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Effect of Extremely High Specific Flow Rates on the Ion-Exchange Resin Sorption Characteristics

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Additional information is available at the end of the chapter

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Abstract

Behavior of the strongly basic, macroporous ion-exchange resin Amberlite IRA 958-Cl is circumstantially explained in the book chapter. Effects of different specific flow rate (SFR) and determination of its optimum value, as well as effects of the empty-bed contact time (EBCT) values on the removal of NOM, arsenic, sulfate, electrical conductivity, bicarbonate and chlorine from groundwater using strongly basic ion exchange resin (SBIX) is examined in this chapter. Determination of the resin's sorption characteristics is also part of the investigation. A new approach of pseudo equilibrium adsorption capacity is presented. Investigations of determination of optimum value of water flow rate and resin's sorption characteristics were conducted with native groundwater and native groundwater with addition of oxidizing agent. Sodium hypochlorite was added to the raw water with the aim of oxidizing NOM and As(III) to As(V). The intention was to find out whether the resin might be used beyond the range of operating conditions recommended by the manufacturer. Results will provide a better understanding of treatment of groundwater with similar physico-chemical composition which is important when designing a water treatment plants for settlements in areas with such groundwater. Also, prolonging the resin working cycle can ultimately lead to water treatment plants cost reduction. Namely, when the results for the optimum SFR are obtained for a pilot plant system for concrete groundwater of distinct physico-chemical characteristics, it is simple to design a unique ion-exchange water treatment system of any capacity. The obtained results make a sound basis for designing an appropriate plant for the removal of NOM from groundwater of the region of the town of Zrenjanin. The tested resin can also be used in the process of pretreatment of the same water, since it allows the removal of about 50 % of the naturally occurring arsenic.

Keywords: Specific flow rate, resinsorption characteristics, arsenic, natural organic matter

1. Introduction

Natural organic matter (NOM) and arsenic present a major problem when found in drinking water. There have been many published scientific papers on the methods for their removal over the years [1-9]. Groundwater investigated in this chapter is one of the most arsenic and NOM contaminated water in Europe [10], and nevertheless population which inhabits these areas are using this groundwater as a drinking water without any treatment process.

Behavior of the strongly basic, macroporous ion-exchange resin Amberlite IRA 958-Cl [11] will be circumstantially explained in the book chapter. Effects of different specific flow rate (SFR) and determination of its optimum value as well as the effects of the empty-bed contact time (EBCT) values on the removal of NOM, arsenic, sulfate, electrical conductivity, bicarbonate, and chlorine from groundwater using strongly basic ion-exchange resin (SBIX) will be examined in this chapter. Determination of the resin's sorption characteristics is also part of the investigation. A new approach of pseudo equilibrium adsorption capacity will be presented.

Investigations of determination of optimum value of water flow rate and resin's sorption characteristics were conducted with native groundwater and native groundwater with addition of oxidizing agent. Sodium hypochlorite was added to the raw water with the aim of oxidizing NOM and As(III) to As(V). The addition of sodium hypochlorite to water yields hypochloric acid, and the liberated atomic oxygen acts as an efficient disinfection agent and a very strong oxidant. Apart from oxidizing the present NOM and arsenic(III), the liberated nascent oxygen can also oxidize the present inorganic species such as nitrites, iron(II), and the like. This is important because of resin affinity for certain ions and their competition for resin binding sites which can affect NOM and arsenic ion-exchange and adsorption.

The intention was to find out whether the resin might be used beyond the range of operating conditions recommended by the manufacturer. Results will provide a better understanding of treatment of groundwater with similar physicochemical composition which is important when designing a water treatment plants for settlements in areas with such groundwater. Also, prolonging the resin working cycle can ultimately lead to water treatment plants cost reduction.

1.1. Composition and characteristic of dissolved natural organic matter and arsenic

Natural organic matter is frequently found dissolved in groundwater. In most cases, the presence of NOM gives these waters a characteristic yellow color. NOM consists usually of humic substances originated from the geological formations of the location of groundwater

source [12]. Their molecules have a supramolecular structure, formed by condensation of smaller molecules resulting from the degradation of organic matter [13]. Humic matter has a very stable structure, a proof of this being the fact that they have been present in the Earth's crust for thousands of years [13, 14].

Piccolo and Stevenson showed that humic acids exhibit affinity to metal ions from the soil, forming thus the complexes of different stability constants and other characteristics [15].

Humins of the investigated groundwater contains humic acids (HAs) and fulvic acids (FAs). Humins are macromolecular polymers whose structure and characteristics are determined by their origin and process of humification. Like HAs, FAs too, are naturally present in water, soil, and turf. They are formed by chemical and microbiological degradation of plant material (humification). There are opinions that FAs are formed after the constitution of HAs. The FAs are richer in oxygen and poorer in carbon than HAs. Like HAs, FAs contain a number of reactive functional groups including carboxylic, hydroxylic, phenolic, quinonic, and semiquinonic [16]. Molar masses of FAs are smaller than those of HAs. FAs contain more constitutive groups that are structurally similar to carbohydrates, originated from polysaccharides. In the determination of total carbon content (TOC) in groundwater, HAs and FAs make the source of total dissolved organic carbon (C_T). Previous investigations showed that there exists labile (unstable) and non-labile components of NOM [17]. By taking advantage of the fact that labile NOM are sensitive to permanganate, it is possible to determine their fraction by standard method as the permanganate consumption (COD). The fraction of labile organic carbon is designated as C_L , and the fraction of non-labile carbon (C_{NL}) is calculated as the difference between the TOC and C_L . Anderson and Schoenau showed that the FA fraction depends essentially on the content of C_L , and that it is independent of C_{NL} [18]. Labile components of organic matter consist of cell biopolymers such as carbohydrates, amino acids, peptides, amino sugars and fats. Contents of these components in FA fraction is smaller, and because of that it is biologically and chemically more resistant. The HA skeleton contains strongly condensed aromatic structures surrounded by the side chains of aliphatic components. The FA fractions are mainly composed of carbohydrates, microbiological metabolites, and "younger" materials that are not significantly related to the mineral fraction. This explains the strong correlation between C_L and FA content, which is not observed for HAs. The strong correlation between C_{NL} and HAs indicates that C_{NL} consists of the fraction of organic carbon which is stabilized due to the chemical and physical associations with the mineral matrix. The groundwater that contains FAs has a characteristic yellow color.

Arsenic is a very toxic metalloid, occurring in nature in several oxidation states (-3, 0, 3, 5). In natural waters, it is present in its inorganic forms of oxyanions, primary and secondary arsenite, as well as in primary, secondary, and tertiary arsenate [19]. The water pH and redox potential influence dominantly the oxidation state of arsenic in natural waters. At the $pH < 6.9$ dominates $H_2AsO_4^-$, whereas at higher pH it is $HAsO_4^{2-}$. In strongly acidic media, under oxidation conditions the molecular form H_3AsO_4 is dominant, whereas under alkaline conditions, it is AsO_4^{3-} . Under reduction conditions, at the water $pH < 9.2$ dominates the amphoteric neutral molecular species H_3AsO_3 [20]. Arsenic is a constituent component of many ores and by the process of their dissolution reaches groundwater. Apart from natural arsenic,

arsenic in groundwater may be due to anthropogenic activities. Namely, many insecticides and fungicides, wood-protecting agents, chemicals used in semiconductor production, and additives to various alloys and glasses contain arsenic compounds [21]. It is known that prolonged exposure of the human organism to small doses or short exposure to high doses of arsenic causes skin disease and serious disturbance of internal respiratory and digestive organs, blood circulation, and of the nervous system. Also, Ng et al. proved that arsenic is carcinogenic [22].

The EU Drinking Water Directive from 1998 recommended that the maximum tolerable concentration (MTC) of arsenic in drinking water should be 10 µg/L [23]. Three years later, in its revision of the corresponding standard, the US EPA adopted also the same MTC value of 10 µg/L [24]. Because of the geological and mineralogical origin of arsenic in groundwater, its removal is a technologically very complicated and demanding operation.

1.2. Principles of NOM and arsenic removal using strongly basic ion-exchanging resins

Ion exchange is a process used to remove ionic components dissolved in water, the process being based on their high affinity to bind to the ion-exchange resin. As a consequence, ions are captured and exchanged for the resin's ions. When the resin capacity for exchanging particular ions is reached (exhaustion), it is usually regenerated, so that it can be used in repeated cycles. It is reported that the application of special macroporous strongly basic anionic resins is suitable for the removal of NOM from natural waters [25]. These resins are very effective in removing the water coloring matter (humins) and function in the regime of regeneration with sodium chloride [26, 27]. The main principle of NOM removal by these macroporous resins is based on the finding that more than 90% of NOM in groundwater are in fact weak acids represented mostly by molecules and also by dissociated anions and often cations of alkaline earth elements. Molecules of humic acids are large and complex, composed of benzene rings and other interconnected chemical structures. Every NOM molecule contains a number of carboxylic groups. Like carbonic acid, humic acids do not fully dissociate at a neutral pH. Depending on the number of carboxylic functional groups in their molecules, NOM can act as polyvalent species. These NOM properties make, in fact, the basis for their removal from the anionic resin by a saturated solution of sodium chloride. Strong base anionic macroporous exchange resins efficiently exchange chloride for all the anions present in raw water. The anions from water interact with the resin functional groups in dependence of their relative affinity, as well as the rate and dynamics of the ionic exchange. Under ideal conditions, when the resin is saturated, sulfate and anions of organic acids occur adsorb on the surface, while the other anions, such as nitrate, chloride and bicarbonate, are sorbed in the interior of the resin beads. In the initial cycle of ionic exchange, the resin plays the role of a dealkalizer and removes bicarbonates from the raw water. Also, the beginning of the working cycle is characterized by a decrease in the pH of the effluent, which often falls below pH 6. In the further course of the work cycle, the resin adsorbs anions that have a higher affinity than bicarbonate, which is released into the effluent. This is accompanied by a pH increase, which may attain a value that is higher than that of the raw water. In the further course of the working regime, chloride and nitrate are released and their places occupy anions of organic acids and sulfate.

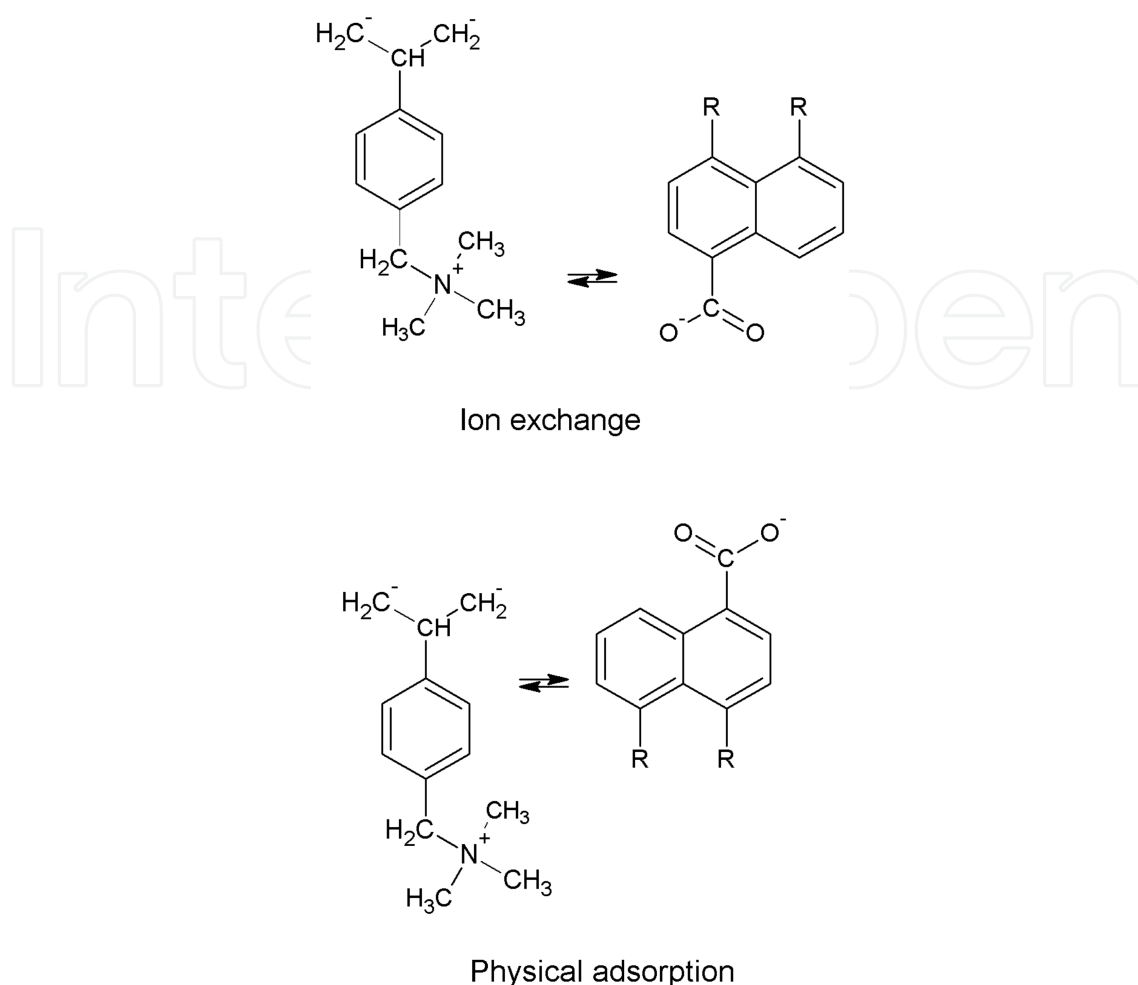


Figure 1. Possible mechanism of reversible sorption of organic molecules on ion exchange resin

Group of authors showed that in a complex solution containing humic acids and arsenic, complex compounds are formed between arsenic and carboxylic groups of humic acids [28]. By investigating this interaction, Warwick et al. found that the deprotonated functional groups of humic acids and arsenic form associates, depending on the pH, ionic strength, and arsenic concentration [29].

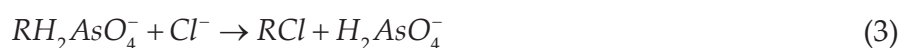
In the process of removal of organic ions, such as those of NOM using anion exchange resin, two sorption mechanisms may be involved, and these are ion exchange and physical adsorption (Figure 1). Ionic exchange includes the transfer of the ions from the ionic exchanger and electrostatic interaction between the ions of functional groups, presented as quaternary ammonium ion-exchanging groups and participation of the carboxylic groups. This interaction is of donor-acceptor type. Quaternary ammonium groups $[-N(CH_3)_3^+]$ are specific active groups which determine the intensity of the ionic exchange. Physical adsorption takes place as the van der Waals interaction between the non-polar (hydrophobic) groups present in the NOM molecules and central structure of the polymer resin to which substituents are attached [30, 31].

The adsorption of arsenic ion on the surface of strongly basic ion exchanging resin may be presented as follows:

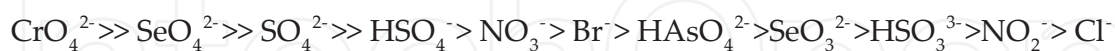


Since the affinity of the acrylic resin with quaternary ammonium groups is higher to doubly charged ions than to the singly charged ones, the efficiency of the ionic exchange is higher at higher pH values, when doubly charged arsenate ions are dominant [32].

Removal of As(III) by ionic exchange is less effective, since at the $pH < 9$ it occurs in water in the form of the molecule H_3AsO_3 [20]. On the other hand, As(V) is present in the form of the anions $H_2AsO_4^-$ and $HAsO_4^{2-}$, which makes the ionic exchange more probable. It is just the specific phenomenon of the occurrence of arsenous acid as an uncharged species that cannot be removed from water which allowed the development of procedures for distinguishing between arsenite and arsenate [33, 34]. Therefore, in order to remove arsenite from water, it has to be oxidized to arsenate. The regeneration of the ion-exchange resin proceeds according to the following reaction:



Regeneration can be done with HCl and NaCl. The use of HCl yields arsenic acid, H_3AsO_4 , which has no influence on the equilibrium of ion exchange and the regeneration is more efficient [32]. The strongly basic resin that has been pretreated by anions, e.g. chloride, is capable of removing a wide spectrum of anions from water, depending on their relative affinities, shown by the following order [35]:



2. Materials and methods

2.1. Specificity of the investigated groundwater and geological survey of aquifer origin

In the period of the Middle Miocene to the Quaternary, the space of the Central and South-Eastern Europe was covered by the Pannonian Sea, formed in the spacious depression between the Alpine, Carpathian, and Dinaridian mountain ranges, where very thick sediment series were deposited. The northern part of Serbia-Vojvodina is situated in the south-east part of this sedimentation zone on an area of 21,506 km². The basic mass of these sediments make the Mesozoic clastites and carbonates along with crystalline schists and granitoids of the Paleozoic

and Proterozoic eras. The town of Zrenjanin is located in the eastern part of the Vojvodina - called the Middle Banat, and the specificity of the location stems primarily from the geological and hydrological characteristics of the terrain. The water-bearing formations in this region were formed in the final phase of the existence of the Pannonian Sea. On the territory of the town of Zrenjanin, in the geological profile to a depth of 400 m, there are several water-bearing strata, separated by strata layers of pure or sandy clay or clayey sands. The thickness of the water-bearing strata is from several meters to about 50 m, most often 10-20 m. The groundwater that can be used as drinking water occurs to a depth of about 400 m. In the upper part, to a depth of about 60 m, an unconfined aquifer (phreatic aquifer) is formed, whereas below it the aquifer is under the pressure (artesian aquifer). The groundwater of the artesian aquifer, to which belongs the investigated water, is by their chemical composition significantly different from the waters of the phreatic aquifer. The investigated water belongs to the type of bicarbonate alkaline waters, with the bicarbonate share of about 85-90% equivalents. The total mineralization is most often lower compared to that of the phreatic water and is in the range 250-1500 mg/L. Content of sodium chloride increases generally with increase in the depth of the artesian aquifer. Local deviations are usually a consequence of tectonic disturbances. The ammonium content is usually below 2 mg/L, although there have been registered very high contents (up to 10 mg/L) at the locations south of Zrenjanin. The iron content often exceeds the maximum tolerable concentration (MTC); it is usually around 1 mg/L and decrease with depth. If compared to the contents in phreatic water, contents of total iron and manganese show a decrease. The artesian water is softer than phreatic water, and its hardness rarely exceeds the limit of 10° dH. Very soft waters (2-5° dH) have been found north of Zrenjanin. Artesian waters are often weakly alkaline, and their temperature is in the range of 15-20°C. In the Zrenjanin region, these waters are of the very characteristic yellow color, have a specific taste, and in many settlements are used as drinking water. People that are accustomed to yellow water are reluctant to change their habit and this represents a problem. Namely, yellow color is due to the presence of undesirable organic (humic) matter. Content of this matter, expressed via the COD, determined by the permanganate method, is in the range of 20-150 mg/L, and in the extreme cases exceeds even 200 mg/L [36]. Up to now, water supply in the Middle Banat region has been based on the exploitation of artesian groundwater. Waters of this aquifer, in addition to marked humic matter load, contain significant amounts of orthophosphate, sodium, and arsenic. The measured arsenic contents are in the range from 0.040 to 0.380 mg/L, so that the Zrenjanin region is in this respect one of the most endangered regions in Europe. The size of the area of the arsenic occurrence suggests the supposition that it is of geological origin. However, there exists the possibility that it has been brought to Vojvodina by the Tisa River, whose water dissolves arsenic minerals of the Carpathian, where there are large deposits of arsenic ores [37]. In some Zrenjanin locations, many domestic and foreign corporations searched for practical groundwater treatment models, but without satisfactory results. A likely reason for this is the methodological research inadequacy for the actual problem. Pilot tests were conducted without a clear project assignment and a defined method of removal of many pollutants for the given case [38]. Groundwater from the Zrenjanin region as a resource outside the natural water cycle is of extremely complex chemical composition, which demands a complex technological treatment. Values of measured physicochemical parameters are given in Table 1.

Parameter	MTC	Groundwater
Color, permanent (°Co-Pt)	5	60
pH	6.8-8.5	8.06
COD (mgO ₂ /L)	2.0	7.73
TOC (mg/L)	/	10.64
Electrical conductivity (µS/cm)	1000	820
Chloride (mg/L)	200	6.97
Bicarbonate (mg/L)	/	645
Sulfate (mg/L)	250	25.6
Arsenic (mg/L)	0.01	0.2658

Table 1. Selected physicochemical parameters of the investigated groundwater

2.2. Strongly basic macroporous ion-exchange resin

To study the removal of dissolved NOM, arsenic bicarbonate, pH value, electrical conductivity, chlorine, and sulfate, an acrylic SBIX type Amberlite IRA 958-Cl, manufactured by Rohm and Haas Company, whose characteristics are given in Table 2 [11] was used. This type of resin has a rigid polymer porous network in which persist an intrinsic porous structure even after its drying. The resin large pores permit access to the interior exchange sites of the bead. They are also referred to as macroreticular or fixed-pore resins. Macroporous resins are manufactured by a process that leaves a network of pathways throughout the bead. This sponge-like structure allows the active portion of the bead to contain a high level of divinylbenzene crosslinked without affecting the exchange kinetics. Unfortunately, it also means that the resin has a lower capacity because the beads contain less exchange sites.

Properties	
Matrix	Crosslinked acrylic macroreticular structure
Functional groups	Quaternary ammonium
Physical form	White opaque beads
Ionic form as shipped	Chloride
Total exchange capacity	≥ 0.8 eq/L (Cl ⁻ form)
Moisture holding capacity	66-72 % (Cl ⁻ form)
Specific gravity	1.05-1.08 (Cl ⁻ form)
Bulk density	655-730 g/L (Cl ⁻ form)
Effective size	470-570 µm
Mean diameter	700-900 µm

Uniformity coefficient	≤ 1.8	
Suggested operating conditions		
Maximum operating temperature	80°C	
Minimum bed depth	600 mm	
Service flow rate	8-30 BV/h	
Regenerants	NaOH	NaCl
Flow rate (BV/h)	2-6	2-6
Concentration (%)	2	10
Level (g/l)	6-40	160-300
Minimum contact time	30 minutes	
Rinse water requirements	5 to 10 BV	
Rinse flow rate	Same as regenerant for first bed displacement, than same as service flow rate	

Table 2. Physicochemical characteristics of the Amberlite IRA 958-Cl macroporous resin and operating conditions recommended by the manufacturer

2.3. Determination of optimal specific flow rate of strongly basic ion-exchange resin

To study the influence of the different SFRs in the process of removal of NOM and arsenic from groundwater, a specially designed pilot plant system 1 was made (Figure 2). The pressure and the amount of water were ensured using the waterworks facilities of the Melenci settlement explained in Section 2.1. The mean operating water pressure and temperature were 3 bar and 18°C, respectively. The composite pressure vessels used for plant construction were Structural type Q-0844 and Q-0635, of total volume of 33.6 L and 14.4 L, respectively. The vessel was filled with 25 L and the later with 10 L of resin. The cross-section area of the tank Q-0844 was 0.034 m², and the resin bed height was 0.735 m. The tank Q-0635 of the cross-section of 0.020 m² had the bed height of 0.5 m. The bigger tank was used for smaller SFRs, from 2 to 80 BV/h, and the smaller one for the SFRs ranging from 100 to 300 BV/h. The control valve (CV) was a Fleck 3150, injector type, with manual control. The pilot plant was equipped with four Franck Plastic flow meters (R), for the flow ranges of 50-500 L/h, 100-1000 L/h, 200-2000 L/h, and 600-6000 L/h, respectively. The plant was also equipped with a Prominent dosing pump (DP), with a Zenner pulse water meter (F) for dosing sodium hypochlorite, and with a vessel for its mixing with water (MT), to achieve a homogeneous solution with a constant chlorine concentration of 0.5 mg/L, determined by the colorimetric method [39] and a micro filter (M). Chlorinated water for the determination of the residual chlorine was sampled via the tap (S). The first part of the study was concerned with the investigation of the effect of different SFR and the determination of its optimum value, as well as of the EBCT value for the removal of NOM and arsenic from groundwater without addition of sodium hypochlorite as oxidizing agent. Sodium hypochlorite was added to the raw water with the aim of oxidizing NOM and As(III) to As(V) in the second part of the study. Special attention was paid to those SFRs that were smaller than 6 BV/h and higher than 30 BV/h, in order to determine the ion-exchange

capabilities and sorption possibilities of using the resin beyond the prescribed range of operating conditions in the treatment of the given groundwater. The first part of the series of measurements was carried out using the resin from the original package of 25 L. The resin was backwashed by standard procedure for 20 min, i.e. to the end of foam formation and appearance of an unpleasant odor. The other two experiments in the series of investigations using either chlorinated or non-chlorinated water were carried out on the resin regenerated according to the procedure described in Section 2.2.1. After the mentioned preparation of the resin, groundwater was passed through the bed in a down flow direction. The EBCT and SFR in these investigations were from 0.5 to 0.0033 h and from 2 to 300 BV/h, respectively. During the experiment, samples of both raw and treated water were taken regularly. Three series of samples of both chlorinated and non-chlorinated water were used to determine the following physicochemical parameters: pH, electrical conductivity, sulfates, bicarbonates, COD, TOC, and total arsenic. All the results represent mean values of three repetitions. Each series of measurements encompassed 30 samples of the effluent and one sample of groundwater. In the first part of the study, involving non-chlorinated groundwater, the overall contact time of water and resin at different SFR values was in average 38.5 h, whereas the average volume of the water passing through the bed was 17,187.50 L. This volume corresponded to 687.5 volumes of the resin in the bed. In the second part of the study, dealing with chlorinated water, the overall contact time of water and resin was in average 34.1 h, at different SFR values. The average volume of groundwater that passed through the bed was 16,650 L, which was equivalent to 666 volumes of the resin.

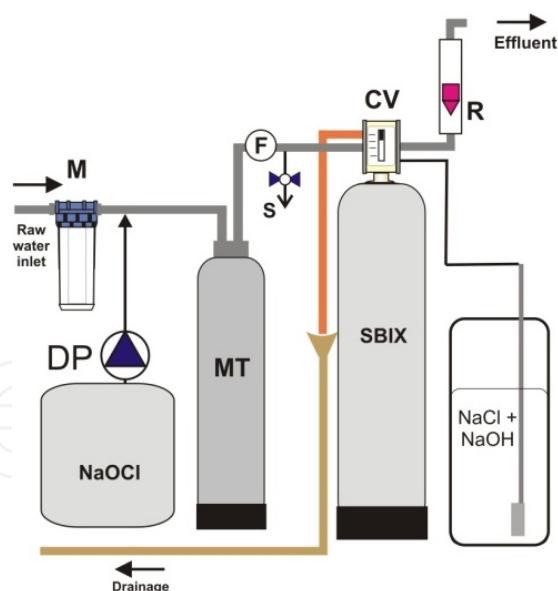


Figure 2. Scheme of pilot plant 1

2.3.1. Regeneration of SBIX

The resin regeneration was carried out in three phases. In the first phase, by opening the control valve, the resin was counterwashed with raw water for 10 min. In the second phase, at a SFR

of 4 BV/h, the regenerant (solution of NaCl (10%) and NaOH (2%)) from the regenerant vessel was injected with the aid of an injector inbuilt in the control valve. The overall contact time of the resin with the regenerant was 120 min in a regime encompassing successive repetition of 10-min passing the regenerant and 10-min of stopped flow. This regeneration method ensured a better dynamic equilibrium between the adsorbed and desorbed humic acid molecules, i.e. NOM and arsenic. In the beginning of the regeneration, the effluent was light yellow, and then became darker, and at the end of the first 10 min, it was of a typical brown color. The effluent began to regain a lighter color after about 80 min of regeneration, to become yellow at about the 100th min, and this color remained to the end of the regeneration. The third phase consisted of the fast rinsing of the resin with raw water, whereby the resin was dispersed in the whole working volume, and this was accompanied by the measurement of the electrical conductivity. When the effluent electrical conductivity dropped to that of the raw water, further washing was stopped. At the same time, the measured pH of the effluent became slightly alkaline, like the raw water. Measurements of the electrical conductivity and pH were necessary to check whether the resin had been freed of the regenerants. After the resin regeneration, the experiments were repeated both with chlorinated and non-chlorinated water, and it was subsequently regenerated two times.

2.3.2. Calculation of flow parameters

In order to study the removal process, it was necessary to calculate the flow parameters and the resins exposure time to the groundwater flowing through pilot plant 1. Specific flow rate was calculated using equation 4, where Q is the flow rate of chlorinated or non-chlorinated groundwater (L/h) and V_{SBIX} is the volume of the resin bed (L). The SFR is expressed in the units of the bed volume per hour (BV/h), and it represents a universal quantity which can be applied to characterize any ion exchanger. Namely, when the results for the optimum SFR are obtained for a pilot plant system for concrete groundwater of distinct physicochemical characteristics, it is simple to design a unique ion-exchange water treatment system of any capacity. The empty bed contact time (EBCT) was expressed and calculated in the way shown in equation 5. The EBCT is used as a measure of the duration time of the contact between the resin granules and water flowing through the bed. The increase in the EBCT value presents increased time available for the adsorption of dissolved matter on the resin beads.

$$SFR = \frac{Q}{V_{SBIX}} \quad (4)$$

$$EBCT = \frac{V_{SBIX}}{Q} \quad (5)$$

2.4. Strongly basic ion-exchange resin sorption characteristics determination

The objective of this research was to experimentally examine the sorption efficiency of NOM and arsenic on Amberlite IRA 958-Cl resin. The aim was to compare experimentally obtained

amounts of NOM and arsenic sorbed on the resin as indicators of the resin sorption capacity with the empirical sorption capacity based on the official data of the resin manufacturer. The investigations were conducted using native groundwater without (first part of investigation) and with addition of sodium hypochlorite (second part of investigation). For this purpose, a pilot plant 2 was designed and manufactured as shown in Figure 3. The main part of pilot plant 2 was the transparent container, manufactured by Atlas, filled with 1.4 L (970 g) of the resin Amberlite IRA 958-Cl. It was equipped with a flow meter (IHTM) for the flow range from 5 to 100 l/h, with a pump (Prominent) and pulse water meter (Zenner) for dosing sodium hypochlorite solution, and a vessel for mixing it with water, to obtain a homogeneous solution with a constant concentration of the residual chlorine. Samples of chlorinated water were taken from the tap. Concentration of the residual chlorine after the mixing vessel was measured by the colorimetric DPD method [39] and was kept constant as in the investigation of optimal flow parameters, at a level of 0.5 mg/L. The dosing system was not used in the first part of investigation, but only in the second one. In the first experiment in the series of measurements, both with native and chlorinated groundwater, a original packing of resin was used, which was backwashed with groundwater for 20 min, that is to the visually observed end of foaming and appearance of an unpleasant odor. The other two experiments in the series of investigation of chlorinated and non-chlorinated water were done using regenerated resin regenerated as described in Section 2.3.1. After the described resin preparation, the water was passed through it in a down flow direction. Samples of both the influent and effluent were taken regularly. Three series of samples of both chlorinated and non-chlorinated water were examined for the following parameters: COD, TOC, and total arsenic. All the measurement results are expressed as mean values of the determined parameters. The characteristics of the NOM and arsenic and of the resin applied as well as the chemical composition of groundwater and applied analytical methods and equipment for the determination of TOC, COD, and arsenic are identical to those described by the authors [40]. According to the resin manufacturer [11], the average sorption capacity of organic matter is 10-15 g of KMnO_4 /L resin. The capacity expressed as COD is between 2.5 and 3.75 g O_2 /L resin. The COD sorption capacity calculated per mass unit of SBIX, taking into account the filling density of 720 g/L, ranges from 3.47 to 5.21 mg O_2 /g resin.

2.4.1. Mathematical expressions of volume and sorption parameters

The efficiency of the removal of NOM and arsenic was followed by determination of COD, TOC, and arsenic concentrations in the effluent as a function of the overall water volume that passed through the SBIX bed, expressed as bed volume (BV). Bed volume is a dimensionless quantity that expresses the water volume as the number of the volume of resin bed (equation 6), where V_{out} is the effluent volume that passed through until the moment of sampling (L) and V_{SBIX} is a constant, standing for the volume of SBIX, and it was 1.4 L in all series of experiments. The BV is a quantity that is not characteristic for only one concrete ion-exchange resin, but is universally applicable to any ion exchanger of any capacity, for the same treated water. The results obtained for BV can be used to calculate the SBIX volume, if one knows the volume of water and vice versa.

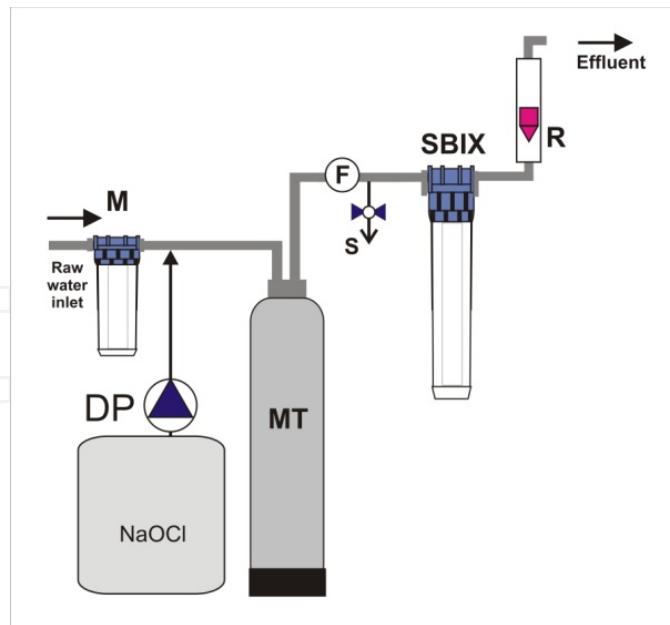


Figure 3. Scheme of pilot plant 2

$$BV = \frac{V_{out}}{V_{SBIX}} \quad (6)$$

NOM and arsenic content in the total volume of investigated chlorinated or non-chlorinated water during the whole experiment are calculated in the following way:

$$COD_{total} = V_{total} \cdot CODC_{in} \quad (7)$$

$$TOC_{total} = V_{total} \cdot TOCC_{in} \quad (8)$$

$$As_{total} = V_{total} \cdot AsC_{in} \quad (9)$$

where COD_{total} (mg O₂) and TOC_{total} (mg TOC) stand for the differently expressed total amounts of NOM; As_{total} (mg) is the total amount of arsenic - the two quantities representing in fact the resin load; V_{total} (L) is the total volume of water treated in the experiment, whereas $CODC_{in}$ (mg O₂/L) and $TOCC_{in}$ (mg O₂/L) designate the NOM concentration in the influent, and AsC_{in} (mg/L) is the corresponding arsenic concentration.

The overall load of the resin with organic matter and arsenic is calculated as shown in equations 10, 11, and 12, where COD_{load} (mgO₂/g) and TOC_{load} (mg TOC/g) represent the overall amounts of NOM; As_{load} (mg/g) the total amount of arsenic to which the resin was exposed in the experiment, and m represents the mass of the resin (g).

$$COD_{load} = \frac{COD_{total}}{m} \quad (10)$$

$$TOC_{load} = \frac{TOC_{total}}{m} \quad (11)$$

$$As_{load} = \frac{As_{total}}{m} \quad (12)$$

The amounts of NOM and arsenic that came in contact with the resin due to the volume of chlorinated or non-chlorinated water that passed through the bed in the real time of the experiment are calculated in the following way:

$$COD_{in} = V_{out} \cdot CODC_{in} \quad (13)$$

$$TOC_{in} = V_{out} \cdot TOCC_{in} \quad (14)$$

$$As_{in} = V_{out} \cdot AsC_{in} \quad (15)$$

where COD_{in} (mg O₂) and TOC_{in} (mg TOC) stand for the amount of the NOM; As_{in} (mg As) is the amount of arsenic, and V_{out} (L) is the volume of water that passed to the moment of sampling.

Contents of NOM and arsenic in the instantaneous sample, i.e. in the effluent after the flow of a given volume of chlorinated or non-chlorinated water, are calculated as follows:

$$COD_{out} = V_{out} \cdot CODC_{out} \quad (16)$$

$$TOC_{out} = V_{out} \cdot TOCC_{out} \quad (17)$$

$$As_{out} = V_{out} \cdot AsC_{out} \quad (18)$$

where COD_{out} (mg O₂) and TOC_{out} (mg TOC) are the differently expressed amounts of NOM; As_{out} (mg As) is the amount of arsenic that was not sorbed onto the resin and is found in the effluent from the pilot unit, whereas $CODC_{out}$ (mgO₂/L) and $TOCC_{out}$ (mg TOC/L) are the concentrations of NOM in the effluent determined by the two different methods. Finally, AsC_{out} (mg/L) represents the arsenic concentration in the effluent.

The amounts of NOM and arsenic that in a given time instant of sampling, after collecting the effluent volume V_{out} (L), were sorbed onto the SBIX are calculated in the following way:

$$COD_{ads} = COD_{in} - COD_{out} \quad (19)$$

$$TOC_{ads} = TOC_{in} - TOC_{out} \quad (20)$$

$$As_{ads} = As_{in} - As_{out} \quad (21)$$

where COD_{ads} (mg O₂) and TOC_{ads} (mg TOC) are the adsorbed amounts of dissolved organic matter, and As_{ads} (mg) the amount of arsenic adsorbed.

The sorption efficiency can be presented by the following expressions:

$$E_{COD} = \frac{(CODC_{in} - CODC_{out})}{CODC_{in}} \cdot 100(\%) \quad (22)$$

$$E_{TOC} = \frac{(TOCC_{in} - TOCC_{out})}{TOCC_{in}} \cdot 100(\%) \quad (23)$$

$$E_{As} = \frac{(AsC_{in} - AsC_{out})}{AsC_{in}} \cdot 100(\%) \quad (24)$$

where E_{COD} and E_{TOC} are the efficiencies of sorption of NOM, and E_{As} is the efficiency of arsenic sorption, all expressed as the corresponding percentages.

2.5. Calculation of equilibrium adsorption capacity of SBIX toward NOM

Effects of NOM adsorption by measuring of effluent NOM concentrations (C) in mg/L, during the experiments were shown in the dependence of cumulative time ($\Sigma\tau$) in hours, i.e. number of effluent's bed volumes (BV). Shapes of these curves are the primary overview of adsorption process kinetics toward starting, breakpoint, and pseudo-equilibrium stages. The big challenge and most important scope of this work was pathway to calculation of mass of the adsorbent (m) in g, in the mass transfer zone (MTZ) [1, 1x] corresponding to each experimental sampling, i.e. measuring point. Elucidation of the m values was significant operation for reaching the final target, which represents the determination of Amberlite IRA-958 pseudo-adsorption capacity toward NOM. It was supposed that the mass of exhausted resin is proportional to effluent NOM concentrations in the moment of sampling time. Based on the obtained percent

equation data, all masses of the resin corresponding to effluent NOM concentrations were calculated using the mathematical expression (25).

$$m = \frac{C}{C_0} \cdot M \quad (25)$$

Adsorbed amount of NOM (α) in mg O₂ at each sampling point was calculated as shown:

$$\alpha = (C_0 - C) \cdot V \quad (26)$$

where V is the volume of the effluent between two samplings (L).

Regarding the fact that samples have been taken randomly, calculation of the adsorption process rate as represented in equation 27 was an essential step:

$$VADS = \alpha / \tau \quad (27)$$

where *VADS* (mg/h) is adsorption rate and τ (h) is time between two sampling points.

Obtaining *VADS* data was a real contribution to equalize the adsorption process during the contact time of the complete experiment. Adsorption capacity of Amberlite IRA-958 in the time of experiment duration - specific adsorption capacity (*ADC*) in mg/gh - was calculated using equation 28:

$$ADC = VADS / m \quad (28)$$

The mutual relation of *ADC* values at measured *C* values was described as exponential regression plot. General equation form of the curve was represented (equation 29).

$$ADC = \beta \cdot e^{-\delta \cdot C} \quad (29)$$

β (L g⁻¹ h⁻¹) and δ are empiric adsorption coefficients obtained from the experimental data and calculated from the plot $\ln ADC$ vs. *C* (equation 30) as intercept and slope, respectively.

$$\ln ADC = \ln \beta - \delta \cdot C \quad (30)$$

The total *ADC* (*ADC_a*) in mg/gh, during the experiment, was calculated by integration of the surface above the curve using the following equation 31:

$$ADC_a = \left[(C_{\max} - C_{\min}) \cdot ADC_{\max} \right] - \int_{C_{\min}}^{C_{\max}} \beta \cdot e^{-\delta \cdot C} dC \quad (31)$$

where C_{\max} and C_{\min} are the highest and lowest measured values of C , and ADC_{\max} is the maximal value of ADC .

Value of adsorption capacity of the resin (Q_{pe}) in mg O_2 of NOM per gram of the resin at pseudo equilibrium was calculated as a function of overall experiment time ($\Sigma\tau_{\max}$) in h, using following equation 32:

$$Q_{pe} = ADC_a \cdot \Sigma\tau_{\max} \quad (32)$$

Investigated adsorption process is flow and time dependent. There is no equilibrium at every sampling point, but only the adsorption capacity could be recorded in the appointed time. Dynamic adsorption kinetics is different to batch experiments adsorption kinetics [41-46]. The difference is that time of adsorption in batch processes is infinitely and equilibrium could be detected with differences depending of time and temperature. In dynamic fixed bed adsorption, process time is defined and finite when sampling. During the adsorption and sampling as well, lasting irreversible adsorption is a consequence of constant addition of adsorbate which is dominant with regard to reversible equilibrium.

3. Results and discussion

The following results present data obtained during the determination of optimal specific flow rate, sorption characteristics, and kinetics of strongly basic ion-exchange resin.

3.1. Results obtained during determination of optimal specific flow rate of strongly basic ion-exchange resin

During the changes of SFR and EBCT, significant data of measured parameters were obtained. Dependence of measured parameters and flow rate values in experiments with non-chlorinated and chlorinated water are shown in Figures 4-7. Figure 4 presents the dependence of pH value and bicarbonate content in the effluent and SFR values (A) and influence of SFR on electrical conductivity and chloride concentrations (B) in both non-chlorinated and chlorinated water.

In the initial sorption contact of groundwater with the resin, an abrupt decrease in the effluent pH effluent was noted. This observation was especially pronounced in the case of chlorinated water. A high affinity of the resin to bicarbonate ions in the initial phase of ion exchange lead to the increase in the effluent acidity. The minima of the pH and bicarbonate concentration were observed at the lower SFR values compared to those measured in non-chlorinated water. These results are the consequence of the presence of the nascent

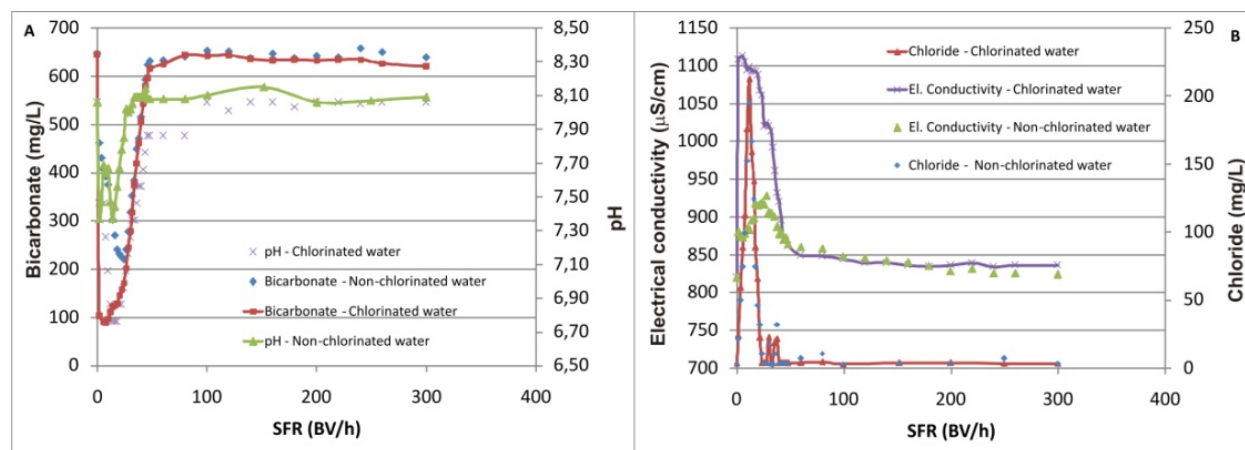


Figure 4. Influence of SFR on the bicarbonate and pH (A), and electrical conductivity and chloride (B) content

oxygen in chlorinated water, which accelerates ionic exchange of chloride for bicarbonate on the resin. The initial intensive exchange of these ions is gradually counterbalanced by the adsorption of the anions of humic acids taking place to the SFR of 50 BV/h, since the sites at which the dynamic equilibrium of sorption and desorption of bicarbonate is shifted to the interior of the resin granules, while humic acid binds to the functional groups on their outer surface. At the end of the investigated range of SFR, the HCO_3^- concentration in the effluent remained almost constant and asymptotically reached the concentration in the groundwater. At higher SFR, effluent pH value approached the pH value of the raw water as a consequence of the change in the bicarbonate concentration. After the value of SFR 50 BV/h, the resin is in the chloride form. Figure 4(A) also shows that in the initial part of the working cycle of resin with chlorinated water, there has been an immediate decrease of bicarbonates in the effluent already at SFR 2-6 BV/h after which the contents of bicarbonates slowly rises to SFR 50 BV/h, where the bicarbonates till the very end of the working cycle reach the concentration similar to that in raw water. The enormous increase in the chloride concentration at small SFR takes place simultaneously with the marked decrease in the content of bicarbonate in the effluent Figure 4(B). This chloride concentration rise, a singly charged small and high diffusion rate, results in the increase in the measured conductivity. A higher increase in the chloride concentration was observed in the case of chlorinated water, which is understandable taking into consideration the release of chloride from hypochloric acid. The differences in the peaks of chloride concentration and electrical conductivity in the effluent for chlorinated and non-chlorinated water are certainly a consequence of the generation of nascent oxygen, which also activates the resin's functional groups and thus contributes to a more effective ion exchange.

The effect of nascent oxygen on the oxidation of As(III) to As(V) is evident from the fact that in a wide range of SFR, from 2 to 300 BV/h, the total arsenic concentration in the effluent of chlorinated water was constantly below the MTC value [47] (Figure 5(A)). On the other hand, in the case of non-chlorinated water, the arsenic concentrations in the effluent at the $\text{SFR} < 100$ BV/h were by 10 times and at $100 < \text{SFR} < 300$ BV/h even by 17 times

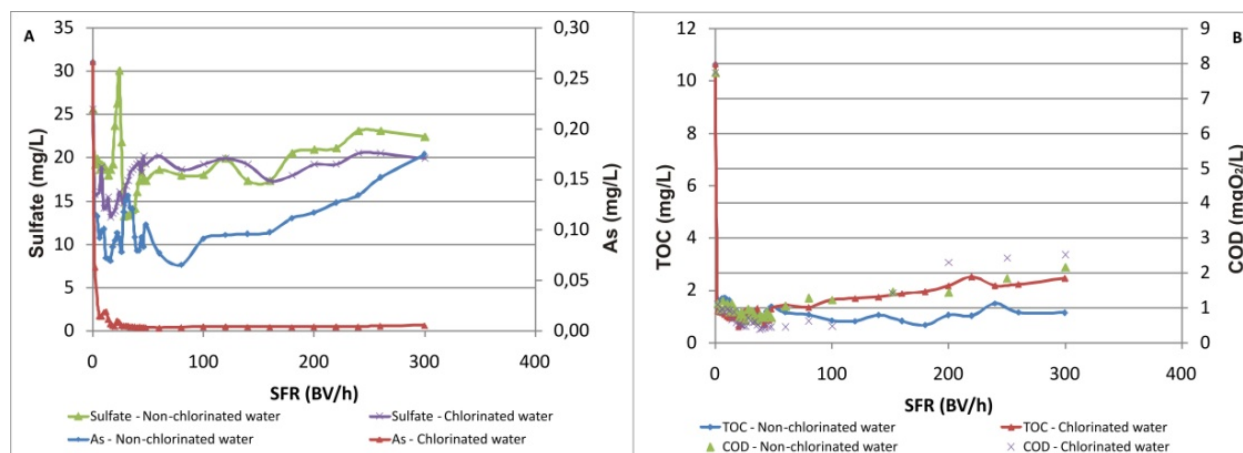


Figure 5. Changes in the sulfate and arsenic concentration (A) as well as NOM concentration (B) of the effluent with SFR

higher. Also, it is evident that the presence of atomic oxygen in chlorinated water hinders desorption of sulfate from the resin and changes the position of sulfate anions in the Clifford series [35]. This effect was especially pronounced at smaller SFR values of about 25 BV/h, when desorption of sulfate ion was observed. At $170 < \text{SFR} < 300$ BV/h, the sulfate removal was more efficient in the case of chlorinated water. At low SFR, the effect of the oxidant on the removal of NOM is more pronounced. In the effluent of the water treated with oxidant, this is evidenced as the lower values of both COD and TOC (Figure 5(B)). At the SFR between 2 and 50 BV/h, there is a competition between humic acids, arsenic, and sulfate with bicarbonate and chloride, which is especially pronounced in the presence of nascent oxygen. With the increase in SFR of chlorinated water, the measured NOM contents in the effluent were higher, which means that NOM removal from non-chlorinated water was higher under these flow conditions. Evidently, the resin's functional groups exhibit a lower affinity toward the newly formed, smaller, organic molecules resulting from the NOM degradation than to the original NOM molecules from the groundwater. Thus, the NOM concentration measured as COD in chlorinated effluent reaches tolerable level of 2 mg O₂/L [47] at 180 BV/h. In the case of non-chlorinated water, this value was not reached until 275 BV/h, suggesting that in such a medium the resin shows a higher affinity to NOM. The effect of contact time of the resin with chlorinated and non-chlorinated water on the NOM removal is presented in Figure 6(A). Changes of arsenic content in the effluent as a function of the contact time of chlorinated and non-chlorinated water are presented in Figure 6(B). As can be seen, more intensive changes in the NOM concentration take place at shorter contact times. To an EBCT value of about 0.05 h, it comes out that the adsorption-desorption processes are especially pronounced in chlorinated water. At longer contact times, the COD and TOC values of the effluent become apparently constant. It is evident that in the shortest time of contact of water with the resin, the arsenic removal was most efficient in the presence of nascent oxygen. This is a consequence of the oxidation-reduction processes by which is generated As(V), which exhibits remarkable adsorption affinity to the resin.

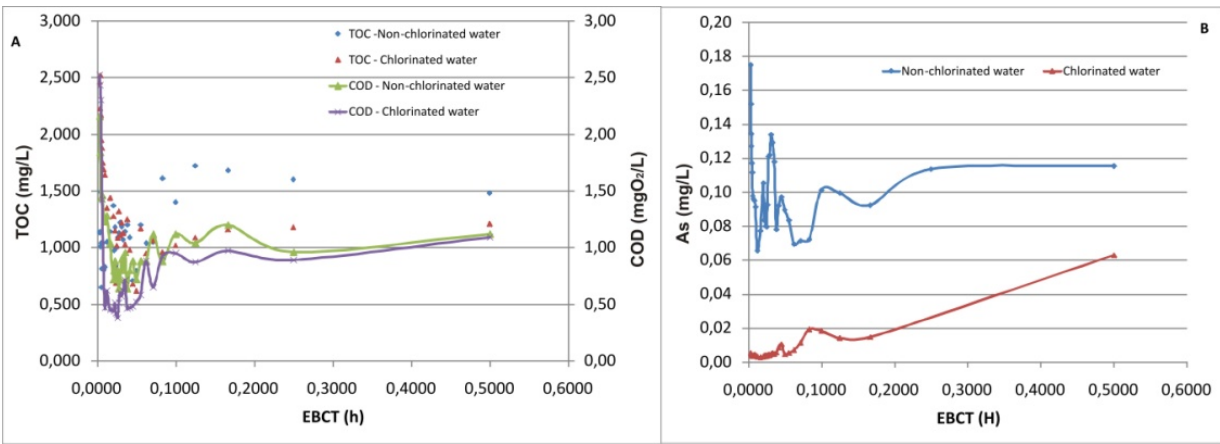


Figure 6. Influence of EBCT on the NOM (A) and arsenic (B) removal

3.2. Results obtained during strongly basic ion-exchange resin sorption characteristics determination

During the investigation of optimal specific flow rate of strongly basic ion-exchange resin, it has come to the conclusion that optimal flow rate of the Amberlite IRA-958 was 40 L/h, i.e. SFR of 30 BV/h \pm 5% when used on described groundwater. This research was conducted in order to determine resin sorption characteristics based on the experimental data and data given by the manufacturer [11]. Based on the data given by the manufacturer, one gram of the resin can adsorb from 3.47 to 5.21 mgO₂ NOM expressed as COD. Investigated groundwater contains 7.73 mgO₂/L NOM, expressed as COD. The calculation shows that one gram of SBIX may adsorb the NOM from 0.45 L to 0.67 L of such water. Taking into account the mass of the resin of 970 g, it can be calculated that the overall volume of the groundwater from 436.5 L to 650 L may be effectively treated with the used the SBIX. If this is expressed via the BV values, the expected adsorption capacity of the resin for NOM is in the range from 312 BV to 464 BV.

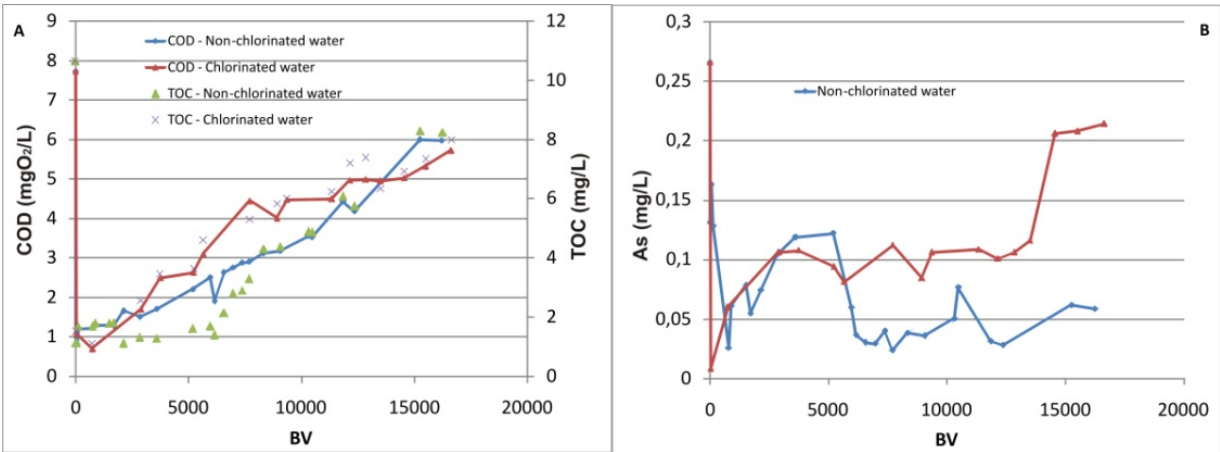


Figure 7. Changes of NOM (A) and arsenic (B) content in the effluent as a function of the overall volume of raw water passed through the SBIX

In the initial part of the sorption process, at small volumes of raw water of about 2,900 BV, as well as at the large volumes of over 13,500 BV, the NOM removal from chlorinated water is more efficient. In the first part of the operation cycle, the nascent oxygen generated from hypochloric acid causes NOM degradation and more efficient sorption of the degradation products of HAs and FAs compared to the native humins present in non-chlorinated water. These processes take place in the environment of the ion competition, as described by authors [40]. At increased volumes of groundwater passing through the system, surface adsorption is a dominant process, by which organic matter accumulates on the outer surface of the resin pearls. In this process, native HAs from non-chlorinated water are more efficiently bonded to the resin functional groups than the smaller molecules formed by the degradation of humin under the influence of nascent oxygen. Due to the larger number of the newly formed molecules in the effluent of chlorinated water at a smaller overall volume of water passing through the system, the resin's saturation and COD limit of 2 of mgO_2/L [47] is attained faster, at about 3,000 BV. At the same time, the adsorption of larger molecules on the resin that was in contact with non-chlorinated water is slower, and the COD limit appears at 4,000 BV. From the analysis of TOC values of the effluent from chlorinated water, it comes out that the changes of this parameter with the volume of treated water are similar to the changes observed for the COD. However, the TOC changes in the effluent of non-chlorinated water show that up to the value of about 8,000 BV, the NOM removal expressed via TOC is more efficient than if expressed via COD, and after that these values become proportionally equivalent. This difference can be explained by the fact that in the absence of the oxidant in water, the COD determination by the permanganate method gives lower results. Namely, permanganate is not a sufficiently strong oxidizing agent to oxidize entirely the humic matter, but only its more easily oxidizable part - fulvic acids. On the other hand, the TOC method encompasses all the dissolved NOM, and this is the reason for the discrepancy between the COD and TOC results presented in Figure 7(A). In the initial phase of resin saturation, the NOM molecules that are more easily oxidized (that is C_L) are preferentially adsorbed on the resin. With the increase in the amount of adsorbed NOM, proportionally to the volume of treated water above 8,000 BV, the resin affinity to sorption of organic matter becomes lower and larger amounts of easily oxidized NOM remain in the effluent, so that the changes in COD and TOC are proportional, which is evident from Figure 7(A). Namely, the appearance of COD and TOC curves above 8,000 BV becomes identical, since the COD value of, for example, 3 and 6 mgO_2/L is proportional to the TOC values of 4 and 8 mg/L . As can be seen from Figure 7(B), the arsenic concentrations in the effluent from chlorinated water are below the MTC of 0.01 mg/L only up to about 700 BV. By monitoring the effect of the further groundwater flow, it can be seen that arsenic removal is approximately equally efficient up to about 5,000 BV, from both chlorinated and non-chlorinated water. At the BV values above about 7,000, the effect of nascent oxygen on arsenic removal represents a complex process. In the investigated groundwater of complex composition, a number of redox reactions can take place in parallel. The reactions of HA degradation dominate over the reactions of As(III) oxidation. With the increase in the volume of treated water exceeding 5,000 BV, the amount of arsenic removed was twice larger when the treated water contained hypochlorite. In the presence of the oxidizing agent, the processes of NOM sorption in competition with arsenate binding to SBIX are more pronounced. The

increased concentrations of arsenic in the effluent from chlorinated water appear as a consequence of arsenic desorption. Desorption process was especially pronounced at the volumes exceeding 14,000 BV, taking place simultaneously with the tendency of lowering arsenic concentrations in the effluent from non-chlorinated water.

The expressions (6)-(21) were used to calculate concentrations of NOM and arsenic in the overall volume of groundwater in the experiments with chlorinated and non-chlorinated water, amounts of NOM and arsenic in the effluent during the experiment, as well as the amounts of NOM and arsenic adsorbed on the SBIX. Total amounts of NOM and As that passed through the resin as well as amounts that charged the resin are presented in Table 3.

Sorption characteristics	$COD_{total} (gO_2)$	$COD_{load} (gO_2/g)$	$TOC_{total} (g)$	$TOC_{load} (g/g)$	$As_{total} (g)$	$As_{load} (g/g)$	BV
No chlorine	175.65	0.181	241.86	0.249	6.039	0.006	16,231
Chlorine present	179.90	0.185	247.71	0.255	6.186	0.006	16,623

Table 3. Experimentally obtained resins sorption characteristics

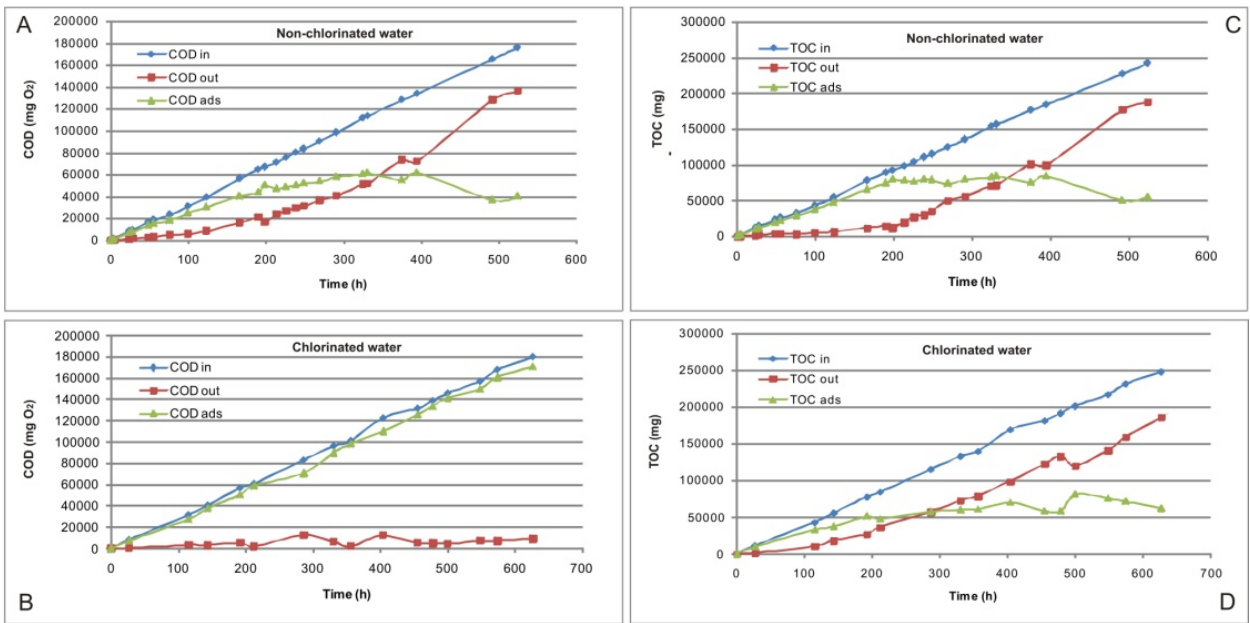


Figure 8. Dependency of NOM in non-chlorinated (A), (C) and chlorinated water (B), (D) adsorbed on the SBIX and one remained in the effluent during the course of the experiment

NOM fractions, which are more difficult to oxidize, remained in the effluent, and the more easily oxidized NOM compounds were adsorbed onto the resin. The assumption of NOM desorption is supported by the fact that at the longest experimental time, the COD_{ads} was 35% smaller than the adsorbed NOM at the intersection of the COD_{out} and COD_{ads} curves, as shown in Figure 8(A). Simultaneously, the COD in the effluent (COD_{out}) increased 2.2 times as large. The ratio between the maximum value for the COD_{ads} (before beginning NOM desorption) of

61,674 mg O₂ and the resin mass of 970 g describes the capacity of the resin for NOM sorption from the non-chlorinated water, with a value of 63.58 mg O₂/g. The NOM sorption process in chlorinated water (Figure 8(B)), without desorption, occurred throughout the experiment. The amount of the more easily oxidized fractions was very high; therefore, the COD_{ads} values were similar to the COD_{in} values. The total dissolved NOM sorption process in the non-chlorinated water, which was monitored by determining the TOC, was similar to the monitored COD (Figure 8(C)). After 10,900 BV, NOM in the effluent exceeded the NOM adsorbed onto the SBIX. The appearance of NOM desorption can be concluded from the fact that at the longest experimental time, the TOC_{ads} was 35% smaller than the TOC_{ads} at the intersection of the TOC_{out} and TOC_{ads} curves. At the same time, the TOC in the effluent (TOC_{out}) increased 2.2 times as large. As shown in Figure 8(D), the TOC_{out} increased 3.2 times as large, and the amount of NOM adsorbed on the resin remained nearly constant. The NOM desorption began at 7712 BV when oxidant was used. This means that the resin adsorption capacity for NOM in the non-chlorinated water was higher than in the chlorinated water.

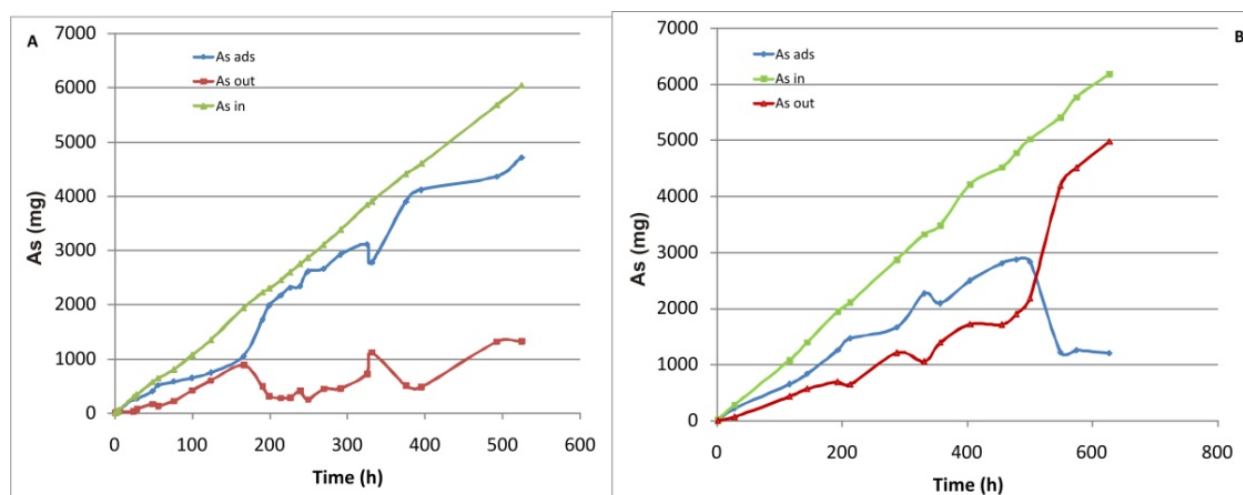


Figure 9. Dependence of the amounts of As contained in non-chlorinated (A) and chlorinated water (B) (As_{in}), adsorbed on the SBIX (As_{ads}) and remaining in the effluent (As_{out}) on the duration time of the experiment

Arsenic sorption process in the non-chlorinated water occurred throughout the entire experiment without the occurrence of desorption was shown in Figure 9(A). The only exception was at 166 h, when a short-lasting, dynamic equilibrium between the adsorbed and desorbed arsenic occurred. The amount of arsenic adsorbed during the experiment was very large, and the As_{ads} value was constantly approaching the value for As_{in} . The pH of the investigated groundwater was 8.06, at which the $HAsO_4^{2-}$ ions of As(V) and H_3AsO_3 molecules of As(III) dominate compared with the total arsenic content [20, 48]; therefore, As_{out} mostly represents the amount of As(III), and As_{ads} mostly represents the amount of As(V). The investigated resin was very effective at removing arsenates that were naturally present in the groundwater without the addition of the oxidant. The arsenates formed by the oxidation of arsenites with nascent oxygen simultaneously with competitive reactions of humin oxidation were adsorbed on the resin to a lesser extent, and after contact times exceeding 500 h, they desorbed and went

into solution (Figure (9B)). Presence of arsenic desorption is supported by the fact that the As_{ads} was 2.13 times smaller than the As_{ads} at the intersection of the As_{out} and As_{ads} curves. It is at this point that desorption process for arsenic actually begins. Contemporaneously, the As in the effluent (As_{out}) increased 1.96 times as larger. The exchange capacities of arsenic sorbed were calculated for the highest values of As_{ads} for both parts of the investigation. Total exchange capacity of adsorbed arsenic As_{ads} for non-chlorinated and chlorinated water was 0.045 eq/L and 0.028 eq/L, respectively. Lower level of adsorption in the chlorinated water is consequence of competition of arsenic anions and smaller molecules originated from NOM oxidation for resin binding sites. Threshold limit value of arsenic [47] was met at 40.48 BV in experiment with chlorinated water. As can be concluded on the basis of Figure 9, the investigated resin is very effective in removing arsenates that are naturally present in groundwater, without addition of the oxidant. The arsenates formed by the oxidation of arsenite by nascent oxygen under the conditions of the simultaneous occurrence of the competitive reactions of humin oxidation are adsorbed on the resin to a lower extent, and at the contact times exceeding 500 h, they are desorbed and passed to the solution.

Equations 22-24 were used to calculate the sorption efficiency on the resin of the NOM (expressed via COD and TOC) and arsenic. Figure 10 shows the sorption efficiency of NOM expressed as E_{COD} and E_{TOC} .

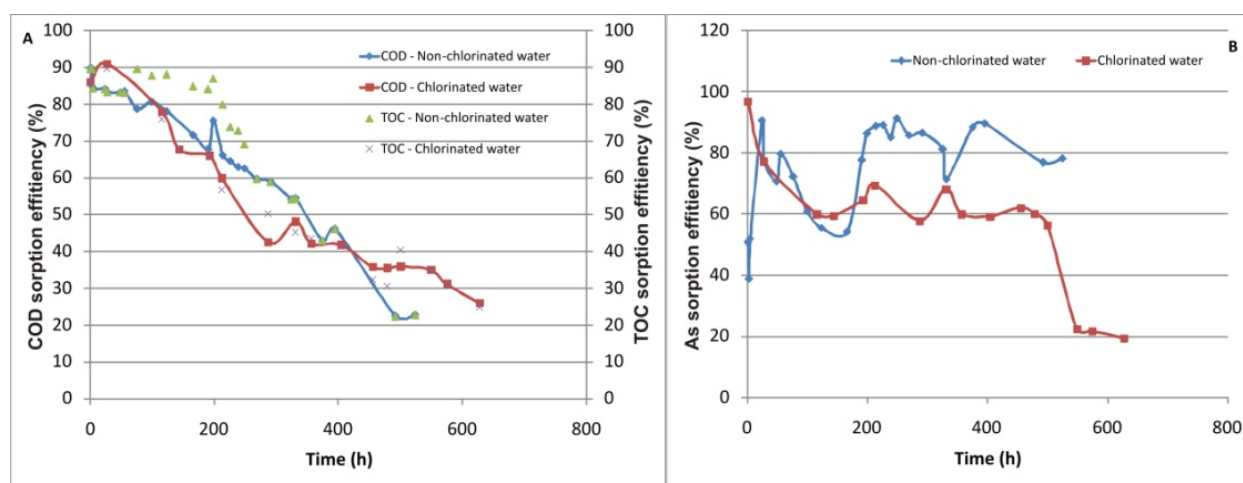


Figure 10. Changes of the efficiency of NOM sorption on SBIX expressed via COD and TOC (A) and arsenic (B) with the time of treatment of chlorinated and non-chlorinated water

As can be seen from Figure 10, the efficiency of NOM sorption expressed as E_{COD} decreases with time in the experiment with non-chlorinated water, and the changes are almost linear. On the other hand, the analogous dependence for chlorinated water is of a different pattern. In the initial part of the experiment, to 100 h, as well as after 400 h, the efficiency of NOM sorption from chlorinated water is more pronounced. This means that the conditions of the presence of the oxidant in the groundwater in the beginning of resin saturation and at the end of this process favor the sorption of NOM, expressed either as E_{COD} or E_{TOC} , compared to the desorption processes. The course of the changes of E_{TOC} , reflecting definitely the overall content

of humic substances, shows that the preferential sorption of NOM is pronounced in one-third of the overall treatment cycle, that is between the 48th and 395th h of the experiment. The large humin molecules are more readily adsorbed than the smaller molecules formed by their degradation. Since the efficiency of NOM removal by the resin decreases with time, the outer sorption layers become more attractive to smaller molecules, so that they are more competitive, and at the longest time, the NOM sorption from chlorinated water is more efficient. As can be seen, the efficiency of arsenic removal from chlorinated water is high only in the beginning of the working cycle. Evidently, the presence of the oxidant, which converts As(III) to As(V), does not contribute to the efficiency of arsenic removal. If one considers the entire working cycle of the resin, the average efficiency of arsenic removal from chlorinated water is about 60%, and from non-chlorinated water it is about 80 %.

3.3. Results obtained by using a new approach for determination of equilibrium adsorption capacity of SBIX toward NOM

Obtained experimental results were applied in the equations 25-32 to calculate the important kinetic behavior of SBIX toward NOM. Calculated ADC values were decreased exponentially during the experiment as shown at Figure 11(A). Curve of exponential regression kinetically represents interface of passed (under the curve) and adsorbed (above the curve) quantity of NOM per mass unit of SBIX in time. The empirical coefficients β and δ (equation 29) were calculated at the base of equation 30, i.e. empirical linear equation (Figure 11(B)). Coefficients β and δ were calculated from linear equation (Figure 11(B)) $\ln A(DC) = -0.704 C + 1.471$ and amounts $4.355 \text{ Lg}^{-1}\text{h}^{-1}$ and 0.70, respectively.

Empirical equation form of the obtained curve and regression coefficient were $ADC = 4.355 e^{-0.70C}$ and 0.961, respectively. By utilization of equations 31 and 32, respectively, the total specific adsorption capacity and adsorption capacity of the resin at pseudo equilibrium were calculated. The values of ADC_a and Q_{pe} were 14.41 mg/gh and $10.935,31 \text{ mg/g}$, respectively.

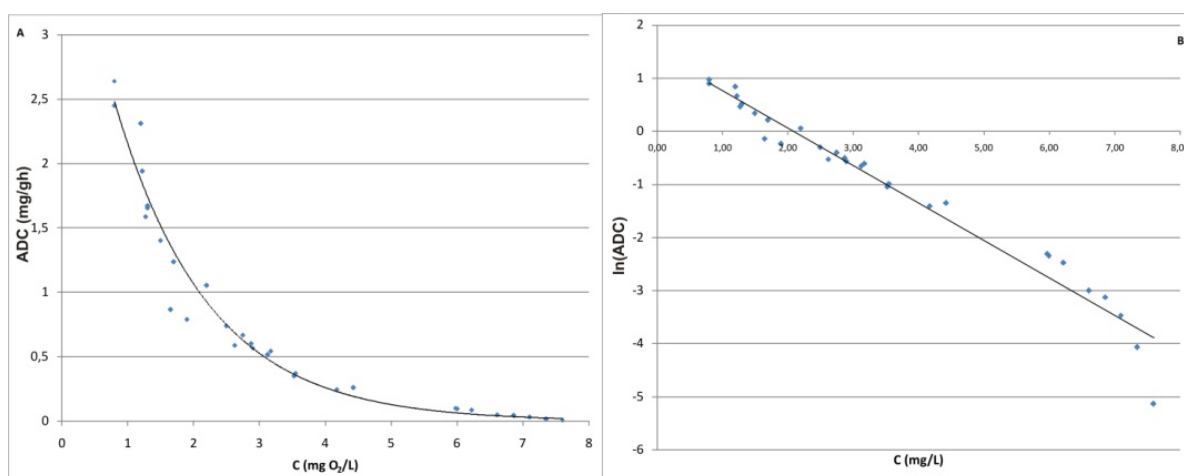


Figure 11. (A) Changes of specific adsorption capacity of SBIX to NOM during the experiment and (B) Linear form of exponential curve ADC vs. C for calculation of β and δ

4. Conclusion

A comparison of the efficiency of NOM removal from native groundwater and the same water with addition of sodium hypochlorite as oxidizing agent showed that at smaller SFR values up to 50 BV/h, the process was more effective in the presence of the oxidant. However, at the SFR values that were up to ten times higher compared to the maximum values given in the manufacturer's declaration, the NOM removal was more efficient in the absence of the oxidant. Namely, the NOM level in the effluent originated from the native groundwater was below MTC of 2 mg O₂/L at a SFR value that was 9.2 times higher, whereas under the oxidative conditions this was observed at the SFR that was by 6 times higher than the declared maximum SFR value. The arsenic removal to the level below the MTC of 0.01 mg/L was more efficient in the presence of the oxidant and shorter SFR compared to the minimum and at 10 times higher SFR values compared to the maximum value of SFR declared by the resin manufacturer. In the absence of the oxidant, only native As(V) was removed, and the process was essentially less effective because of the competition with sulfate ions. It was shown that at small BV values, of up to 700, the removal of NOM and arsenic is more efficient in the presence of the oxidant, whereas in the major part of the working cycle, the efficiency of their removal is higher from non-chlorinated water. The values obtained for the resin adsorption capacity for NOM from non-chlorinated water are by about 15 times higher than the corresponding value given in the specification of the resin manufacturer. New approach to the determination of resin sorption capacity, through definition of specific adsorption capacity, at pseudo-equilibrium showed that investigated resin possesses very high affinity to NOM. Occurrence of NOM desorption, measured as COD, was observed in the treatment of non-chlorinated water, as well as by measuring the adsorbed TOC in the case of both chlorinated and non-chlorinated water. Desorption of arsenic from the resin surface was observed only in the case of treatment of chlorinated water. Namely, when the results for the optimum SFR are obtained for a pilot plant system for concrete groundwater of distinct physicochemical characteristics, it is simple to design a unique ion-exchange water treatment system of any capacity.

The obtained results make a sound basis for designing an appropriate plant for the removal of NOM from groundwater of the region of the town of Zrenjanin. The tested resin can also be used in the process of pretreatment of the same water, since it allows the removal of about 50% of the naturally occurring arsenic.

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