SELECTIVE ION EXCHANGE FOR REMOVAL OF INORGANIC TRACE CONTAMINANTS FROM WATER

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Introduction

Various natural and anthropogenic reasons lead to the presence of heavy metals in natural waters: (i) Mobilisation from soils or rocks during the natural water circulation, (ii) discharge of effluents of actual or former mining, (iii) discharge of waste effluents e.g. from the mineral processing and metal finishing industries, (iv) unlawful discharge of waste water into the underground by individuals, v) leaching of solid waste from landfill deposits or unlawful waste deposition, and (vi) oxidation of sulphides by nitrate input after applying fertilizers in agriculture.

Relevant metal contaminants are mercury, cadmium, arsenic, nickel, uranium, and chromium because of their toxicity. Corresponding with the local situation further metals causing undesirable effects (copper, cobalt, molybdenum, barium, selenium, antimony) may be encountered in concentrations of up to 100 µg/L, in exceptional cases even 2000 µg/L. Because of the well-known harmful effects of heavy metals on human health the concentrations of the inorganic species in drinking water should not exceed standards established by WHO or by individual countries (1).

The speciation of most of the metals strongly depends on the composition of the aqueous phase and may be comprised of free cations, inorganic complexes, complexes with natural organic substances or complexes with strong complexing agents. Among the metals eliminated in the respective studies, mercury can be present in a number of forms and, through interactions with the components of the water matrix, can be transformed into a variety of structures. The most commonly known forms include elemental mercury, divalent mercury and methyl mercury. The speciation of divalent transition metals includes cations Me^{2+} but also complexes with different ligands, depending on the background composition of the water. Chromium is usually present as monovalent oxide anions $HCrO_4^-$. Uranium forms stable complexes with carbonate ions and is present as e.g. $UO_2(CO_3)_2^{2-}$ carbonato complex species (2).

Basic principles of elimination

In raw waters of drinking water supplies heavy metals normally occur at trace concentration levels of up to several 100 µg/L at the maximum while the components of the background composition of natural waters have much higher concentrations. Removal of trace contaminants can be achieved by a variety of demineralisation methods, including membrane processes, chemical precipitation, and sorption processes. However, in most cases only the toxic contaminants have to be eliminated. As a consequence, a selective removal without affecting the background composition is desirable. Such a selective separation is not possible by means of membrane processes. Application of lime precipitation methods is limited by the solubility of hydroxides, which, in some cases, does not allow reaching the required standards. Furthermore, there is an often unwanted softening. A selective elimination of target contaminants in the trace concentration range is exclusively possible by means of ion exchangers. Among the suitable materials weakly basic resins offer particular advantages (3).

Elimination of heavy metal cations

Divalent heavy metal cations can be eliminated from natural waters by adsorption onto weak base anion exchangers. The adsorption is due to the presence of a nitrogen atom in the functional group. Its free electron pair leads to coordinative bonding of transition metals. Nitrogen atoms are also part of the functional groups of weakly basic anion exchangers. As a consequence, they are also able to adsorb heavy metal species. Unlike in cation exchangers, however, the charge of the metal cations is not compensated by negative charges of the functional groups. Therefore, to maintain electroneutrality, the adsorption of metal cations has to be accompanied by the simultaneous adsorption of an equivalent amount of anions. As a total, the process develops as the adsorption of heavy metal salts. Using cadmium and sulphate as an example, the service cycle can be written as (3):

$$\overline{R-NH_2} + Cd^{2+} + SO_4^{2-} \quad \Leftrightarrow \quad \overline{R-NH_2\left(Cd^{2+},SO_4^{2-}\right)} \tag{1}$$

R designates the resin matrix; overbarred symbols refer to the resin phase. The elimination of heavy metal salts other than $CdSO_4$ develops in a similar way.

Protons are strongly preferred over heavy metal species by the nitrogen atoms of the functional groups. With decreasing pH, therefore, the uptake of acids increases and the metal salts are removed. Consequently, desorption of heavy metals can be achieved by treatment with a sufficiently strong acid.

$$\overline{R-NH_2\left(Cd^{2+},SO_4^{2-}\right)} + H_2SO_4 \quad \Leftrightarrow \quad \overline{R-NH_3^+HSO_4^-} + CdSO_4 \tag{2}$$

Because of the strong preference of acids the exchanger cannot be reused in this form. In a second step of the entire regeneration it has to be reconverted to the free base form by means of caustic.

$$\overline{R-NH_3^+HSO_4^-} + 2\,NaOH \quad \Leftrightarrow \quad \overline{R-NH_2} + Na_2SO_4 + 2\,H_2O \tag{3}$$

The advantage of this kind of process lies in the fact that alkaline earth cations being the main constituents of natural waters do not undergo coordinative bonds with the nitrogen atoms. As a consequence, there is an extreme selectivity for heavy metal salts. The disadvantage of this process is that the rate of adsorption is generally small and cannot be increased.

Elimination of heavy metal anions

Selective removal of a spectrum of oxy anions is also possible by means of weakly basic anion exchangers. The reason is due to the protonation of weakly basic exchangers even a neutral pH and to the strong preference of e.g. chromate and also $UO_2(CO_3)_2^{2-}$ over sulphate [4]. Elimination of chromate, therefore, develops as:

$$\overline{R\text{–}(N(R')_2 \bullet H_2O)_2} + (CrO_4^{2-}) \quad \Leftrightarrow \quad \overline{R\text{–}(NH(R')_2^+)_2\ (CrO_4^{2-})} + 2\,OH^- \tag{4}$$

In natural waters the release of hydroxyl ions is buffered by the presence of carbonic acid. Regeneration is achieved by using sodium hydroxide solutions:

$$\overline{R\text{–}\ (N(R')_2^+)\ CrO_4^{2-}} + 2\,NaOH \quad \Leftrightarrow \quad \overline{R\text{–}(N(R')_2 \bullet H_2O)_2} + 2\,Na^+ + CrO_4^{2-} \tag{5}$$

Elimination of uranium species follows the same principle:

$$\overline{R\text{–}(N(R')_2)_2 \bullet H_2O} + UO_2(CO_3)_2^{2-} \quad \Leftrightarrow \quad \overline{R\text{–}(N(R')_2)_2^{2+}\ UO_2(CO_3)_2^{2-}} + 2\,OH^- \tag{6}$$

In the case of uranium removal regeneration has to follow a different way. Application of NaOH leads to a conversion of divalent to tetravalent uranium carbonato complex anions which are very strongly bound and which are only partly displaced (4). Regeneration has to start with a strong acid to convert the complex anions to UO_2^{2+} cations which cannot be sorbed by the anion exchanger acidic conditions.

$$\overline{R{-}(N=(R')_2)_2^{2+}\,UO_2(CO_3)_2^{2-}} + H_2SO_4 \Leftrightarrow \overline{R-(N=(R')_2)_2^{2+}\,SO_4^{2-}} + UO_2^{2+} + H_2CO_3 + CO_3^{2-} \qquad (7)$$

In a second step NaOH is applied to convert the anion exchangers to the free base form:

$$\overline{R{-}N(R')_2^{+}\,SO_4^{2-}} + 2\,NaOH \Leftrightarrow \overline{R{-}N(R')_2 \bullet H_2O} + 2\,Na^{+} + SO_4^{2-}) \qquad (8)$$

Materials and methods

Exchange resins

For the investigations only commercially available weakly basic anion exchangers have been applied. A manifold of resins were applied to find out the most effective once for the removal of each heavy metal. **Table 1** summarizes the exchangers used in the experiments that are reported (5, 6).

For the laboratory scale experiments the resins were subjected to a standard pre-treatment with hydrochloric acid and sodium hydroxide. In the pilot scale experiments the resins were used as delivered after intensive rinsing.

Table 1: Ion exchange resins applied in the experiments

Name	Manufacturer	Matrix	Functional Group
Duolite A7	Rohm and Haas	Phenol - Formaldehyde	Primary and secondary amine
Amberlite IRA67 / PWA 8	Rohm and Haas	Acrylic – DVB	Tertiary and secondary amine
Purolite A 845	Purolite Intern.	Acrylic – DVB	Tertiary and secondary amine

Column Installations

The laboratory scale experiments were carried out using filter columns of 2 3 cm inner diameter and bed heights of to 5-30 cm. Raw water from a reservoir was pumped across the columns in upstream direction. pH was measured and recorded and samples were taken from the effluent. In the laboratory scale experiments the raw water consisted of tap water from the Research Center spiked with the respective heavy metal. Throughput amounted to 5-20 bed volumes per hour (BV/h) during service cycle and to 2 – 2.5 BV/h during regeneration, which was carried out in counterflow. (7).

Pilot scale experiments for elimination of traces of mercury and chromate were carried out in the framework of a cooperation project with Tsinghua University, Beijing, China. The pilot plant had two columns of 25 cm diameter, each containing 75 L of exchanger material. Downstream throughput amounted to 10 - 20 BV/h. Regeneration was again carried out in counterflow (8).

Further pilot scale experiments for removal of traces of natural uranium were carried out in Germany. The respective plant contained two columns of 0.5 m diameter, each filled with 300 L of exchanger material. No regeneration was carried out.

Heavy metal concentrations in feed and effluent were determined by means of AAS or ICP-MS of samples obtained from automatic samplers.

Results and discussion

Removal of cations

Results from pilot scale experiments with respect to elimination of mercury species from contaminated lake water close to Haikou, Hainan Island, China are shown in

Figure 1. For this experiment the weakly basic exchanger Purolite A 845 was applied. The polluted feed water contained about 1.7 µg/L Hg. Up to a total throughput of about 16,000 BV the effluent mercury concentration was smaller than the drinking water standard of 1 µg/L. No regeneration could be carried out at the site (8).

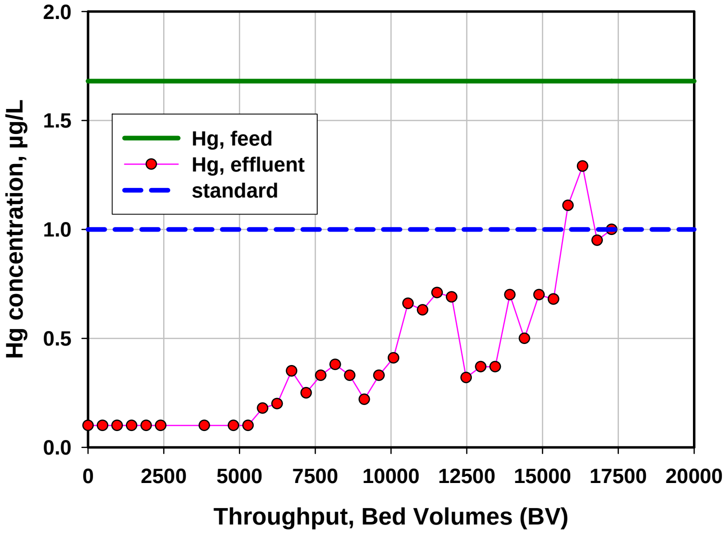

Figure 1: Development of mercury elimination at Haikou, Hainan, China. Resin: Purolite A 845, throughput: 20 BV/h.

Removal of oxy anions

Removal of oxy anions has been demonstrated in the pilot scale in the framework of the cooperation project with Tsinghua University, Beijing. Experiments were carried out at Shenyang, Northern China using a contaminated groundwater bearing 90 µg/L of hexavalent chromium. Purolite A 845 and Duolite A 7 were applied in the experiments. For the acrylic anion exchanger Purolite A 845 repeated service cycles of about 4,500 BV between two regenerations could be achieved. In constrast to this result, the development of the breakthrough curve for Duolite A7 reveals an unusually long service cycle (**Figure 2**). After 40,000 BV throughput the effluent Cr concentration was only 25 µg/L and still far below the drinking water standard of 50 µg/L (8). Analysis of the development showed that chromate oxidised the exchanger and was thus converted to chromium hydroxide.

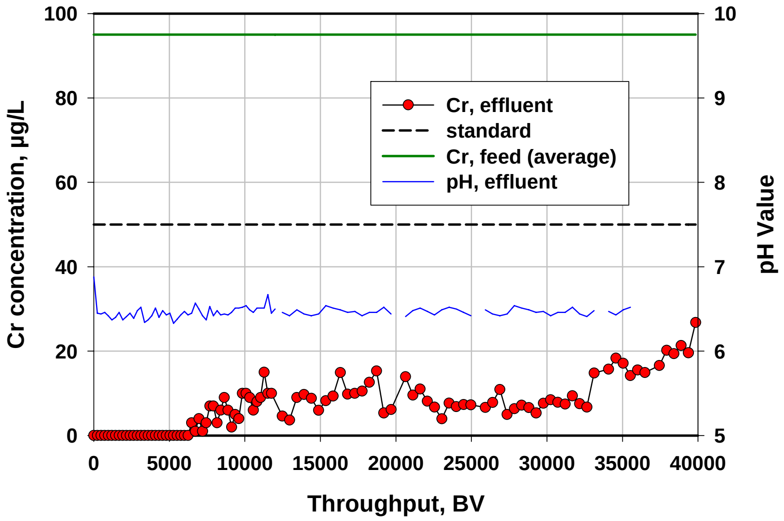

Figure 2: Development of Cr(VI) concentration in pilot scale experiments at Shenyang, China. Resin: Duolite A7, throughput: 20 BV/h.

Regeneration is possible; because of the oxidation, however, the exchanger is not re-usable. Despite this problem, the length of the service cycle seems to be long enough to use the exchanger in a one-time application.

Removal of natural uranium has been investigated in the laboratory and pilot scales. **Figure 3** shows results from pilot scale experiments in a municipal water work for a relatively small feed concentration of 10 – 13 µg/L. Up to t total throughput of 60,000 BV the effluent concentration was below 0.1 µg/L (left). Analysis of standard anions demonstrated that no change of the background composition occurs. Furthermore, no release of organic compounds or amines by the anion exchangers could be detected.

Regeneration of the uranium loaded exchangers has also been studied. By treating the resin with 0.5 molar H_2SO_4 in the first step and with 1 molar NaOH in a second step a nearly complete elution of the uranium was achieved.

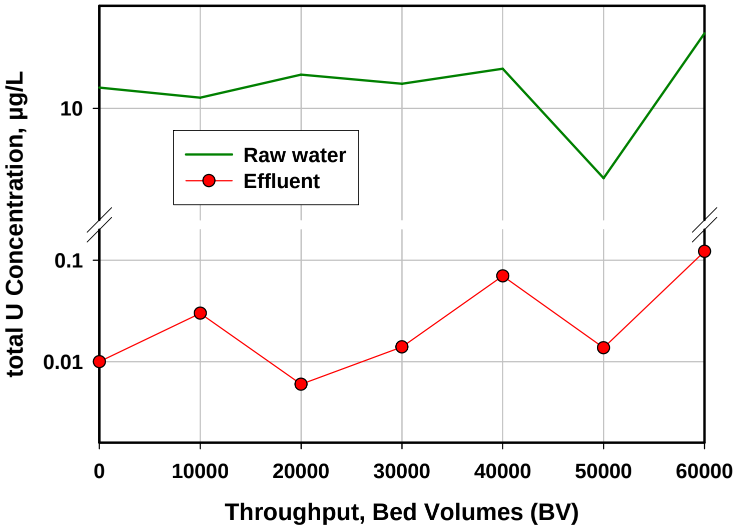

Figure 3: Development of uranium elimination in two pilot scale experiments.
Resin: Amberlite IRA 67 / PWA 8, throughput: 20 BV/h.

Conclusions

The experiments have demonstrated that weakly basic anion exchangers in their free base form allow an efficient elimination of heavy metals, both of divalent cations and oxy anions. The successful removal of cadmium, mercury, nickel, uranium, and chromium has been demonstrated in the pilot scale with real raw waters. Depending on the raw water concentrations operation times of up to 10,000 BV can be obtained.

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