Elimination of trace heavy metals from drinking water by means of weakly basic anion exchangers

Wolfgang H. Höll, Christian Bartosch, Xuan Zhao and Shijun He

ABSTRACT

Weakly basic anion exchangers exhibit a unique selectivity for adsorption of heavy metals such as mercury, copper, lead, zinc, nickel and cadmium. Furthermore, some types of exchangers show a marked preference for chromate over sulphate anions. Application of the respective ion exchange processes may, therefore, offer a promising way to remove traces of hazardous heavy metals very efficiently from the raw water of drinking water supplies. The respective ion exchange processes have been demonstrated both at laboratory and semi-technical scales for the elimination of heavy metal cations (cadmium, mercury, lead, nickel) and of chromate anions from spiked tap water and contaminated groundwaters. In all cases the effluent concentrations of filters could be decreased well below the parametric values of the European Drinking Water Directive.

Key words | anion exchangers, cadmium, chromate, drinking water, heavy metals, mercury, nickel

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INTRODUCTION

In raw waters of drinking water supplies heavy metals can occur in elevated concentrations for different reasons:

1. The natural groundwater or surface water may originate from sources or areas in which the soil or rock contains heavy metals. These can be mobilised during the natural circulation of water. This problem is found in many countries, mainly in regions rich in ores of a variety of metals.

2. Solid metal sulphides in the subsoil are mobilised because of chemical reactions with oxidising substances. This is mainly caused by the input of nitrates into the soil during fertiliser addition in agriculture and the subsequent transport into deeper layers. In Germany about 20 waterworks observe an increase in nickel concentrations which is caused by this type of mobilisation. In some wells the concentrations have already reached 200 μg/l (IWW 1996).

3. Effluents from working or abandoned mines contain heavy metals at elevated concentrations. These metals are mobilised in the open rock structure because of the direct contact with oxygen and subsequently washed out. Such waters are encountered, for example, in regions of eastern Germany with intensive mining. However, it also occurs in many other countries.

4. Mineral processing and metal finishing industries produce large amounts of waste effluents which contain a variety of harmful metals such as chromium, mercury, cadmium, lead and nickel. In many cases these effluents are discharged into open water or sewage systems without adequate purification. Consequently, these wastes are transported to rivers or lakes which serve as raw water sources for drinking water. This problem is frequently encountered in developing countries with insufficient wastewater treatment. In many cases wastewaters containing heavy metals penetrate into the groundwater because of the unlawful discharge of wastewaters into the soil.

Relevant metal contaminants are mercury, cadmium, nickel, lead, chromium and arsenic, because of their

toxicity. Depending on the local situation further metals causing undesirable effects (e.g. copper, cobalt, molybdenum, barium, selenium and antimony) may be encountered.

Because of the well-known harmful effects of heavy metals on human health the concentrations of the inorganic species of metals in drinking water should not exceed certain standards. For the European Union the respective parametric values are given by the Directive 98/83/EG (Hein & Schwedt 2000).

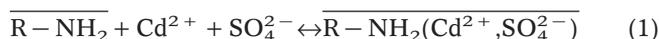## SELECTIVE ELIMINATION OF HEAVY METALS

Problem

In raw waters of drinking water supplies heavy metals normally occur only in trace concentrations of up to several 100 μg/l at the maximum. The components of the background composition of natural waters have much higher concentrations. This is important with respect to the elimination of the trace contaminants. Most heavy metals cations can be eliminated by means of lime precipitation processes (Overath *et al.* 1998). However, this type of treatment is by no means selective because it is necessarily combined with a softening process which is often not required. Selective elimination is possible by means of heavy metal selective ion exchangers which exhibit a sufficiently high affinity for heavy metals. Application of such resins in the calcium form has successfully been demonstrated for nickel removal (Rahm & Overath 1997). Unfortunately, such exchangers are actually not allowed for the treatment of food and drinking water. Chromate-selective exchange resins do not exist.

Selective elimination of metal cations

The ability of selective exchange resins to selectively adsorb transition metals is generally due to the presence of electron donor atoms (e.g. nitrogen or oxygen) in their functional groups. By this means these resins have Lewis base properties and can undergo coordination bonds with Lewis acids (Saldadze *et al.* 1970; Saldadze & Kopylova 1972).

Weakly basic exchangers possess nitrogen atoms in their amino groups. At pH values above 5, therefore, they can adsorb transition metal ions. If a weakly basic resin in its free base form is in contact with a heavy metal bearing solution, metal cations will be adsorbed. However, to maintain the condition of electroneutrality in the liquid and exchanger phases, this uptake of metal cations has to be accompanied by a parallel adsorption of equivalent amounts of anions of strong acids, preferably of sulphate (Höll 1996). Using cadmium and sulphate as an example, the service cycle can be written as:

$$\overline{R-NH_2} + Cd^{2+} + SO_4^{2-} \leftrightarrow \overline{R-NH_2(Cd^{2+},SO_4^{2-})} \qquad (1)$$

The elimination of heavy metal salts other than $CdSO_4$ develops in a similar way. Unlike heavy or transition metals alkaline earth ions have extremely poor Lewis acid properties. As a consequence their adsorption is practically excluded. This means that weakly basic resins exhibit an extremely selective adsorption of heavy metal salts.

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.

$$\overline{R-NH_2(Cd^{2+},SO_4^{2-})} + H_2SO_4 \leftrightarrow \overline{R-NH_3^+ HSO_4^-} + CdSO_4 \qquad (2)$$
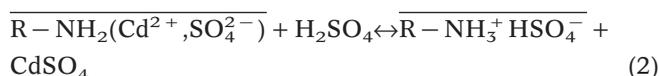
The uptake of sulphuric acid develops as a reaction-coupled exchange process for which only slightly more than the stoichiometric amount of acid is needed. Because of the strong preference for the acid the exchanger cannot be reused in this form but has to be reconverted to the free base form in a second step of the entire regeneration. For this neutralisation sodium hydroxide can be applied:
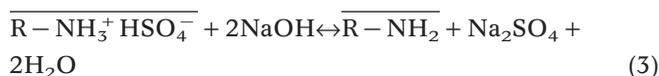
$$\overline{R-NH_3^+ HSO_4^-} + 2NaOH \leftrightarrow \overline{R-NH_2} + Na_2SO_4 + 2H_2O \qquad (3)$$

Table 1 | Ion exchange resins applied in the experiments

Name	Manufacturer	Matrix	Functional group
Duolite A7	Rohm and Haas	Phenol—formaldehyde copolymer	Secondary amine
Duolite A 365	Rohm and Haas	Polystyrene	Tertiary amine
Amberlite IRA 67	Rohm and Haas	Poly-acrylamide	Tertiary amine
Purolite A 830	Purolite International	Polystyrene	Secondary amine
Purolite A 832	Purolite International	Polystyrene	Secondary amine
Purolite A 845	Purolite International	Poly-acrylamide	Tertiary amine
Fuji PEI CS	Fuji Comp.	Chitosan	Secondary amine

Again, a reaction-coupled exchange process develops which needs only a small excess amount of NaOH over the stoichiometric quantity.

Elimination of chromium (VI)

In natural water and at neutral pH chromium usually occurs as CrO_4^{2-} and $HCrO_4^-$. Chromate species cannot be eliminated in a similar selective method as described above. However, it is well known that chromate anions are preferred over the usual anions of natural waters by all types of anion exchangers. As a consequence, a preferred elimination should be possible by means of weakly basic exchangers which are sufficiently protonated in neutral solutions. This property is found with acrylic weakly basic resins (Höll 1998). Assuming $HCrO_4^-$ species is present, the elimination by means of the resin in the free base form can be written as:

$$\overline{R-NH_2 \cdot H_2O} + HCrO_4^- \leftrightarrow \overline{R-NH_3^+ \, HCrO_4^-} + OH^- \quad (4)$$
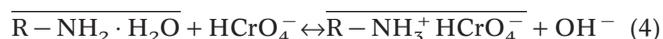
Because of the much higher concentration of sulphate and chloride a small exchange for hydroxyl ions occurs. Consequently, the above-mentioned elimination of chromate leads to a slight temporary increase of the effluent pH. This increase can, however, be suppressed by pre-neutralising the exchanger with a NaCl solution. This does not affect the uptake of chromate species. The exchange of chromate species in trace concentrations for OH^- has no measurable influence on the pH value.

For regeneration the exchanger has to be converted to the free base form by means of caustic or lime.

$$\overline{R-NH_3^+ \, HCrO_4^-} + NaOH \leftrightarrow \overline{R-NH_2 \cdot H_2O} + Na^+ + HCrO_4^- \quad (5)$$
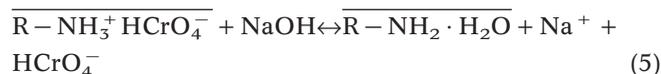
Due to the strong preference for hydroxyl ions at high pH values regeneration needs only slightly more NaOH than the stoichiometric amount.

METHOD

Exchange resins

For the investigations only commercially available weakly basic anion exchangers have been applied. The resins and their manufacturers are listed in Table 1.

For all experiments the resins were submitted to a standard pre-treatment with hydrochloric acid and sodium hydroxide. The exchangers were applied in the free base form after intensive rinsing with (distilled) water without sieving out narrow particle size fractions.

Table 2 | Concentrations of the main components of tap water from the Karlsruhe Research Centre

Parameter	Concentration, mg/l
Calcium	98.1
Magnesium	12.6
Sodium	18.9
Chloride	35.6
Nitrate	4.5
Sulphate	76.1
DOC	0.5–1.5

Figure 1 | Cadmium concentration and pH value in the effluent (resin: Duolite A7, throughput: 20 BV/h).

Data relating to the resins have been published by the manufacturers.

Raw waters

For the experiments in the laboratory, spiked tap water of the Karlsruhe Research Centre was used. This water has been spiked with the respective amounts of heavy metal salts (chlorides, nitrates or sulphates). Table 2 shows the concentration of the main components of this tap water. In one experiment for chromate removal, contaminated groundwater taken from an area close to Karlsruhe was used.

Larger scale experiments for nickel removal were (and are currently) carried out at Rasseln water-works which belongs to the NVV (Niederrheinische Verkehrs- und Versorgungs- GmbH, Mönchengladbach).

Column installations

The column experiments were carried out in several test installations. The filter columns for the laboratory scale experiments had an inner diameter of 2 or 3 cm and the bed height amounted to 5–30 cm. Raw water from a reservoir was first pumped to an intermediate vessel from which it was conducted across the filter in an upstream

direction. pH was measured and recorded and samples were taken from the effluent. For further experiments a larger column was used with a diameter of 5 cm containing 1 l of resin material. In this case the operation was downstream. For both sizes of installation, throughput was adjusted to 5–20 bed volumes per hour (Höll 1996). Heavy metal concentrations in the effluent were determined by means of atomic absorption spectroscopy analyses of samples taken by means of an automatic sampler. Furthermore, the effluent pH was measured and recorded. Throughput of raw water was varied between 5 and 40 bed volumes per hour (BV/h). Throughput during regeneration was usually 2–2.5 BV/h. The design of the larger installations for the field tests at Rasseln is similar, but with downflow operation during the service cycle and counterflow regeneration.

RESULTS AND DISCUSSION

Elimination of cadmium

Figure 1 shows the breakthrough curve of a cadmium removal experiment with the exchanger Duolite A7 in the laboratory. For about 7,000 bed volumes the effluent concentration is below the limit of measurement for flame AAS of 1 μg/l and, therefore, below the desired maximum
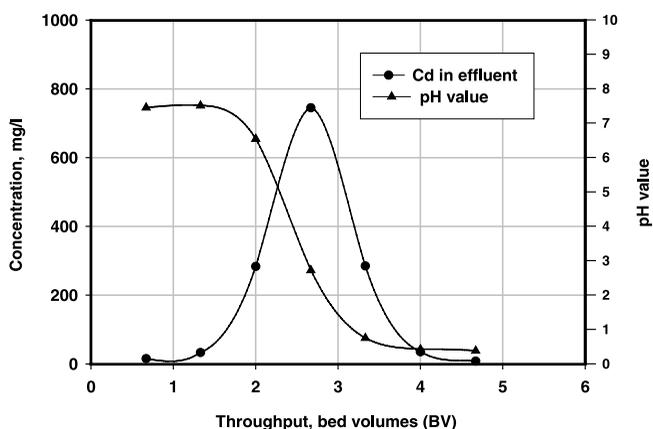
Figure 2 | pH value and cadmium concentration in the effluent of regeneration with sulphuric acid (1 mol/l) (resin: Duolite A7, throughput: 2.5 BV/h).

Figure 3 | Concentration of mercury in feed and effluent (exchanger: Fuji PEI CS 07, throughput: 20 BV/h).

concentration of 5 μg/l. Similar and even better results could be obtained with other exchangers. For the given background composition, and especially for the chloride concentration, a very satisfactory elimination was achieved. With Cl^- concentrations exceeding 100 mg/l an increased formation of cadmium chloro-complex anions leads to a less effective elimination (Zhao 1999).

Due to the non-suppressed exchange of sulphate for hydroxyl ions the effluent pH is initially greater than 8. However, it drops rather quickly and corresponds with the feed pH after 2,000 BV.

In the above experiments the DOC had been increased to 6 mg/l by means of commercially available humic acid. Apart from eliminating cadmium the exchanger also decreased the DOC to about 1 mg/l. This effect is characteristic for the use of weakly basic exchangers. No deterioration of the metal uptake was observed. With Duolite A7 no irreversible fouling due to the organic matter was observed.

Figure 2 shows the development of cadmium concentration during regeneration with 1 molar H_2SO_4. As can be deduced, about 4 BV of concentrated acid are required. The displacement of metal salts coincides with the development of pH which, therefore, can be used for process control. The amount of cadmium displaced is approximately equal to the amount eliminated in the service cycle. Experiments with cadmium-bearing sulphuric acid
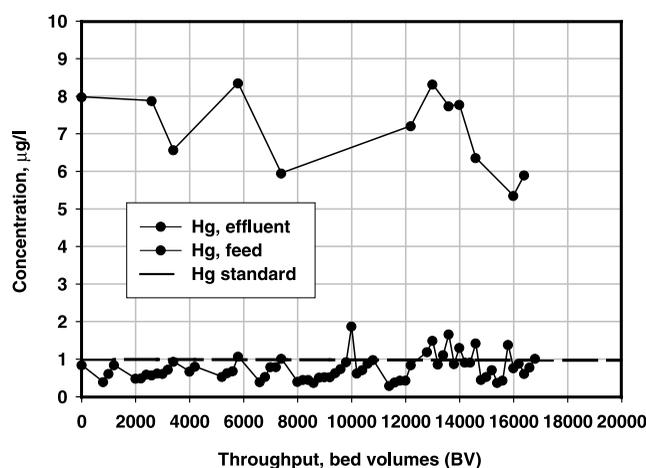
demonstrated that the spent acid could be re-used after increasing its H_2SO_4 concentration to the initial value.

During elution of heavy metal species by means of sulphuric acid only minor amounts of humic substances are released. Most of the humic substances are eluted during the second regeneration step, the treatment with NaOH.

Elimination of mercury

Figure 3 shows results of the elimination of mercury by means of the chitosan-based exchanger Fuji PEI CS 07. Feed concentration amounted to 8 μg/l. Apart from a few samples the effluent concentration was <1 μg/l until the end of the experiment after a total throughput of 16,000 bed volumes (Zhao 1999).

As in the preceding case a complete displacement of mercury from the exchanger is achieved by means of a few bed volumes of sulphuric acid (Zhao 1999).

Elimination of further metals

The elimination of nickel has been investigated at a much higher feed concentration of 1230 μg/l. As has been shown in earlier papers significant amounts of nickel
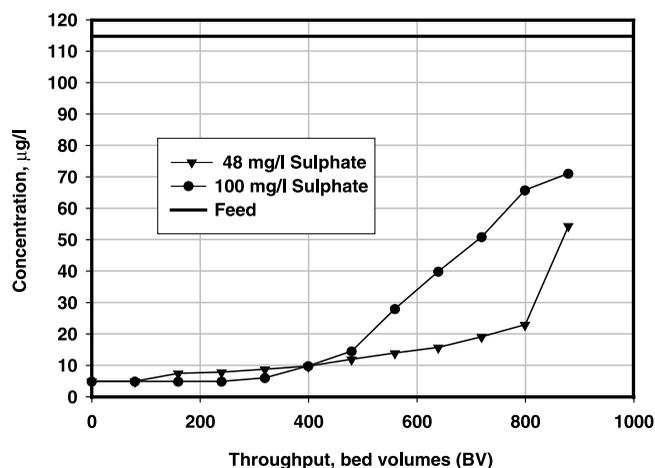
Figure 4 | Breakthrough curves from chromate removal from spiked tap water at different sulphate concentrations (exchanger: Amberlite IRA 67. throughput: 20 BV/h).

Figure 5 | Concentration of chromate in the effluent of regeneration (resin: Purolite A 845, throughput: 2 BV/h).

(35 µg/l) have been found only after a total throughput of 1,500 BV (Höll 1998).

Similar favourable results were obtained for the elimination of zinc from an effluent of a former mine (Höll 1998) and of lead. Zinc was detectable in the product water only after a total throughput of 1,850 BV. Lead was decreased from 100 µg/l to less than 5 µg/l.

Results of experiments in which mercury, cadmium and lead were added to tap water demonstrated that mercury removal was even better than in the experiments without other metals. This coincides well with earlier results of the simultaneous elimination of copper and nickel. In that case the copper removal was better if the exchanger had been pre-saturated with nickel (Höll 1996).

Figure 6 | Concentration of total chromium in the effluent of the treatment of a contaminated groundwater (resin: Amberlite IRA 67, throughput: 20 BV/h).

Removal of chromium(VI)/total chromium

Figure 4 shows results of the chromate elimination by means of the exchanger Amberlite IRA 67 at two different sulphate concentrations of the feed water. Comparison of the two breakthrough curves reveals the preferred uptake of chromate, which however, is affected at elevated sulphate concentrations. At feed concentrations of about 115 µg/l of chromate and 100 µg/l of sulphate, the limit of chromate is exceeded after 700 BV (He 1999).
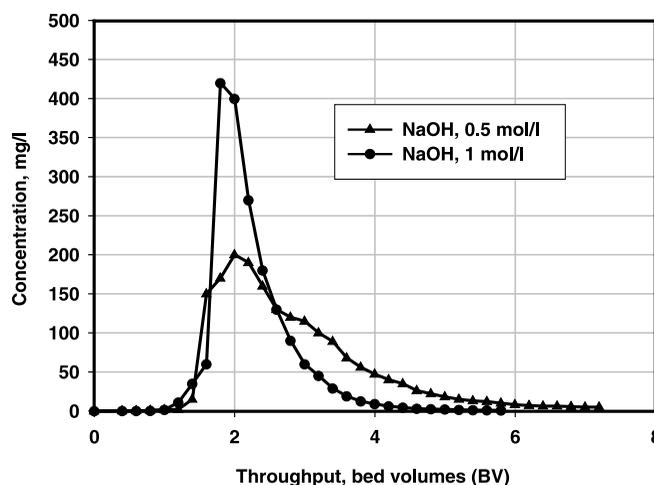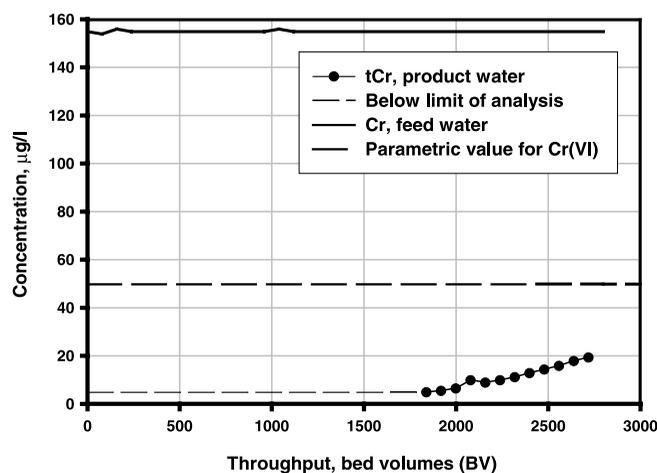
The development of regeneration after an experiment without increasing the sulphate concentration is shown in Figure 5. Chromate is quantitatively displaced from the resin by means of 4 bed volumes of 1 molar NaOH. As for the metal cations, chromate is concentrated in a relatively small volume which can easily be post-treated.

Figure 6 shows the results of an experiment with a contaminated groundwater containing about 160 µg/l total chromium. Up to a throughput of 1,800 bed volumes the concentration of chromium was below the limit of
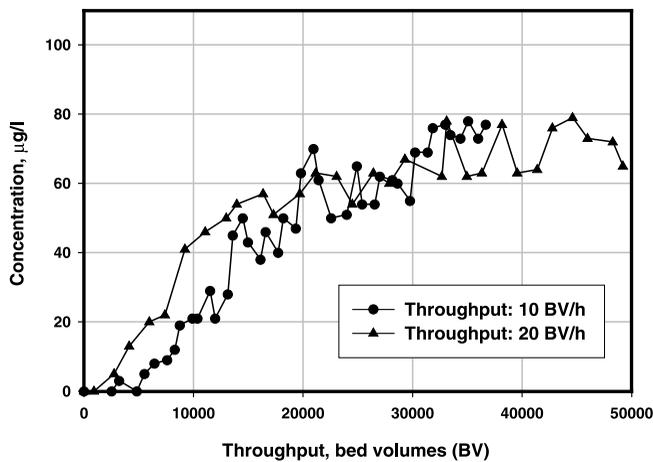
Figure 7 | Concentration of nickel in the effluent of a semi-technical filter (resin: Duolite A 7, resin volume: 45 l, raw water: spiked groundwater of Rasseln waterworks).

Figure 8 | Development of nickel, zinc, and DOC concentrations in the first regeneration step.

measurement by AAS. At the end of the experiment (2,750 BV) the effluent concentration had just reached 20 µg/l.

Experiments at the semi-technical scale

The elimination of nickel is currently being investigated at the Rasseln waterworks close to Mönchengladbach in the framework of a bmbf research project. At this location the groundwater of one of the wells has nickel concentrations of 70–100 µg/l. Two kinds of columns containing 2×10 l and 45 l exchanger, respectively, are in service. Bed heights amount to about 1 m. Due to practical reasons the mixed well water of all the wells is spiked with nickel to reach an approximately constant feed concentration of 100 µg/l. In addition to nickel the groundwater also contains about 35 µg/l of zinc. It is the objective of the investigations to decrease the nickel concentration below 20 µg/l. Results from the larger semi-technical installation are given in Bartosch (2001, figures 13–15).

Figure 7 shows the development of nickel concentration in the effluent at two different throughputs. Until a total throughput of 8,000 BV is reached, nickel concentrations below 20 µg/l are encountered. However, the filter performance strongly depends on the rate of filtration.
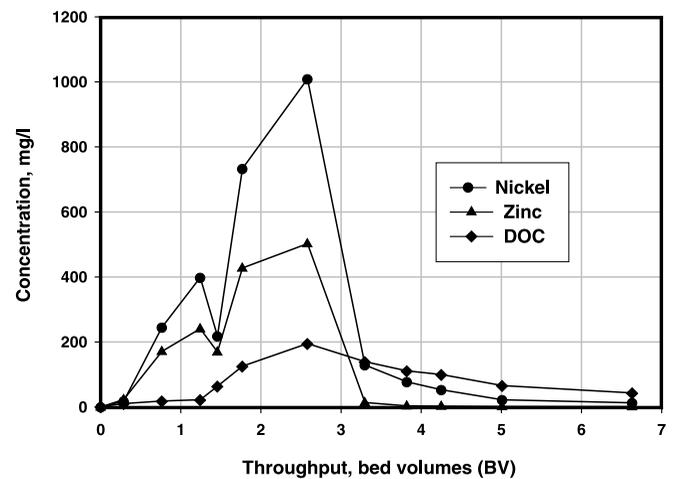
Figure 8 shows the development of the first regeneration step with 5 BV of sulphuric acid. Unlike the laboratory tests no smooth nickel peak was observed. Obviously the development depends on the reactions of the acid with co-adsorbed humic acid species. Protonation of these substances leads to a consumption of acid and, thus, to an intermediate increase/decrease of pH. Results of regeneration reveal that not only nickel but also zinc has been adsorbed during the service cycle. Although the zinc concentration in the groundwater is only about 35 µg/l relatively high values are encountered in the spent acid. This indicates its preferred uptake. The breakthrough performance of zinc has not been measured. The development of DOC demonstrates that part of the adsorbed organic substances are displaced by sulphuric acid.

The development of pH value and DOC concentration in the effluent of the second regeneration step are shown in Figure 9. The diagram shows that the main part of the DOC is released during this treatment step.

CONCLUSIONS

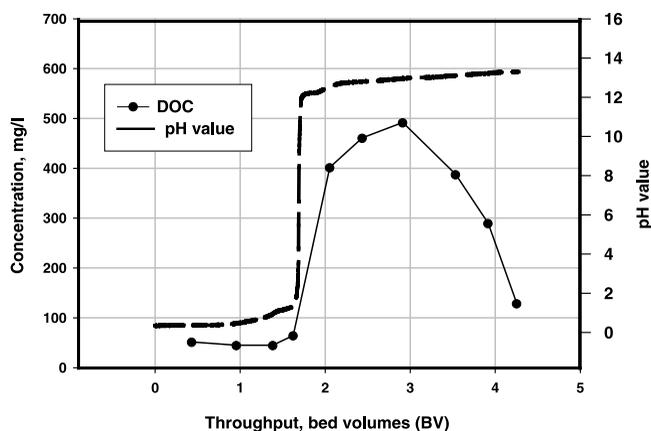The results of the laboratory-scale column tests have demonstrated the following:

Figure 9 │ Development of pH value and DOC concentration in the second regeneration step (solution: NaOH, 1 mol/l, resin: Duolite A7, throughput: 2.8 BV/h).

- The application of commercially available weakly basic ion exchangers allows an extremely selective elimination of trace amounts of a variety of hazardous cationic heavy metals, and a preferred elimination of chromate anions from raw waters of drinking water supplies.
- Elimination can be carried out in simple standard installations which can easily run automatically.
- In all cases the effluent concentrations can easily be decreased below the parametric values of the European Directive for Drinking Water.
- At usual throughputs long service cycles are possible.
- Regeneration is simple and requires standard chemicals. Furthermore, the volumes of the spent regenerant solutions are small. Therefore, the final discharge of the concentrated metals is simple.

Although no cost evaluation has been made so far, it can be concluded that the proposed elimination leads not only to simple, but also to cheap, processes.

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