

Application of Iron Based Nanoparticles as Adsorbents for Arsenic Removal from Water

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Arsenic contaminations of groundwater in several parts of the world are the results of natural and/or anthropogenic sources, and have a large impact on human health. Millions of people rely on groundwater for drinking water supply; therefore, contamination of these sources represents a strong limitation to their civil and urban development. Due to the toxicity and potential carcinogen effect, in 2001 the World Health Organization has reduced the maximum allowable concentration of arsenic in drinking water to 10 µg/L. This new limit has been then adopted by numerous countries, such as Italy.

Among the methods used to reduce arsenic concentration, the adsorption process has often proved to be the most suitable in the case of drinking water sources. Adsorption efficiency strongly depends on the type of adsorbents. In the case of arsenic contaminated groundwater, a number of media have been tested so far (alumina, iron-based), some of which providing good removal. However, there is still an high interest in new media capable of providing better performances, i.e. longer duration of the column plants where the adsorption process is usually implemented at the full-scale. Recently there has been increasing interest on the application of nanoparticles and nanostructured materials as efficient and viable alternatives to conventional adsorbents in the removal of metals from water. Due to their small size, they possess a large surface area and a high surface area to volume ratio. These characteristics improve the adsorption capacity of the nanoparticles and make them potentially suitable for the application where higher removal efficiency are required.

The present work investigates the application of a new nano-adsorbent for arsenic removal from water. The media was produced in laboratory and made by magnetite nanoparticles. These iron-based nanoparticles, characterized by a very small size (9 nm), showed high removal rate, providing a specific adsorption capacity at equilibrium of about 8.25 [mg As/g ads]. Among the investigated models, the pseudo-second order best fitted the experimental data of the kinetic tests. Comparisons made with the performance provided by commercial adsorbents and other materials confirms the use of magnetite nanoparticles for the removal of arsenic as a promising technique.

1. Introduction

Arsenic is a widely diffused metalloid, commonly found in all the environmental matrices. High levels of arsenic have been measured in many groundwaters worldwide as a consequence of either natural or anthropogenic sources. Since it has been recognized toxic and potentially carcinogen, the World Health Organization (WHO, 2004) reduced the arsenic maximum contaminant level (MCL) in drinking water from 50 to 10 µg/L (Sharma and Sohn, 2009). This new limit has been then adopted by numerous countries, such as Italy. Thus treatment of As contaminated water with improved or completely new technologies to provide safe drinking water to the community is an urgent issue at present.

Several physico-chemical techniques have been developed to this purpose (Ng et al., 2004). The most commonly used technologies are: oxidation, co-precipitation followed by adsorption onto coagulated flocks, lime treatment, ion exchange, adsorption onto various solid media and membrane filtration (Choong et al.,

2007). Among them, precipitation usually requires high chemical dosages and produces high volumes of sludge which need proper treatment and disposal. Furthermore, the addition of chemicals to the water may negatively alter its quality in view of the use as drinking water source. Ion exchange is highly efficient, provided that interfering ions are absent or at very low concentration. Membrane filtration, although capable of producing a very high quality permeate, it recovers only a fraction of the treated water volume while the remaining fraction is wasted as concentrate stream. This represents a severe drawback in the case of drinking water sources.

The above limitations have frequently made the adsorption process to be preferable with respect to the alternative technologies. It is capable of reducing arsenic concentration below the MCL without the need of chemical addition; total treated volume of water is recovered and no sludge are being generated. However, its efficiency is strongly dependent on the type of adsorbent (Mohan and Pittman, 2007). Extensive studies have been performed to determine performances and optimal operating conditions of numerous natural or commercial media. For instance, activated carbons

Among all the tested adsorbents, iron and activated alumina based adsorption have been more widely used for treatment of As contaminated groundwater. Activated alumina (AA) was the first adsorptive medium to be successfully applied for the removal of arsenic from water supplies. The reported adsorption capacity of AA ranges from 0.003 to 0.112 g of arsenic per gram of AA. It is available in different mesh sizes and its particle size affects contaminant removal efficiency. Several different studies have established the optimum pH range as 5.5-6.0, and demonstrated greater than 98% arsenic removal under these conditions (Jain and Singh, 2012).

Adsorption on iron-based (IB) is a more recent treatment technique for arsenic removal, but it is considered to be one of the most promising solution. This has led to the development of a great number of products, such as granular ferric hydroxide, zero valent iron, iron coated sand, modified iron and iron oxide based adsorbents. The studies conducted with IB media have revealed that the affinity of this media for arsenic is strong under natural pH conditions, relative to AA. This feature allows IBS to treat much higher bed volumes without the need for pH adjustment, as compared to AA (Jain and Singh, 2012).

Recent advances in nanoscience and nanotechnology have led to the development of a number of nanoparticles for the environmental remediation of various contaminants from groundwater (Zhang, 2003). Due to their high specific surface area and reactivity, nanoparticles are considered as a suitable option for fast removal of contaminants from aqueous solution (Huber, 2005). Nanostructured metal oxides such as mesoporous alumina (Kim et al., 2004), titanium oxide (Pena et al., 2006), nanocomposites comprised of aluminiumoxide nanoparticles (AluNPs) incorporated in macroporous polyacrylamide-based cryogels (Önnby et al., 2014), iron oxide (Tang et al., 2011), hydrous cerium oxide (Li et al., 2012) have attracted the attention of researchers due to their great capability of arsenic removal. Nevertheless, the study of other nanomaterials is still of a wide interest (Tsytnev et al., 2014).

The main purpose of this preliminary work was to investigate the adsorption characteristics of magnetite nanoparticles for arsenic removal from water at high contamination level. 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 are widely used in radar absorbers, magnetic recording devices, heat resistant alloys, powder metallurgy, injection molding, a variety of additives, water treatment and many other areas. They have an uniform particle size, high purity and low contents of carbon, nitrogen, oxygen, sulfur, phosphorus and other harmful elements.

The experimental activity was conducted through batch tests, investigating both the adsorption kinetics and equilibrium.

2. Materials and methods

2.1 Adsorbents

The magnetite nanoparticles were produced in laboratory by following the procedure reported in detail in Ruzmanova et al. (2013). Briefly explained, a FeCl_3 solution in 2M of HCl and 1M of Na_2SO_3 is mixed to a 0.85M ammonia solution on 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).

The resulting model size of the pure magnetite nanoparticles was 9 nm (Figure 2).

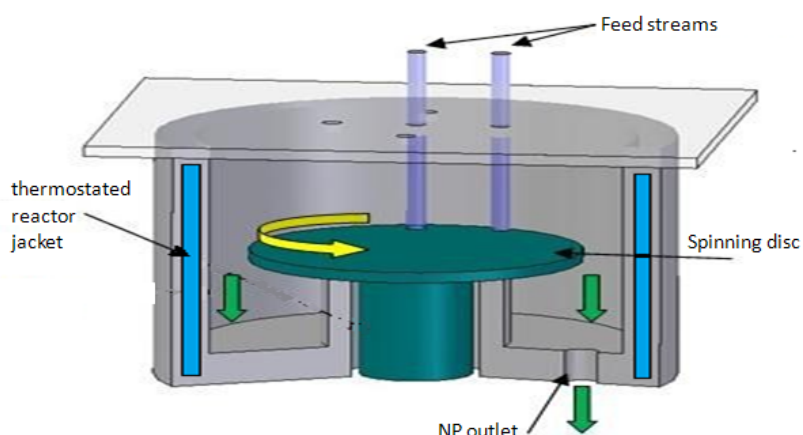


Figure 1: Scheme of the spinning disc reactor

2.2 Chemical solutions

Arsenic aqueous solutions at various concentrations were 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 μ L H₂O₂ (30% v/v) to the solutions. All chemical were of analytical grade and were used without a further purification.

2.3 Analytical methods

Arsenic concentration in aqueous solutions 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 μ g/L. pH values were continuously monitored during the batch tests by using the standard probe HI8418 by HANNA Instruments.

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

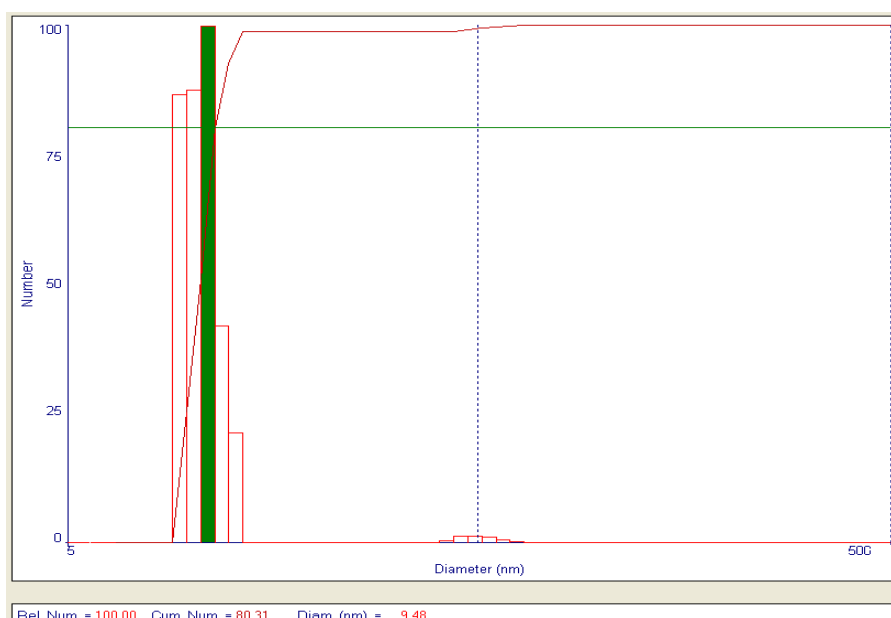


Figure 2: Particle Size Distribution of the used nanoparticles of magnetite

2.4 Adsorption kinetics

Kinetics of the adsorption process on 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 24 h, found to be enough to reach equilibrium conditions.

The initial arsenic concentration in solution (at time $t=0$ of the test), C_0 , was posed equal to 10 mg/L: such a value, which is significantly higher than the concentrations usually found in naturally contaminated groundwater, was chosen based on the need to ensure reproducible data since it was the first time this adsorbent was tested. The solid to liquid (S/L) ratio was fixed to 5 g/L.

Periodical sampling of the liquid solution was performed until the mass transfer process reached equilibrium conditions. Each sample was then filtered by using a syringe equipped with a 45 μm 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_{ads} , which represents the mass of arsenic adsorbed per unit mass of adsorbent, was calculated by applying the following equation:

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

where C_0 and C_e are the initial and final (at equilibrium) arsenic concentration in solution, respectively, V is the solution volume and m is the mass of the adsorbent material.

2.5 Kinetics modeling

The best fitting of the experimental data by the following models was found based on the value of the correlation coefficient (R^2): 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

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

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_{wm} and q are the Weber-Morris rate constant and constant, while K_0 and α are the Bangham constants.

3. Results

Table 1 shows the values of concentration, removal percentage, pH and adsorption capacity calculated at the different times during the kinetic tests.

Table 1: Experimental results of the kinetic tests

Time (min)	0	5	10	15	30	60	90	120	150	180	240	300	360	420
$C(t)$ (mg/L)	10.2	5.9	3.9	3.2	2.1	1.0	1.2	0.7	0.4	0.4	0.3	0.1	0.1	0.0
Removal (%)	-	42.2	61.8	68.6	79.4	90.2	88.2	93.1	96.1	96.1	97.1	99.02	99.02	100.0
pH (unit)	6.0	4.0	3.8	3.7	3.6	3.5	3.5	3.5	3.4	3.4	3.4	3.4	3.4	3.4
$Q(t)$ (mg/g)	0.0	0.9	1.3	1.4	1.6	1.8	1.9	1.9	2.0	2.0	2.0	2.0	2.0	2.0

The mass transfer process by adsorption of arsenic onto magnetite was very rapid, as can be seen in Figure 3, representing the solution concentration time-profile. After about 3 h, the equilibrium conditions were likely to be established: indeed, the following variations of arsenic concentration in solution were negligible.

It is interesting to notice that all the As in the sample was adsorbed by the nanoparticles within 420 min, whereas the limit of As for potable water in Italy, equal to 0.1 mg/L, was reached within 300 min. At this point, a purification from As of the sample equal to 99% was achieved.

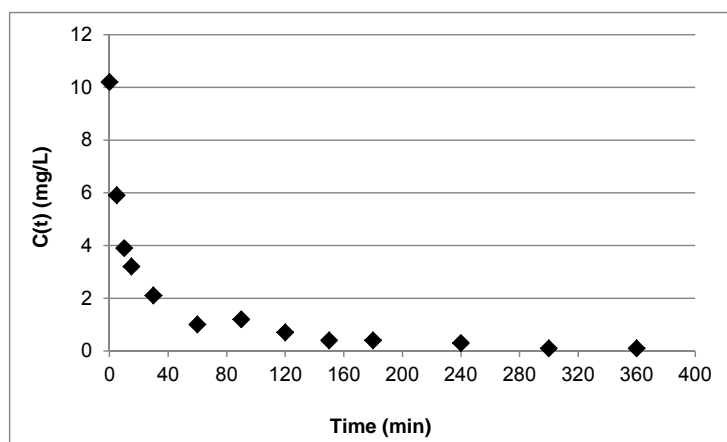


Figure 3: Arsenic concentration time-profile during the kinetic test

The best fitting of the kinetic data was obtained by the pseudo-second order model ($R^2=0.9944$): the corresponding fitting line had the following equation

$$\frac{t}{Q(t)} = 1.344 + 0.5618t$$

Based on the above equation, it was possible to calculate the equilibrium adsorption capacity, Q_{ads} , and the rate constant, k'_2 . The following values were obtained: $Q_{ads}=1.8$ (mg/g), $k'_2=0.03$ (g/mg min).

4. Conclusions

Based on this preliminary study, the use of nanomagnetite particles for the removal of arsenic from water appears to be promising: a very high rate of adsorption was observed, with the limit of As concentration for drinking water achieved after only 300 min. However, the specific adsorption capacity at equilibrium was very low as compared to the values reported by the literature using other media (Jain and Singh, 2012). Nonetheless, it must be taken into account that the initial contaminant load adopted in the present study was very high as compared to the more common cases of natural contamination. Therefore, further experiments

will be carried out for investigating the removal capability of nanomagnetite particles at lower arsenic concentration.

It is noteworthy that magnetic particles offer the possibility of easy recovery (and possibly reuse) by means of a magnetic trap: this suggests the need of a deeper understanding of this kind of adsorbent.

To this purpose, the following studies will also address a detailed characterization of the media and the effects of pH on the removal rate.

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