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Original scientific paper

Removal of inorganic As⁵⁺ from a small drinking water system

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Abstract: The drinking water from a small drinking water system contained arsenic in a concentration of about 50 µg/L. Chemical analyses showed that the pentavalent form of arsenic was present. Since the MCL value is 10 µg/L, it was necessary to implement a technological treatment to make the water suitable for drinking. In order to do so, two technologies were suggested: activated alumina and α-FeOOH (TehnoArz, TA) adsorption media. Experiments using both adsorption media were performed on a laboratory scale. It was possible to remove arsenic to below 1 µg/L. The maximal adsorption capacity was found to be 12.7 mg of As⁵⁺ per gram of α-FeOOH. Moreover, all the important physico-chemical parameters of the water remained practically unchanged after the treatment. Only a slight release of iron from the media was observed. The Fe–As bond was studied by means of chemical analysis and X-ray powder diffraction. Finally, in addition to showing the capability of arsenic removal by α-FeOOH, a comprehensive optimization of the technological parameters of the selected technology is provided.

Keywords: drinking water; arsenic; activated alumina (AA); goethite; adsorption.

INTRODUCTION

In 2004, arsenic became to be regarded as a highly toxic substance by the US EPA and European Union with a maximum level of contamination MCL of 10 µg/L. It was confirmed that arsenic causes skin, liver, lung, and kidney cancer. Arsenic naturally occurs in water because of mineral dissolution from the parent rock and abandoned coal mines. Due to human pollution, 21 countries around the world are affected by arsenic contamination of groundwater.¹ Anthropogenic activities, such as mining and smelting and the use of pesticides, wood preservatives and fossil fuels have resulted in a dramatic effect on the levels of natural environmental arsenic. Bangladesh and the West Bengal State in India have the most severe arsenic problems, with concentration in mg/L range.^{2,3}

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Arsenic occurs in the oxidation states -3 , 0 , 3 and 5 , yielding a variety of inorganic and organic compounds. In short, the inorganic species consist of arsenate and arsenite, while the organic consist of monomethylarsonic acid and dimethylarsonic acid. Other arsenic-containing organic compounds are also found in the environment, such as arsenobetaine, methylarsonate (MA), dimethylarsonate (DMA) and trimethylarsine oxide (TMAO). The toxicity decreases in the order arsine $>$ inorganic As^{3+} $>$ organic As^{3+} $>$ inorganic As^{5+} $>$ organic As^{5+} $>$ arsonium compounds and elemental arsenic.⁴

The methods for the removal arsenic are explained in detail in the literature.^{1,5} The existing removal processes include oxidation using Fenton's reagent, catalytic materials such as manganese dioxide coated sand, black iron removal material BIRM, green sand, UV irradiation, dissolved oxygen oxidation followed by a powdered activated carbon, coagulation by Fe- or Al-salts, ion exchange, activated alumina, AA, and membrane separation. It is very important to establish the form in which the arsenic is present in the water, because the pentavalent form is easier to remove than the trivalent form.

Lafferty⁶ studied the efficiency of iron oxides in the removal of arsenic from water. According to literature data,⁷⁻¹² goethite showed a very good adsorption capacity for organic and inorganic arsenic species. Goethite is, therefore, a promising adsorption media for the removal of inorganic As^{5+} from water. Sherman¹³ studied the mechanism of arsenate (AsO_4^{3-}) ion sorption to oxide hydroxides ($\alpha\text{-FeOOH}$). At the pH and pore water concentrations of the reservoir, arsenite remained sorbed to labile iron solid phases until they underwent reductive dissolution.¹⁴ Also, Tripathy reported an enhanced efficiency of arsenic removal by alum coated activated alumina.¹⁵

The aim of this study was to investigate which of the two chosen adsorption media is the most adequate for As^{5+} removal and to provide the optimum parameters of selected technology for small communities.

EXPERIMENTAL

Materials and analytical methods

Activated alumina (AA) was obtained from Alcan Chemicals, the Netherlands, and TehnoArz (TA) from Tehnobiuro, Slovenia; TA is a commercial name for $\alpha\text{-FeOOH}$.

All the employed chemical substances were of a high degree of purity (p.a.).

Analyses of Fe^{2+} , Mn^{2+} , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} , were done spectroscopically using a Cary instrument, based on standard methods (DIN 38406, DIN 38405-D19).

The concentrations of K^+ and Na^+ were measured by atomic absorption spectrometry using a Perkin-Elmer 1100 B spectrometer with the appropriate source of radiation (DIN 38406 E-13, E-14, E-15).

Ca^{2+} , Mg^{2+} and HCO_3^- were determined titrimetrically by standard methods (DIN 38409 H6).

The pH was measured using a pH meter MA 5740, after calibration with buffers of pH 4.0 and 7.0 (DIN 38404-C5).

X-Ray powder diffraction data was collected with an AXS-Bruker/Siemens/D5005 diffractometer using $\text{CuK}\alpha$ radiation at 293(1) K. The samples were PSD fast scanned and measured in the 2θ range 10–80°. The measuring times were from 47 to 52 h with a step of 0.014 and a scanning speed of 2 s per step. The values for the divergence and anti-scattering slit were fixed at 0.2 mm. The X-ray diffraction pattern was indexed with the help of automatic indexing programs TREOR and ITO. For the determination of the end product, the Search/Match program was used.¹⁵

The concentrations of arsenic were analysed using a Perkin–Elmer Elan 6100 ICP–MS instrument. All samples were filtered through a 0.45- μm filter (Whatman Autovial), acidified and stored at 5.0 °C until analysed. Arsenic analysis using ICP has a relative standard deviation of less than 5 %.

Water sampling, characteristics and purification

The water well is situated under the Pohorje Hill and rises from an abandoned mining site. Arsenic may have been released into the environment through the mining process. A groundwater aquifer is the source of the water. The internal pressure is high enough to push the water up to the surface. The water flows from the rock through a 2.5 cm diameter tube. The water flow has been constant at 18000 m³ per year for a long period of time (over 100 years).

The water samples were taken directly at the spring, according to the water quality sampling guidance on the preservation and handling of samples standard method (ISO 5667-3; 96). All water samples were stored in brown glass bottles and kept cool (at 4.0 °C) during transport to the laboratory, where they were processed the day after sampling campaign. The water was odourless, colourless and tasteless. All measured parameters are presented in Table I. Three replicates were made for all measurements and very good reproducibility was obtained. There was no iron, manganese, nitrite or phosphate in water, as can be seen from Table I. According to the EU legislation, the concentration of arsenic is too high. Thus, it should be removed before the water is used for drinking.

Two water purification procedures were selected: adsorption on activated alumina (AA) and on goethite $\alpha\text{-FeOOH}$ (TA).

The water was filtered through an AA column of diameter 3.2 cm and height 1.0 m at a velocity of 10 to 40 m/h.

The water was filtered through a TA column of diameter 3.2 cm and height 30 cm at a velocity of about 10 m/h (Fig. 1).



Fig. 1. Laboratory equipment for arsenic removal with $\alpha\text{-FeOOH}$ (TA) filter media.

Adsorption studies

The equilibrium adsorption measurements consisted of mixing various amounts of adsorbent (1–2 g) with a fixed mass of test liquid in stoppered flasks, which were shaken for at least 24 h (the time required for each system to reach equilibrium had previously been determined by contact time experiments). Preliminary purging was necessary to eliminate the effects of oxidative coupling of the adsorbates. The adsorbent was subsequently separated by filtration and the filtrate analysed by ICP–MS for residual adsorbate concentration.

RESULTS AND DISCUSSION

Preliminary tests made using HPLC–HG–AFS¹⁶ showed that the drinking water source contained As in the inorganic pentavalent form.

The obtained results of physico–chemical analyses are presented in Table I for both arsenic removal procedures.

TABLE I. Physico–chemical parameters of the water before and the after treatment procedures

Parameters	Water	AA	TA
pH	7.6	7.8	7.6
$c(\text{As}) / \mu\text{g L}^{-1}$	50	6	0.2
$c(\text{Na}^+) / \text{mg L}^{-1}$	4	11	4
$c(\text{K}^+) / \text{mg L}^{-1}$	1.5	1.5	1.5
$c(\text{Ca}^{2+}) / \text{mg L}^{-1}$	53	50	55
$c(\text{Mg}^{2+}) / \text{mg L}^{-1}$	44	40	43
$c(\text{Fe}^{2+}) / \text{mg L}^{-1}$	< 0.05	< 0.05	< 0.05
$c(\text{Cl}^-) / \text{mg L}^{-1}$	6	6	6
$c(\text{NO}_3^-) / \text{mg L}^{-1}$	15	15	15
$c(\text{SO}_4^{2-}) / \text{mg L}^{-1}$	22	23	20
$c(\text{HCO}_3^-) / \text{mg L}^{-1}$	330	330	330

The removal of arsenic from the drinking water was successful. As presented in Table I, the pH value increased from 7.6 to 7.8 after treatment with AA. The concentration of Na^+ remained practically unchanged when using TA, while the concentration increased after adsorption on AA. Slight oscillations were observed for the concentrations of Ca and Mg ions.

The concentrations of arsenic ions were reduced to under the MCL value by both the employed methods. The experiments were repeated several times and the results were always the same as presented in Table I.

It is clear that water purified in this way agrees with the standards for drinking waters.

The Freundlich model is defined by Eq. (1):

$$q = K \gamma_e^{1/n} \quad (1)$$

where q is the mass adsorbed per mass of media (mg/g) and γ_e is the equilibrium concentration of adsorbate (mg/L).

The parameters of the model were calculated from measured data (Fig. 2): $K = 25.1$ and $1/n = 0.1439$. The model reasonably described the experimental values.

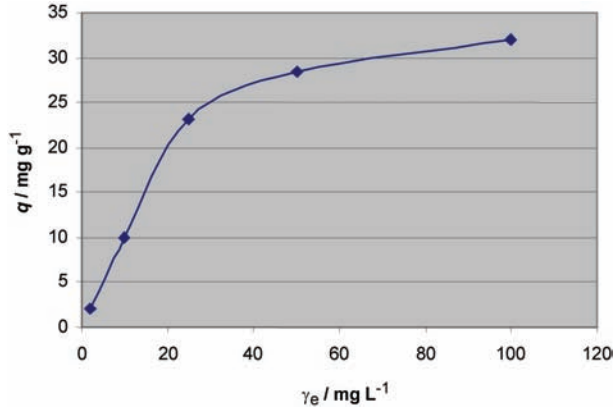


Fig. 2. Experimental adsorption isotherms at 25 °C and pH 7.6.

Tests showed that the AA and TA filtration efficiency was quite high. If q is the mass adsorbed per mass of media (mg/g), γ_0 is the As^{5+} influent concentration (mg/L) and γ_1 is the As^{5+} effluent concentration (mg/L), the bed life Y , the volume of water that can be treated per mass unit of AA (L/g), can be calculated:

$$Y = \frac{q}{\gamma_0 - \gamma_1} \quad (2)$$

Since q for AA was determined as 2 mg/g,¹⁷ Y for AA was calculated to be 48.8 L/g. Y for TA was determined as 311 L/g, according to Eq. (2).

Thus, the adsorption capacity using TA was much higher than when AA was used. Therefore, the following parameters were suggested:

- Water flow: 0.50 m³/h;
- Daily water need: 2.0 m³/d;
- $\gamma(\text{As})$: 0.050 mg/L;
- TA mass: 2860 g;
- TA height: 1.0 m;
- Column diameter: 22 cm;
- Contact time: 275 s;
- Pump power: 0.75 kW.

If the water flow is assumed at 2000 L/d, $\gamma(\text{As})$ is 0.050 mg/L and the adsorption capacity 12.74 mg/g, the TA bed life was calculated as 443 days or approximately 1.2 year. After this period, it would have to be replaced.

The release of iron ions from the medium was monitored. From Fig. 3 it is seen that the concentration of iron ions increases slightly. After 50 days, the

concentration was still below 0.01 mg/L. It could be concluded that the concentration will not rise above the 0.02 mg/L before replacement of the media.

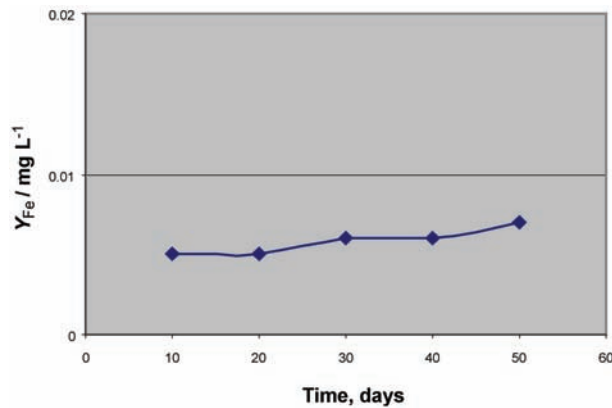


Fig. 3. The release of iron ions with time.

The type of the Fe–As bond was characterized, in addition to chemical analysis, also by X-ray powder diffraction analysis. With powder diffraction analyses, arsenic as AsO_4^{3-} forms a strong bond to $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$. The mechanism has not yet been fully explained. Powder diffraction analysis of TA, shown in Fig. 4, showed that the arsenic was bound to Fe in the form $\alpha\text{-FeOOH}$ and Fe_2O_3 .

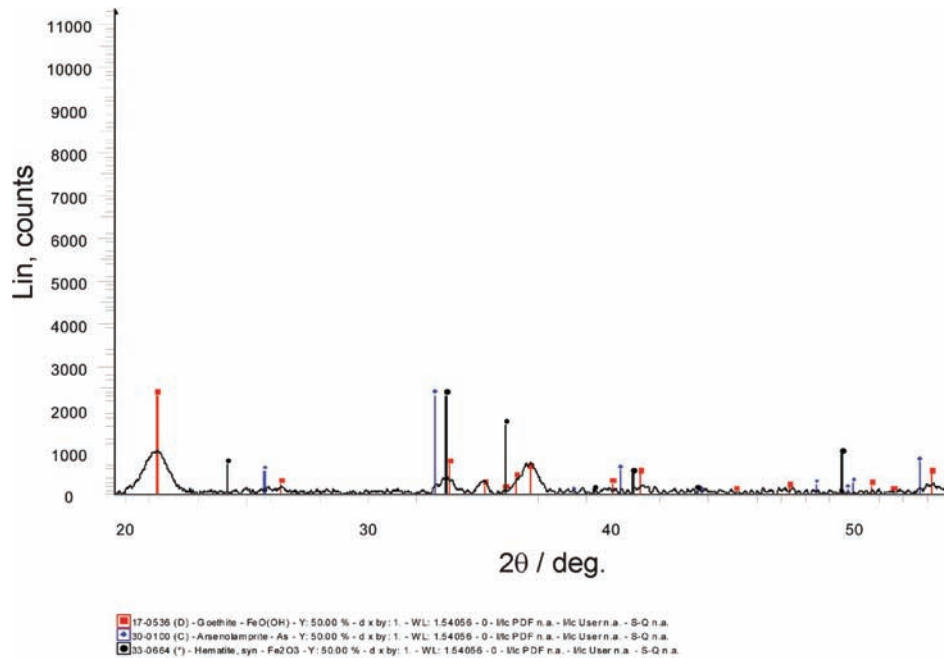


Fig. 4. Powder X-ray diffraction pattern of TA.

First, 1.0 g of TA was stirred in a water sample with 20 mg/L As^{5+} . After the equilibrium had been attained, it was dried and subjected to X-ray powder diffraction analysis. The same material was mixed with rainwater and left first for a week, and then for a month. The As concentrations were measured in the water before and after stirring. The As ions were bound strongly to the TA and they did not re-dissolve into the water, thus the concentration of arsenic in all samples did not change. Also, X-rays powder diffractograms were made for both dried samples: they did not differ one from the other at all. All three diffractograms were very similar to the shown in Fig. 4. This proved that the spent material could be discharged to a landfill without the fear of As leaking to the ground water sources.

TA adsorption is cost effective. It was calculated that the capital cost would be 11,740 Euros and the operational costs, including maintenance, would be at the same level. Thus, the process could be fully implemented for such a small water plant.

CONCLUSIONS

$\alpha\text{-FeOOH}$ was shown to be the most adequate adsorption media for arsenic removal for a small water system. The mass concentration of pentavalent arsenic in the source water was about 50 $\mu\text{g/L}$. The results showed that arsenic was removed below the MCL value of 10 $\mu\text{g/L}$ by adsorption on activated alumina and $\alpha\text{-FeOOH}$. The obtained adsorption capacity of $\alpha\text{-FeOOH}$ was 12.7 mg/g, and the determined contact time was 4.5 min. For small ground water systems, the implementation of $\alpha\text{-FeOOH}$ (TA) adsorbent is more efficient than activated alumina. X-Ray powder diffraction analysis proved that arsenic as AsO_4^{3-} forms a strong bond to TA.

ИЗВОД

УКЛАЊАЊЕ As^{5+} ИЗ МАЛОГ СИСТЕМА ЗА ПИЈАЋУ ВОДУ

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Вода из малих система за пијаћу воду садржала је арсен у концентрацији од око 50 $\mu\text{g/L}$. Хемијске анализе су показале да је арсен присутан у петовалентном стању. Пошто је MCL вредност 10 $\mu\text{g/L}$, неопходно је применити технолошки третман да би се вода учинила погодном за пиће. За то се предлажу две технологије: са употребом активираних алумина и $\alpha\text{-FeOOH}$ као адсорпционих медијума. Изведени су експерименти на лабораторијском нивоу који користе оба адсорпциона медијума. Било је могуће смањити концентрацију арсена на испод 1 $\mu\text{g/L}$. Нађен је максимални адсорпциони капацитет од 12,7 mg As^{5+} по граму $\alpha\text{-FeOOH}$. Такође, сви важни физичко-хемијски параметри остали су практично неизмењени након третмана. Уочено је само незнатно ослобађање гвожђа из медијума. Испитивана је веза Fe-As хемијском анализом и дифракцијом x-зрака праха. Коначно, уз приказ капацитета уклањања арсен помоћу $\alpha\text{-FeOOH}$ дата је и детаљна оптимизација технолошких параметара одабране технологије.

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