\mu\text{g/L}$ ) (Chiavola et al., 2016b).

Alumina has been widely investigated due to its potential capacity of adsorbing a wide range of contaminants, such as arsenic. In particular, activated alumina (AA), prepared by thermal dehydration of aluminium hydroxide, has a high surface area and a distribution of both macro- and micro-pores, which make it more suitable for efficient uptake. The United Nations Environmental Program agency has classified AA adsorption among the best available technologies for arsenic removal from water (Jain and Singh, 2012).

Several studies have been performed to evaluate the adsorption capacity of  $\text{TiO}_2$  for As(V) and As(III) removal from water. Nanocrystalline titanium dioxides ( $\text{TiO}_2$ ), with an average particle size of 6 nm, showed to have the ability to remove both arsenate and arsenite (Pena et al., 2006). Tchieda et al. (2016) observed similar values of the maximum adsorption capacity at equilibrium (about 8 mg/g) of synthesized alumina, powder alumina, and  $\text{TiO}_2$ -coated alumina calcinated at 450°C, under similar operating conditions. The results obtained highlighted the beneficial effect due to either the reduced particle size of the adsorbent or the  $\text{TiO}_2$  coating.

Based on these previous results, it was decided to investigate in the present study the arsenic adsorption capacity of magnetic core nanoparticles prepared with different coatings consisting of pure titania, pure AA and a mix of titania and AA. For each sample, the uptake capacity was measured through kinetic experiments.

## 2. Materials and methods

### 2.1 Adsorbents

Three different adsorbent media were tested: (1) ferromagnetic nanoparticles with a  $\text{SiO}_2$  core shell and activated alumina (AA) coating (FM/Al); (2) ferromagnetic nanoparticles with a  $\text{SiO}_2$  core shell and titanium dioxide ( $\text{TiO}_2$ ) coating (FM/ $\text{TiO}_2$ ); (3) ferromagnetic nanoparticles with a  $\text{SiO}_2$  core shell and activated alumina and titanium dioxide coating (FM/Al- $\text{TiO}_2$ ).

The core-shell  $\text{SiO}_2/\text{Fe}_3\text{O}_4$  nanoparticles (FM) were prepared by two steps. Firstly,  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were synthesized using a spinning disk reactor. Due to the excellent micromixing conditions achieved by this device, the magnetite nanoparticles precipitate immediately and are washed by distilled water using a centrifuge (De Caprariis et al., 2012) (Figure 1).

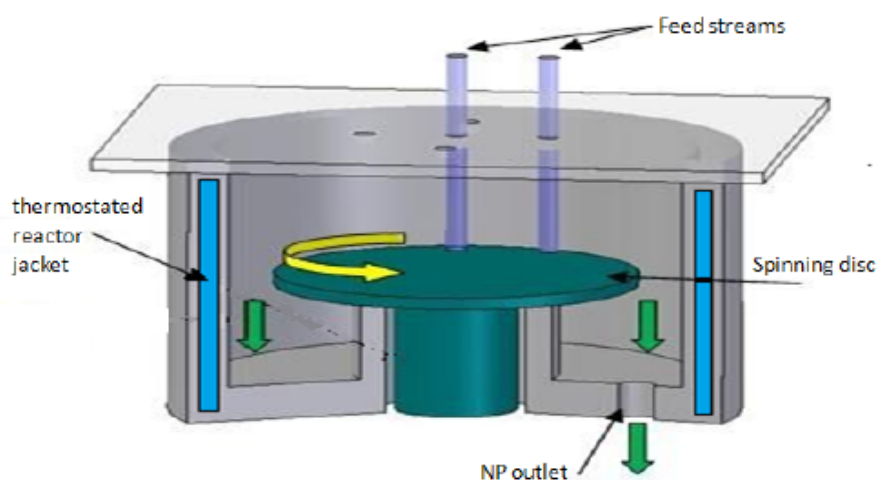


Figure 1: Scheme of the adopted spinning disk reactor.

Then, FM nanoparticles were prepared by dispersing  $\text{Fe}_3\text{O}_4$  particles in distilled water, followed by the addition of  $\text{C}_2\text{H}_5\text{OH}$  (Sigma Aldrich). Tetraethyl ortosilicate (TEOS), preliminarily diluted in  $\text{C}_2\text{H}_5\text{OH}$ , was added drop-wise to the  $\text{Fe}_3\text{O}_4$  particle suspension. Then, an aqueous solution of  $\text{NH}_3$  (30 wt %) was added and the TEOS hydrolysis and condensation were allowed under overnight gentle stirring. The obtained FM particles were washed in a centrifuge using firstly water/ethanol mixtures, and then distilled water. Finally, they were dried and calcinated at  $450^\circ\text{C}$  for 30 minutes (Ramp  $10^\circ\text{C}/\text{min}$ ).

FM/Al nanoparticles were prepared by adding 8.98 g of  $\text{SiO}_2/\text{Fe}_3\text{O}_4(\text{FM})$  to water and putting it in the sonicator for 5 minutes with 8 g of  $\text{Al}_2\text{O}_3$  (AA). After 10 minutes mechanical mixing, the mixture was centrifuged and then washed for two times. Finally, it was calcinated at  $450^\circ\text{C}$  for 45 minutes (ramp of  $10^\circ\text{C}/\text{min}$ ).

FM/ $\text{TiO}_2$  nanoparticles were prepared by adding 8.98 g of  $\text{SiO}_2/\text{Fe}_3\text{O}_4(\text{FM})$  to water and putting it in the sonicator for 5 minutes with 8 g of TTIP. After 10 minutes mechanical mixing, the mixture was centrifuged and then washed for two times. Finally, it was calcinated at  $450^\circ\text{C}$  for 45 minutes (ramp of  $10^\circ\text{C}/\text{min}$ ).

FM/Al- $\text{TiO}_2$  nanoparticles were prepared by adding 4 g of  $\text{Al}_2\text{O}_3$  to 50 mL water and mixing it for 10 minutes continuously. Then, 8.98 g of  $\text{SiO}_2/\text{Fe}_3\text{O}_4(\text{FM})$  were added to water and the mixture was sonicated for 5 minutes along with 4 g of TTIP. After 10 minutes mechanical mixing, the mixture was centrifuged and then washed for two times. Finally, it was calcinated at  $450^\circ\text{C}$  for 45 minutes (ramp of  $10^\circ\text{C}/\text{min}$ ).  $\text{TiO}_2$  accounted for 37.5% of the adsorbent by weight.

## 2.2 Chemical solutions

Arsenic aqueous solution was obtained by adding arsenic solution (99% in As(V)) in 0.5 N nitric acid, supplied by CHEBIOS, to deionized water. Arsenic was always maintained in the pentavalent form by adding  $100\ \mu\text{L H}_2\text{O}_2$  (30% v/v) to the solutions. All chemicals were of analytical grade and were used without a further purification.

## 2.3 Analytical methods

Arsenic concentration in aqueous solution was measured by using an Atomic Absorption Spectrophotometer (Agilent Technologies 240Z AA supplied with the GTA 120 Zeeman graphite tube atomizer) at the wavelength of 193.5 nm, following the 3113 B. Electrothermal Atomic Absorption Spectrometric Method (APHA, 2005).

Standard solutions of arsenate were used for calibration. The As(V) detection accuracy was  $0.22\ \mu\text{g}/\text{L}$ .

pH values were continuously monitored during the batch tests by using the standard probe HI8418 by HANNA Instruments.

## 2.4 Adsorption kinetic experiments

Kinetics of the adsorption process on the different magnetite nanoparticles were determined by means of batch experiments, performed in a jar –tester (Velp Scientifica, Italy), stirred at a constant rate of 120 rpm. The batch duration was always fixed at 24 h.

The initial arsenic concentration in solution (at time  $t=0$  of the test),  $C_0$ , was posed equal to  $500\ \mu\text{g}/\text{L}$ : such a value was chosen as a representative of a very highly contaminated groundwater, with the aim to evaluate removal capability of these new adsorbents under excessive load. The solid to liquid (S/L) ratio was fixed to  $1.5\ \text{g}/\text{L}$ .

The liquid solution was sampled from the adsorption kinetic experiments at regular time intervals ( $t=0, 60, 180, 360, 480$  and  $1440\ \text{min}$ ), in order to follow the mass transfer process under the achievement of the equilibrium conditions.

Each sample was then filtered by using a syringe equipped with a  $45\ \mu\text{m}$  PV filter and the filtrate was analyzed to determine the residual arsenic concentration in solution.

The amount of the arsenic adsorbed onto the media was calculated based on the mass balance of arsenic between solid and liquid phases. The adsorption capacity of the adsorbent at equilibrium,  $Q_{\text{ads}}$ , which represents the mass of arsenic adsorbed per unit mass of adsorbent, was calculated by applying the following equation:

$$Q_{\text{ads}} = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and final (at  $t=1440\ \text{min}$ ) arsenic concentration in solution, respectively,  $V$  is the solution volume and  $m$  is the mass of the adsorbent material.

All the experiments were repeated three times and the data were averaged.

## 2.5 Kinetics modeling

The experimental data from the adsorption tests were fitted by different models, and the best one was found out based on the value of the correlation coefficient,  $R^2$ . The following models were applied to the purpose: zero, first, second, saturation, pseudo-first-, pseudo-second-order, Weber-Morris and Bangham.

The linear forms of the model equations shown below was used to determine the best agreement between the experimental and the predicted data.

Zero order

$$C(t) = C_0 - k_0 \cdot t \quad (2)$$

First order

$$\ln C(t) = \ln C_0 - k_1 \cdot t \quad (3)$$

Second order

$$\frac{1}{C(t)} = \frac{1}{C_0} + k_2 \cdot t \quad (4)$$

Pseudo-first-order

$$\ln(Q_{ads} - Q(t)) = \ln Q_{ads} - k'_1 \cdot t \quad (5)$$

Pseudo-second-order

$$\frac{t}{Q(t)} = \frac{1}{k'_2 \cdot Q_{ads}^2} + \frac{t}{Q_{ads}} \quad (6)$$

Saturation

$$\frac{1}{t} \ln \frac{C_0}{C(t)} = -\frac{1}{K_s} \frac{C_0 - C(t)}{t} + \frac{k}{K_s} \quad (7)$$

Weber-Morris

$$Q(t) = k_{diff} \cdot t^{1/2} + q \quad (8)$$

Bangham

$$\ln \left[ \ln \left( \frac{C_0}{C_0 - Q(t) \cdot m} \right) \right] = \ln \left( \frac{K_0 \cdot m}{V} \right) + \alpha \cdot \ln t \quad (9)$$

where  $C(t)$  and  $Q(t)$  stand for the concentration in solution and the amount of arsenic adsorbed per unit weight of adsorbent, respectively, at time  $t$ ;  $k_0$ ,  $k_1$ ,  $k_2$ ,  $k'_1$ ,  $k'_2$  represent the rate constants of the zero, first, second, pseudo-first and pseudo-second order model, respectively;  $K_s$  and  $k$  indicate the semi-saturation and the rate constants, respectively, of the saturation model;  $k_{diff}$  and  $q$  are the rate constant for intraparticle diffusion and a constant, respectively, where  $q$  provides an insight into the thickness of the boundary layer of the particles; in Eq. (9),  $K_0$  and  $\alpha$  are the Bangham constants.

## 3. Results

Figure 2 shows the adsorption capacity of FM/Al, FM/TiO<sub>2</sub> and FM/Al-TiO<sub>2</sub> calculated based on the arsenic concentration time profile during kinetic experiments.

It can be noted that the all the adsorbents performed a very rapid removal process. Particularly, FM/TiO<sub>2</sub> and FM/Al-TiO<sub>2</sub> showed the best adsorption kinetic and reached equilibrium after about 6 h of contact time, whereas FM/Al took a longer time. Furthermore, the TiO<sub>2</sub>-containing media showed a similar arsenic profilesince the beginning of the test, with a very slight difference between the residual concentrations left over in solution at each time. Therefore, it can be concluded that the presence of titanium dioxide plays a key role in determining the adsorption capacity of these nanomaterials.

It is noteworthy that arsenic concentration was reduced to below the limit set on drinking water (i.e. 10 µg/L) after 3 h and 6 h with FM/TiO<sub>2</sub> and FM/Al-TiO<sub>2</sub>, respectively; by contrast, the residual concentration in solution at the end of the test (time  $t=24$  h) with FM/Al was still much higher, i.e. 32 µg/L As.

At  $t=24$  h, arsenic removal efficiency was 93.52%, 99.24% and 99.20% for FM/Al, and FM/TiO<sub>2</sub> and FM/Al-TiO<sub>2</sub>, respectively.

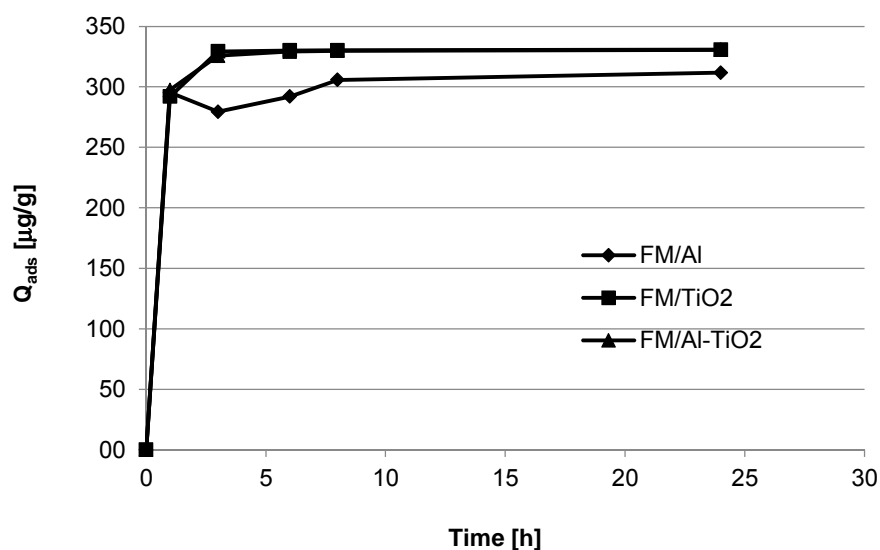


Figure 2: Arsenic adsorption capacity time-profiles by the three magnetic nanoparticles media.

About the kinetic models applied to the experimental data, the Table 1 shows the values calculated for the constants and  $R^2$  of each model and for the three adsorbents.

The best fitting kinetic model was found to be the pseudo-second one for all the adsorbents.

Table 1: Summary of fitting data for each kinetic model for the three magnetic nanoparticles adsorbents

| Model         | Constant unit                                | FM/Al    |                | FM/TiO <sub>2</sub> |                | FM/Al-TiO <sub>2</sub> |                |
|---------------|----------------------------------------------|----------|----------------|---------------------|----------------|------------------------|----------------|
|               |                                              | k        | R <sup>2</sup> | k                   | R <sup>2</sup> | k                      | R <sup>2</sup> |
| Zero          | k <sub>0</sub> (μg/L min)                    | 0.1546   | 0.2024         | 0.1629              | 0.1895         | 0.1617                 | 0.1873         |
| First         | k <sub>1</sub> (L/min)                       | 0.0011   | 0.3787         | 0.0022              | 0.3605         | 0.0021                 | 0.3604         |
| Second        | k <sub>2</sub> (L/μg min)                    | 0.00002  | 0.6897         | 0.0002              | 0.5766         | 0.0001                 | 0.4316         |
| Pseudo-first  | k <sub>1</sub> ' (1/min)                     | 0.0055   | 0.5762         | 0.0127              | 0.8107         | 0.0114                 | 0.8793         |
| Pseudo-second | k <sub>2</sub> ' (g/μg min)                  | 0.0002   | 0.9997         | 0.0008              | 0.9999         | 0.0007                 | 0.9999         |
| Saturation    | k (mg/L min)                                 | 0.0102   | 0.9975         | 1.5000              | 0.8876         | 1.1333                 | 0.9578         |
| Weber-Morris  | k <sub>diff</sub> (μg/g min <sup>1/2</sup> ) | 0.8127   | 0.5438         | 0.9316              | 0.3878         | 0.8473                 | 0.4614         |
| Bangham       | K <sub>0</sub> (g)                           | 886.0649 | 0.4606         | 716.9386            | 0.6873         | 700.6372               | 0.8247         |

The values of the maximum adsorption uptake predicted by the model were very similar to those measured experimentally in all the cases.

#### 4. Conclusions

The objective of the present study was to investigate the arsenic adsorption capacity of magnetic core nanoparticles prepared with different coatings consisting of pure titania, pure activated alumina and a mix of titania and activated alumina. Kinetic experiments showed very high efficiency of the adsorption process by all the tested media. However, the presence of TiO<sub>2</sub> coating significantly enhanced the removal rate, with the faster process observed in the case of titania coating only. By contrast, the residual concentration in solution

at the end of the test (time  $t=24$  h) with activated alumina coating-nanoparticles was still much higher, i.e. 32  $\mu\text{g/L}$  As. For all the adsorbents, the best fitting kinetic model was found to be the pseudo-second one. Being the performance so promising, further studies will be soon carried out to investigate the adsorption capacity of the  $\text{TiO}_2$ -coated magnetic core nanoparticles at higher arsenic load.

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