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THE INFLUENCE OF SELECTED FACTORS ON THE REMOVAL OF ANIONIC CONTAMINANTS FROM WATER BY MEANS OF ION EXCHANGE MIEX®DOC PROCESS

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Abstract: The study of the effectiveness of the removal of anionic natural organic matter (fulvic acids-FA and humic acids-HA) and inorganic anions (F^-, Br^-, NO_3^-) in MIEX®DOC process was performed. The influence of physico-chemical parameters of feed water on the process performance was investigated. The ion exchange process was carried out using strongly basic, macroporous polystyrene resin MIEX® by Orica Watercare. The synthetic feed waters differ in composition, i.e. concentration of FA and HA (ca. 6 and 12 mg/L), anions content (F^-, Br^-, NO_3^-) and of various alkalinity (ca. 20 and 120 mg/L as $CaCO_3$) were used. The study confirmed the possibility of application of MIEX®DOC process for removal of anionic contaminants from water. It also showed the significant impact of feed water parameters on the process effectiveness. Moreover, the strong dependence of anions (F^-, Br^-, NO_3^-) removal, FA and HA concentration on the resin dose was revealed.

INTRODUCTION

MIEX®DOC system is an interesting ion exchange process significantly different from the conventional ion exchange usually applied in water treatment plants. In this process ion exchange takes place on a resin which is suspended in treated water. The separation of the suspended resin from the treated water is carried out in a separated gravitational settler or in the reaction chamber. 90−97% of the settled resin is usually recycled to the reactor, but the portion of fresh resin also must be added. The non-recycled resin is constantly directed to regeneration process. Such a performance of the process enables the constant water treatment and avoids the need of regeneration breaks, which must be made when traditional ionite beds are used. The granulation of MIEX® resin is almost 5 times smaller comparing with traditional ionites. Thus, the higher specific surface and the improvement of the ion exchange are obtained.

The interesting results and conclusions of studies which can be useful for modernization of technological systems with MIEX®DOC process can be found in the literature [3, 5, 7−10, 13]. It has been proved that MIEX® resin is very efficient for the removal of natural organic matter (NOM) from water and it is able to exchange anions present in surface water, i.e. sulfates, sulfides, bromides, nitrates and arsenates [3, 7, 13]. It can be also used for the removal of ions responsible for water hardness [2]. The efficient removal of anionic organic (DOC^-) and inorganic (e.g. Br^-) substances is a crucial step of water treatment process as their appearance in water may cause the formation of disinfection byproducts (trihalomethanes and bromates). The efficiency of the MIEX®DOC process depends mainly on the amount and type of contaminants and thus on the competitiveness between ions present in treated water.

The application of MIEX® resin in water treatment posses many advantages, i.e.:

- the decrease of values of water contamination indicators such as dissolved organic carbon (DOC), color, absorbance at 254 nm;
- the increase of coagulation effectiveness and the decrease of the required coagulant dose;
- the decrease of filter washing frequency;
- the elongation of sorption bed lifetime;
- the decrease of disinfectant doses;
- a partial support of other treatment processes (e.g. during the increase of water load with contaminants);
- the avoidance of blockage of micro- and ultrafiltration membranes (so called fouling);
- an easy integration with other unit processes e.g. coagulation, activated carbon adsorption, membrane filtration etc. [1, 4, 6, 10–12].

The aim of the study was to investigate the impact of selected water parameters on the effectiveness of the removal of anionic organic and inorganic contaminants from water in MIEX®DOC process.

MATERIALS AND METHODS

The synthetic waters differing in composition, containing fulvic (FA) and humic (HA) acids, anions (F^-, Br^-, NO_3^-) and substances responsible for water alkalinity dissolved in deionized water were used during the treatment. The standard humic acid powder was supplied by Sigma-Aldrich, fulvic acid powder by Beijing Multigrass Formulation Co. Ltd, and anions and alkaline compounds, i.e. KBr, NaF and $Mg(NO_3)_2$, $CaCl_2$, $NaHCO_3$, by POCH.

In the ion exchange process the macroporous anion exchange resin MIEX® by Orica Watercare of granules size 150 μm was used. The resin was dosed to water in the form of suspension and it was regenerated using 10% NaCl solution. The applied doses were equal to 1, 2.5, 5, 8, 10 and 15 mL/L, while contact and sedimentation times were established at 30 minutes.

The characteristic of investigated waters was obtained by means of physico-chemical measurements of:

- total and dissolved organic carbon (TOC, DOC) content using HiperTOC analyzer by ThermoCorporation;
- absorbance at 254 nm (UV254) using UV/VIS CE 1021 spectrophotometer by Instruments;
- color using Spectroquant NOVA 400 photometer by Merck,
- anions (F-, Br-, NO3-) concentration using DX-120 ion chromatograph by Dionex;
- total alkalinity by means of titration method.

The effectiveness of MIEX®DOC process was determined on the basis of DOC, absorbance at 254 nm (UV_{254}), color and anions content measurements.

Table 1. Characteristics of synthetic feed water

Parameter		Synthetic water				
	W1 FA	W2 HA	W3 FA, HA, F^-, Br^-, NO_3^-, low DOC	W4 FA, HA, F^-, Br^-, NO_3^-, high DOC	W5 FA, HA, F^-, Br^-, NO_3^-, alkalinity 20 mg/L $CaCO_3$	W6 FA, HA, F^-, Br^-, NO_3^-, alkalinity 120 mg/L $CaCO_3$
pH	5.34	5.72	6.19	6.09	6.30	7.32
Temperature,°C	20.0	20.0	20.0	20.0	20.0	20.0
Conductivity, mS/cm	0.016	0.011	0.215	0.228	0.282	0.446
Turbitity, NTU	0.44	2.44	1.69	2.55	1.69	1.79
TOC, mg/L	5.79	6.37	6.57	13.1	6.29	8.90
DOC*, mg/L	5.33	5.82	5.63	11.9	5.95	7.95
Absorbance*, UV_{254}^{1m}	18.8	44.1	21.5	58.0	31.2	32.9
Color*, mgPt/L	34	94	47	102	50	47
F^-, mg/L	Not added		10.6			
Br^-, mg/L	Not added		1.04			
NO_3^-, mg/L	Not added		105			
SUVA**, $m^3/gC \cdot m$	3.53	7.58	3.82	4.87	5.24	4.14

TOC – total organic carbon, DOC – dissolved organic carbon,
* Samples filtered via 0.45 µm filter, ** specific ultraviolet absorbance UV_{254}/DOC

RESULT AND DISCUSSION

One of the main parameters that determine the efficient MIEX®DOC process performance is the proper resin dose. Next, the time of the resin contact with water is found to be important. The study presented in [10] discussed the impact of the contact time on the process and indicated that the highest efficiency was obtained for contact time range of 15−30 minutes. The elongation of the process did not affect the contaminants removal. In the presented study the dependences of contaminants type and concentration and MIEX® resin dose on the MIEX®DOC process effectiveness were investigated, while the time of resin contact with water was set up constant and equal to 30 minutes. In Tables 2 and 3 the decrease of fulvic and humic acids concentration obtained for synthetic waters containing separately humic or fulvic acids (Tab. 2) and their 1:1 ratio mixture (two different total acids concentrations) (Tab. 3) are presented.

Table 2. The results of W1 (FA) and W2 (HA) feed waters analyses

Resin MIEX® dose, mL/L	Parameter					
	DOC, mg/L		Absorbance, UV_{254}^{1m}		Color, mgPt/L	
	W1	W2	W1	W2	W1	W2
0	5.33	5.82	18.8	44.1	34	94
1	3.85	5.18	13.0	39.6	24	86
2.5	2.89	4.98	9.6	33.0	20	72
5	2.88	4.50	7.2	27.5	12	60
8	2.17	4.29	5.2	19.3	9	42
10	2.13	3.34	4.5	17.3	10	38
15	n/m*	n/m*	n/m*	n/m*	n/m*	n/m*

* non-measurable

Table 3. The results of W3 (low DOC) and W4 (high DOC) feed waters analyses

Resin MIEX® dose, mL/L	Parameter					
	DOC, mg/L		Absorbance, UV_{254}^{1m}		Color, mgPt/L	
	W3	W4	W3	W4	W3	W4
0	5.63	11.9	21.5	58.0	47	102
1	3.77	11.5	18.7	47.2	20	79
2.5	2.58	8.29	13.5	39.5	17	51
5	2.04	6.71	9.0	28.3	10	37
8	0.96	4.35	3.6	17.9	6	15
10	0.86	3.93	2.7	15.5	5	15
15	0.64	3.24	2.4	13.3	3	15

The anion-exchange MIEX® resin effectively removes dissolved organic compounds which are formed during natural processes occurring in surface water. Thus, the values of water color, DOC and UV_{254} absorbance are successively decreased. It was found that the concentration of organic contaminants present in water decreased and depended on the type of natural organic matter (NOM). MIEX®DOC process favors the removal of substances of low molecular weight below 10 kDa, which are difficult to be removed by conventional treatment methods (e.g. coagulation). The results of the study presented in Table 2 confirm the theory, because fulvic acids were removed in greater extent. According to the literature the average molecular weight of fulvic acids is equal to 2 kDa. The dependence of the removal of organic substances on the resin dose was found to be crucial. The increase of the dose resulted in the more efficient decrease of contaminants content indicators, i.e. DOC, UV_{254} absorbance and color. Moreover, the stronger dependence of the process effectiveness on the resin dose was observed for 1 to 5 mL/L doses comparing with 8–15 mL/L ones for which the removal of contaminants was comparable. It was also observed that when organic compounds (FA, HA) were present in water in the form of the mixture (W3, Tab. 3) their removal was more efficient than in the case of separated solution (Tab. 2).

The dose of the resin determining MIEX®DOC process efficiency also depended on the concentration of contaminants present in water. The required resin dose was lower (Tab. 3) for synthetic feed waters of lower organic compounds concentration (W3). In that case the resin dose equal to 8 mL/L resulted in the decrease of DOC by 83% (the final DOC concentration below 1 mg/L), absorbance by 83% and color by 87% (6 mg Pt/L). For the same resin dose applied for feed water of higher organic substances content (W4) the obtained removal rate of DOC was equal to 63% (DOC concentration 4.3 mg/L), of absorbance – 69% and of color – 85% (15 mg Pt/L). The last value was found to be sufficiently high. The results indicated that treatment of waters of high organic contaminants content required higher resin dose. However, the application of high resin doses causes the formation of significant amounts of post-regeneration wastewaters.

It was also found that MIEX®DOC process effectiveness depended on the presence of carbonate ions in water. Thus, the treatment of synthetic feed waters of different alkalinity, i.e. 20 mg/L and 120 mg/L as $CaCO_3$ was performed. The results of the experiment considering the removal of organic compounds and anions (F^-, Br^-, NO_3^-) are shown in Tables 4a and 4b, respectively.

The results revealed that the increase of the resin dose resulted in the increase of anionic contaminants removal. However, the chemical composition of feed water (which differed in alkalinity) had a significant impact on MIEX®DOC process effectiveness. It was observed that in waters with higher alkalinity (120 mg/L as $CaCO_3$) the removal of both, dissolved organic compounds (Tab. 4a) and anions (Tab. 4b) was less efficient, especially in the case of fluorides. The final parameters of treated waters were lower in the case of solutions with 20 mg/L as $CaCO_3$ of initial alkalinity than those with 120 mg/L as $CaCO_3$. The rule was valid for all applied MIEX® resin doses. Probably, carbonates and chlorides present in water competed with other substances for active sites of MIEX® resin

Table 4a. The results of W5 (alkalinity-20 mg/L as $CaCO_3$) and W6 (alkalinity-120 mg/L as $CaCO_3$) synthetic feed waters analyses – organic compounds removal

Resin MIEX® dose, mL/L	**Parameter**					
	DOC, mg/L		**Absorbance, UV_{254}^{1m}**		**Color, mgPt/L**	
	W5	**W6**	**W5**	**W6**	**W5**	**W6**
0	5.95	7.95	32.9	31.2	50	47
1	5.78	7.53	25.8	24.7	32	27
2.5	3.73	5.83	15.1	15.7	13	14
5	3.64	5.32	11.3	12.6	8	10
8	3.52	4.58	8.9	9.1	6	8
10	2.86	4.17	6.8	7.5	5	8
15	2.82	4.06	4.3	6.9	4	8

Table 4b. The results of W5 (alkalinity-20 mg /L as $CaCO_3$) and W6 (alkalinity-120 mg/L as $CaCO_3$) synthetic feed waters analyses – anions removal

Resin MIEX® dose, mL/L	Parameter					
	F^-, mg/L		Br^-, mg/L		NO_3^-, mg/L	
	W5	**W6**	**W5**	**W6**	**W5**	**W6**
0	10.6	10.6	1.04	1.04	105	105
1	n/m*	10.4	n/m*	0.94	n/m*	n/m*
2.5	n/m*	n/m*	n/m*	0.79	n/m*	96.8
5	10.0	10.2	0.44	0.73	54.4	62.5
8	8.4	10.3	0.40	0.49	33.9	53.3
10	6.2	9.7	0.38	0.47	30.8	44.6
15	4.8	8.5	0.27	0.37	19.3	31.9

* non-measurable

and acted as process inhibitors. Thus, their concentration was found to be a crucial factor significantly influencing the effectiveness of the process.

It was found that the competitiveness between anionic organic and inorganic compounds, and their affinity to the MIEX® resin active sites was of a great importance. The results indicated that the highest affinity to the resin active sites was revealed by fulvic acids Tab. 2) as well as by bromides and nitrates (Tab. 4b), while it was lower in the case of fluorides. The removal rates of Br^- and NO_3^- were higher than those of DOC and depended on water alkalinity. The study presented in [3] indicates that the removal of bromides can also depend on DOC concentration in treated water. In the case of higher DOC concentration (ca. 9 mg/L) the higher removal rate of bromides was obtained comparing with the results measured for 3.5 mg/L as DOC (for 20 mg/L as $CaCO_3$ alkalinity solutions).

CONCLUSIONS

In the presented study the application of strongly basic macroporous MIEX® resin for ion exchange was shown to be a sufficient method of removal of anionic organic compounds as well as bromides and nitrates from water. It assures the elimination of anions from water, thus it can be supposed that the disinfection byproducts formation, e.g. trihalometanes or bromates is decreased. The effectiveness of the process was found to depend on many factors. The study showed that the dose of the resin and the chemical composition of feed water connected with the competitiveness of compounds for active sites of the resin were of the greatest importance. It was shown that the increase of the resin dose favored the removal of contaminant. Moreover, carbonates and chlorides were found to be main process disruptors.

In order to increase the quality of water treated by MIEX®DOC process it can be combined with other unit operations, i.e. microfiltration or ultrafiltration (so called integrated/hybrid systems). The study presenting the application of such systems were discussed at [11, 12].

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WPŁYW WYBRANYCH CZYNNIKÓW NA USUWANIE ANIONOWYCH ZANIECZYSZCZEŃ Z WÓD W PROCESIE WYMIANY JONOWEJ MIEX®DOC

W artykule przedstawiono wyniki badań efektywności usuwania anionowych form naturalnych substancji organicznych (kwasów fulwowych i humusowych) oraz anionów w procesie MIEX®DOC. Badano wpływ składu fizyko-chemicznego wód na efektywność usuwania zanieczyszczeń anionowych w procesie MIEX®DOC. W procesie wymiany jonowej użyto silnie zasadową, polistyrenową makroporowatą żywicę MIEX® firmy Orica Watercare. Oczyszczano wody modelowe o zróżnicowanym składzie, tj. różniące się stężeniem kwasów fulwowych i humusowych (ok. 6 i 12 mg/l), zawierające aniony (F^-, Br^-, NO_3^-) oraz charakteryzujące się różną zasadowością (ok. 20 i 120 mg/l $CaCO_3$). Uzyskane wyniki badań potwierdziły możliwość zastosowania procesu MIEX®DOC do usuwania zanieczyszczeń anionowych z wód. Wykazano istotny wpływ składu chemicznego oczyszczanych wód na efektywność procesu MIEX®DOC oraz ścisły związek pomiędzy usunięciem anionów (F^-, Br^-, NO_3^-), stężeniem kwasów fulwowych i humusowych a wielkością zastosowanej dawki żywicy.