

Arsenic removal using iron colloids



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Drinking water contaminated with arsenic can be treated using filters in which arsenic is adsorbed onto iron colloids. However, the performance of these systems may not be optimal, depending on the composition of the water. Eawag has now investigated the processes involved – and how the design of future filters could be optimized.

Worldwide, more than 100 million people – mainly in developing countries – are affected by excessive concentrations of arsenic in drinking water. Groundwater is tapped as an alternative to scant or polluted surface waters, but in many areas it contains natural (geogenic) arsenic dissolved from rocks and sediments. As water supplies in developing countries are often decentralized, there is a need to find solutions at the household or community level. In recent years, a variety of arsenic mitigation strategies have been developed in severely affected countries, such as Bangladesh; the success of these approaches depends on local circumstances [1]. For those regions where it is not possible to avoid arsenic-tainted water altogether, filter systems have been developed to permit removal of the toxic element (see Box). Particularly promising are sand filters that either take advantage of iron occurring naturally in water or contain additional iron in the form of filings or nails [2]. In these systems, iron colloids are formed which adsorb arsenic, thereby removing it from the water. However, the performance of the filters varies according to the water composition. For example, it has been shown that colloid formation decreases sharply within the first 30 days, leading to inadequate arsenic removal.

If these systems are to be optimized, a fundamental understanding of the chemical and physical processes in the filters is required. We therefore used electron microscopy methods, combined with chemical analysis of samples, to study the following questions:

- How are the iron colloids produced and what are their properties?
- Under what conditions are dissolved substances adsorbed onto existing surfaces (iron nails/filings, iron colloids), forming new layers?

Experimental set-up. As part of Christine Wenk's Master's thesis, the Kanchan filter was reconstructed and tested at laboratory scale. Since the removal efficiency depends on the water composition, we studied various synthetic waters. While all of these showed the elevated arsenic content characteristic of arsenic-tainted groundwaters, we varied the concentrations of calcium, silicon and phosphorus. The waters produced were allowed to

pass through a bed of iron nails corresponding to the Kanchan filter for several weeks (Fig. 1). Arsenic removal was determined by measuring the concentrations of arsenic in the effluent. In addition, to obtain information on corrosion rates for the iron nails used, the oxygen content of the filtered water was analysed. Electron microscopy techniques were used to examine the surface

Fig. 1: Bed of iron nails.



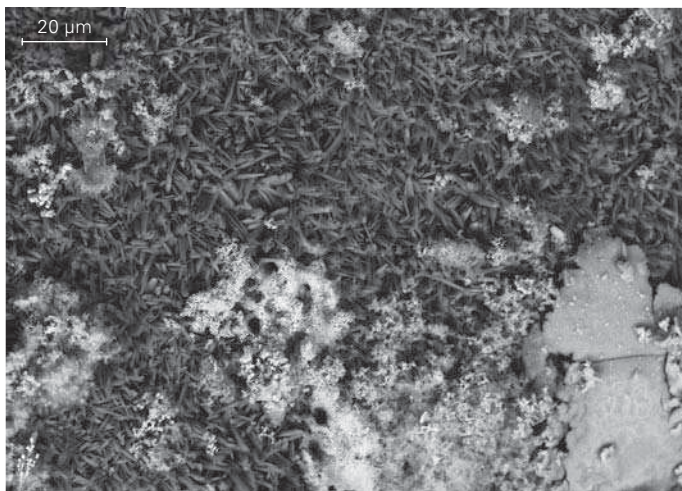


Fig. 2: Coating of calcite (dark areas) and iron colloids (light areas), which formed on iron nails after filtration with phosphate-free water.

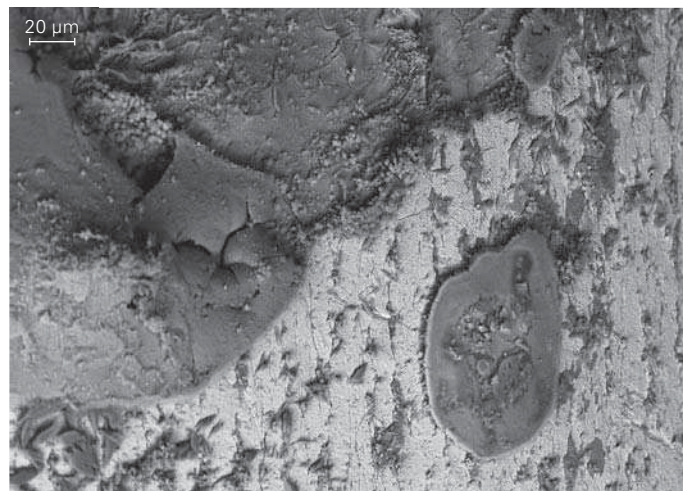


Fig. 3: If water containing phosphate is used for filtration, the surface of the iron nails remains largely clean (light areas).

of the corroded nails and of the iron(III) oxide/hydroxide colloids (particles between 1 nm and 1 μm) produced by the corrosion process.

Surface analysis of iron nails by environmental scanning electron microscopy. With the ESEM, in contrast to conventional scanning electron microscopy, non-conductive samples can also be imaged without special preparation. Depending on the signal type, information is acquired on the topography or the elemental composition of the specimen.

Initially, we worked with a phosphate-free water, which, however, contained calcium and silicon. It was shown that, after filtration, the surface of the nails is completely covered by a coating of dark crystals, with isolated lighter areas. Figure 2 is a backscattered electron image, providing both topographical and chemical information: bright areas represent heavy elements, and darker regions correspond to lighter elements. The chemical composi-

tion of the two phases can be directly determined in the SEM by means of energy dispersive X-ray analysis. In this technique, the atoms in the sample are excited by the electron beam and emit X-rays with an energy characteristic of a specific element. We identified the darker areas as calcite crystals (CaCO_3) and the lighter areas as iron-rich colloids. The iron particles were formed in the course of corrosion and became attached to the surface of the calcite crystals. With water containing phosphate, in contrast, calcite formation is suppressed and the iron nails remain uncoated. In Fig. 3, the light areas clearly indicate that the surface of the iron nails is still largely free of coating layers.

Overall, our observations accord very well with the results concerning oxygen consumption and iron corrosion. In the absence of phosphate and with a high calcium content, a dense layer of calcite forms on the iron nails. This is undesirable, as the calcite reduces iron corrosion, i.e. the formation of iron(III) oxide/hydroxide colloids. Conversely, in the presence of phosphate,

Principle of filter systems used for arsenic removal

In Bangladesh, the main type of filter used comprises layers of sand and cast iron turnings (SONO filter) [3], while the type of device preferred in Nepal is the Kanchan filter, in which water first runs through a bed of iron nails (Fig. 1) and is then passed through a biosand filter [4]. In both cases, iron(III) oxides/hydroxides are produced – either from dissolved iron(II) already contained in the water, which oxidizes when groundwater is pumped to the surface, or as a result of corrosion from metallic iron(0) in the filings/nails. These iron colloids adsorb the dissolved arsenic and form larger particles, which can then precipitate or be deposited on sand grains or on the iron itself.

The performance reported for filters of both types varies from good to inadequate, according to the specific type of water and other factors. The form, composition and properties of the iron(III) oxides/hydroxides depend on the water composition. At the same time, phosphate, calcium and silicate present in the water are incorporated into the iron(III) oxides/hydroxides, which impedes the removal of arsenic. In addition, the oxidation of iron is coupled with the oxidation of arsenic(III) to the more readily removable arsenic(V) species – but this process is also significantly influenced by the water composition and the flow conditions in filters.

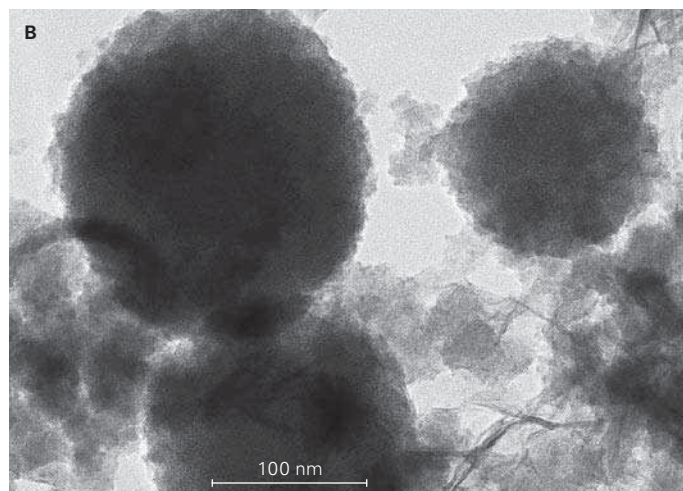
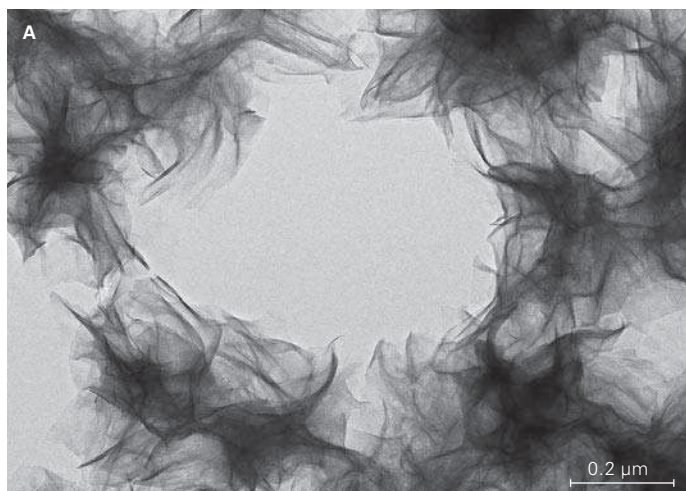


Fig.4: Lepidocrocite (A) and ferrihydrite (B), iron colloids that form in the filter system if the water contains sodium bicarbonate (A) or sodium bicarbonate and silicon (B). Both types of colloid adsorb arsenic.

calcite formation is prevented; as a result, the surface of the iron nails remains cleaner and the rate of corrosion higher. In fact, however, this finding was surprising because phosphate is also used as a corrosion inhibitor in water pipes.

Analysis of iron colloids by transmission electron microscopy. In the transmission electron microscope (TEM), samples are illuminated by electrons and therefore need to be thin. The newly formed iron(III) oxide/hydroxide colloids are generally only a few 100 nm thick and are highly suitable for analysis in the TEM. With this method – unlike the above-described ESEM, where larger samples can be directly inserted into the microscope – the colloids first have to be mounted on appropriate holders.

We first analysed iron colloids that had formed during the filtration of water which contained sodium bicarbonate but was silicon- and phosphate-free (Fig. 4A). We identified these colloids as lepidocrocite, an iron oxide/hydroxide mineral (γ -FeOOH) with an orthorhombic crystal structure (crystal system with three unequal axes at right angles to each other). If silica is now added to the water, the crystallization of lepidocrocite is prevented and ferrihydrite (structural formula not yet established), another iron oxide/hydroxide mineral, is formed (Fig. 4B). Dissolved arsenic can be adsorbed onto both types of colloid and is thus removed from the water.

If phosphate is added to the water, amorphous iron phosphate colloids are formed, but – as a result of the binding of phosphate to the iron colloids – the adsorption of arsenic is decreased and less arsenic is removed from the water overall. However, this negative effect of phosphate on arsenic removal is partly offset by the more rapid corrosion of iron turnings in contact with water containing phosphate.

How can arsenic filters be improved? The Kanchan filters that were reconstructed at laboratory scale and tested under various conditions rely on the corrosion of iron nails. The measurement

of oxygen concentrations showed that, although iron corrosion does not decline sharply within the first 30 days, arsenic removal is reduced from 90 % at the outset to approx. 60 %. The main reason seems to be that less iron(III) is released and the formation of iron(III) oxides/hydroxides is thus also decreased. However, after the initial deterioration in arsenic removal efficiency, it appears to stabilize at the 60 % level in subsequent months. One possible way of improving the filter system would be to use two nail beds separated by a space containing air. After passing through the first filter, the water would then be oxygenated again and the corrosion process would be restarted; as a result, the arsenic content would be reduced to an acceptable level. Another option would be periodic removal of the corrosion layers, e.g. by breaking up the nail bed and applying mechanical friction (vigorous shaking). ○ ○ ○

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