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REMOVAL OF POLLUTANTS FROM DRINKING WATER BY COMBINED ION EXCHANGE AND ADSORPTION METHODS

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Complex ion exchange and adsorption methods were used for drinking water purification. Na-clinoptilolite was applied for selective removal of ammonium ions. The ion exchange capacity was 0.47 mg NH_4^+ /g, and 0.2 mg NH_4^+ /L breakthrough concentration was kept. The spent clinoptilolite was regenerated by 10-20 BV of 20 g NaCl/L at pH >12, then backwashed with purified water. Granulated activated carbon was used for removal of humic acids. The adsorption capacity was 91 mg/g of adsorbent. The average effluent concentration was <1 mg of humic acid/L. New adsorbent was used for arsenic removal, prepared by precipitation of $\text{Fe}(\text{OH})_3$ on Al_2O_3 as support material. The breakthrough capacity at 0.05 mg As/L was 0.10 mg of As/g adsorbent. For the regeneration of the spent adsorbent, 15-30 BV of a 1 M NaOH solution was used. The results showed that the removal of ammonium and arsenic ions as well as humic acids was selective and was not affected by other components of the raw water.

INTRODUCTION

In Hungary, mainly in the southern plain, there are large areas where drinking water contains more ammonium and arsenic ions than the recommended concentration. Furthermore, ammonium and arsenic ions are accompanied by high amounts of humic acids (about 10-15 mg/L), dissolved gases (mostly methane), and high temperatures (>30°C). The drinking water has to be purified before consumption. Poor disinfecting efficiency is caused by the reactions between these pollutants and chlorine. Now, only the dissolved gases are being removed from the deep-well waters.

The processes used for the removal of ammonium ions from drinking waters include air stripping, nitrification, break point chlorination, and ion exchange. The properties of synthetic and natural zeolites as ion exchangers for

removal of ammonium ions have been discussed in great detail (Hlavay 1982; 1983; Klieve 1980). Recently laboratory, field, and pilot plant experiments were carried out for selective removal of ammonium ions from waters by Hungarian natural zeolite tuff (Hlavay 1988). The influent NH_4^+ concentration ranged between 1.5-2.2 mg/L, while the effluent was <0.2 mg/L. The ion exchange capacity of the zeolite was found to be 0.35 mg NH_4^+ /g zeolite. Cyclic operation of the three-columns set-up gave drinking water of the desired quality. These results show that the ion exchange process using natural zeolite seems to be an appropriate and economical technology for purifying drinking waters.

Arsenic in water supply systems is a great problem in many areas of Hungary. About 400 000 inhabitants consume drinking water containing As ions higher than the

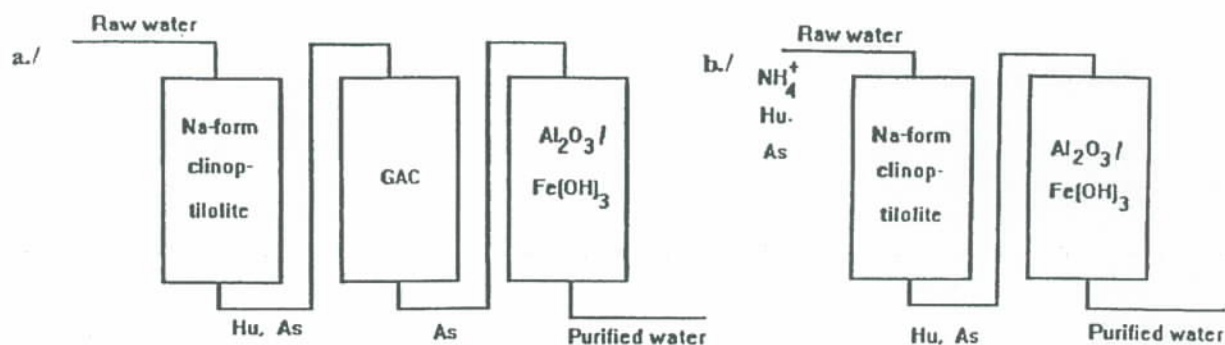


Fig. Experimental set-up.

permitted concentration. In natural waters, inorganic arsenic is present as arsenate and arsenite, depending on the pH and Eh conditions (Ferguson and Gavis 1972). In oxygenated waters, arsenic acid species (H_3AsO_4 , H_2AsO_4^-) are permanent while under mildly reducing conditions, arsenious acid species (H_3AsO_3 , H_2AsO_3^- , and HAsO_3^{2-}) become stable. Different methods have been used for arsenic removal from waters. Technologies included are lime softening, precipitation with ferric salts, ferrous sulfide beds, ion exchange, and adsorption onto activated carbon and alumina (Patterson 1973). Generally, chemical processes were successful, in particular those including coagulation and precipitation with ferric salt and lime. Disadvantages of the chemical methods are that a huge amount of hazardous waste is produced, mostly amorphous precipitates, and the safe disposal of the materials has not been solved yet. Application of ion exchange and adsorption methods is limited for large-scale water purification (Sato 1980; Bellack 1971; Shigetomi 1980; Elson 1980; Gullledge 1973; Gupta 1978). The recommended concentration of arsenic ions in drinking water has recently been set as 0.05 mg/L by the Hungarian National Health Institute (in agreement with USEPA). New adsorbents have been applied for removal of excess arsenic ions prepared from porous supports treated chemically on their surface (Hlavay 1984). The adsorption behaviour of the different adsorbents was investigated in static and dynamic experiments. Experimental results were compared to the Langmuir and Freundlich isotherms (Dzombak 1990).

The aim of this work was to develop a complex and simple ion exchange and adsorption method in laboratory scale for purification of drinking water containing high amounts of ammonium and arsenic ions as well as humic acids. The results of model experiments can provide data for the scale-up of a field and pilot plant study. Water is supplied from a deep well situated in Eperjes, a village in Csongrad County. Chemical components of the model water are characteristic for the southern part of Hungary.

EXPERIMENTAL

Laboratory experiments were carried out by 3.4 cm i.d. x 18 cm columns. Bed volumes (BV) of ion exchangers and adsorbents were 80 mL, and the columns were operated in a down-flow mode. The average exhaustion flow rate was about 5 BV/h. Three ion exchange columns set up in series were filled with Na-clinoptilolite (Hlavay 1982), granulated activated carbon, and $\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$ (Hlavay 1984), respectively. Natural zeolite was mined at Tokaj Mountain in northern Hungary from an open pit mine. $\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$ adsorbent was prepared as follows:

Table 1. Chemical composition of the raw water.

Component	Concentration, mg/L
COD	6.9
Humic acid	11.0
NH_4^+	1.0
NO_2^-	<0.05
NO_3^-	<1
Fe	0.16
Mn	<0.02
Cl^-	34.2
HCO_3^-	800
Na	270
K	2.6
Ca	10.2
Mg	4.5
As	0.14
pH	8.26
Dissolved gas	50 L/m ³

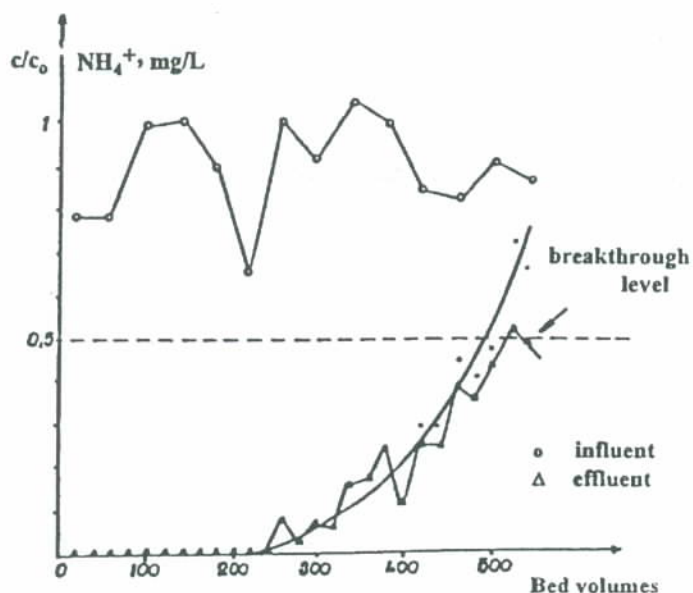


Fig. 2. Breakthrough curve for ammonium ions.

granules of 0.5-1.0 mm of activated Al_2O_3 were formed and $\text{Fe}(\text{OH})_3$ was freshly precipitated onto the surface of the particles. The resulting iron(III)-hydroxide impregnated porous adsorbent was dried at room temperature, packed into an ion exchange column and washed with water to remove the excess reagent. Raw water was loaded to the top of the first column and the prepurified water was led from the bottom of this column to the top of the second column, and so on (Fig. 1). Drinking water from a deep well (a small village in Csongrád County) was used. The components of the raw water were analysed, and the results are shown in Table 1. The exhaustion experiments were cyclically carried out and the regeneration of the spent adsorbents was also studied.

Analytical procedures

Samples were taken twice daily from all columns and the influent water. The ammonium ion concentration was measured by the Hungarian Standard (MSZ 1980). A spectrophotometric method using the silver-diethyl-dithiocarbamate complex of arsine was applied for the determination of arsenic ions in the 1-100 $\mu\text{g}/\text{L}$ range. Arsenic ions are reduced to arsine by $\text{Na}(\text{BH}_4)$ and arsine reacts with SDDC in pyridine (Hungarian Standard, MSZ 1987). The humic acid concentration was measured by spectrophotometric method (Standard Methods 1989). The pH, COD, calcium, magnesium, sodium, potassium, and iron ion concentration of the effluent were also monitored.

Table 2. Chemical composition of influent and effluent water.

Component	Concentration, mg/L	
	Influent	Effluent
NH_4^+	0.88	<0.1
Humic acid	11.2	10.6
As	0.14	0.14
Na	263.4	283.1
K	3.1	2.3
Ca	13.0	10.0
Mg	4.5	0.5
Fe	0.16	<0.02
pH	8.52	8.64

RESULTS AND DISCUSSION

Removal of ammonium ion with ion exchange process

The Na-form clinoptilolite was applied as an ion exchanger that preferentially exchanged ammonium ions in the presence of sodium, calcium, and magnesium ions. Exhaustion and regeneration experiments were carried out in four cycles. The average ammonium concentration of the raw water was 0.86 mg/L and that of the effluent water was found as 0.15 mg NH_4^+/L . The volume of the treated water was 48 L (600 BV); the flow rate was kept at 5 BV/h (0.4 L/h filtering rate). The ion exchange capacity was determined up to 0.2 mg NH_4^+/L breakthrough concentration and proved to be 0.47 mg NH_4^+/g zeolite. The breakthrough concentration was chosen at 0.2 mg NH_4^+/L to prevent the formation of chloramines and the problems of bad taste and odour.

Based upon the results, it was found that the ion exchange capacity of the Na-form clinoptilolite was similar to that published earlier (Hlavay et al. 1983). The breakthrough curve prepared for the exhaustion cycle is shown in Fig. 2. It can be seen that the initial ammonium ion concentration of raw water has considerably changed due to the relatively high temperature and pH of the water. Along with the ammonium ions, the concentration of other ions, e.g., Fe, Ca, Mg, and K, as well as humic acids, was also monitored (Table 2). Calcium, Mg, and K ions were ion exchanged with the Na-form clinoptilolite, while humic acids were adsorbed on the hydrated oxides forming the zeolite frame. The iron(III)hydroxide, formed

Table 3. Amount of NaCl solution required for regeneration.

Regenerant required		Flow rate BV/h	Removal of
BV	pH		ammonium ions %
20	12.3	5	80
37	12.3	5	91
10-20	12.3	2.5	98

in the drinking water at pH = 8.5 - 8.6, is adsorbed on the surface of the natural ion exchanger.

Regeneration of the spent clinoptilolite ion exchanger bed was accomplished by a 20 g NaCl/L solution at pH = 12.3, then backwashed with purified water. The amount of regenerant required to remove the ion-exchanged ammonium ions is shown in Table 3. It can be seen that 10 - 20 BV of regenerant was used to remove 98% of the ammonium ions at a flow rate of 2.5 BV/h.

Humic acids removal with granulated activated carbon (GAC)

The second column in the experimental set up (Fig. 1a) was filled up by granulated activated carbon (GAC). Prepurified water was introduced to the top of the GAC column. Concentration of humic acids was determined in the influent and effluent water. Results of the exhaustion cycle are summarised in Fig. 3.

On the basis of the results, it was found that the removal efficiency of humic acids from the prepurified water was about 90%. The GAC was prepared from wood and the adsorption capacity was obtained as 91.1 mg humic acid/g adsorbent. It can also be seen that the $Al_2O_3/Fe(OH)_3$ adsorbent, filled in Column 3 and placed at the end of the experimental set-up (Fig. 1), can further be used for the removal of humic acids. The results are in good agreement with the findings of other research work (Stumm 1987); namely, the weak acids can be adsorbed on the surface of hydrated aluminium and iron oxides. The reactions can be characterised by the mutual application of more processes, e.g., chemical reactions, adsorption, and electrostatic interaction. The pH of the treated water increased, the ΔpH was 0.2-0.3 ($\Delta pH = pH_{initial} - pH_{effluent}$), while the other chemical parameters of the effluent water were not practically changed. During the preparation of active carbons, basic solution is usually applied, so a slight amount of the base can be released into the water.

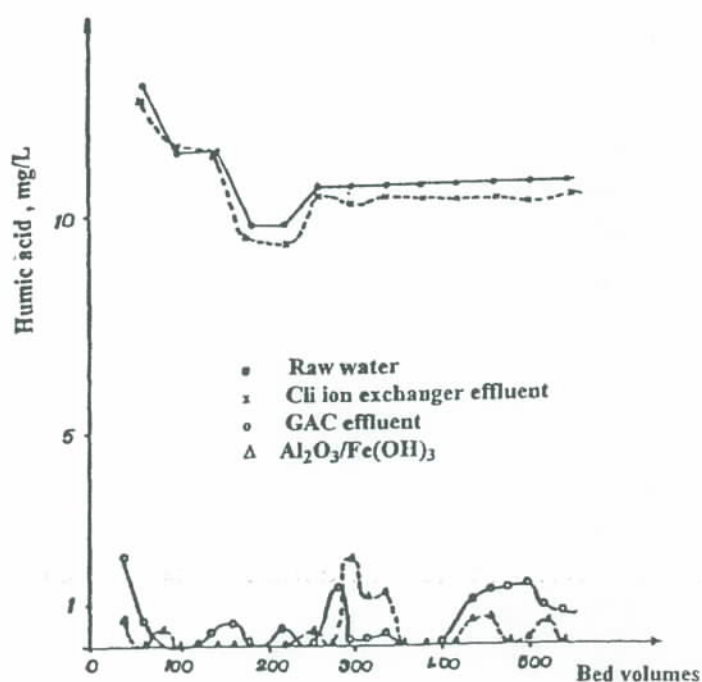


Fig. 3. Humic acid removal by GAC adsorption.

Removal of arsenic ions with $Al_2O_3/Fe(OH)_3$ adsorbent

New adsorbent was used for arsenic removal prepared by precipitation of $Fe(OH)_3$ on aluminium-oxide as a support material (Fig. 4). The exhaustion experiments were studied at different amounts of humic acids in the drinking water. First, prepurified water containing small amount of ammonium ions and humic acids was treated on the $Al_2O_3/Fe(OH)_3$ column (Fig. 1a). The results of exhaustion experiment are summarised in Table 4. Secondly, water containing high amount of humic acids (10.5 mg/L) and arsenic ions was treated by the adsorbent filled in column 2. (Fig. 1b). The results of exhaustion experiment are summarised in Table 5.

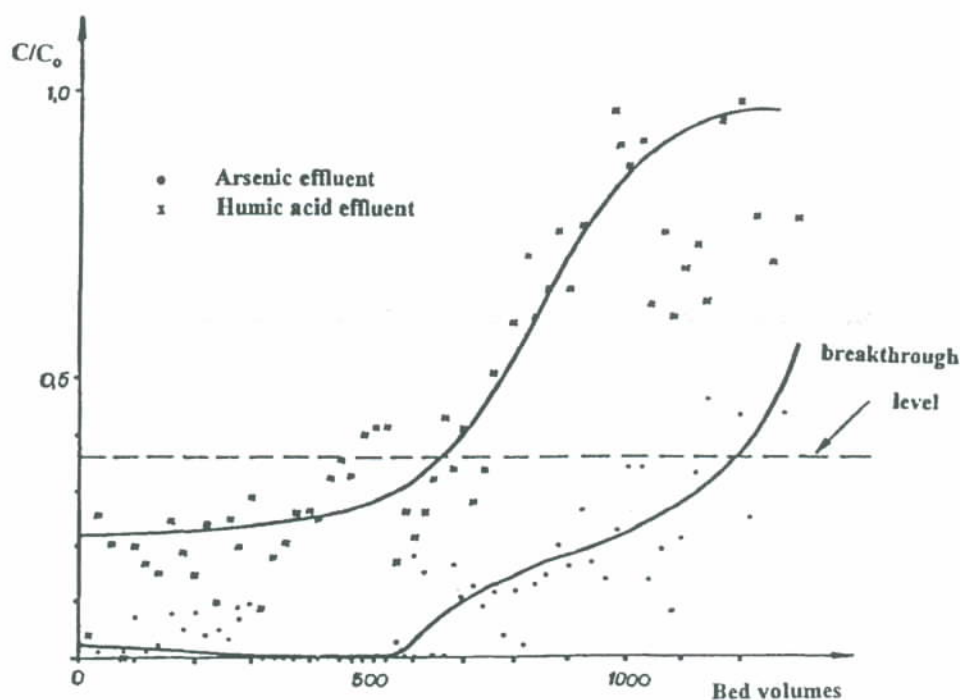


Fig. 4. Arsenic and humic acid removal by $\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$.

Table 4. Results of the removal of the arsenic ions $\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$ adsorbent.

Volume of adsorbent	50 mL
Amount of adsorbent	63.3 g
Average influent As conc.	0.135 mg/L
Average effluent As conc.	0.025 mg/L
Purified water volume	1038 BV; 51.9 L
Average flow rate	5 BV/h; 0.25 L/h
Adsorption capacity up to 0.05 mg As /L	0.09 mg As/g adsorbent
breakthrough concentration	

Comparing the results summarised in Tables 4 and 5, it can be seen that the adsorption capacity proved to be practically the same: 0.1 mg As/g adsorbent for the two experimental set-ups. Part of the humic acids was adsorbed on the surface of the $\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$ adsorbent, but it did not affect the removal of arsenic ions. This means that the adsorption of high molecule humic acids and arsenic ions takes place at different adsorption sites. The reasons for the small adsorption capacity were the chemical composition, the high pH (pH = 8.2 - 8.9), and the different arsenic species of the raw water.

The removal efficiency of the arsenic ions depends greatly on the dominant species of arsine in the raw water. The amount of arsenic ions was determined. It was found that 80% of As ions were in H_2AsO_3^- form, 20% of which were in HAsO_4^{2-} species. The arsenite ions can primarily

be adsorbed by chemical reaction on the surface of iron(III)-hydroxide. Similar to the interaction between the H_2PO_4^- ions and $\text{Fe}(\text{OH})_3$ precipitates (Sigg 1979), the neutral functional group of $\{=\text{FeOH}\}$ reacts with H_2AsO_3^- ions and surface compounds of $\{=\text{FeAsO}_3\text{H}_2\}$, $\{=\text{FeAsO}_3\text{H}\}$, and $\{=\text{FeAsO}_3\}$ can be formed. The chemical reactions can be used for characterisation of the processes taking place on the surface, since the adsorption models by Langmuir and Freundlich were not appropriate to explain the phenomenon (Hlavay 1984).

The spent adsorbents were regenerated by 1 M NaOH with a flow rate of 5 BV/h. The results of the regeneration are shown in Table 6. It can be seen that adsorbed arsenic ions could be removed by 15-30 BV of regenerant with a recovery efficiency of 75-80%. With increasing volume and concentration of the regenerant, the efficiency of the

Table 5. Removal of arsenic and humic acid by the $\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$ adsorbent.

Volume of adsorbent	80 mL
Amount of adsorbent	99.6 g
Average influent arsenic conc.	0.14 mg/L
Average effluent arsenic conc.	0.02 mg/L
Average influent humic acid conc.	10.2 mg/L
Average effluent humic acid conc.	4.5 mg/L
Purified water volume	1225 BV; 98 L
Adsorption capacity up to 0.05 mg As/L breakthrough concentration	0.10 mg As/g adsorbent
Adsorption capacity of $\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$ adsorbent for humic acid	5.6 mg humic acid/g adsorbent

Table 6. Regeneration of spent $\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$ adsorbents (see Fig. 1a).

Regenerant required Bed volume	Removal of As	
	Flow rate, BV/h	%
15	5	75
30	5	80
30	2.5	82

Table 7. Ion contents of raw purified water.

Component mg/L	Raw water	Purified water		
		Cl _i	GAC	$\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$
COD	7.6	7.8	1.3	0.2
Humic acid	11.1	10.5	2.1	0.6
NH_4^+	0.78	<0.1	<0.1	<0.1
Cl ⁻	39.3	38.4	37.5	35.6
Na	263	283	283	224
K	3.1	2.3	2.1	1.5
Ca	4.5	0.5	1.0	0.1
Mg	7.5	5.5	5.5	1.0
Fe	0.12	<0.02	<0.02	<0.02
As	0.14	<0.004	<0.004	<0.004
pH	8.52	8.64	8.89	8.87

regeneration was not improved. This underlines the hypothesis of the chemical reaction between the As ions and the adsorbent, since the complete removal of the surface arsenic compounds could not be achieved by NaOH solution. The ionic concentrations of influent and effluent drinking water determined at each of three columns, respectively, are shown in Table 7. As can be seen from the results, during water treatment, all pollutants were removed up to the recommended concentration. The other components of the given drinking water were changed only on a small scale. The calcium and magnesium concentrations decreased slightly, ferric ions were completely removed, and the pH increased to about $\Delta\text{pH} = 0.3 - 0.4$.

CONCLUSIONS

The water purification system developed is a low-waste technology, since no harmful chemical is produced and released into the environment. The spent clinoptilolite ion exchanger can be regenerated; the ammonia can be air-stripped from the solution; and the regenerant is used again. The spent clinoptilolite was regenerated by 10-20 BV of 20 g NaCl/L at pH >12; then, it was backwashed with purified water. Granulated activated carbon (particle size of 0.5-1.0 mm) was used for removal of humic acids. The average effluent concentration was found to be <1 mg humic acid/L, while the adsorption capacity was >90 mg humic acid/g GAC. A novel adsorbent was developed and used for removal of arsenic ions. The exhaustion experiments were studied by deep-well water containing different amounts of humic acid. The breakthrough capacities, calculated at 0.05 mg As/L, ranged between 0.09-0.1 mg/g adsorbent. For regeneration, 15-30 BV of 1 M NaOH solution was used. The high amount of arsenic ions in the small volume of the regenerant solution may be removed by lime precipitation. The disposal of toxic sludge has to be solved. Removal of ammonium and arsenic ions, as well as humic acids, was not affected by other components in the raw water. Based on the results of the laboratory experiments, the design and construction of field set-ups with a capacity of 0.5-1 m³/d is suggested.

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