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The use of chitosan and pressure-driven membrane processes to remove natural organic matter from regenerative brine recovery

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ABSTRACT

The research on the removal of natural organic matter (NOM) from post-regeneration brine solution, that is, a mixture of NaCl and natural organic substances (fulvic and humic acids) generated during regeneration of MIEX® resin used in the treatment of surface and synthetic water via ion-exchange process is discussed. Different chitosan modifications (powdered chitosan, chitosan-based coagulant and chitosan balls) and pressure-driven membrane processes (ultrafiltration [UF] and nanofiltration, [NF]) were used. A number of treatment process arrangements, such as chitosan-based coagulation and sorption, single-stage membrane processes (UF and NF) and integrated membrane systems (UF+NF) were tested. The research showed the efficient removal of NOM by means of chitosan coagulation at the dose 0.6 g/L and pH = 6, for which 44% decrease of dissolved organic carbon (DOC) concentration was obtained. The high efficiency of post-regeneration brine solution treatment was reached using integrated system of chitosan coagulation and NF. For this system 97% removal of DOC accompanied with the highest, among all investigated systems, relative permeate flux 0.65 was obtained.

Keywords: NOM; MIEX®; Chitosan; Ultrafiltration; Nanofiltration; Water; Brine solution

1. Introduction

Among many conventional methods used in water treatment technology to natural organic matter (NOM) removal, one has to mention the ion exchange, operated with anion-exchange resins, which is more commonly used due to stringent requirements of potable water quality standards [1]. The fundamental of the ion exchange is the replacement of mobile ions present in water with other ions of the same charge, which are carried by either in solid or polymeric substance that contains suitable functional groups [2]. The ion-exchange process with conventional anion-exchange resins is carried out in columns, while the application of MIEX® resin comprised of its direct dosing to treated water, 30 min mixing and separation from water in dedicated devices [3] or by means of pressure-driven membrane processes [4–6]. The depletion of an ion-exchange capacity is a common phenomenon observed during the process, thus their regeneration, usually with NaCl solution [7], is run. The post-regeneration solution, which is a mixture of organic and inorganic contaminants, is regarded as a waste stream of harmful environmental effect due to toxicity and corrosive character. Considering zero liquid discharge systems of water management, the treatment and reuse of post-regeneration brine should be considered. The use of natural biopolymer, chitosan (chitin derivative), produced from sea crustaceans, seems to be appropriate for this purpose [8].

Chitosan is non-toxic, bioactive biopolymer of biodegradable character. The chemical structure of the compound is very complex and comprises of (1,4-β-)-2-acetylamino-2-deoxy-D-glucopiranose and (1,4-β-)-2-amino-2-deoxy-D-glucopiranose-2 [9]. Biological, chemical and physical features of chitosan enable its wide use in many branches of industry (e.g., medicine, environmental protection or biotechnology). Considering the quality, one can distinguish

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technical, pure and ultrapure grades of chitosan. The first one is broadly used in agriculture, water and wastewater treatment; the second is utilized in food and cosmetic industry; while ultrapure chitosan is applied in biomedicine. The discussed biosorbent reveals a sorption affinity towards heavy metals, agglomerated colloidal contaminants, improves colour and turbidity of water and wastewater and enhances the removal of natural organic substances [10]. The natural character of chitosan and its affinity to NOM removal allows to consider it as potentially valuable natural organic fertilizer. On the other hand, in order to recover relatively clean brine from post-regeneration solutions, deprived of smallest NOM fraction, the application of membrane processes, for example, ultrafiltration (UF) and/or, preferably, nanofiltration (NF), should be considered. NF is suggested due to rejection of bivalent ions and recovery of monovalent ions (NaCl) in permeate stream [11].

The aim of the discussed research was to remove NOM from post-regeneration brine solution regarding the reuse of permeate to MIEX® resin regeneration and the efficient solid side stream utilization.

2. Methods

2.1. The subject of the research

Post-regeneration brine solution (Table 1), that is, a mixture of NaCl and NOM (fulvic and humic acids) formed during regeneration of MIEX® resin applied to surface and synthetic water treatment (after 48 operational cycles) was used as the subject of this research.

Many studies performed by Rajca [12–15], and also by Bond et al. [16], Apell and Boyer [17] and Drikas et al. [18], have shown that MIEX® dissolved organic carbon (DOC) process effectively removes NOM from water. The applied MIEX® resin is an anion-exchange, macroporous polymer produced by Orica Watercare. The resin is dosed to treated water in the suspended form, and after separation, it is regenerated using 10%–12% brine solution of NaCl. As a result, post-regeneration brine solution of significant concentration of natural organic substances is generated. In the study of post-regeneration brine solution treatment, various chitosan modifications and pressure-driven membrane processes were used.

2.2. Chitosan

Chitosan applied in the research was supplied by BOC Sciences (USA) as a powder of deacetylation degree ≥ 95%, molecular weight Mw = 500,000 Da, moisture content < 8% and volumetric density ≥ 0.6 g/mL.

For the treatment of post-regeneration brine solution, following modifications of chitosan were used:

- Powdered chitosan – sorption (2 g of chitosan/L of post-regeneration brine solution);
- Chitosan-based coagulant – coagulation (50 g of chitosan/L in 0.025 N HCl solution in deionized water; doses: 0.1, 0.2, 0.4 and 0.6 g/L, pH = 6 and 7);
- Chitosan balls – sorption (20 g of chitosan balls/L of post-regeneration brine solution). Chitosan balls were obtained by pipetting 1% of chitosan solution in acetic acid to 2M NaOH solution. The formed balls were washed with deionized water until neutral pH of washing effluent was obtained [19].

2.2.1. Coagulation with the use of chitosan solution

The process was carried out in the laboratory flocculator JLT6 by Velp Scientifica at a fast mixing rate of 200 rpm for 1 min and a slow mixing rate of 30 rpm for 30 min followed by 30 min of sedimentation. After the latter process, samples were centrifuged for 10 min at 3,000 rpm. Chitosan-based coagulant (chitosan solution) was dosed to post-regeneration brine solution during the fast mixing stage, next solution pH was adjusted and the slow mixing stage (flocculation) was carried out [19].

2.2.2. Sorption with the use of chitosan powder and chitosan balls

The process was carried out in Erlenmeyer flasks of volume 250 mL by shaking 50 mL portions of the post-regeneration brine solution with proper doses of tested adsorbents at 160 rpm and 20°C temperature for 24 h. Laboratory shakers by ELPIN Plus and GFL were used. The purified solution was separated from a sorbent using paper filter and next the solution was centrifuged as in case of coagulation [19]. In the industrial scale the separation of sorbent would be performed by microfiltration process.

2.3. UF and NF and integrated processes

Membrane processes, that is, UF s and NF, were also used to post-regeneration brine solution treatment. The processes were applied as single-stage operations, as two-stage systems or as an enhancement for chitosan-based coagulation process (integrated systems). Following treatment arrangements were tested:

- Single-stage UF,
- single-stage NF at various transmembrane pressures,
- integrated UF+NF system and
- integrated chitosan-based coagulation-NF system.

Membrane filtration was carried out in a pressurized device consisting of a steel cell (of capacity 400 mL) and magnetic stirrer (Fig. 1) operated in the dead-end mode. Flat sheet, polymeric, polyvinylidene fluoride (PVDF, 30,000 Da) UF membranes by GE Osmonics and NF270 (polyamide, 200–400 Da) and NF membrane by Dow Filmtec were used. The separation area of the membrane was equal to 35.25 cm^2.

Table 1
Parameters of brine solution generated during regeneration of MIEX® resin

Parameter	Value
pH	7.40
Conductivity, mS/cm	9.23
Colour, mg Pt/L	750
Absorbance UV_{254}, 1/cm	6.45
DOC, mg/L	127.6

Filtration processes were conducted for 1 h. Removal rates of colour, DOC and absorbance were calculated from the Eq. (1).

$$R = \left(1 - \frac{C_p}{C_n}\right) \times 100\% \quad (1)$$

where R – retention coefficient (%), C_n – concentration of n component in the feed (mg/L), C_p – concentration of n component in the permeate (mg/L).

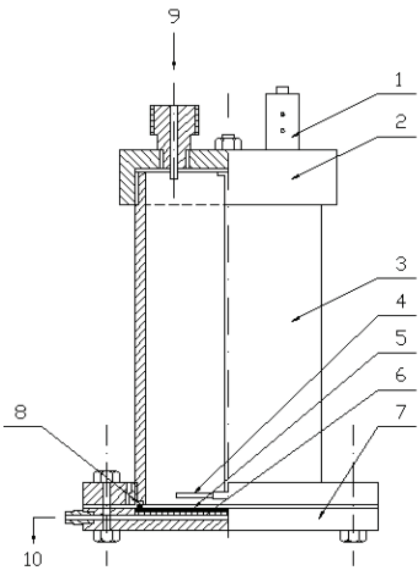

Fig. 1. The scheme of the apparatus for dead end membrane filtration. (1) Safety valve, (2) upper collar, (3) membrane cell, (4) magnetic stirrer, (5) membrane, (6) perforated plate, (7) bottom collar, (8) gasket, (9) gas supply, and (10) permeate.

2.4. Analytical methods

Raw and purified post-regeneration brine solutions were analyzed in regard to DOC content by means of HiPerTOC analyzer by Thermo Elektron Corporation (Germany), UV absorbance (UV254 nm) using UV/VIS CE 1021 spectrophotometer by Cecil Instruments (UK) and colour by means of NOVA 400 photometer by Merck Millipore (Germany).

3. Results and discussion

3.1. Removal of natural organic substances by chitosan

In Table 2, the results of the treatment of post-regeneration brine solution by means of chitosan are shown.

The study revealed that the coagulation with chitosan-based coagulation solution was the most efficient process. For all investigated contamination indicators (absorbance, colour and DOC), the efficiency of the process increased with chitosan-based coagulant dose increase, while it decreased with the increase of solution pH. The highest applied coagulant dose, that is, 0.6 g/L was found to be the best one, while pH = 6 was the preferable one. At such conditions 64%, 62% and 44% decrease of colour, absorbance and DOC, respectively, was obtained. The effective removal of NOM by means of chitosan-based coagulation was also discussed by Fabris et al. [20], who considered the coagulant use in treatment of water dedicated to potable purposes.

Coagulation process with the use of aluminium or iron coagulants to treat post-regeneration brine solutions was also considered. The treatment process revealed satisfactory results; however, the use of external, aggressive chemicals disqualified the solid deposit from further use to fertilizing purposes and caused its proper utilization issues.

Static sorption methods examined in this study were found to be the least efficient in removal of NOM from treated brine solution (Table 2). In this research, chitosan

Table 2
Results of the treatment of post regeneration brine solution by means of chitosan

No. sample	Method	Dose, g/L	pH reaction	Colour[a], mg Pt/L	Absorbance[a], UV_{254}, 1/cm	DOC[a], mg/L
0	–	–	7.4	750	6.45	127.6
1	C	0.1	7.0	493	3.79	105.5
2	C	0.2	7.0	472	3.74	97.82
3	C	0.4	7.0	411	3.33	88.82
4	C	0.6	7.0	369	2.91	86.23
5	C	0.1	6.0	429	3.38	92.12
6	C	0.2	6.0	373	3.04	90.63
7	C	0.4	6.0	305	2.72	76.39
8	C	0.6	6.0	267	2.45	71.37
9	S chitosan	2.0	3.0	390	3.18	99.93
10	S chitosan	2.0	5.0	520	4.12	115.1
11	S chitosan	2.0	7.5	710	5.16	123.7
12	S balls	20	3.0	313	2.90	84.74
13	S balls	20	5.0	439	3.53	100.2
14	S balls	20	7.5	650	4.82	112.9

0, Brine solution; C, coagulation; S, static sorption.

[a] Sample prefiltration with 0.45 μm filter.

powder and balls were tested. The impact of pH on the efficiency of both tested sorbents was examined. It was observed that with the pH increase (3.0, 5.0 and 7.5), the efficiency of sorption decreased regardless of the sorbent form applied and contaminant examined. The percentage decrease in colour at applied pH levels was equal to 48%, 30% and 5%, respectively, for powdered chitosan, and 58%, 41% and 13%, respectively, for chitosan balls. Absorbance measurements indicated on 51%, 36% and 20% parameter decrease for powdered chitosan in regard to solution pH and for chitosan balls it was 55%, 45% and 25%. The decrease of DOC observed for chitosan powder was 21%, 9% and 3% for solution pH 3.0, 5.0 and 7.5, respectively, while for chitosan balls 33%, 21% and 11% of DOC removal in respect to pH was noted. Nevertheless, chitosan balls revealed higher treatment efficiency than the powdered form of the sorbent. It resulted from the large porous surface of the hydrogel balls, which was much higher than for powdered chitosan. The higher efficiency of contaminants removal observed for solutions of lower pH was probably caused by interactions between contaminants and amine functional groups present in chitosan structure, which were based on electrostatic attraction [21].

3.2. UF, NF, integrated processes

In Table 3, the results of investigations on the treatment of post-regeneration brine solution by means of single stage or integrated membrane processes arrangements are shown.

The analysis of experimental results indicated that the single-stage UF was the least efficient treatment process, while systems based on NF integrated either with UF or coagulation with chitosan were comparable and suitable for NOM removal. The removal of the measured parameters obtained for UF system was 3%, 28% and 16% for colour, absorbance and DOC, respectively, while for other systems 97% decrease in colour, 99% decrease in absorbance and 98% removal of DOC were noted. Additionally, in case of single-stage NF, the impact of transmembrane pressure on the contaminants removal efficiency was tested. It was found that the pressure increase within the range of 0.25–1.0 MPa resulted in the decrease of treatment efficiency. It was caused by the application of the higher driving force, due to which contaminants could quickly diffuse to permeate. The treatment of waste brine solution generated during MIEX® resin regeneration by means of different membranes was investigated by Kabsch-Korbutowicz and Urbanowska [22]. The authors observed 19 to ca. 60% removal of NOM by means of polyethersulphone (PES) UF membranes, 20%–40% removal rates were revealed by UF membranes made of regenerated cellulose (RC) and 40%–60% contaminants rejection was obtained for PES NF membranes. The results obtained by Kabsch-Korbutowicz and Urbanowska [22] were slightly worse than those observed within this research.

3.3. Capacity of membrane processes

Considering the application of membrane processes to NOM removal, the susceptibility of a membrane to fouling by solution components, which may significantly affect the hydraulic capacity of a process, should be checked. Inconveniences related to membrane processes regarding decreases in hydraulic performance of membranes are caused by concentration polarization, gel layer formation on the surface of the membrane, accumulation of impurities on a membrane surface or inside its pores (fouling), precipitation of sparingly soluble salts forming inorganic deposits (scaling). The severeness of fouling is indicated by the so-called relative permeate flux and may vary from 0 to 1.0. The lower the value of the indicator is, the higher the membrane surface and pores fouling occur. In Fig. 2 changes in relative permeate flux observed for single-stage UF and NF are shown, while in Fig. 3 the impact of the transmembrane pressure on the NF process capacity is presented. In Fig. 4 relative permeate flux noted for integrated systems, that is, UF+NF and chitosan-based coagulation+NF are given.

The lowest relative permeate fluxes were noted for single-stage UF and NF and after 1 h of filtration they were 0.55 for UF (Fig. 2) and 0.33, 0.45 and 0.50 for NF carried out at transmembrane pressure 0.25, 0.5 and 1.0 MPa (Fig. 3), respectively. Such values indicated on membrane fouling occurrence, however, in refer to results obtained by Kabsch-Korbutowicz and Urbanowska [22], the phenomenon was of a moderate character. Kabsch-Korbutowicz and Urbanowska [22] examined UF membranes made of different materials (PES and RC) and PES NF membranes. They obtained very low relative permeate fluxes during the treatment of similar feed and the value of the parameter for UF PES varied from 0.1 to 0.4 and depended on the membrane cut-off, which was 30 and 5 kDa. The highest relative permeate flux was noted for RC UF membrane (0.65) and resulted from hydrophilicity of the membrane material. In this research, UF, PVDF, hydrophobic membrane of cut-off 25 kDa was used. Despite cut-off

Table 3
Results of the treatment of post-regeneration brine solution by means of membrane processes

Treated method	pH	Colour[a], mg Pt/L	Absorbance[a], UV_{254}, 1/cm	DOC[a], mg/L	Chlorides, mg/L
Brine solution	7.40	750	6.450	127.6	–
UF, 0.25 MPa	7.76	730	4.630	106.5	40,413
NF, 0.25 MPa	8.65	25	0.038	1.04	34,812
NF, 0.5 MPa	9.35	27	0.049	3.08	38,570
NF, 1.0 MPa	9.44	29	0.071	3.34	38,966
UF+NF, 0.25 MPa	8.30	25	0.082	3.50	40,378
C[a] chitosan+NF, 0.25 MPa	7.20	22	0.082	3.88	30,842

[a] Coagulation by chitosan, dose 0.6 g/L, pH 6.0.

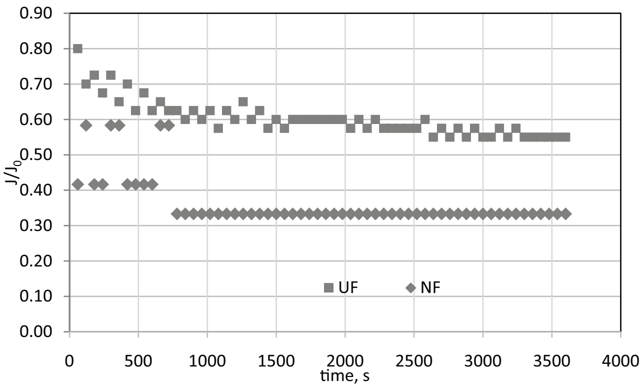

Fig. 2. Changes in relative permeate flux observed for single-stage UF and NF, 0.25 MPa, J_0 for UF 18.9 × 10^{-6} m^3/m·s, J_0 for NF 6.62 × 10^{-6} m^3/m·s, J_0 – volumetric flux of deionized water, J – volumetric permeate flux during the brine solution treatment with UF and NF.

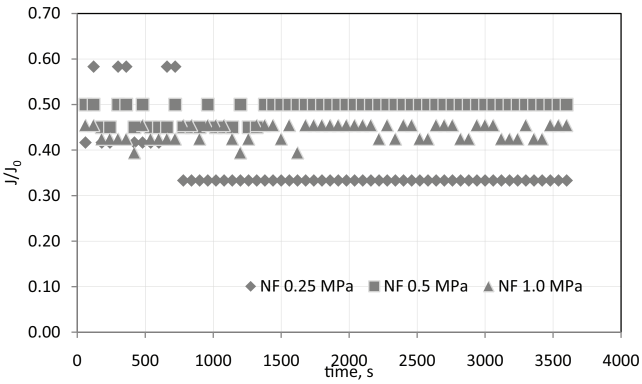

Fig. 3. Changes in relative permeate flux observed for single-stage NF at various transmembrane pressures, J_0 for 0.25 MPa – 6.62 × 10^{-6} m^3/m·s, 0.5 MPa – 9.46 × 10^{-6} m^3/m·s, and 1.0 MPa – 15.6 × 10^{-6} m^3/m·s.

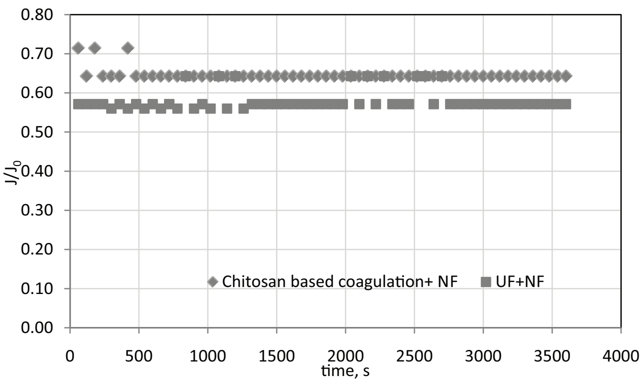

Fig. 4. Changes in relative permeate flux observed for integrated systems, 0.25 MPa, J_0 for UF 18.9 × 10^{-6} m^3/m·s, J_0 for NF 6.62 × 10^{-6} m^3/m·s.

similar to UF PES membrane used in the study by Kabsch-Korbutowicz and Urbanowska [22], the measured relative permeate flux was five times greater (0.55). The results obtained for NF membranes were comparable.

The highest relative permeate fluxes were observed for integrated systems (Fig. 4), whereas the better performance was observed for the system in which NF was preceded by coagulation with chitosan (0.65). It indicated that such a configuration was the preferable one among all investigated systems, as it characterized with satisfactory capacity and efficient contaminants removal (Table 2). It was assumed that the research on process optimization would allow to obtain even better results. Thus, the studies are to be continued.

4. Summary and conclusions

- Chitosan-based coagulation was found to be the most efficient in NOM removal from post-regeneration brine solution among all tested chitosan-based sorption methods.
- Integrated systems, that is, UF+NF and chitosan-based coagulation+NF enabled to efficiently recover brine NaCl solution depleted of NOM (humic and fulvic acids) and the purified solution could again be applied to MIEX® resin regeneration.
- The transmembrane pressure had an impact on NOM removal by means of NF, that is, the higher the transmembrane pressure was, the lower contaminants removal efficiency was noted.
- The use of chitosan, that is, the derivative of chitin produced from sea organisms shells enables to utilize this side product, which, after sorption of NOM remains in the mixture (concentrate produced in integrated chitosan coagulation+NF) and it can be further used as a soil amendment agent for fertility enhancement.

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