

Arsenic removal with selective hybrid adsorbers

Dr Stefan Neumann, manager technical marketing and chemicals purification at the Ion Exchange Resins business unit of LANXESS and head of the respective application laboratory, reports about recent developments and improvements in the application of specific hybrid adsorbers to remove arsenic from drinking water

Anion exchange resins modified with special iron oxides are suitable for the efficient removal of arsenate and also arsenite ions from drinking water by selective adsorption¹ (Figure 1). However, further development work² was needed in order to make the process technically feasible also on a small scale and to overcome certain obstacles, i.e.

- The interference of other anions, namely silicate, with arsenate during the adsorption process, resulting in a significant reduction of capacity for arsenic uptake.

- A significant drop in capacity to a lower level after repeated conventional regeneration of the adsorber material.

Additionally, a practical procedure has been developed and tested for the removal of arsenic on a household scale, employing a commercially available filter system

The arsenic problem and how to solve it

The health of millions of people around the globe is endangered by arsenic contamination of their drinking water.

This is the case not only in India, China or Bangladesh, but also in parts of the United States of America, Great Britain, Germany and Italy, due to the washing out of natural mineral sources and, to a lesser extent, to anthropogenic influences such as wastewater from mining and industry. The World Health Organization (WHO) has recommended³ a threshold of 10 ppb (parts per billion) of arsenic as the maximum concentration limit (MCL) in drinking water. This threshold is generally accepted in many countries. Nevertheless, millions of people only have access to drinking water containing 50 ppb of arsenic or even more. Arsenic is highly toxic to higher organisms and humans. Changes to the skin and other damage to health,

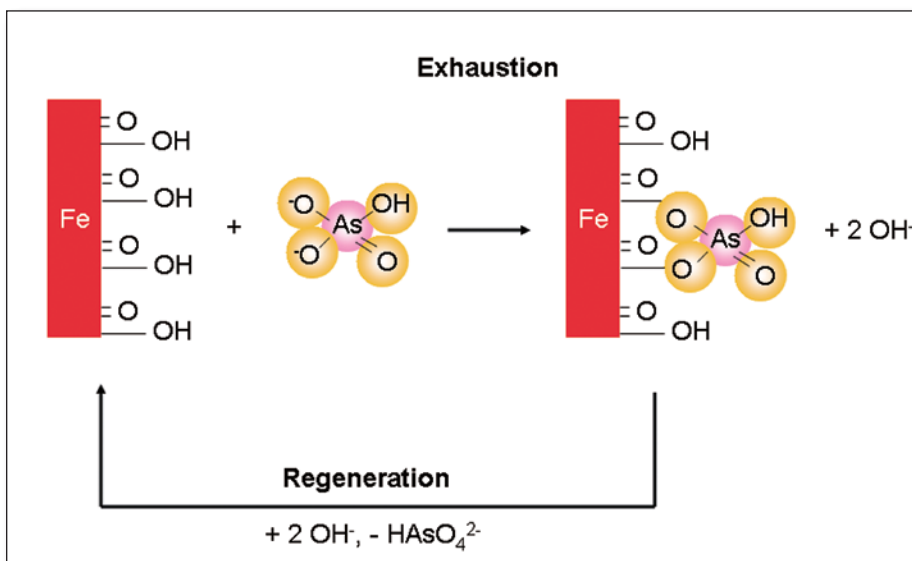


Figure 1: Simplified mechanism of As(V) adsorption on FeO(OH)-based materials.

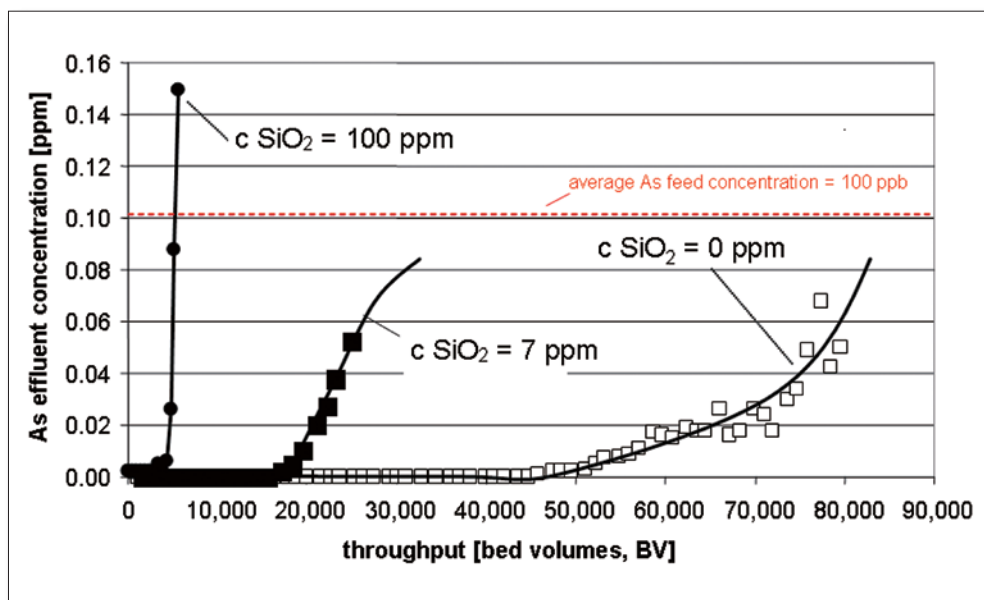


Figure 2: Influence of silicate concentration on arsenic adsorption to Lewatit® FO 36 (feed: pH 7, approximately 100 ppb As(V), 160 mg/L HCO₃⁻, 50 mg/L Cl⁻, 13 mg/L SO₄²⁻, 0.18 mg/L H₂PO₄⁻; volume/depth of filter bed: 100 mL/280 mm; diameter of column: 22 mm; specific velocity: 20 – 30 BV/h).

culminating in vascular diseases or cancer, are particularly prevalent in the case of long-term exposure.

Modified ion exchange resins have been successfully applied to cope with this problem. Based on decades of experience in water treatment and on the joint expertise in the fields of ion exchange resins and iron oxides, LANXESS has developed Lewatit® FO 36. This is a hybrid material composed of a regular polystyrene based weak base anion exchanger and an inorganic iron oxide phase (approximately 15% by weight) distributed almost uniformly throughout the pores of the resin matrix. Production of this material was launched by LANXESS in 2008. As a dust-free, flowable substance with a standard grain size and good mechanical stability, the product is tailored to the requirements of industrial water treatment. After the saturation limit has been reached, it can be regenerated with a solution of sodium hydroxide in brine, enabling it to be used repeatedly in an eco-friendly, cost-effective way. Lewatit FO 36 is currently already being used at a total of three facilities in Italy and Germany to remove arsenic from well water on an industrial scale.

Coping with interfering anions

Several anions such as HPO₄²⁻, HCO₃⁻ and – most importantly in many regions of the world – H₃SiO₄⁻, have been shown to efficiently interfere with arsenate adsorption. As a result, the performance of the hybrid adsorber is significantly deteriorated in the presence of these ions, as shown in Figure 2 above for a laboratory experiment with silica at different concentration levels. In the presence of 100 ppm of silica, the arsenic capacity drops to only 0.45 g/L of adsorber resin, compared to 7.0 g/L in the absence of silicates.

As silicates are quite frequently present in drinking

water, a way to overcome the interference with arsenic adsorption is highly in demand. This could be achieved by employing a two-step adsorption process (Figure 3, overleaf) which has recently been developed in our laboratories and is about to be patented⁴. This process can lead to an increase in operating capacity (OC) of the hybrid adsorber by a factor in the range of five to seven, compared to the one-step process. For example, at a silica concentration of 100 ppm, an OC of 3 g of arsenic per litre of resin could be obtained instead of about 0.45 g/L with the conventional setup.

The process consists of two steps (Figure 3). In the first step, the raw water

containing both silica and arsenic is filtered through a conventional strongly basic resin (standard basic anion exchanger, SBA), namely Lewatit MonoPlus M600, exhibiting low selectivity for silica. Silicates therefore pass through the filter while the arsenic is adsorbed.

When the capacity limit of the SBA for arsenic is reached after about 10 h of operation, regeneration of this filter is carried out as the second step of the process by means of a concentrated solution of either seven per cent of sodium chloride or sodium sulphate. The latter leads to enhanced liberation of arsenic from the SBA. This regeneration takes about 1 h. The spent regenerant solution then contains all the arsenic originally bound to the SBA. It is subsequently filtered over a column containing the arsenic selective hybrid adsorber (ASHA), thus taking up the arsenic washed down from the SBA. The filtered brine can subsequently be reused to regenerate the SBA.

A further advantage in this process results from the fact that a smaller amount of hybrid adsorber, i.e. About 50% by volume, is required, compared to the volume of the SBA. As a result, overall operating costs for the two-step process are expected to be in the same range as for the conventional one-step procedure. An additional benefit of the two-step process arises from the fact that practically all the brine/sodium sulphate solution used for regeneration can be recycled. This is especially important because operation cycles of the SBA are much shorter than those of the ASHA, thus requiring large quantities of the regenerant.

Improving regeneration efficiency

Even when the hybrid adsorber is employed for just one cycle of arsenic removal and discarded afterwards, cost for this water

treatment will not exceed one Euro per cubic metre, according to LANXESS estimates. However, a key advantage of ion exchange resins compared to other filter materials used for water treatment is the fact that simple and efficient regeneration is normally possible, allowing for repeated use of the material. This helps to design processes which run even more cost-efficiently than a nonrecurring use of the resin.

Unfortunately, the original capacity of the adsorber cannot be restored in total after repeated standard regeneration cycles. Instead, the actual capacity stabilises at a lower level. Currently, this level lies at about 50% of the initial capacity and is reached after two regeneration cycles in the case of dynamic adsorption employing a column setup. This is especially the case at high concentrations of silicates in the raw water. In order to improve this unsatisfactory situation, modifications of the regeneration process were investigated, namely:

1. Reduction of the sodium hydroxide concentration in the brine used for regeneration from four per cent to two per cent;
2. Introduction of a second step into the regeneration cycle, consisting of a conditioning treatment of the resin with brine which is little by little acidified to pH 4.5 in order to omit substantial loss of iron by formation of iron chlorides.

As a result of the first modification, capacity loss was slowed down by about a factor of two, now allowing for four cycles before the capacity drops to the 50% level. However, a lower silicate concentration in the 2% NaOH-experiment might also contribute to this improvement. In the second case, the initial capacity could almost completely be restored by the

conditioning treatment. Similar results have been obtained in the presence of phosphate or silicate ions. These findings have yet to be confirmed by further experiments.

For both process modifications, reasons for the observed improvements are not yet clear. In the first case, the beneficial effect of a reduced concentration of sodium hydroxide might arise from reduced “chemical stress” to the iron oxide. This might give rise to a smaller extent of ageing which means a change in crystal morphology of the oxide. This morphology is crucial for the adsorptive activity of the material. Loss of iron from the resin, on the other hand, turns out to be relatively unlikely. Plugging of pores or fouling of the resin could also explain a reduced capacity. The acidified brine used in the after-treatment might neutralise traces of sodium hydroxide which are still present in the resin, thus preventing long-term damage to the resin or the iron component. The effect of phosphate or silicate ions could be due to blocking of arsenic-binding sites which is not reversible under standard regeneration conditions. However, the acidic after-treatment might then be able to unblock these sites.

Further investigations are underway to clarify the situation and to develop a superior regeneration strategy which can be employed in large-scale water treatment.

A household solution for arsenic removal

Laboratory tests have shown that the hybrid adsorber can be used to fill filter cartridges and – like commercially available standard cartridges for softening water – be deployed on a localised basis on the move or for household use where a central supply of drinking water is not available. The flow chart representation (Figure 4) shows the experimental setup of such a pitcher test.

One single cartridge containing only around 125 mL of adsorber was used to treat around 1,400 litres of water over three months (Figure 5). This cuts arsenic content from approximately 100 ppb (100 micrograms per litre) to less than 10 ppb, i.e. below the MCL recommended by the WHO. Further experimental confirmation of this result under a variety of field conditions has yet to be obtained. The cartridge system was used in an on-demand mode, as is typical of household applications, and even went through a series of drying cycles in the course of the test period. Despite this rough treatment, the filter remained in operation for three months, ultimately yielding operating capacities of around 1.1 g of arsenic per litre of resin which are quite comparable to those from large technical systems operated under much smoother and better controlled conditions

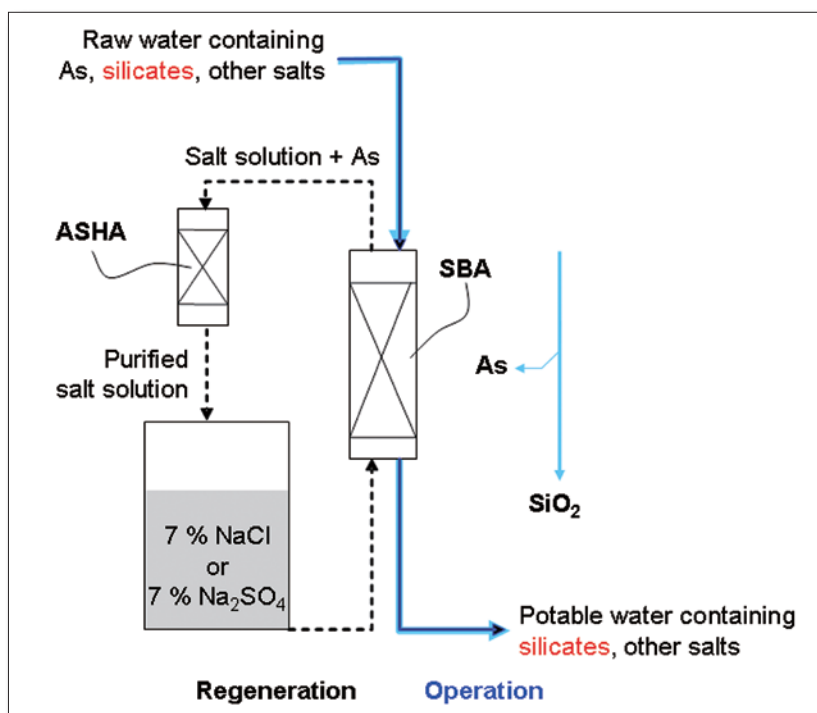


Figure 3: SBA/ASHA-process (schematic) for efficient removal of arsenic from raw water containing silicates.

Results and outlook

The selective removal of arsenic from drinking water with an iron oxide-based

hybrid adsorber resin has been shown to be a feasible process both on an industrial scale and on a household scale using a simple pour-through device. Introducing a two-step adsorption process has made it possible to overcome the competing effect of high silica loads on these adsorbers. Variations of the regeneration conditions have provided an entry into improved regeneration procedures which give rise to an enhanced recovery of the initial capacity of arsenic adsorption.

Besides developing an automated two-step operation process, future efforts will concentrate on the optimisation of the regeneration process in order to enhance the lifetime of the adsorber at maximum operating capacity. [WWA](#)

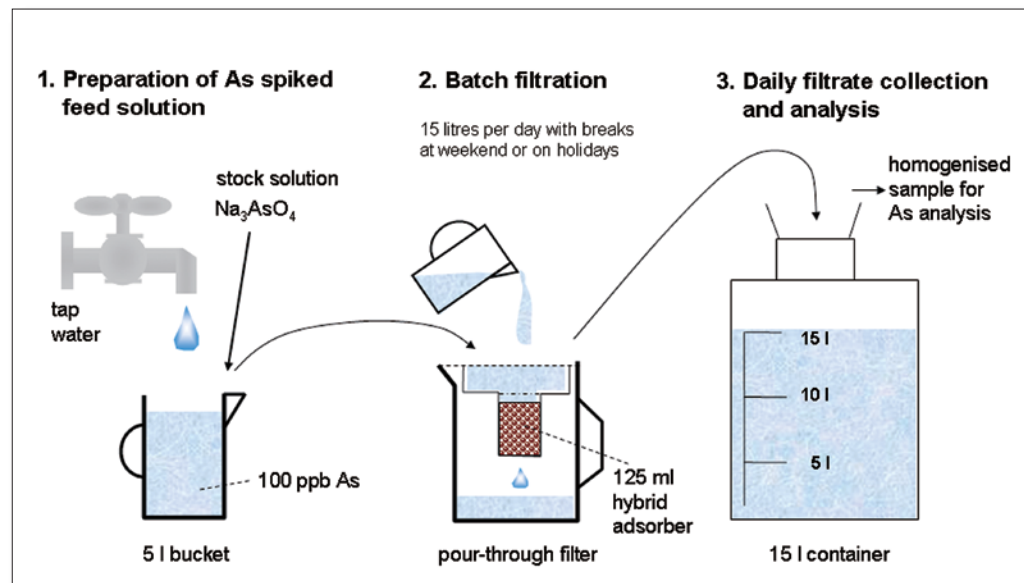


Figure 4: Flow diagram illustrating the setup of the pitcher test.

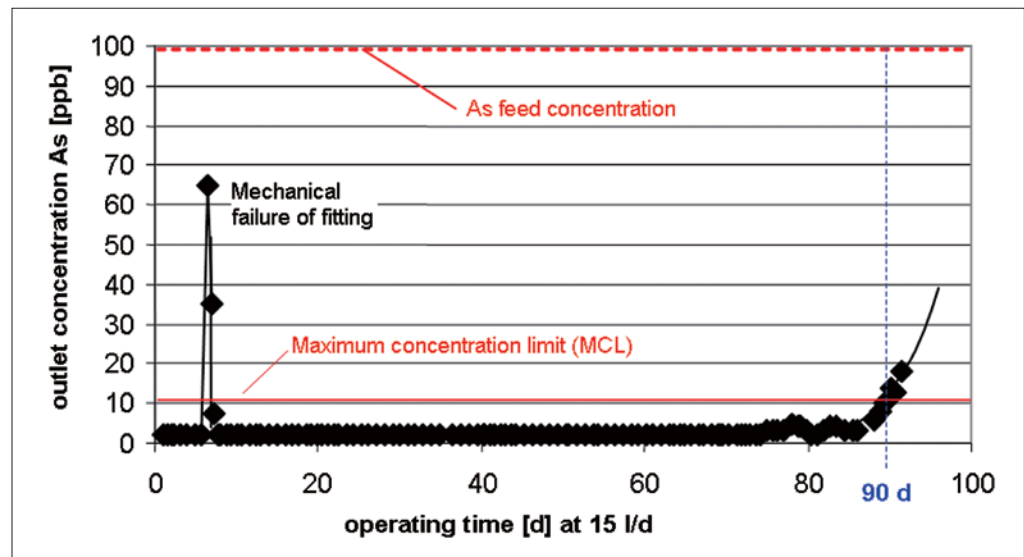


Figure 5: Breakthrough curve for arsenic obtained in the pitcher test (ion concentrations in tap water [mg/L]: Mg^{2+} 12; Ca^{2+} 63; SO_4^{2-} 43; Cl^- 44; NO_3^- 11; CO_3^{2-} 168; PO_4^{3-} 0.2; SiO_2 5.3; Na^+ , K^+ not determined).

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