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MIEX[®]DOC RESIN CAPACITY FOR NATURAL ORGANIC MATTER (NOM) REMOVAL

The study aimed to achieve near-complete saturation of the adsorption capacity of the MIEX[®]DOC resin with dissolved organic compounds in order to quantitatively assess its sorption potential. The experimental procedure was conducted using a laboratory-scale continuous-flow reactor containing 25 cm³ of the MIEX[®]DOC adsorbent, with a packing density of approximately 500 cm³/dm³. The influent water matrix consisted predominantly of humic-type organic matter, with a concentration of approximately 9 g C/m³. Under conditions devoid of competition from inorganic anions and at a resin bed volume ratio reaching 16 000 m³/m³, the MIEX[®]DOC adsorbent achieved a saturation capacity of 29 mg C/cm³. This saturation level can be considered proximate to the maximum adsorption capacity, as the removal efficiency of organic substances under these conditions did not exceed 2%. Furthermore, this value is consistent with the operating ion-exchange capacity of the resin for organic constituents characterized by low charge density, approximately 4 meq/g C. The adsorption saturation profile demonstrated that the application of a “high-rate” (HR) reactor enables a satisfactory quality of treated water utilizing approximately 19% of the estimated capacity of the MIEX[®]DOC resin. In contrast, implementation of a “high-rate counter-current” (HR-CC) reactor configuration allows for at least a twofold increase in capacity utilization, reaching approximately 40%.

1. INTRODUCTION

Adsorption is a water treatment method valued for its ability to remove dissolved substances, particularly organic compounds. It is an equilibrium-driven process, which enables high removal efficiency at low adsorbent utilization. However, progressive saturation of the adsorbent leads to a decline in its adsorption efficiency. As a result, most adsorbents exhibit variable efficiency, and the trade-off between removal efficiency and

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adsorbent utilization presents a significant operational challenge. The technological objective of the process – namely, the substantial reduction of organic compound concentrations – often conflicts with the economic goal of maximizing adsorbent capacity usage.

The powdered magnetic anion exchange resin (MIEX[®]) process [1], introduced at the turn of the 20th and 21st centuries, demonstrated a pathway toward partial reconciliation between technological efficacy and economic feasibility in organic contaminant removal. Firstly, the use of fine-grained adsorptive media results in a higher adsorption rate compared to the same adsorbent in coarser, granular form. Secondly, the observation that a substantial fraction of natural organic matter (NOM) consists of organic macroanions enabled the application of ion exchange resins as adsorbents. These resins offer the advantage of relatively low-cost and technically straightforward regeneration, which can be performed on-site, thereby improving operational flexibility and cost-effectiveness. Thirdly, the incorporation of a magnetic component enabled efficient separation of the adsorbent, thereby facilitating its recovery for regeneration and subsequent reuse. Fourthly, the fine-grained nature of the material allows for hydraulic transport, enabling effective removal from the reactor and reintroduction into the system. As a result, the adsorption process transitions from batch to continuous operation, enabling dynamic control over removal efficiency and/or adsorbent capacity utilization. The continuity of operation, combined with the ability to perform effective and cost-efficient on-site regeneration (i.e., rapid and economical restoration of adsorptive capacity), renders the capacity of the adsorbent less critical for achieving process objectives under economically rational conditions. Nevertheless, any unused adsorptive capacity represents an opportunity for further optimization of process economics.

A well-established strategy for improving adsorbent capacity utilization involves the use of multiple reactors arranged in series [2]. In the first reactor, a highly saturated adsorbent is brought into contact with water containing a high concentration of dissolved organic carbon (DOC). Under these conditions, the adsorption equilibrium shifts toward high adsorbent saturation and low removal efficiency. In contrast, the last reactor contains relatively fresh adsorbent, which interacts with water of lower organic content, allowing for the attainment of sufficiently low DOC concentrations in the treated effluent.

A similar system has been implemented for ion exchange processes utilizing powdered magnetic resin [3]. It consists of two high-rate (HR) reactors [4] arranged in series, in which the powdered resin is transported counter-current to the flow of treated water (high-rate counter-current system: HR-CC). The first reactor contains resin with a high degree of saturation, while the second operates with resin of low saturation. The high degree of adsorbent saturation in the first chamber results from its direct feed with raw water and the absence of regenerated resin input. Only partially exhausted resin exiting the second reactor is directed into the first reactor, where it continues to adsorb organic constituents under high loading conditions. The adsorbent deficit in the second

reactor is compensated by the addition of regenerated resin. Regeneration is performed exclusively on the highly saturated resin withdrawn from the first reactor.

Beyond its cognitive relevance, investigating the performance of highly saturated MIEX[®]DOC resin and quantifying its capacity with respect to DOC is crucial to the design and operation of the first reactor in the HR-CC system.

The primary parameter used to evaluate the capacity of ion exchange resins is the operating ion exchange capacity [5]. For the MIEX[®]DOC anion exchange resin, various sources estimate this value to range 0.40–0.52 meq/cm³ [6–10], with discrepancies likely arising from methodological inconsistencies. A key limitation of this indicator is its lack of direct correlation with fundamental parameters describing the removal of organic compounds. Therefore, establishing such a clear relationship – particularly with respect to the mass of DOC removed – is essential for improving the interpretability and applicability of this capacity measure.

This study aimed to address four key questions: What is the real saturation level of MIEX[®]DOC resin with organic compounds (expressed in mg DOC/cm³) achievable under extreme loading conditions? Can this saturation level be equated with the adsorbent's capacity for DOC removal? Does the progression of adsorbent capacity exhaustion have implications for the operation of the HR-CC system? And finally, does the value of high or full resin saturation (mg DOC/cm³) correspond in any meaningful way with its operating ion exchange capacity (meq/cm³)?

2. MATERIALS AND METHODS

A cylindrical reactor was used with a diameter of 5 cm and a height of 9 cm. 25 cm³ of regenerated MIEX[®]DOC resin was introduced into the reactor. The resin volume was measured following a 20-minute sedimentation period. Water was supplied at a flow rate of 3 dm³/h in an upward direction from the bottom to the top of the reactor. A high adsorbent concentration of 500 cm³/dm³ was assumed, indicating that the working resin occupied twice the volume of the sedimented resin (1 000 cm³/dm³). Mixing of the resin by the upward water flow alone proved insufficient; therefore, it was supplemented by a mechanical paddle stirrer with a cross-sectional area of 0.5 × 2.0 cm. The stirrer's rotational speed was adjusted to match the target volume of dispersed resin within the reactor (50 cm³), which corresponded to a resin layer approximately 2.55 cm high. Above the working resin layer, a 6 cm water layer was maintained to prevent excessive carryover of fine resin beads from the reactor. The outflow tube was positioned 8.6 cm above the reactor bottom.

Raw water samples were collected once daily. Treated water samples were taken at variable time intervals, ranging from 30 to 60 min during the initial phase of the process

and up to 12 h toward the end of the experimental cycle. The treatment cycle was terminated after 96 h (4 days) of reactor operation, at which point the efficiency of DOC removal had decreased to merely 2%.

The source of natural organic matter was an unnamed drainage stream originating from the Wielkie Torfowisko Batorowskie peat bog in the Stołowe Mountains (sampling point: 50°27'29.97"N; 16°23'16.87"E), which constitutes a right-bank tributary of the Czerwona Woda stream. The water from this source contains substantial amounts of colored organic substances of humic origin, with no detectable presence of other contaminants. A key characteristic of the organic constituents in this water is their complete (100%) affinity for removal via anion exchange, as confirmed by a preliminary kinetic test conducted prior to the flow-through experiments. For the study, the raw water was diluted with demineralized water to achieve the target DOC concentration of approximately 9.0 g C/m³. The physicochemical parameters of the raw water are summarized in Table 1.

Table 1

Raw water parameters

Parameter	UV ₂₅₄ [m ⁻¹]	Color [g Pt/m ³]	DOC [g C/m ³]	SUVA ₂₅₄ [m ³ /(g C·m)]
Value	37.82	51.27	9.06	4.17

Only standard indicators characterizing the process were evaluated for the treated water, namely: dissolved organic carbon (DOC), color, and ultraviolet absorbance at 254 nm (UV₂₅₄). Before analysis, all water samples were passed through membrane filters with a pore diameter of 0.45 µm. The analytical procedures were conducted in strict accordance with the protocols outlined in the “Standard Methods for the Examination of Water and Wastewater” (DOC, UV₂₅₄, and SUVA₂₅₄) [11] or PN-EN ISO 7887:2012 regarding color [12]. The DOC was measured using the IL550 TOC-TN Hach–Lange analyzer, which applies the high-temperature (950 °C) catalytic oxidation method (5310 B). The color (method C, λ = 410 nm) and UV absorbance at 254 nm (method 2910 B) were determined spectrophotometrically using the Shimadzu UV-1800 spectrophotometer with a quartz cuvette, light path length of 3 cm. In qualitatively evaluating the amount of organic substances removed, the SUVA₂₅₄ (Specific UV Absorbance) parameter (method 2910 C) was used, which is derived from the DOC and UV absorbance (UV₂₅₄/DOC) [13].

3. RESIN SWELLING AND LOSS

Quantitative assessment of powdered ion exchange resin within the reactor – and more broadly, within the entire water treatment system – requires consideration of two

critical phenomena: resin swelling and resin loss. Both factors are also essential for evaluating the specific removal rates of NOM and the saturation level of the adsorbent's capacity.

The amount of ion exchange resin introduced into the reactor did not remain constant throughout the experiment. Resin beads were carried out of the system along with the flowing water, resulting in adsorbent losses. Due to the need to maintain the current saturation state of the adsorptive material, these losses were not replenished. To assess the extent of resin loss, measurements of resin content within the reactor were conducted during the study. Sampling was performed after 12, 24, 48, 72, and 96 h of operation.

The measured volume of ion exchange resin is influenced by the swelling effect of resin beads. Swelling upon contact with a solvent is an inherent property of polymeric ion exchange resins, as well as many other natural and synthetic materials. As demonstrated in the previous study [14], a given portion of MIEX[®]DOC resin occupies its minimum volume in a regenerated state and in contact with demineralized water. Upon introduction into natural water, the swelling effect increases the resin volume. Continued operation of the resin, including progressive saturation of its adsorption capacity, leads to further volumetric expansion, which stabilizes after exceeding a certain threshold value of bed volume (BV) ratio (the volume of treated water divided by the volume of resin within the reactor).

In the previous study [14], the threshold BV value was established at $400 \text{ m}^3/\text{m}^3$, corresponding to a swelling degree of 15% relative to the volume of regenerated resin immersed in demineralized water. Maximum swelling was observed under relatively low resin loading conditions, suggesting that the swelling degree of resin operating under typical reactor loads (BV : $1\,000$ – $2\,000 \text{ m}^3/\text{m}^3$) remains relatively stable. In the present experiment, the BV level of $400 \text{ m}^3/\text{m}^3$ was reached after approximately 3.5 h of reactor operation within a total experimental cycle of 96 h. Therefore, it was assumed that the adsorbent reaches its maximum swelling almost immediately.

All experimental data were only referenced to the absolute measure of resin content, namely the regenerated resin in contact with demineralized water, referred to as the absolute resin dose (ARD) according to the previous research [15]. To investigate the relationship between ARD and the volume of saturated, swollen resin (saturated resin dose, SRD), the entire remaining volume of adsorbent after the experiment (19.1 cm^3 as SRD) was collected, regenerated, rinsed with demineralized water, and remeasured, yielding a volume of 16.5 cm^3 (ARD). This indicates a final swelling degree of approximately 16%, which closely aligns with the value established in the previous study [14]. The total loss of adsorbent material, measured as ARD , amounted to 8.5 cm^3 , representing 34% of the initial volume of 25 cm^3 . Such a significant resin loss is attributed to the small scale of the experimental setup.

In evaluating the temporal progression of adsorbent loss, it was assumed that the swelling degree relative to the ARD remained constant at 16% for each of the five measurements taken between 12 and 96 h of reactor operation. Based on this assumption,

ARD values were determined for each time point and subsequently approximated using an exponential function (Fig. 1), resulting in a continuous profile of resin content variation within the reactor.

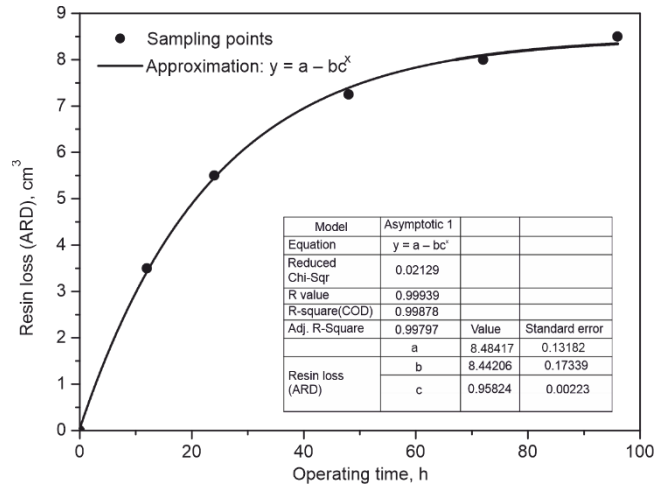


Fig. 1. Resin loss model incorporating swelling effect (resin content expressed as ARD)

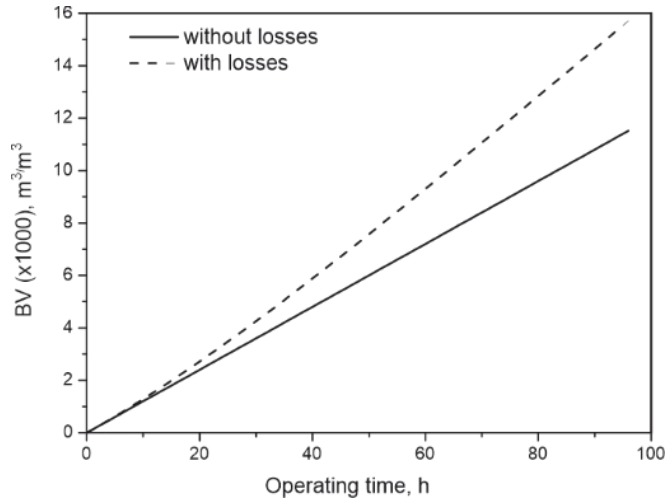


Fig. 2. Impact of resin losses on actual bed volume ratios (*BV*) during experimental reactor operation cycle

The data obtained from this approximation were subsequently used to determine the actual values of the bed volume ratio, which represents one of the key indicators of adsorbent loading. The real *BV* values were calculated according to:

$$BV_{n+1} = BV_n + \Delta BV_{n+1} = BV_n + \frac{V_{n+1} - V_n}{\frac{1}{2}(ARD_{n+1} + ARD_n)} \quad (1)$$

where V denotes the volume of water introduced into the reactor and n refers to the measurement point. The simulation results, along with their comparison to theoretical values (excluding resin losses), are presented in Fig. 2.

4. RESIN CAPACITY

The model water used in the study was characterized by a high concentration of dissolved organic carbon at 9.06 g C/m³ and significantly elevated color (51.3 g Pt/m³). These values were selected to exhaust the adsorbent capacity within a relatively short period. Due to the absence of competing inorganic anions, only organic compounds were subject to removal by the resin material. The relatively high ultraviolet absorbance (37.8 m⁻¹), and particularly the SUVA₂₅₄ value (4.2 m³/(g C·m)), indicate a predominance of high-molecular-weight and aromatic fractions of humic substances with hydrophobic properties [16]. The relationship between SUVA₂₅₄ values and the efficiency of DOC removal via anion exchange is not unequivocally interpretable. However, in the case of MIEX®DOC resin, statistically higher removal efficiencies tend to correlate with elevated SUVA₂₅₄ values – particularly those exceeding 3.0 m³/g (C·m) [17].

Changes in the parameters of treated water during the reactor operation cycle are presented in Fig. 3. Despite the high concentration of organic substances and the extremely short contact time between water and adsorbent (1 min), the initial removal efficiency was high. The DOC concentration decreased to 2.5 g C/m³ (removal efficiency: 72%), color to 8.5 g Pt/m³ (83%), and absorbance at 254 nm to 6.5 m⁻¹ (83%). These results indicate a strong affinity of the organic matter present in the raw water for binding to the MIEX®DOC adsorbent material. Preferential removal of DOC fractions characterized by high SUVA₂₅₄ values was also confirmed. During the initial phase of the reactor operation cycle, the SUVA₂₅₄ value decreased to approximately 2.7 m³/(g C·m), indicating selective elimination of organic constituents with higher SUVA₂₅₄ values. Once the resin became saturated, its selectivity decreased, resulting in SUVA₂₅₄ values remaining within the range of 3.4–3.8 m³/(g C·m).

As anticipated, the high resin loading resulted in rapid and substantial depletion of its adsorption capacity. After only 16 h of reactor operation, the system exceeded a bed volume value of 2000 m³/m³, which typically represents the upper limit of MIEX®DOC adsorbent loading in technical installations. Under these conditions, the DOC, color, and UV₂₅₄ absorbance indicators decreased by 37%, 49%, and 48%, respectively.

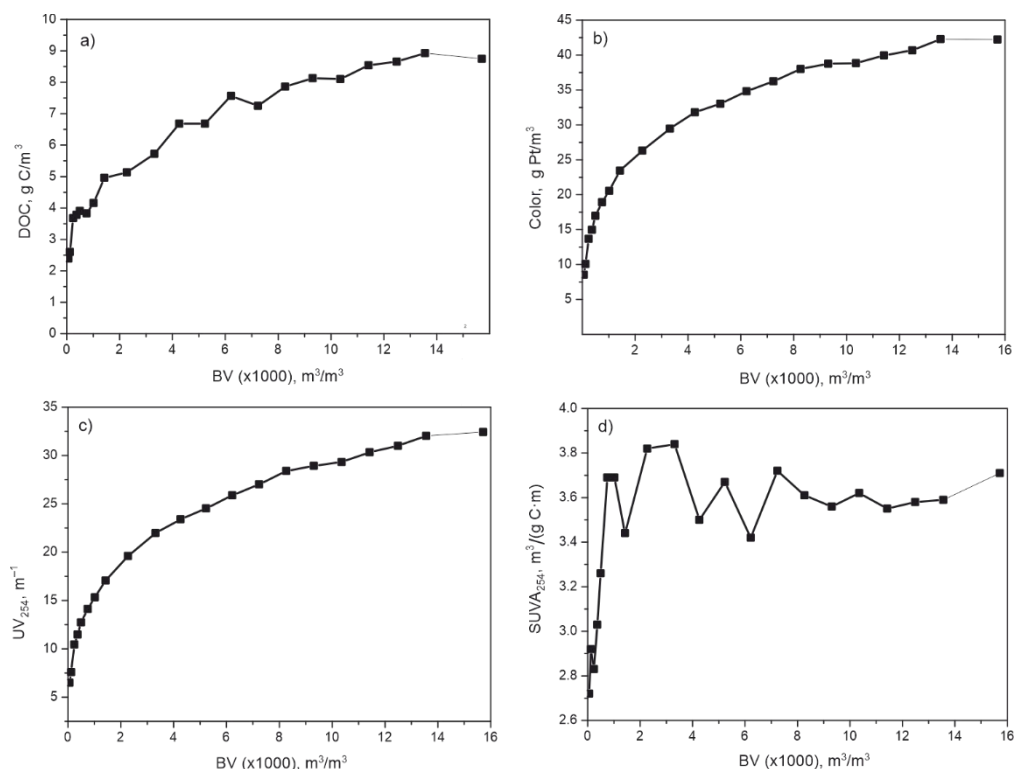


Fig. 3. Treated water quality parameters during reactor operation cycle:

- a) $\text{DOC}_0 = 9.06 \text{ g C/m}^3$, b) $\text{Color}_0 = 51.3 \text{ g C/m}^3$,
 c) $(\text{UV}_{254})_0 = 37.8 \text{ m}^{-1}$, d) $(\text{SUVA}_{254})_0 = 4.2 \text{ m}^3/(\text{g C} \cdot \text{m})$

At the end of the reactor operation cycle, the bed BV ratio reached nearly $16\,000 \text{ m}^3/\text{m}^3$ – approximately eight times higher than the standard operational limit. At this stage, the reductions in DOC, color, and UV_{254} absorbance were 2, 18, and 14%, respectively. These low values, particularly in terms of DOC, indicate that the adsorbent was approaching exhaustion of its capacity to remove organic substances. Consequently, the total amount of organic carbon removed may be used to estimate the adsorption capacity of MIEX[®]DOC resin with respect to DOC.

The DOC load retained by the MIEX[®]DOC resin material represents the difference between the load supplied to the reactor and the load discharged from it. The supplied load remained constant over time due to the stable DOC concentration in the raw water and a constant flow rate of treated water. In contrast, the discharged load varied depending on the changing efficiency of DOC removal. The cumulative DOC load (L) in the reactor effluent at a measurement point $n + 1$ was calculated according to:

$$L_{n+1} = L_n + \Delta L_{n+1} = L_n + (V_{n+1} - V_n) \frac{DOC_{e(n+1)} + DOC_{e(n)}}{2} \quad (2)$$

where DOC_e means DOC concentration in the effluent. During the initial phase of operation, when concentration changes in the effluent were significant, measurements were conducted every 0.5–2 h. In the final phase of the cycle, when these changes became negligible, samples were collected at intervals of 6–12 h.

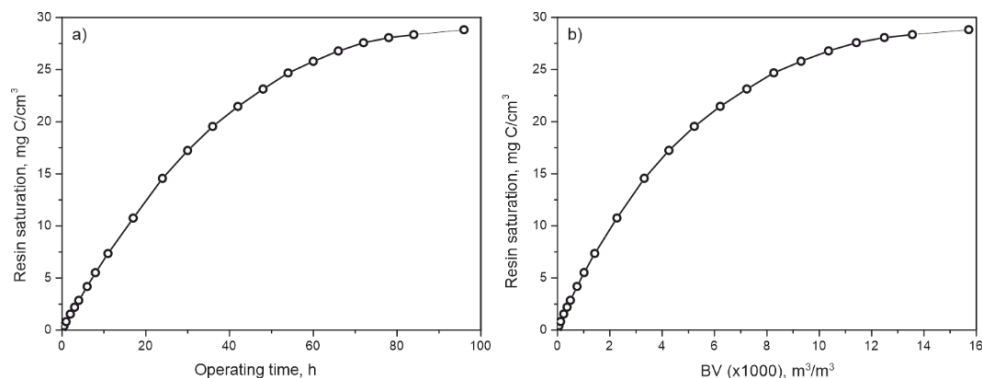


Fig. 4. MIEX[®]DOC resin saturation profile as a function of:
a) reactor operating time, b) bed volume ratio (BV)

Changes in the DOC load removed by MIEX[®]DOC resin, as a function of both time and bed volume ratio, are presented in Fig. 4. A key observation is the typical variation in binding rates of removed constituents, characteristic for adsorption processes. Fresh resin was capable of adsorbing approximately $0.8 \text{ mg C}/(\text{cm}^3 \cdot \text{h})$, whereas resin nearing exhaustion retained only about $0.04 \text{ mg C}/(\text{cm}^3 \cdot \text{h})$. Organic compounds exhibiting high color and ultraviolet absorbance were removed with increased efficiency (Fig. 3).

Addressing the key issue of the specific adsorption capacity of MIEX[®]DOC resin, the study demonstrated that its value near full saturation (DOC removal efficiency: approximately 2%) reached $28.8 \text{ mg C}/\text{cm}^3$ of resin. It is important to emphasize that this value was obtained at a BV of approximately $16 \text{ 000 m}^3/\text{m}^3$. Under typical operating conditions, BV values are maintained within the range of $100\text{--}2000 \text{ m}^3/\text{m}^3$, corresponding to DOC adsorption capacities of 5.5 and $9.6 \text{ mg C}/\text{cm}^3$, respectively.

Considering the final DOC concentrations – approximately $4 \text{ g C}/\text{m}^3$ for $BV = 1000 \text{ m}^3/\text{m}^3$ and around $5 \text{ g C}/\text{m}^3$ for $BV = 2000 \text{ m}^3/\text{m}^3$ – it can be concluded that the former value is more representative of typical operational conditions. Under these circumstances, the adsorbent utilizes approximately 19% of its estimated capacity. This result is consistent with other reports indicating that organic constituents occupy only a small fraction of the MIEX[®]DOC resin capacity – typically in the range of a dozen or so percent [10, 18].

However, it should be noted that the experimental conditions in this study differed significantly from those in the referenced works.

The HR-CC system enables operation with higher adsorbent saturation in the first reactor. In this configuration, DOC concentrations in the effluent from the saturated adsorbent reactor may be higher. At intermediate DOC concentrations ranging from 5 to 6 g C/m³, the MIEX[®]DOC resin utilizes approximately 33–41% of its estimated capacity. This indicates that the use of an HR-CC reactor allows for significantly improved utilization of the adsorbent's capacity, albeit at the expense of increased capital investment.

Natural organic matter represents a specific class of ionic molecules referred to as macroanions. These compounds are characterized by a low charge associated with a relatively high molecular mass. As a result, ion exchange processes can remove substantial mass quantities while utilizing only a small fraction of the resin's ion exchange capacity. The experiment under analysis was designed to create conditions that promote near-complete saturation of the adsorbent with organic compounds: (1) high DOC concentration, (2) very high *BV* value, and (3) absence of competition from inorganic anions.

In the case of MIEX[®]DOC resin, various methodologies – each based on inorganic anion exchange – have yielded operational ion exchange capacities in the range of 0.40–0.52 meq/cm³ [6–10]. According to multiple literature sources [19–22], the content of dissociated functional groups in NOM molecules typically falls within the range of 2–6 meq/g. Assuming a carbon content within NOM of approximately 50% [22], this corresponds to a functional group density of 4–12 meq/g C.

Assuming the extreme values of ion exchange capacity and NOM charge density, the estimated DOC adsorption capacity of MIEX[®]DOC resin ranges from 3.3 to 26.0 mg C/cm³. Compared to the value of approximately 29 mg C/cm³ obtained under particularly favorable DOC separation conditions in the present study, it can be inferred that ion exchange capacity is related to DOC adsorption potential. Higher calculated capacities are associated with low charge density, which typically characterizes high-molecular-weight NOM fractions. The presence of such fractions in the tested water is indicated by a high SUVA₂₅₄ value ($> 4 \text{ m}^3/(\text{g C} \cdot \text{m})$). Enhanced DOC adsorption is also supported by the preferential removal of NOM constituents with elevated SUVA₂₅₄ values (Fig. 3).

Ultimately, it can be concluded that the two distinct approaches to describing the adsorption capacity of MIEX[®]DOC resin are interrelated. However, this relationship depends on the structural characteristics of natural organic matter. The maximum adsorption value obtained in this study may serve as a reference point for evaluating the degree of adsorbent capacity utilization, while acknowledging that both the properties of NOM and the operational conditions of the process can influence this value.

5. CONCLUSIONS

- Under conditions of extremely high MIEX[®]DOC resin loading (raw water DOC concentration: approximately 9 g C/m³, *BV* 16 000 m³/m³), the adsorbent was capable

of retaining approximately 29 mg C/cm³. However, it should be noted that the achieved adsorption value is partially dependent on the aforementioned process conditions. In this case, a significant contributing factor was the absence of competition from inorganic anions.

- The saturation value is not strictly equivalent to the adsorbent's capacity, as further removal of organic compounds from water was still possible under such extreme conditions. However, the very low removal efficiency (approximately 2%) indicates that, at this level of saturation, the adsorption capacity no longer holds practical significance, and the observed adsorption value closely approximates the true capacity of the adsorbent.

- The saturation profile of the adsorbent capacity demonstrated that, when using a conventional high-rate reactor, sufficiently treated water quality can be achieved with approximately 19% utilization of the estimated MIEX[®]DOC resin capacity. In contrast, the application of a high-rate counter-current reactor allows for at least twice the capacity utilization – approximately 40%.

- The relationship between the DOC adsorption capacity of MIEX[®]DOC resin and its operational ion exchange capacity is complex. This is primarily due to the heterogeneous structure of natural organic matter, both in terms of molecular size and associated charge. Nevertheless, the conducted study demonstrated that the measured DOC adsorption capacity closely aligns with the range estimated based on the resin's ion exchange capacity and the charge density of NOM. Paradoxically, higher DOC adsorption capacities are associated with lower charge densities – a phenomenon observed in this experiment. The high adsorption value of 29 mg C/cm³ corresponded well with the operational ion exchange capacity of the resin for organic constituents exhibiting low charge density, approximately 4 meq/g C.

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