Synthesis and Characterization of Nanometric Titania Coated on Granular Alumina for Arsenic Removal

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The adsorption process is widely used for the treatment of drinking water sources containing high levels of arsenic. The choice of the adsorbent is crucial for the efficiency of the process. Very good performances were obtained in the past by activated alumina, while more recent studies have shown that also other media such as titanium oxide can provide high removal rates.

In the present work, four types of adsorbents were tested for their removal capability of pentavalent arsenic from liquid solutions. Specifically, it was investigated if modifications of activated alumina by coating with titanium oxide nanoparticles or by reducing particle size might improve their performance.

The adsorbents were firstly characterized by X-ray diffraction, BET specific area measurement and SEM analysis. Then, kinetics, equilibrium isotherm experiments were conducted in batch mode at fixed pH.

All the tested adsorbents showed satisfactory arsenic removal, with the best performance obtained by the mesoporous γ-alumina which had the lowest grain size. The titanium coating did not appear to significantly improve adsorption capacity. The kinetic data were best fitted by the pseudo-second order model, while both the Freundlich and the Langmuir equations well represented the adsorption isotherm data.

1. Introduction

Recently, a wide number of water sources have been found naturally contaminated by high levels of arsenic. This represents a serious threat to people which uses these sources for drinking water supply. To address the problem, water treatment is often the only possible solution when alternative non-contaminated sources are not nearby available. The treatment process must be capable of reducing arsenic concentration below the maximum allowable limit for drinking water, which has been recommended by the World Health Organization (WHO) to be fixed below 10 μg/L.

Several different processes can be applied for this purpose, e.g. chemical precipitation, membrane separation, ion exchange, adsorption. Among these processes, adsorption has been widely applied for removing arsenic in the case of drinking water, since it offers more advantages (e.g. no chemical requirements neither modification of water organoleptic characteristics). However, the adsorption process efficiency may significantly vary, depending on many factors among which the type of adsorbent media plays a key role. Therefore, the adsorbent choice is fundamental to guarantee a high arsenic removal. Many commercial media have been tested so far (Reed et al., 2000), such as iron hydroxide (Thirunavukkarasu et al., 2003), activated carbon (Patanayak et al., 2000) and activated alumina (Guha and Choudhuri, 1990). Furthermore, a number of experimental studies has been performed with the purpose to find out new media having superior performances as compared to the commercial ones (Glocheux et al., 2013).

Among the tested media, activated alumina (AA) has been widely used in the past since has a strong selectivity to arsenate ion (Sing and Pant, 2006). The arsenic removal capacity of activated alumina is pH sensitive and therefore requires pre- and post- pH adjustment (EPA, 2003a,b). Several different studies have established the optimum pH range as 5.5-6.0 (Jain and Singh, 2012). The need of pH adjustment is a drawback, particularly in the case of drinking water treatment, where physical-chemical water characteristics must be carefully checked and maintained. Therefore, there is still space to improving the AA capacity for arsenic removal. Several emerging proprietary media, commonly referred to as modified AA, have been proposed, which contain alumina in a mixture with other substances such as iron and sulfur. In some instances, these media have greater overall adsorptive capacities, enhanced selectivity towards arsenic, and/or greater overall operational flexibility than conventional AA, thus making them more cost-effective.

Titanium dioxide (TiO_2), commonly used for environmental applications, is a promising material for removing arsenic (Pirilä et al., 2011). The advantages of TiO_2 include good adsorption activity, physical and chemical stability, non-toxicity, resistance to corrosion, commercial availability and inexpensiveness.

In the present study, the treatment capacity of arsenic-contaminated water by different types of adsorbents was experimentally investigated. The media differed by granule sizes, the presence of titanium oxide impregnation and preparation procedure. Their capacity was evaluated through batch tests to investigate kinetics and isotherms of the removal process.

2. Materials and methods

2.1 Adsorbents
The experiments were performed using the adsorbent media listed in table 1.

Table 1: Tested adsorbent media and their main properties

Media	Composition	Average grain size [μm]	Average specific surface [m^2/g]
Al_2O_3-Sigma	Al_2O_3	106	155
Al_2O_3-γ	Al_2O_3	20	110
Al-Ti	Al_2O_3+TiO_2	150	155
Adsorbsia[TM]	Ti	106	200

Al_2O_3-Sigma was a commercial alumina supplied by SIGMA ALDRICH and in the powder form. It was used as a reference media.

Al_2O_3-γ was a mesoporous γ-alumina, provided by the Laboratoire des Sciences des Procédés et des Matériaux (LSRM) of CNRS Université Paris 13. It was produced by oxidation of metallic aluminum plates through a liquid mercury-silver layer at room temperature in humid atmosphere (Vignes et al., 2008). After the growth was completed, the samples were homogeneously impregnated with trimethylethoxysilane (TMES: $(CH_3)_3$-Si-C_2H_5O) vapor at room temperature until saturation, followed by the thermal treatment at 1300 °C to obtain θ-Al_2O_3 polymorph. The material was then grinded and sieved in order to obtain a powder of 20 μm average grain size. The specific area of this material was 110 m^2/g as measured by BET method (Coulter SA3100) and its mass density was approximately 0.15 g/cm^3 (Khatim et al., 2013).

Al-Ti indicates a nanometric titania coated onto commercial granular alumina, synthesized by LSRM. Titanium tetraisopropoxide was dissolved in 20 mL isopropanol and hydrolyzed with 50 mL of distilled water. Distilled water was added drop wise under stirring and the white precipitate of hydrous oxide was produced instantly. The mixture was stirred for 20 minutes after the end of addition of water. The amorphous precipitate was separate by decantation and washed two or three times with distilled water for a complete removal of alcohol. The supernatant liquid was removed. This hydrous oxide precipitate was slowly added to 10 mL of peroxide. The precipitate dissolved completely by reaction with peroxide and formed a transparent orange sol of titanium-hydrogen peroxide complex. This transparent orange sol slowly thickened with time and transformed into the gel. The coating of Al_2O_3 by TiO_2 nanoparticles was done by impregnation of particles of alumina in the transparent orange sol of titanium-hydrogen peroxide complex, and gently shacked until its transformation into a gel. The viscous gel was then further dried under a lamp for 8-12 h.

Adsorbsia[TM] is a titanium-based adsorbent supplied by Dow Chemical Company. It is usually provided with a granular size of 118-250 μm; in the present experiments it was previously grinded and sieved at 106 μm so as to have a comparable size to the reference media Al_2O_3-Sigma.

2.2 Adsorbent characterization

The adsorbent media were characterized by the following techniques: (1) image analyses and elemental composition by a Scanning Electron Microscope (SEM) ZEISS model AURIGA provided by Microanalysis EDS 123 Mn-K eV supplied by Bruker, (2) X-ray diffraction analysis performed by PHILIPS apparatus model PW1830DY3558 with a copper anticathode Cu-Kα (I=30 mA and V=40 kV).

2.3 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 bidistilled water. The pH of the solution was always adjusted to be between 6.5 and 7 (which is the more common value found in drinking water) by adding 0.1 M nitric acid or a sodium hydroxide solution. Arsenic was always maintained in the pentavalent form by adding 100 μL H_2O_2 (30% v/v) to the solutions. All reagents were of analytical grade and were used without a further purification.

2.4 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). The As(V) detection accuracy was 0.22 μg/L. pH values were measured using the standard probe HI8418 by HANNA Instruments. All the experiments were repeated three times and the data were averaged.

2.5 Adsorption kinetics

Kinetics of the adsorption process on the selected media were determined by using the usual batch technique. The initial arsenic concentration (at time t=0 of the test) was fixed equal to 400 μg/L, in order to simulate the highest content in contaminated groundwaters potentially available for drinking water supply. The mass density of adsorbent was 50 mg/L in the case of alumina-γ and about 15 mg/L for the others. Completely mixed conditions between solution and adsorbent were assured by using a shaking table provided with a Certomat-R apparatus, rotating at 160 rpm.

Periodical sampling of the liquid solution was performed until equilibrium conditions of the mass transfer process were reached. Each sample was then filtered by using a syringe equipped with a 45 μm PV filter and the filtrate 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 material at time t, $Q_{ads}(t)$, which represents the mass of arsenic adsorbed per unit mass of adsorbent, was calculated by applying the following equation:

$$Q_{ads}(t) = \frac{V \cdot (C_0 - C(t))}{m} \tag{1}$$

where C_0 and $C(t)$ are the arsenic concentration in solution calculated at time t=0 (the beginning of the test) and at any time t during the test, respectively, V is the solution volume and m is the mass of the adsorbent material.

The kinetics of the adsorption process were modeled by applying the pseudo-first-order and pseudo-second-order models.

The best fitting model was considered that one providing the higher value of the correlation coefficient (R^2) between the experimental and the predicted data.

2.6 Adsorption isotherms

Isotherms of the adsorption process were determined using the same apparatus as that of the kinetic experiments. Temperature was always maintained at 22±2°C. Different masses of adsorbent were used, while initial concentration of the arsenate solution was fixed at 400 μg/L for Al_2O_3-γ, Al_2O_3-Sigma and Al-Ti.

Based on the kinetic tests, the equilibrium time, i.e. the duration of each test, was fixed at 24 h. At the end of this time, the plate shaking was stopped; a sample was withdrawn from the solution and filtrated by using a syringe fitted with a 45 μm PV filter. The filtrate was finally analyzed to measure the residual arsenic concentration.

The amount of the adsorbed arsenic per unit mass of adsorbent was calculated by means of Eq(2).

$$Q_{ads} = \frac{V \cdot (C_0 - C_e)}{m} \tag{2}$$

where C_e and Q_{ads} represent the arsenic concentration in solution and the adsorption capacity at equilibrium (i.e. at t=24 h).

The experimental results were then fitted by the Freundlich and the Langmuir model equations. The best fitting model was considered that one providing the higher value of the correlation coefficient (R^2) between the experimental and the predicted data. Once the best model was found, the characteristic coefficients of the model equation were calculated.

3. Results

3.1 Adsorbent characterization
Figure 1 shows representative SEM images of the tested adsorbents, while the following Figure 2 the results of XRD images of Al_2O_3-γ and Figure 3 the EDS analysis.

The SEM images show a non-uniform surface, with slits and cracks in the alumina-based media. White particles or particles aggregates of different sizes can be noticed on the material surface of the titanium dioxide coated-alumina (Figure 1b).
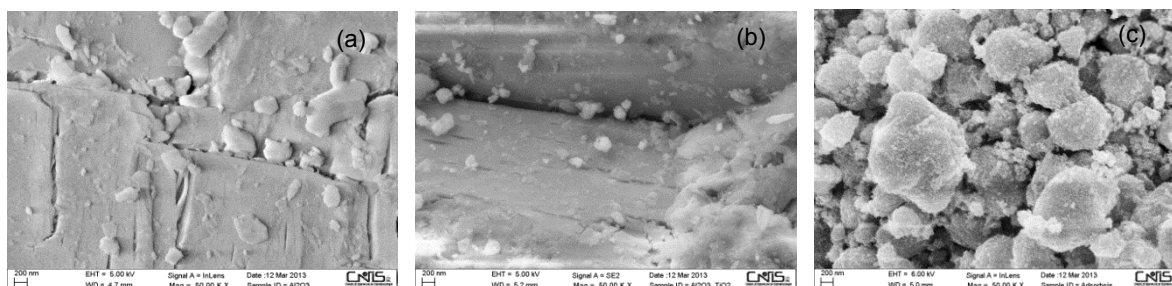

Figure 1: SEM images of (a) Al_2O_3-$_{Sigma}$, (b) Al-Ti, (c) Adsorbsia^{TM}

In the case of Adsorbsia^{TM}, the SEM images highlights the prevalent presence of titanium oxide fine particles, which represent the main component of the media, as confirmed by the elemental composition analysis, showed thereafter.
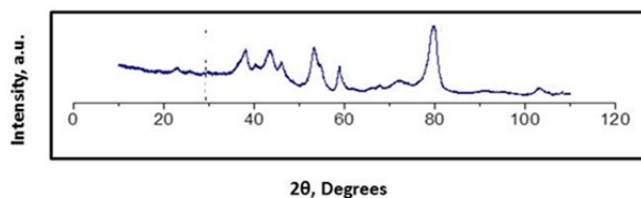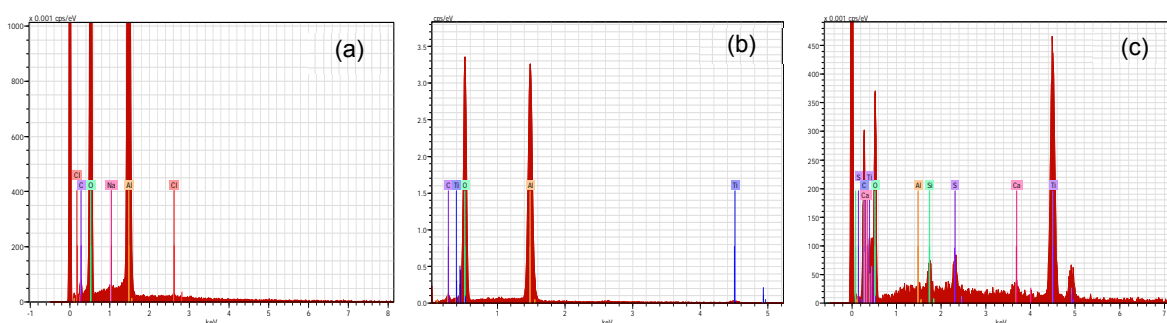

Figure 2: XRD images of Al_2O_3-γ

Figure 3: EDS analysis of (a) Al_2O_3-$_{Sigma}$, (b) Al-Ti, (c) Adsorbsia^{TM}

3.2 Adsorbent kinetics and isotherms
Figure 4 shows the kinetics profiles obtained with the tested media. The most rapid trend was observed with Al_2O_3-γ, which reached the adsorption equilibrium conditions in the first few hours. So did Adsorbsia, while the lowest kinetic rate was observed with Al_2O_3-$_{Sigma}$. The specific adsorption uptakes at equilibrium were very similar in all the cases, with values in the range 7.4-7.6 mg/g.

The best fitting of the kinetic data was obtained by the pseudo-second order model for all the adsorbents tested: the values of the adsorption uptake at equilibrium predicted by the model were very similar to those measured experimentally.

Figure 5 shows the results of the isotherms experiments in terms of specific adsorption uptake, Q_{ads}, versus the arsenic concentration in solution, C_e, at t=24 h. Table 2 lists the isotherms parameters of the Freundlich and Langmuir models, calculated by fitting the experimental data.

It can be noted that the highest value of Q_{ads} was achieved by Al_2O_3-γ: this is in agreement with the value of Q_{max} determined through the Langmuir model, which was significantly higher than the values found for the other media. The lowest uptake was achieved by Adsorbsia, while both Al_2O_3-$_{Sigma}$ and Al-Ti performed very similarly.

Fitting by the Freundlich and Lagmuir models both provided a pretty good agreement for all the tested media, with only a slightly higher value of R^2 in the former case.
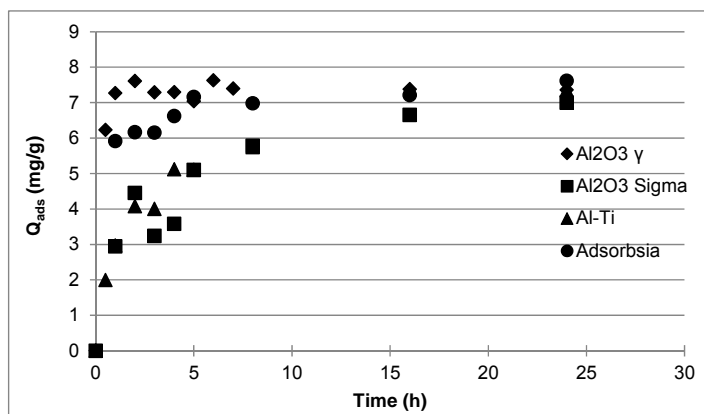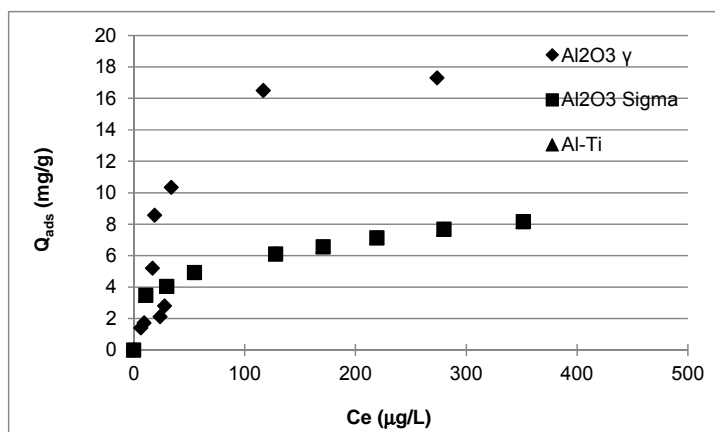

Figure 4: Kinetic profiles of the tested media

Figure 5: Isotherm profiles of the tested media

Table 2: Isotherm data of the tested media

Media	Freundlich			Langmuir		
	n	K_F $(mg/g)(L/mg)^{1/n}$	R^2	Q_{max} (mg/g)	K_L (L/mg)	R^2
Al_2O_3-$_{Sigma}$	3.937	1.799	0.989	8.636	26.930	0.987
Al_2O_3-γ	1.449	0.487	0.689	26.596	7.833	0.529
Al-Ti	3.891	1.779	0.988	9.497	18.804	0.984
Adsorbsia[TM]	1.622	1.346	0.999	6.443	0.249	0.997

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4. Conclusions

All the tested adsorbents showed satisfactory arsenic removal, with the best performance obtained by the mesoporous γ-alumina which achieved the highest specific adsorption uptake and was able to carry out the more rapid adsorption process. It is worth noting that Al_2O_3-γ was produced in laboratory with the lowest grain size: this likely determined the very fast kinetic of the mass transport process as compared to the other media which all had a much higher particle size.

The presence of titanium did not seem to appreciably improve process performance of alumina-based media.

It must be pointed out that the reported adsorption capacity by activated alumina ranges within a wide interval (3-112 mg/g according to Jain and Singh, 2012) and is strongly dependent on the pH, being the acidic conditions more favourable to arsenic removal. This holds also for titanium-based media, whose performance are reported to be higher at a lower pH (Pirilä et al., 2011). Since in the present work all the experiments were performed at about neutral conditions, there is the need to further investigate the arsenic removal capability of the same media under different pH conditions.

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