Arsenic adsorption and desorption cycles for groundwater remediation

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Abstract Arsenic is a critical pollutant for groundwater, severely reducing the quality of water for human utilization and aquatic life, even at low concentrations.

Adsorption is one of the most suitable technologies to reduce arsenic content within acceptable levels. Several studies rely on the usage of activated carbons to remove arsenic from water, but they rarely deal with the reutilization of spent carbons. This is a critical issue because the economy of adsorption processes strongly depends on the capacity of cyclically use the sorbent without replacing it after exhaustion.

In a former paper, we showed that NaCl solutions effectively regenerate arsenic-spent carbons and produce saline solutions from which arsenic can be effectively precipitated. In this work, we report new experimental studies aimed to support the design of an adsorber based on a set of columns operated in either adsorption, desorption or water rinsing mode. In particular, experiments were performed on a model groundwater contaminated with 3 mg/L As(V), in order to understand how the use of the same activated carbon in consecutive adsorption-regeneration cycles modify its adsorption capacity over time. The experiments indicated that activated carbon can be proficiently used in multiple cycles, preserving more than 90% of its original adsorption capacity.

Keywords: Arsenic; activated carbon; desorption; regeneration, adsorption cycles.

1. Introduction

Arsenic is one of the most poisonous inorganic pollutants of drinking and ground waters and its maximum allowable concentration is strictly regulated by most of the world nations. Italian regulations adopt to European laws that defined a maximum arsenic limit in drinking water as low as 10 μg L^{-1} and a limit for sewage discharge of 500 μg L^{-1}.

The International Agency for Research on Cancer (IARC) stated that arsenic is carcinogenic to humans. Long-term exposure to arsenic contamination in water is associated with skin pigmentation changes, skin lesions and hard patches on the palms and soles of the feet (hyperkeratosis). These pathologies may be precursors to skin cancer. Besides, long-term exposure to arsenic may also cause cancers of the bladder and lungs. Adverse health effects potentially associated with long-term ingestion of inorganic arsenic include myocardial infarction, neurotoxicity, diabetes, pulmonary disease and cardiovascular disease. Arsenic also contributes adverse pregnancy outcomes and infant mortality, with impacts on child health and cognitive development.

Arsenic is more toxic in its lower oxidation state (e.g. As^{-3}, As(0) and As^{+3}) respect to the most abundant As^{+5} and, in order to remove it from water, this element must be transferred and confined onto a solid phase. Precipitation is an effective method to reduce arsenic below 1 μg L^{-1} (Cheng *et al.*, 1994; Scott *et al.*, 1995; Hering *et al.*, 1996; Garelick *et al.*, 2005; Ricci Nicomel *et al.*, 2016), but the current techniques used for precipitation, coagulation and filtration (or flocculation) produce large amount of sludge. Their volume is related to the mass of coagulant rather than to the effective arsenic content (e.g. Cheremisinoff, 2003; Metcalf and Eddy, 2005). For example, using iron (III) chloride as coagulant, the sludge volume is about 5% of the treated flow rate, i.e. 5 metric tons of sludge for each 100 metric ton of treated water. In Italy, the costs for the disposal of sludge containing heavy metals is in the range 150-200 € per metric ton. Therefore, intense sludge dewatering is required. This operation implies additional capital and operational costs to reduce water content, usually below 30% but sometimes even below 5-10% (e.g. Cheremisinoff, 2003; Metcalf and Eddy, 2005).

Adsorption or ion exchange are effective treatments by which arsenic is transferred more or less selectively, from the liquid to the surface of a sorbent or an ion exchange resin. Simple adsorption on microporous granular activated carbon can reduce the concentration of arsenic below regulation limits with a relatively inexpensive material (between 1000 and 2000 € per metric Ton) when compared with commercial resins or other functionalized sorbent. The mechanical properties of granular activated carbon also allow its use in multiphase reactors with mobile solid phase, as fluidized beds, trickle beds, pulsed beds, etc.. These units provide a more effective use of the sorbent, which leaves the reactor saturated at the inflow concentration of the treated waste stream. This option

allows to maximize the amount of arsenic loaded on the activated carbon and to minimize the volume of exhaust carbon to be disposed.

Our research group recently demonstrated that exhaust activated carbons containing as much as 0.12 mg/g of arsenic can be effectively regenerated by desorption using sodium chloride solutions at 0.1 or 0.5 M (Di Natale *et al.*, 2013). This arsenic content corresponds to the equilibrium adsorption capacity with a natural water solution containing about 3 mg L^{-1} of arsenic. In particular, a 0.1 M NaCl solution allows recovering more than 90% of the arsenic. Besides, the study indicated that adsorption is actually reversible, i.e. the desorbing solution has an arsenic concentration corresponding to the value retrieving from the adsorption isotherms on the same activated carbon operated in the same conditions of desorption step. These evidences open to the opportunity of developing an adsorption process with sorbent regeneration and reuse. For example, such a process can consider an arsenic-contaminated stream flows through the adsorber, consisting in a moving bed of granular activated carbon (a trickle or a pulsed bed for example), and leaves it depurated. The spent carbon leaving the adsorber should be sent by a conveyor to the regeneration section where it is treated with NaCl solution and rinsed with fresh water. After regeneration, the carbon can be recirculated in the column. A sorbent purge and addition of fresh carbon can be also considered. The desorption solution can be then treated by precipitation/coagulation and filtration process (e.g. Hering, 1996; Hesami, 2013) and a small amount of sludge containing high levels of arsenic is then obtained. An effective separation of arsenic from water and the minimization of the associated solid waste can be thus achieved.

The aim of this work is to provide preliminary information to understand the feasibility of this process. In particular, experimental data are needed to verify how the use of the same activated carbon in consecutive adsorption-desorption cycles modify its arsenic uptake capacity over time. Besides, experimental evidences are needed to verify if arsenic is released during the water rinsing step.

2.   Materials and methods

Aquacarb 207EA^{TM} is a commercially available non-impregnated granular activated carbon, produced by Sutcliffe Carbon starting from a bituminous coal. This material has a narrow particle size distribution with an average diameter of 1.2 mm. Its main chemical and physical characteristics are reported in Di Natale *et al.* (2013). At the beginning of each test, a sorbent dose m=0.75 g was carefully rinsed with distilled water and oven dried for 48 h at 120°C.

All the chemicals used in this work were AR grade supplied by Sigma Aldrich. The stock solutions for adsorption experiments were prepared by dissolving a given quantity of sodium arsenate hepta-hydrate ($Na_2HAsO_4 \cdot 7H_2O$) in a natural water whose main properties are reported in Table 1. NaCl solutions were prepared with AR grade sodium chloride powder in the same natural water. All the labware was previously soaked in 1 M HNO_3, triply rinsed with distilled water and oven dried.

Adsorption and desorption tests followed the experimental conditions explored by Di Natale *et al.* (2013). This is based on the repetition of experimental tests with the clean natural water artificially polluted with arsenic. The experimental runs were carried out in batch mode in a P.I.D. controlled thermostatic oven at 20°C and without any additional stirring of the sample. Each adsorption-desorption cycle starts with the preparation of a sample consisting of V=100 mL of c_0=3±0.1 mg L^{-1} arsenic solution. Preliminary blank tests on arsenic solutions without addition of sorbent showed that the experimental procedure did not lead to any reduction of arsenic concentration unrelated to sorbent effects. Furthermore, blank tests on model solution without arsenic addition showed that the activated carbon did not lead to appreciable ions release to the solution.

Table 1. Natural water properties

pH	8.0
Electric conductivity, μS cm^{-1}	242
Fixed residue at 180°C, mg L^{-1}	160
Salinity, mM	4.59
[Ca^{++}], meq L^{-1}	1.632
[Mg^{++}], meq L^{-1}	1.050
[Na$^+$], meq L^{-1}	0.100
[K$^+$], meq L^{-1}	0.015
[HCO$_3^-$], meq L^{-1}	2.426
[SO$_4^{-2}$], meq L^{-1}	0.400
[Cl$^-$], meq L^{-1}	0.073
[NO$_3^-$], meq L^{-1}	0.060

Finally, batch kinetic tests indicated that arsenic adsorption and desorption both reached equilibrium conditions within 72 hours. These were chosen as reference test time for all the experiments.

During the generic j-th adsorption-desorption cycle, the sample solution is contacted with the activated carbon from cycle j-1th. When the equilibrium was established, the solution was filtered in a ceramic Hirsch funnel with a vacuum pump to assure a rapid and efficient separation of the granular sorbent. The filtered solution was then analyzed for pH and arsenic concentrations, c_j.

The amount of arsenic adsorbed per unit mass of carbon during the cycle, q_j, was calculated with the mass balance:

$$q_j = \frac{V}{m}\left(c_0 - c_j\right) \qquad (1)$$

The exhaust carbon was then treated with V_d=75 mL of NaCl solution at 0.01, 0.05 and 0.1 M. As a benchmark solution, we also performed tests with distilled water.

After equilibration, the leaching solution is filtered and analyzed to establish the concentration c_{dj}. Once c_{dj} is measured, the mass of arsenic desorbed from the carbon, q_{dj}, is determined as:

$$q_{dj} = \frac{V_d}{m}c_{dj} \qquad (2)$$

The solid after the desorption step was separated and rinsed with unpolluted natural water in a glass column to elute excess sodium and chloride until pH and electric conductivity of the inflow water were restored. The liquid velocity is kept at 7.5 cm s^{-1}. The rinsing water was periodically analyzed to detect traces of arsenic during the process, which resulted always negligible.

The total arsenic concentration in solution, c_j and c_{dj}, were measured by Atomic Absorption Spectrometer (Varian Spectra AA 220), using a flame-hydride generation method (F-HG-AAS) with NaBH$_4$ as reducing agent (Clesceri et al., 1998). Detection limits are 1-20 μg/L. This method requires a preliminary reduction of the samples. For this purpose, a hydrochloric acid aqueous solution (HCl, 1M), with potassium iodide (KI 1% w/w) as reducing agent, was used for sample reduction and dilution. To account the presence of NaCl in the desorption solutions, analytical tests were performed with standard addition methodology, i.e. by dilution of arsenic samples with NaCl solutions at the same sample concentration containing given amount of arsenic, from 2.5 to 10 μg/L. Standards were prepared by dilution with NaCl solution.

To assure the accuracy, reliability, and reproducibility of the collected data, all tests were performed in triplicate and average values only were reported. The accuracy of analytical techniques was checked by the evaluation of the relative standard deviation (RSD) of each sample analysis. Typical values of the RSD for arsenic were below 4%. Among each replica of a repeated test, the variance in arsenic concentration was of the order of 5%. Since adsorption capacity q_j is calculated by mass balance, the error propagates along the calculation of the adsorption

capacity doubling and resulting equal to 10%. Instead, q_{dj} estimation is accurate within 5%.

3. Results and discussion

In the investigated experimental conditions, the arsenic adsorption tests led to a reduction of arsenic concentration from 3.0 mg L^{-1} to an equilibrium concentration spanning between 2.2 and 2.5 mg L^{-1}, with an average adsorption capacity of around 0.12 mg g^{-1}. This value was far lower than that observed for arsenic solution in distilled water, but is consistent with the former evidences for groundwater (e.g. Muniz et al., 2009). This is also similar to the adsorption capacity exploited by fly ashes (Balsamo et al., 2010). Actually, the adsorption model reported in Di Natale et al. (2008), based on the competition between arsenic, chloride and hydroxides ions allows estimating a value between 0.18 and 0.4 mg g^{-1}. Therefore, the presence of other anions in the actual natural water conditions are responsible for a reduction of arsenic uptake from 2 to 3.3 times with respect to expectation.

The performances of the activated carbon during the cycles are compared in terms of the ratio between equilibrium concentrations at cycle j and cycle 1, c_j/c_1 and in terms of the ratio between adsorption capacities at cycle j and 1, q_j/q_1. The first ratio indicates the effect of cyclic use of the carbon on its capacity of lowering arsenic concentration in the adsorption solution to a fixed value. The second ratio indicates how arsenic is recovered from the activated carbon during each test of the cycle.

Figures 1 shows the experimental results in terms of c_j/c_1 ratios. Experiments indicate that during the cycles, the activated carbon exploits a small worsening of its performances, similar for the three sodium chloride solutions used for regeneration, within the 10% of the fresh sorbent performances. Differently, the solids treated with distillate water immediately experience a 20% increase in c_j, which corresponds to the condition of negligible adsorption in the investigated conditions. This worsening of the activated carbon performances lies within the experimental error, but is likely to be related also to the unavoidable loss of materials during solid handling during the filtration operations. Indeed, the sorbent mass was registered at the beginning of each cycle and, in spite of our best efforts, between 0.03 and 0.06 g of sorbent were lost during the 11 cycles.

This bias can be reduced plotting the experimental ratios q_j/q_1 during cycles, as in Figure 2. This ratio clearly indicate that, on average, the adsorption capacity slightly decreased after the first cycle, probably due to the presence of high affinity adsorption sites (i.e. almost irreversible), but then remain within 10% of its value (and within the experimental uncertainness) for as much as 11 cycles. In other words, a satisfying regeneration level was reached. Besides, we also noticed that arsenic adsorption is almost independent on concentration of NaCl adopted, while after about five cycles, the 0.1 M solution appears the most promising option.
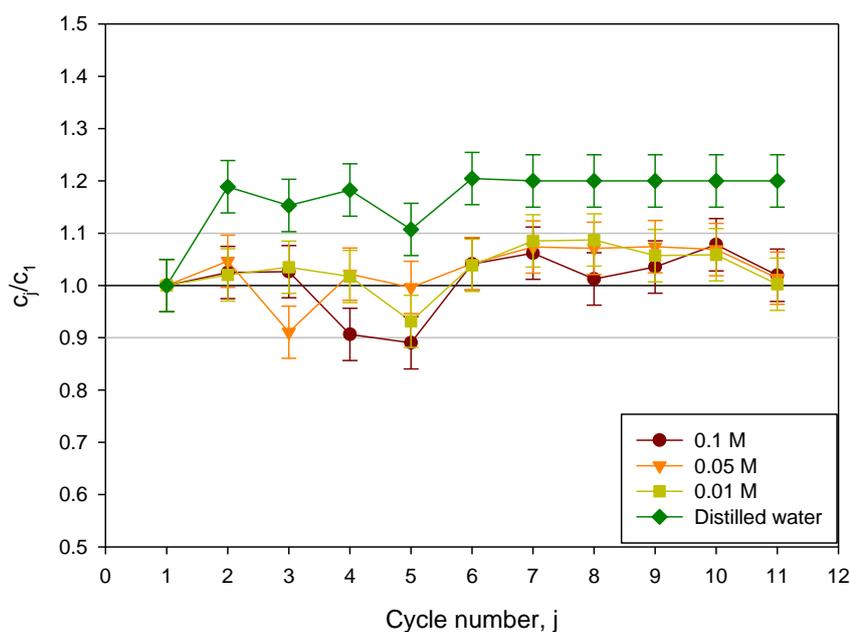
Figure 1. Values of the ratio c_j/c_1 for the j-th cycle for the different NaCl solutions and for distilled water.
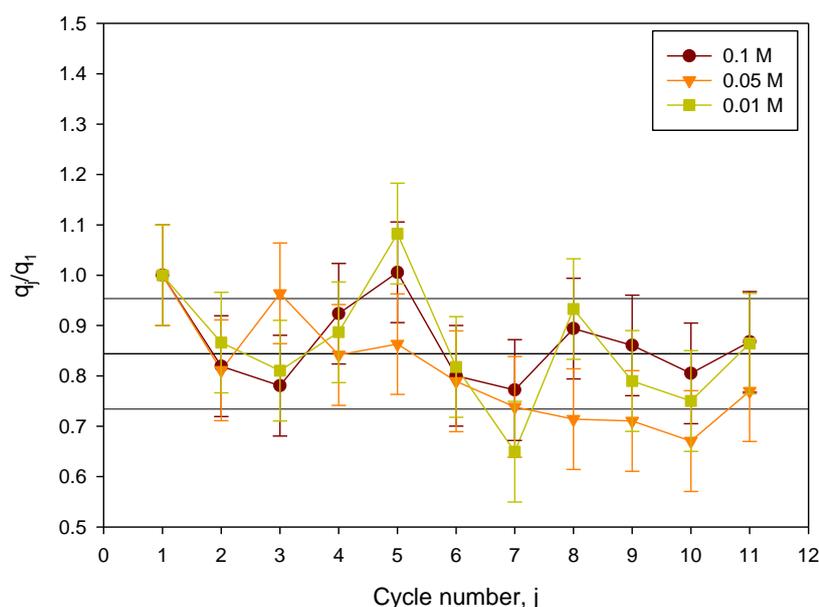
Figure 2. Values of the ratio q_j/q_1 for the j-th cycle for NaCl solutions at different concentration.

Finally, the experimental tests on desorbed activated carbon rinsing with water indicated the absence of any appreciable (>1 μg/L) arsenic leaching. This is consistent with the very limited desorption occurring in distilled water. The highest levels of arsenic (around 0.9 μg/L), were observed at the beginning of rinsing procedure. The rinsing process is usually completed by flushing an overall water volume of 90, 150 and 240 ml for 0.01, 0.05 and 0.1 M NaCl solutions, respectively.

As observed by Di Natale *et al*. (2013), effective arsenic desorption (>90% of total arsenic uptake) can be achieved

with 25 mL of NaCl 0.1 M solution per gram of sorbent. About 80% desorption was observed with 10 mL g^{-1}. Even better desorption are reached with 0.5 M solutions (>95% at 10 mL/g). The results of this study confirmed that, even when exposed to a liquid volume of sodium chloride as high as 100 mL g^{-1}, the performances of the activated carbon were slightly affected by the exposition to chloride and sodium ions. Besides, efficient rinsing, during which negligible amount of arsenic were released, assures acceptable restoration of sorbent properties and allows its reuse for subsequent cycles. Indeed, rinsing is very

important, because the high competition between arsenic and residual chloride solution in the carbon pores may strongly reduce the arsenic adsorption capacity in the next cycle. This was eventually verified by performing tests without rinsing (data not shown). In this case, arsenic adsorption was not preserved in the cycle sequence and after five cycles, the activated carbon was not effective anymore.

The possible restoration of activated carbon capacity with NaCl desorption open the route for the design of a cyclic adsorption-desorption process. Indeed, since the carbon preserves its uptake capacity once exposed to as much as 100 mL g^{-1}, with up to 10 mM of NaCl per gram, we can admit that the same will occur once it is exposed to lower NaCl dosage. If for example, we suppose to run the cycle process with with 25 mL of 0.1 M NaCl solution, or with 10 mL g^{-1} of 0.5 M NaCl solution, arsenic can be concentrated in a liquid stream at pH 8 and containing chloride whose volume is 5.3 to 13.3 times smaller than the polluted stream. This led to a relevant reduction of the amount of water to be treated by precipitation, ideally using iron chloride, which is expected to provide the best removal of arsenate among the other coagulant, as suggested, for example, by Hesami *et al*. (2013), Hering *et al*. (1996) or Ricci Nicomel *et al*. (2016).

4. Conclusions

This paper reports experimental data on the cyclic usage of activated carbon for arsenic adsorption from a model natural water. Experiments indicated the possibility of running effective adsorption cycles with activated carbon. However, further efforts are needed to better address some relevant aspects, such as the effect of sulfates and other anions concentration in solution. Moreover, the assessment of process kinetics and preliminary economic estimation will be the next step of this project.

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