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journal or publication title	Chemosphere
volume	92
number	2
page range	196-200
year	2013-06-01
URL	http://hdl.handle.net/2297/34668

doi: 10.1016/j.chemosphere.2013.03.024

The research article is originally published at *Chemosphere*
An Elsevier Journal

<http://www.journals.elsevier.com/chemosphere/>

The original publication is available at: <http://dx.doi.org/10.1016/j.chemosphere.2013.03.024>

Decontamination of Spent Iron-Oxide Coated Sand from Filters Used in Arsenic Removal

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Please Cite the article as: I.M.M. Rahman, Z.A. Begum, H. Sawai, T. Maki and H. Hasegawa, Decontamination of spent iron-oxide coated sand from filters used in arsenic removal, *Chemosphere*, 92(2): 196–200, 2013.

Abstract

Sand filters devised with iron-rich adsorbents are extensively promoted and deployed in the arsenic-prone south and south-east Asian countries (*e.g.* Bangladesh). The approach offers superior performance in removing arsenic while the spent sludge from the sand filters is an issue of concern due to the possibility of toxic releases after being discarded. In this work, a new technique is proposed for the treatment of spent iron-oxide coated sand (IOCS) from filters used in arsenic removal. Chelant-washing of the arsenic-loaded IOCS is combined with the solid phase extraction treatment to accomplish the objective. The unique point of the proposed process is the cost-effective scheme, which includes the option of recycling of the washing solvent beside the decontamination of the spent arsenic-rich sludge.

Keywords

Arsenic removal; Sand filter; Iron-oxide coated sand (IOCS); Spent sludge; Chelant washing

1.0 Introduction

Contamination of groundwater with arsenic is reported from a number of countries of the world, and the largest population at risk is in Bangladesh, followed by West Bengal in India (Mohan and Pittman, 2007). The major natural source of arsenic in the groundwater is the leaching from geological formations (Vaishya and Gupta, 2003). Several methods are proposed for end-of-the-pipe treatment of the arsenic-contaminated groundwater to be used for drinking purpose, including ion exchange resins, membranes and adsorption onto coagulated flocs or sorptive media (Mohan and Pittman, 2007). Public water treatment facilities are uncommon in the rural areas of the developing countries (e.g. Bangladesh), and some of these techniques may need to be scaled down for private use. Furthermore, simplistic design, minimum maintenance or operating cost are some factors that require to be considered (Rozell, 2010). Arsenic removal by low-cost adsorbents has been the most promising technique which meets all the mentioned criteria offering reliable and efficient performance (Hsu et al., 2008). In the arsenic-prone south and south-east Asian countries, the present focus on arsenic removal is the use of iron-containing adsorbents as they are both economical and effective (Ramaswami et al., 2001). Household filters for arsenic removal using iron-rich adsorbents are deployed and evaluated in a number of reports (Khan et al., 2000; Sutherland et al., 2002; Cuda, 2005; Leupin et al., 2005; Hussam and Munir, 2007; Anjali et al., 2008; Petrusevski et al., 2008).

Amorphous iron oxide or ferrihydrite, a common coating of subsoil particles, possess a high adsorption capacity for different ions, including arsenic (Pierce and Moore, 1982). Quartz sand coated with iron salts has also been used for the removal of arsenic from groundwater (Joshi and Chaudhuri, 1996). Sorptive filtration using sand coated with iron is a relatively new approach for treating metal-contaminated drinking water, and numerous varieties are reported in literature such as, Ce(IV)-doped iron oxide (Zhang et al., 2003), iron impregnated quartz sand (Vaishya and Gupta, 2003), silica-containing iron(III) oxide (Zeng, 2003), iron-oxide coated sand (IOCS) modified with sulfate (Vaishya and Gupta, 2006), iron-

oxide-coated polymeric materials (Katsoyiannis and Zouboulis, 2002), and IOCS either reclaimed from other treatment processes (Hsu et al., 2008) or from special preparation (Thirunavukkarasu et al., 2003; Gupta et al., 2005). While adsorbents coated with iron are frequently considered as filter media to design the effective arsenic removal systems, the stability and disposal of sludge evoke concerns (Ford, 2002; Badruzzaman, 2003; Dixit and Hering, 2003). Several options are suggested or practiced for minimizing the possible risks of contaminant release from the sludge material such as, disposal into deeper pits when the amount is large, sub-aqueous disposal by burying in mud or mixed with organic matters, encasement in concrete to restrict the environmental exposure and so forth (Badruzzaman, 2003; Leupin et al., 2005).

In this work, we proposed a new approach for the treatment of spent IOCS from sand filters used in arsenic removal. The process includes washing treatment of high arsenic containing spent IOCS with chelant followed by solid phase separation of the chelant and metals from the effluent.

2.0 Experimental

2.1 Instruments

An iCAP 6300 model inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Fisher Scientific, Waltham, MA) was used for metal analysis. A fully automated TOSOH 8020 model high-performance liquid chromatography system (Tosoh, Tokyo, Japan) was used for the verification of EDTA concentration in solution. A Navi F-52 pH meter (Horiba Instruments, Kyoto, Japan) and a combination electrode was used for pH measurements. A GL-SPE vacuum manifold kit (GL Sciences, Tokyo, Japan) combined with a CAS-1 air pump (AS ONE, Osaka, Japan) was used to perform the solid phase extraction. A 4-housing E-Pure water purification system (Barnstead/Thermolyne, Dubuque, IA) was used to prepare the deionized water, and is referred to as EPW hereafter.

2.2 Reagents and materials

Analytical grade commercial products were used throughout. As(V) stock solution (10 mM) was prepared from sodium arsenate heptahydrate (Kanto Chemical, Tokyo, Japan). EDTA is used as the reference chelant, and the corresponding stock solution (10 mM) was prepared from disodium dihydrogen ethylenediamine tetraacetate dihydrate salt (Kanto Chemical, Tokyo, Japan). Solutions of working standards were prepared by dilution with EPW on a weight basis. The solution pH was adjusted in the range of 4–8 using either HCl or NaOH (1 M). The buffer reagents used to maintain the system pH were 2-(*N*-morpholino)ethanesulfonic acid (Sigma-Aldrich, St. Louis, MO) and 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (Nacalai Tesque, Kyoto, Japan) for pH 4–6 and 7–8, respectively.

Silica gel-bonded solid phase extraction (SPE) material, namely AnaLig TE-01, was used for the separation of chelant and metals from the washing effluents. The product is commercially available from the IBC Advanced Technologies (American Fork, UT) and procured from GL Sciences (Tokyo, Japan). The SPE system contains proprietary polymeric organic material, and the separation mechanism is attributable to molecular recognition and macrocyclic chemistry (Izatt et al., 2000).

Low-density polyethylene bottles (Nalge Nunc, Rochester, NY, USA), perfluoroalkoxy tubes and micropipette tips (Nichiryo, Tokyo, Japan) were used throughout the experiments. Before use, laboratory wares were first soaked in the Scat 20X-PF alkaline detergent (Nacalai Tesque, Kyoto, Japan) overnight, and then in 4 M HCl overnight, followed by rinsing with EPW after each step.

2.3 Preparation of IOCS

Commercial filter sand of the geometric mean size of 0.6 mm was used. The sand was acid-washed (pH 1) for 24 h followed by three times washing with EPW, and drying for 20 h at 100 °C. The two-step procedure adopted for the preparation of IOCS was similar to that of Benjamin et al. (1996), with the modifications from Thirunavukkarasu et al. (2003) and

Nguyen et al. (2006). In step 1, a mixture of 2 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (80 mL) and 10 M NaOH (1 mL) was added to 200 g of the dried sand, agitated, heated at 110 °C (4 h), and then at 550 °C (3 h). The sand sample, after cooling, was washed with EPW till the complete washing out of the black colored fraction. In step 2, the aforesaid mixture of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NaOH was added to 100 g of the sand sample obtained in Step 1, heated at 110 °C (20 h), cooled, mechanically grinded, sieved for grain separation, followed by further heating at 110 °C (20 h). The dried IOCS was then stored in capped bottles.

2.4 Determination of iron content in the IOCS

Acid digestion treatment of IOCS, as described by Thirunavukkarasu et al. (2003), was conducted to determine the iron content. A 1 g of IOCS was added to 50 mL of 10% HNO_3 , heated to boiling, and continued for 2 h. The treatment dissolved the iron-coating on the sand surface completely, and produced a yellow-colored solution. The solution was made up to 1 L with EPW, filtered through the 0.45 μm cellulose membrane filters (Advantec, Tokyo, Japan), and subjected to ICP-OES measurements.

2.5 Treatment of arsenic-contaminated groundwater with IOCS

Synthetic groundwater having the main characteristics of groundwater available in the arsenic-prone regions of Bangladesh is prepared following the procedure as described elsewhere (Roberts et al., 2003; Leupin and Hug, 2005; Leupin et al., 2005), and spiked with arsenic (10 μM). The simulated arsenic-contaminated groundwater (40 mL) was then added to 20 g of the IOCS for batch treatment. The samples were shaken at 180 rpm on an EYELA Multi Shaker MMS rotary shaker co-equipped with the EYELA incubator FMS (Tokyo Rikakikai, Tokyo, Japan) for 24 h at 25 °C.

2.6 Washing treatment of the arsenic-loaded IOCS

Arsenic-loaded IOCS (0.5 g) was treated with 0.05 M EDTA (5 mL), shaken for 24 h in the SHK-U4 rotary shaker (Iwaki Glass, Tokyo, Japan) with a speed of 180 rpm at room

temperature. The resultant solution was filtered through the cellulose membrane filters of 0.45 μm pore size (Advantec, Tokyo, Japan).

2.7 Recovery of the chelant from the washing solution

SPE material packed into 5 mL column was used for the recovery of chelant from the washing solution obtained after the treatment of arsenic-loaded IOCS. Detail methodology adopted for the SPE column conditioning and optimization of the separation process is described elsewhere (Hasegawa et al., 2011; Rahman et al., 2011). The washing solution was allowed to pass through the SPE column at the flow rate of 0.2 mL min^{-1} . The metal ions were captured within the SPE column during the flow process followed by recovery of the chelant as the column effluent. The SPE column was regenerated via back-washing with HNO_3 (1 and 6 M) and reused.

3.0 Results and discussion

3.1 Performance of IOCS in arsenic removal

A time-limited study was conducted to find out the time required to attain the equilibrium during IOCS-arsenic contact as well as to check the arsenic removal performance of IOCS. The IOCS dosage was maintained at 20 g L^{-1} and the initial As(V) concentration was 10 μM (~ 0.75 mg L^{-1}). Thirunavukkarasu et al. (2003) observed a maximum removal of As(V) in the pH range of 5–8 with the IOCS prepared by the similar method. Hence, the system pH was controlled at 7 during our experiments.

The variation in the residual arsenic concentration with contact time (Fig. 1a) showed a high initial rate of removal followed by a slower subsequent removal rate that gradually approached an equilibrium condition. The high concentration difference between the bulk solution and adsorption sites initiate the rapid removal at the initial hours while the rate tended to be slowed down with the saturation of the adsorbent sites at the late hours. It was observed that the concentration of arsenic decreased with time up to 240 min and then the curves seem to be flattened *i.e.* approaching to the equilibrium within 360 min or 6 h. In Fig.

1b, arsenic removal rate (%) as a function of time is shown, and it is observed that about 75% arsenic from the bulk solution was adsorbed by IOCS within the initial 15 min. The arsenic concentration in the adsorbent phase was estimated to be 0.037 mg of As(V) adsorbed in g⁻¹ IOCS during the 6 h adsorption period.

3.2 Washing treatment of arsenic-loaded IOCS

IOCS samples that were used for arsenic removal experiment were dried, and treated with EPW and EDTA to check the leaching extent of arsenic and iron. The findings are graphically represented in Fig. 2. It can be observed that the amount of arsenic or iron leached from the samples treated with EPW is significantly low. Arsenic concentration in the EDTA-treated samples was also insignificant while the amount of iron is notable. The results of the acid digestion studies confirmed that the iron content of IOCS was 42.6 mg g⁻¹, while the arsenic adsorbed in the IOCS after treatment with arsenic-contaminated water was estimated to be 0.037 mg g⁻¹. The As(V) has no known affinity for the EDTA and the amount adsorbed in IOCS was also comparatively low, which may be the result of such a negligible leaching. Jessen et al. (2005) reported that 0.02% of the total arsenic pool can possibly be leached due to desorption following an estimation that about 37–40% of the adsorbed arsenic is located in the surface structural layer and remain mobile. Hence, there is a shear risk of the release of that arsenic from the filter sand precipitates. Iron has a strong affinity for the EDTA and the leached iron (4.1–7.4%) was assumed to be present as the Fe-EDTA complex in the solution. It can be assumed that the iron-coating in the surface layer of the IOCS was leached in solution when treated with EDTA, which also trapped the mobile fraction of the arsenic pool.

3.3 Recovery of arsenic and iron from the washing solution

The leaching of arsenic or arsenic-associated iron is always a concern. The surface layer of IOCS containing the mobile arsenic pool is separated in the solution by the washing treatment with EDTA. Therefore, the treated IOCS can be discarded in the environment without any additional risk or can be recycled. However, EDTA is also an environmental

hazardous material, and it should either be degraded or recovered before its release to the surroundings. Due to the high cost involvement in the operation with EDTA, the option for recovery and recycling is the most feasible option (Juang and Wang, 2000a, 2000b; Hasegawa et al., 2010). A macrocycle-immobilized solid phase extraction material AnaLig TE-01 was used for the recovery the arsenic and iron from excess EDTA containing solution. The findings, in terms of pH, are shown in Fig. 3. The experimental pH was restricted within the range of 4–8 considering the inferior solubility of EDTA in water at lower pH (Ueno et al., 1992) and the liquefying possibility of the silica gel base of the SPE column at higher pH (Vogelsberger et al., 1992). The extraction and recovery behavior for iron is very much similar within the pH range studied while the tendency was more or less comparable for arsenic. A scheme is proposed for the treatment of spent IOCS from the sand filters based on the outcome (Fig. 4).

4.0 Conclusions

A simple approach for the treatment of IOCS from household filters used in arsenic removal is discussed. The IOCS has notable capability of arsenic removal from the contaminated water. The arsenic-loaded IOCS is subjected to washing treatment with EDTA, which extracts the Fe-coating on the sand along with the adsorbed arsenic. The arsenic and iron in the EDTA solution is then treated with a SPE system to separate out the elements from the chelant solution. The SPE system can be regenerated via back washing with HNO₃. The EDTA solution is available for subsequent recycling, and thus minimizes the cumulative cost-factor and potential environmental concern.

Acknowledgement

This research was partially supported by the Grants-in-Aid for Scientific Research (24310056 and 24-02029) from the Japan Society for the Promotion of Science.

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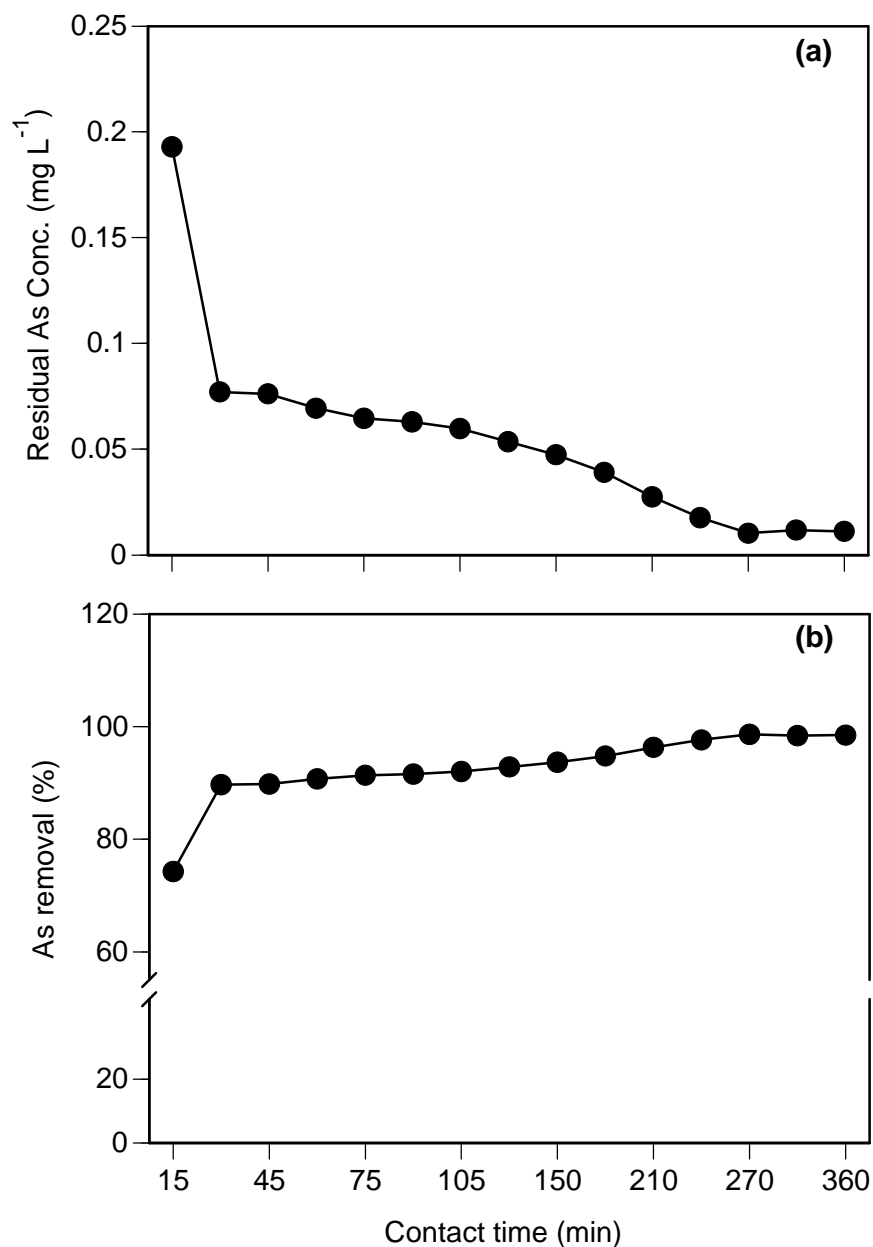


Figure 1. Arsenic adsorption on IOCS: (a) time course for residual arsenic concentrations and (b) arsenic removal with time. Sample: 10 μM ($\sim 0.75 \text{ mg L}^{-1}$) As(V), pH: 7, IOCS dose: 20 g L^{-1} , $n = 3$.

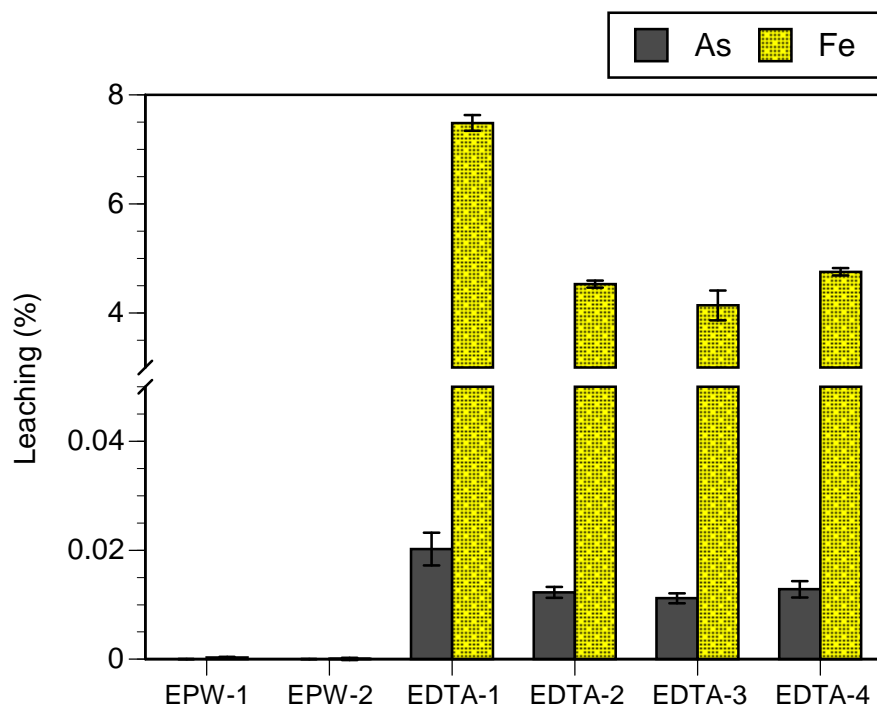


Figure 2. Leaching rate of arsenic and iron from the arsenic-loaded IOCS after the washing treatment. Sample– As-loaded IOCS (0.5 g), EPW– 5 mL, EDTA– 0.05 M (5 mL), $n = 3$.

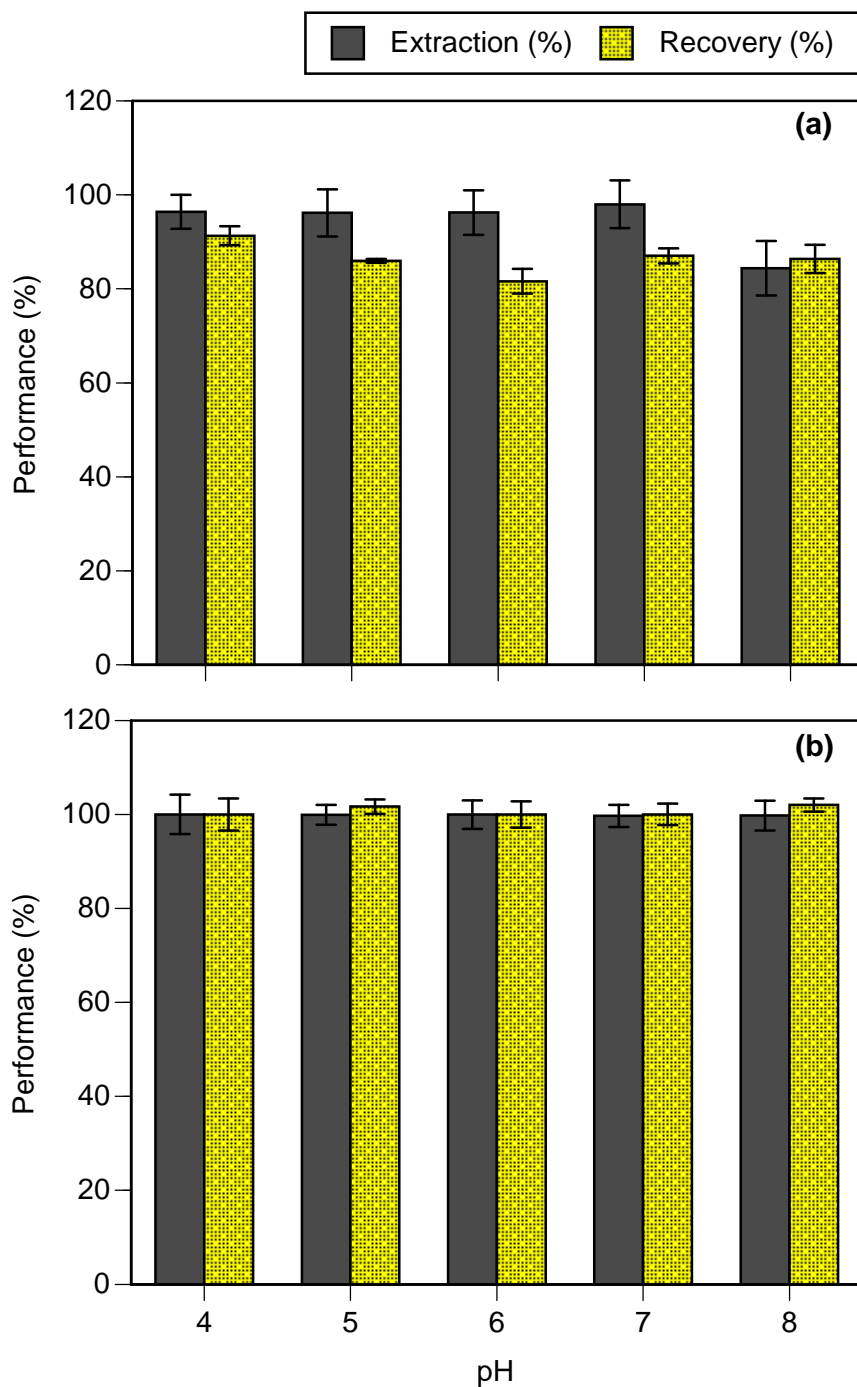


Figure 3. Extraction and recovery behavior of the AnaLig TE-01 in terms of pH for the separation of (a) arsenic and (b) iron from EDTA containing aqueous solution. Sample solution– (a) As(V)– 10 μ M and (b) Fe(III)– 10 μ M, EDTA– 0.05 M, matrix– H₂O, pH– 4 to 8, $n = 3$.

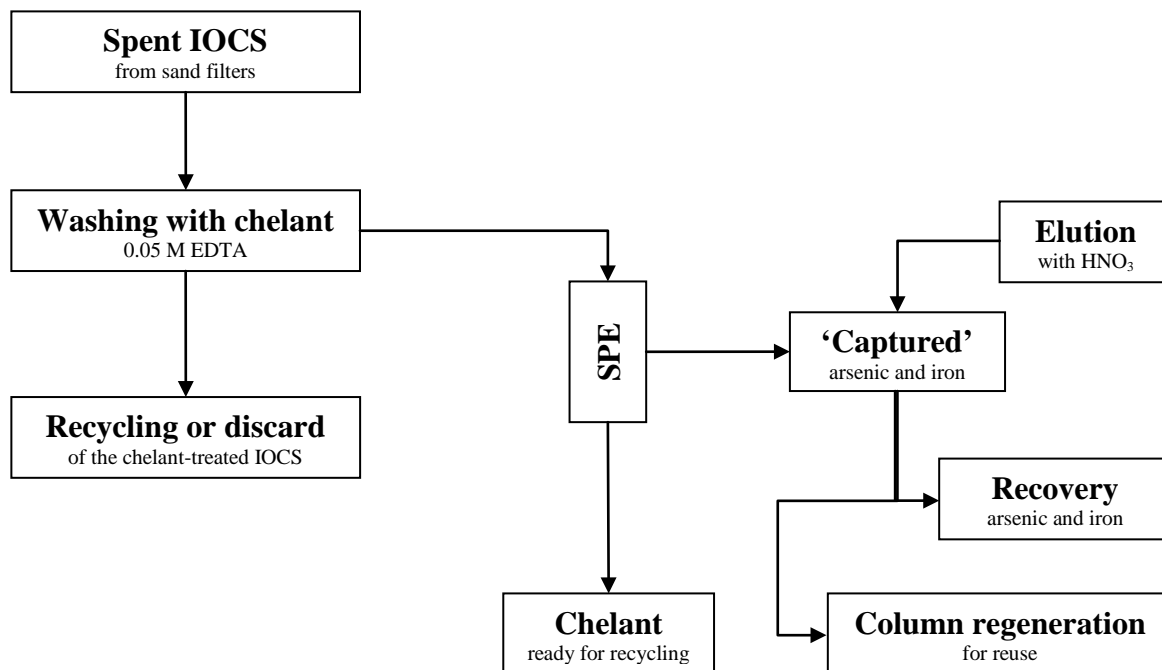


Figure 4. Scheme for the treatment of spent IOCS from the sand filters