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Properties of anion exchange resins exhausted by humic compounds

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ABSTRACT

The loading of anion exchange resins with humic compounds adsorbed during industrial water treatment processes has been investigated. It has been found that humic compounds are uniformly distributed throughout the bead. Fresh and exhausted anion exchange resins have been studied with respect to their ability to be loaded with Fe(III) oxides. The results show that anion exchangers containing humic compounds retain iron better than fresh ones. The uptake may be due to catalytic oxidation and contact coagulation at the surface.

Keywords: Anion exchange resins; Humic compounds; Exhausted resins; Iron sorption

1. Introduction

During their service time in water demineralization, e.g. in the power generating industry, strong and weak base anion exchange resins irreversibly accumulate a variety of organic molecules, usually designated as fouling, from the respective raw waters. Furthermore, strong base exchangers are subject to a slow degradation of their quaternary ammonium groups. There are several reasons why such exhausted anion exchangers can no longer be applied for further demineralization [1]:

- Their total exchange capacity has decreased up to 20%, and weak base capacity up to 40%, respectively;
- Rinsing after regeneration requires large volumes of treated water;
- The required elimination of strong and weak acids is no longer achieved.

On a world scale, the exhausted anion exchange resins stemming from power generation industry represent a large quantity of wastes. So far, there is no reuse or recycling of such exchanger materials for further applications. Exhausted resins are simply discharged to landfill deposits.

Information from literature shows that there is no common and generalizing approach to the change of ion exchange performance during exhausting processes. The fouling mechanism depends on the kind of organic substances and pH and may be either predominantly physical adsorption or predominantly ion exchange [2,3]. Sorption of humic compounds onto anion exchange resins was found to be directly proportional to the (negative) charge density of humic acids and inversely proportional to their molecular weight [4]. The existing literature, however, does not present neither information about structural changes of anion exchangers exhausted with humic compounds nor allow any conclusion about the change of their properties.

In previous investigations of the properties of anion exchangers that were exhausted in water treatment processes it has been shown that the resins loose part of their exchange capacity, but, at the same time, show an

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enhanced affinity to transition metal ions, particularly to iron and copper [5]. As a consequence, such exhausted resins represent new polyfunctional sorption materials whose properties are directly due to the interactions between the remaining anion exchange resin structure and the irreversibly adsorbed humic compounds. The main objectives of the present studies are to elucidate the mechanism of the humic compounds retention by anion exchange resins under the industrial water treatment processes and transformation of exhausted resins sorption properties by example of interaction with Fe(II) dissolved compounds to open opportunities to create new polyfunctional sorption materials.

2. Materials and methods

2.1. Anion exchange resins

Commercially available styrene-divinyl-benzene anion exchange resins of different porosity, basicity and grain-form type, with various functional groups were applied in the present research. Characteristic data of anion exchange resins used are given in Table 1.

Samples of exhausted anion exchange resins were received from different Ukrainian power plants located in the Dnjepr River basin, where they had been in service for demineralization processes. The feed waters were pretreated by conventional methods (liming, coagulation, flocculation, and filtration) [6]. Accumulation of humic compounds developed through periodical cycles of sorption and regeneration by means of NaOH carried out during a period of 1–5 years. During their service time these anion exchangers were regenerated 2000–10,000 times.

2.2. Experimental

To assure that all resin samples contain the same ionic form (chloride) of functional groups conditioning with NaCl has been applied. Samples of fresh or exhausted resins were stored in a column (1 cm diameter and 10 cm bed height) and initially washed with deionized water. In the second step they were treated with 5 bed volumes of 5% NaCl solution at a specific flow rate of 10 bed volumes/h (BV/h). Finally, all resins were again washed with deionized water.

For determination of humic compounds on the exhausted exchangers 2 mL of anion exchanger material was contacted for 24 h with 100 mL of an eluent consisting of a mixture of 2% NaOH and 10% NaCl at 45°C.

Uptake of iron compounds was achieved by treating 10 cm^3 exchanger material in a column with 10 L (= 1000 bed volumes) of a solution containing 6.0 mg/L Fe(II) dissolved in de-chlorinated tap water. The flow rate during loading amounted to 20 BV/h. The composition and pH value of this solution are summarized in Table 2. The total amount of iron retained by the exchangers has been determined by the differences of concentration between feed solution and effluent and by desorption of retained iron by means of 1M HCl solution. Average values are listed in Fig. 4.

2.3. Analyses

The content of humic compounds in exhausted anion exchange resins was determined titrimetrically as permanganate oxidizability (mg/L O_2) of the filtrate decanted after elution with the mixture of NaOH and NaCl. The resulting filtrate was also characterized by means of size exclusion chromatography to determine the molecular-weight distribution of the organic components [7]. Iron concentration in the solution passed through sorption

Table 2
Composition of Fe(II) model solution

Fe^{2+}, mg/L	6 ± 0.1
Na^+, mg/L	93.5
K^+, mg/L	23.5
Ca^{2+}, mg/L	63.6
Mg^{2+} , mg/L	11.52
HCO_3^- , mg/L	202.52
Cl^- , mg/L	12.3
SO_4^{2-}, mg/L	65.7
pH	7.2 ± 0.2
Permanganate oxidizability, mg/L O_2	1.8

Table 1
Characteristic data of anion exchange resins

Commercial name	Total exchange capacity for specified ionic form, eq/L	Porosity	Basicity	Grains
Dowex MWA-1	1.3 (FB)	Macroporous	WBA	Spherical, polydispersive
Dowex Marathon MSA	1.1 (Cl)	Macroporous	SBA Type I	Spherical, monodispersive
Dowex Marathon 11	1.3 (Cl)	Gel	SBA Type I	Spherical, monodispersive
Dowex Mono A2-500	1.2 (Cl)	Gel	SBA Type II	Spherical, monodispersive

WBA – weak base anion exchange resin; SBA – strong base anion exchange resin; FB – free base column was determined photometrically applying an UNICO spectrophotometer.

The internal structures of fresh and exhausted anion exchange resin beads were studied by means of stereomicroscopy. Macrophotos were taken using a SteREO Discovery V20 Carl Zeiss stereomicroscope, which allows a tree-dimensional observation in transmitted, reflected and combined light at a maximum magnification of 80. Sampling included performing bead cuts using mechanical micropreparative methods and fixing of the beads bead using silicate glue sticks.

Environmental scanning electron microscopy (ESEM) was used to analyze structural changes of anion exchange resins surfaces after adsorption of both, humic compounds and iron substances, respectively. Magnification during these surface studies ranged from 500 to 10,000.

Energy dispersive X-ray spectroscopy (EDX) was applied for investigations of elemental iron distribution across bead cuts and surfaces of Fe-loaded ion exchange resins.

3. Results and discussion

3.1. Humic compounds

The concentration of humic compounds in the feed water analyzed during service cycle was in the range of 5–10 mg/L O_2. Fig. 1 shows a chromatogram from the characterisation of the humic compounds in the Dnjepr river water. The shares of different molecular masses that can be deduced from this chromatogram are listed in Table 3.

From the quantity of humic compounds of the exhausted resin samples mobilized during the above-mentioned elution procedure (expressed in mg $KMnO_4$ oxygen) and the volume of the samples their loading could be calculated. The results are summarized in Table 4 and reveal that the highest value (6.0 mg/mL O_2) has been found for the weak base macroporous anion exchange resin Dowex MWA-1 which is known as a scavenger for organic matter [7].

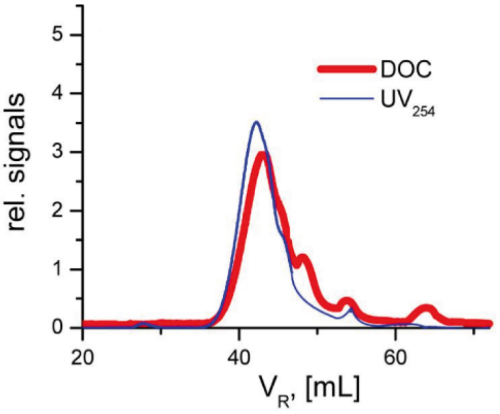

Fig. 1. Size exclusion chromatogram of humic compounds in feed water of the Dnjeper River basin.

Table 3
Molecular weight distribution of humic compounds in feed water of the Dnjeper River

Molecular weight, Da	% of fraction
6000–4500	23
4500–3000	52
3000–1000	8
1000–200	14
200–1	2

Table 4
Content of humic compounds in exhausted anion exchange resin samples

Commercial name	Humic compounds content, mg/mL O_2
Dowex MWA-1	6.00
Dowex Marathon MSA	1.80
Dowex Marathon 11	2.93
Dowex Mono A2-500	2.70

Changes in the appearance of both macroporous and gel-type anion exchange resins can be seen in the macrophotographs of cuts of single particles (Figs. 2 and 3). For the macroporous exchanger Dowex MWA-1 the exhausted particle shows a uniform colour indicating that the full volume of the resin is homogeneously loaded with humic compounds.

The strong base gel-type anion exchanger Dowex Marathon 11 bead (Fig. 3b) seems to show a darker outer zone and a lighter core. The intensity of the brown colour is higher, nevertheless, the content of humic compounds found in the elution amounts to only half of that of the Dowex MWA-1.

3.2. Sorption of iron

Comparison of the performance of fresh resins and exhausted resin material reveals an increased uptake of iron in general by the exhausted anion exchangers. This "uptake" can be due to different possible mechanisms (sorption of Fe^{2+} onto Lewis base sites of resin structure and humic substances; catalytic oxidation at the surface, formation/precipitation of $Fe(OH)_3$ as solid compounds at the surface). However; no discrimination between these possibilities could be made. The results are plotted in Fig. 4. The amount of iron "loading" is considerably higher for the weak base resins (app. 6.5 mg/mL Fe) than for the strong base ones (2.8–3.9 mg/mL Fe). Obviously, the presence of humic compounds increases the uptake by 8–60%.

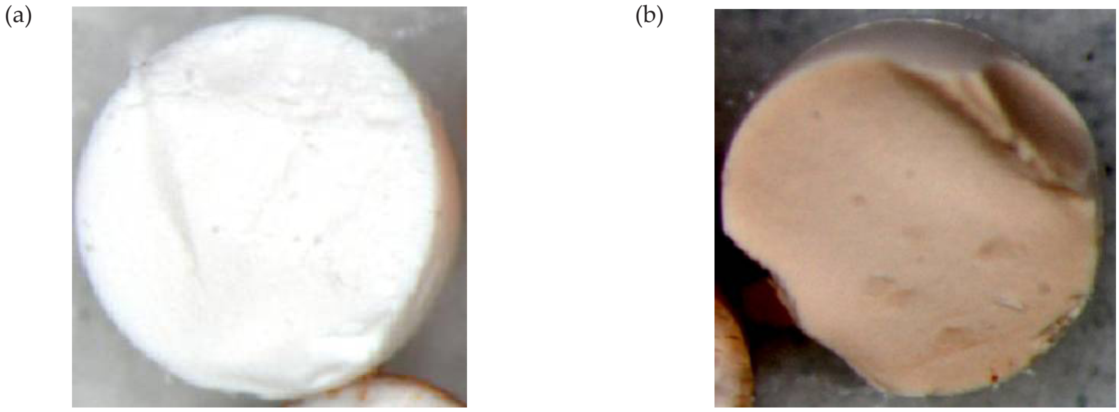

Fig. 2. Fresh (a) and exhausted (b) beads of the macroporous Dowex MWA-1.l.

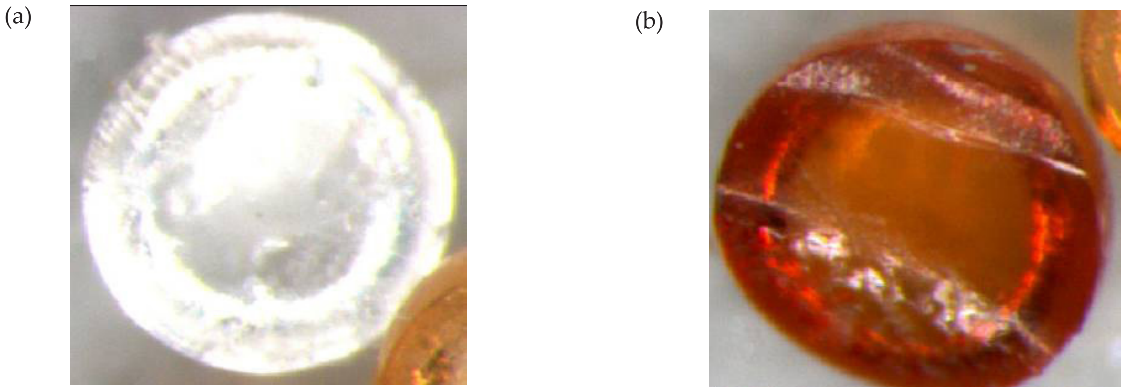

Fig. 3. Fresh (a) and exhausted (b) samples of the gel-type Dowex Marathon 11 resin.

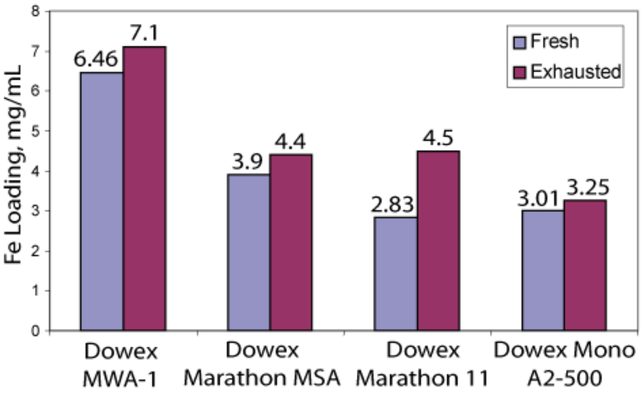

Fig. 4. Iron sorption by fresh and exhausted anion exchange resins.

Fig. 5 shows cuts of beads of the fresh and exhausted anion exchange resin Dowex MWA-1 after treatment with the iron-bearing solution. The pictures of the fresh and the exhausted particle, both after contact with the Fe-bearing solution show the typical colour of Fe^{3+} oxides which demonstrates that Fe^{2+} was oxidized to Fe^{3+}. Furthermore, no colour and hence no Fe^{3+} oxides can be detected in the inside of the beads which means that Fe(II) has not invaded the resin phase. It should also to be noted that the iron oxide coating of the exhausted bead seems to be denser than on the fresh resins.

The uptake of iron oxides only on the surface is also found through EDX mapping analysis (Fig. 6) which confirms that iron compounds cover the surfaces of the anion exchange resins of both types. However, beads of each type do not contain any iron traces in the interior.

According to Fig. 5 the formation of iron oxides on the surface depends on the loading with humic compounds. Fig. 7 shows iron oxides on the surface of the strong base gel-type resin Dowex Marathon 11; here non-structured layers are detected on the surface of the fresh resin bead while fine and coarse network structures are observed on the exhausted resin sample.

The structure of iron oxides is different for the macroporous resin Dowex MWA-1. Fig. 8 shows that the surface of fresh resin beads is again not uniformly covered, whereas a more or less homogeneous coating with no network structures is found for the exhausted resin.

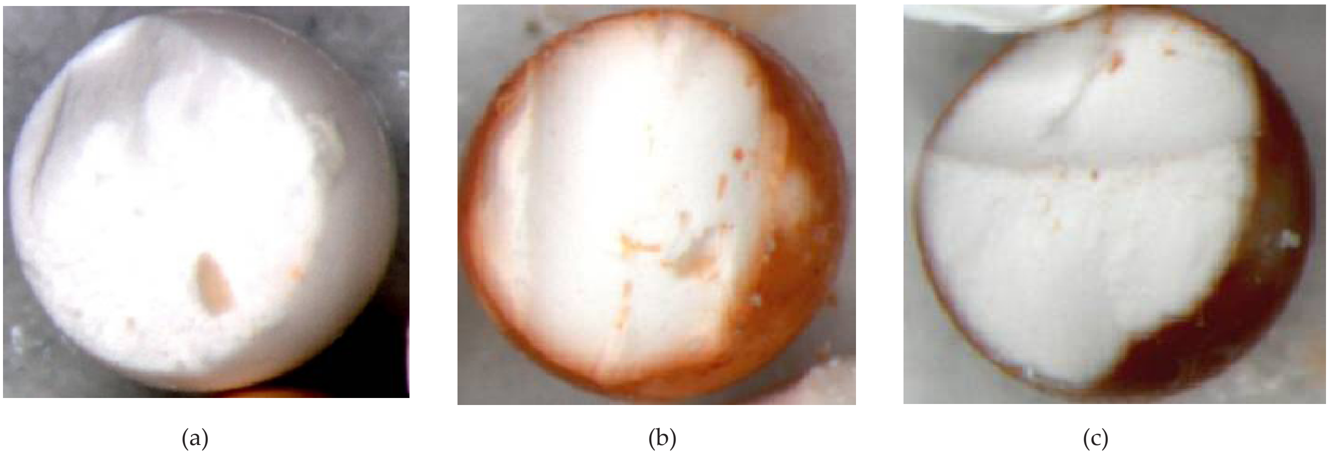

Fig. 5. Fresh and Fe-containing beads of macroporous Dowex MWA-1 resin: untreated (a), treated fresh (b) and exhausted (c).

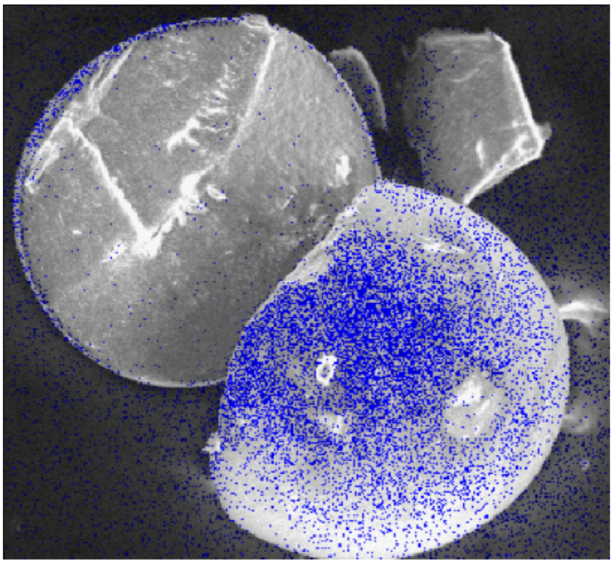

Fig. 6. EDX mapping of exhausted iron containing Dowex MWA-1.

Obviously the interactions between iron compounds and the macroporous anion exchange resin beads are different from those with gel-type resins.

ESEM studies showed that iron oxides precipitate as flocs, which cover the surface of the exchanger beads. Fig. 9 shows an SEM photograph of flocs that are similar to structures formed in conventional flocculation processes at high pH.

In the view of the general surface property changes during iron sorption and the observed formation of flocs, it may be assumed that there is a kind of contact coagulation after a preceding oxidation of Fe^{2+} to Fe^{3+}. The complex mechanism of contact of this coagulation includes i) Fe^{2+} concentration in surface layer due to specific interaction with impregnated surface of ion exchanger, ii) oxidation $Fe^{2+} \rightarrow Fe^{3+}$ process mostly owing to catalytic properties of humic compounds and dissolved oxygen, and iii) formation of flocs on the bead surface due to increasing in probability of particles interaction. This coagulation is obviously much more effective with

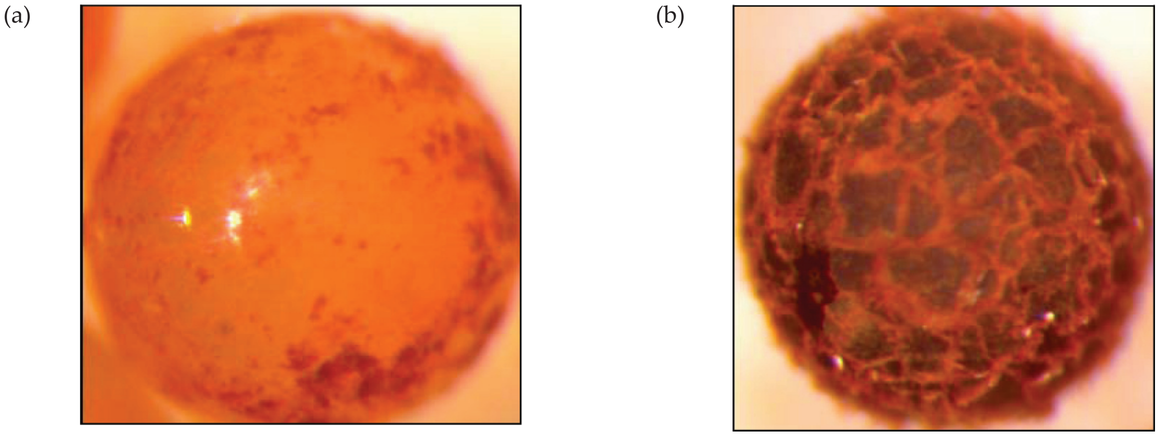

Fig. 7. Formation of iron-layer on gel-type Dowex Marathon 11 anion exchange resin surface: a) fresh sample b) exhausted sample.

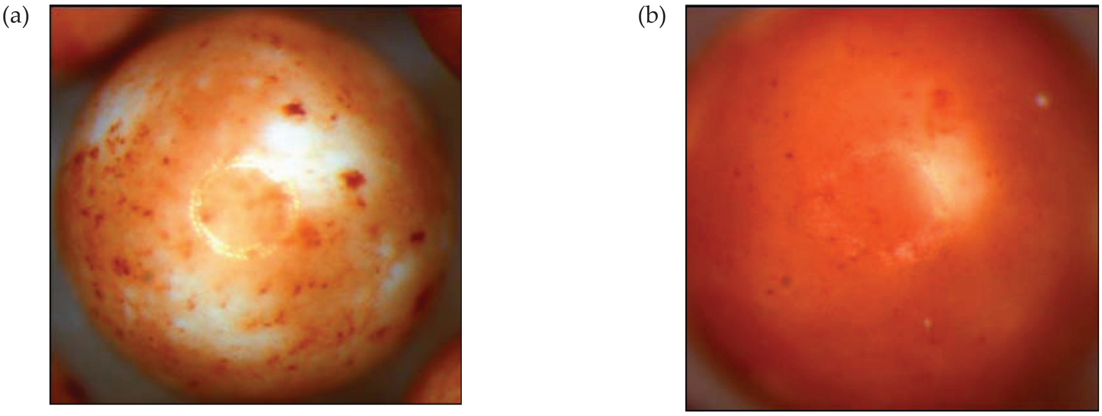

Fig. 8. Formation of iron-layer on macroporous-type Dowex MWA-1 anion exchange resin surface: a) fresh sample b) exhausted sample.

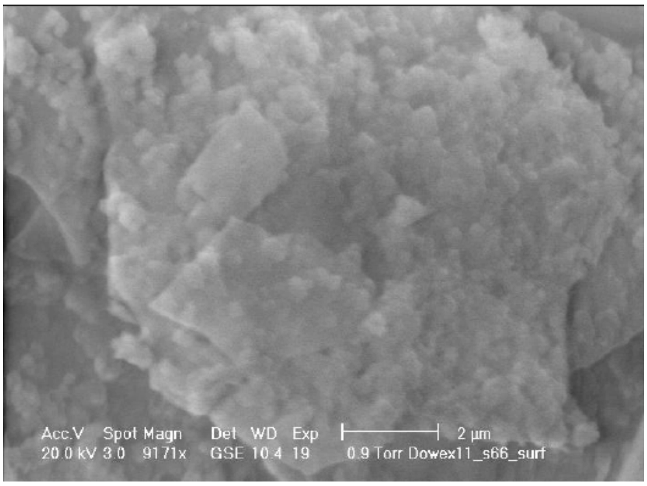

Fig. 9. Flocs of iron compounds on surface of the exhausted resin Dowex Marathon 11.

exhausted anion exchange resins. As a consequence, anion exchange resins exhausted by an irreversible sorption of humic substances might be used for elimination of iron from water.

4. Conclusions

Adsorption of humic compounds has been investigated for a series of anion exchange resins exhausted under industrial water treatment conditions. It has been found that macroporous weak base anion exchange possess the highest loading with humic compounds.

Iron(II) removal experiments have been carried with fresh anion exchange resins and with resins containing humic compounds. The results show that an uptake as Fe(III) hydroxides occurs in both cases. For samples containing humic compounds the quantity of hydroxides retained is higher than for resins without loading with humic compounds. Contact coagulation mechanism may be an explanation for this uptake which is due to interactions between iron substances and humic compounds on the surface.

References

[1] J. Brown and N.J. Ray, Ion exchange in water purification: where do we stand? Ion Exchange Technology. 1984, pp. 14–24.

[2] Y. Tan, J.E. Kilduff, M. Kitis and T. Karanfil, Dissolved organic matter removal and disinfection byproducts formation control using ion exchange. Desalination, 176 (2005) 189–200.

[3] B. Bolto, D. Dixon, R. Eldridge, S. King and K. Linge, Removal of natural organic matter by ion exchange. Wat. Res., 36 (2002) 5057–5065.

[4] E.R. Cornelissen, N. Moreau, W.G. Siegers, A.J. Abrahamse, L.C. Rietveld, A. Grefte, M. Dignum, G. Amy and L.P. Wessels, Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions. Wat. Res., 42 (2008) 413–423.

[5] T. Mitchenko, N. Makarova and H. Schevchuk, Development of novel multifunctional sorbents on a basis of ion exchange resins exhausted in processes of water demineralization. Proc. 4th International Conference on Ion Exchange, Japan, 2007, pp. 558–563.

[6] N.P. Cheremisinoff, Handbook of Water and Wastewater Treatment Technologies. Butterworth Heinemann – Pollution Engineering, 2002.

[7] A. Mitchenko, F. Frimmel, T. Gremm, T.E. Mitchenko and N. Makarova, The efficiency of the humic compounds removal from tap water by sorbents with various nature. Abstracts 2nd International Conference "Interfaces Against Pollution", Miskole, Hungary, 2002, p. 140.

[8] T.H. Boyer and P.C. Singer, A pilot-scale evaluation of magnetic ion exchange treatment for removal of natural organic material and inorganic anions. Wat. Res., 40(15) (2006) 2865–2876.