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Natural organic matter removal from water by complexation–ultrafiltration process with poly(diallyl dimethylammonium chloride)

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ABSTRACT

The efficiency of humic acids (HA) removal from aqueous solutions by complexation-ultrafiltration (COUF) process, in the presence of the cationic water-soluble polymer, poly(diallyl dimethylammonium chloride) (PDADMAC) of different average Mw were studied; also the effect of mass ratio of HA to polymer, pH of solution on the HA removal were evaluated. The results show that the HA rejection on ultrafiltration PBCC membrane (Millipore) varied from 70 to 99.9% with addition of PDADMAC, depending on average Mw, when a HA/polymer mass ratio was changed from 1:1 to 1:7. The solute rejection to some extent improved with an increase in the concentration of polymeric complexing agents due to a higher completeness of the HA binding. It was found that the HA removal change with pH value of the feed solution, owing to protonation of the quaternary amino groups of this polymer.

Keywords: Ultrafiltration; Complexation; Humic acids; Poly(diallyl dimethylammonium chloride)

1. Introduction

The presence of natural organic matter in water is associated with a number of problems and the formation of harmful by-products on chlorination [1–3]. One particular group of contaminants that is present in water supplies and which has brought about concern in the water industry are humic substances (HSs).

Humic substances are complex and heterogeneous mixtures of polydispersed materials formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains (a process called humification). The HSs system is created by the association of various components present in the humification process, such as amino acids, lignins, pectins or carbohydrates, through intermolecular forces (donor–acceptor, ionic, hydrophilic, and hydrophobic). It is evident that the mechanisms of the formation of humic substances can be slightly different, depending on geographical, climatic, physical and biological circumstances, respectively [4,5]. The HSs can be divided into components according to their solubility in different media—humin which is completely insoluble; humic acid (HA) which is insoluble at a pH of 1 and fulvic acid (FA) which is soluble at any pH [4–6].

Humic substances (HSs) constitute a major fraction of the dissolved and particulate organic matter in natural ecosystems [5].

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Regardless of the still unknown structure of HSs and the great efforts to elucidate, it is known that their major functional groups include carboxylic, phenolic, carbonyl, hydroxyl, amine, amide and aliphatic moieties, among others. Due to this polyfunctionality, HSs are one of the most powerful chelating agents among natural organic substances [5,7].

However, in 2005 information gathered using spectroscopic, microscopic, pyrolysis, and soft ionization techniques are not consistent with the "polymer model" of humic substances [4]. Fresh scrutiny of soil processes active in the formation and preservation of humic substances also casts doubt on this model [8,9]. A new concept of HS has thus emerged, that of the supramolecular association, in which many relatively small and chemically diverse organic molecules form clusters linked by hydrogen bonds (H-bonds) and hydrophobic interactions [9,10].

Humic acids constitute the major part of NOM therefore these substances should be extracted from water before chlorination to prevent the formation of chlorinated disinfection by-products (DBPs) [1,5]. The latter, such as trihalomethanes (THMs) and haloacetic acids (HAAs), have been recently recognized to be human carcinogens [1]. Several treatment processes or their combinations are capable of removing NOM from water, for example adsorption [11], ozonization [12], flocculation [13,14], pre-coagulation [15,16], which do not always satisfy the continuing tightening of drinking water standards. The removal of HA from aqueous solutions using membrane-based techniques has been investigated by a number of researches [1,3,15–27].

Pressure-driven membrane methods are often associated with high-energy requirements involved in these processes, and the membrane surface can be fouled. Recently the application of low-pressure membrane filtration such as microfiltration (MF) and ultrafiltration (UF) to produce drinking water has grown in prevalence due to its ability to remove a wide range of contaminants [3]. Therefore of particular interest is the use of the COUF approach as an alternative water treatment method for HA removal. The basic concept of COUF is that—the target ions or molecules are rejected on wide-porous ultrafiltration membranes after binding with high molecular weight water-soluble polymers. The advantages of this process are the low-energy requirements and the high binding capacity of the polymeric complexing agents [21,22].

Tipping and Ohnstad [28] have studied the removal of HS from solution. The degree of complexation was found to increase with $CaCl_2$ concentration, and above a concentration of 2.5 mM of $CaCl_2$, substantial aggregation occurred, at neutral or alkaline pH. According to these authors, the differences in fractions of HS are due to differences in their solubilities—presumably, the higher molecular weight HS have a greater content of complexing ionizable functional groups.

The main objective of this research is to investigate the effect of the polymer molecular weight in the efficiency of HA removal from aqueous solutions by COUF using cationic water soluble polymers such as poly(diallyl dimethylammonium chloride) (PDADMAC), with different average molecular weights of polymer and different NMWCO ultrafiltration membranes.

2. Materials and methods

HA were obtained from Aldrich. Poly(diallyl dimethylammonium chloride) with average molecular weight (Mw) <100 kDa, (PDADMAC 1); average Mw 100–200 kDa, (PDADMAC 2); average Mw 200–350 kDa, (PDADMAC 3); average Mw 400–500 kDa, (PDADMAC 4); were purchased from Aldrich and were used as polymeric complexing agents for HA binding.

The membranes used in this study were flat-disc ultrafiltration membranes of Millipore PB and PL series (PBCC Biomax PES and PLGC Ultracel RC). They are asymmetric regenerated cellulose membranes, with a propylene support, and are considered hydrophilic in nature.

2.1. Preparation of the solution

The glassware or container was rinsed with milliQ water and dried in an oven. Before passing any process solution through the membrane it was flushed with milliQ water.

The HA solution and polymer solution were prepared with milliQ water. Humic acid powder was used to make up the required concentrations for each model solution, the HA solutions were prepared using an ultrasonic bath and 35 min were required for full dissolution of humic acid. The aqueous solution of the polymer was added to HA solution with a concentration of HA of 20 mg l^{-1} at different HA/polymer mass ratio (1:1 to 1:7).

2.2. Filtration protocols

The blended aqueous solutions were stirred for 30 min, after that the feed solution was filtered through the membrane. For constant pressure experiments, nitrogen gas was used to pressurize the feed reservoir. For constant flux experiments, the feed reservoir was pressurized to 20 kPa with nitrogen gas and a peristaltic pump was connected to the permeate line to control the flux. Ultrafiltration experiments were performed in a 200 ml dead-end stirred cylindrical cell (UF stirred cell 76 mm from millipore) with an effective membrane area of 4.18 × 10^{-3} m^2. A stirring speed in the cell was maintained at about 300 rpm. The pH of solutions was adjusted by 0.1 N hydrochloric acid or sodium hydroxide. HA concentration in permeate was determined by a UV-vis spectrophotometer (Perkin Elmer Instrument, USA) at 254 nm.

The rejection coefficient of HA was calculated as

$$R = \frac{C_o - C_p}{C_o} \times 100\% \qquad (1)$$

where C_o, C_p are the HA concentrations in the feed and permeate, respectively. Membrane flux was evaluated following:

$$J = \frac{V}{S_t} \qquad (2)$$

where J is the membrane flux, V is a permeate volume passed through the membrane with an area of S within time t at operating pressure of P.

3. Results and discussion

The effect of the operating pressure on the HA rejection and membrane flux are presented in Fig. 1. As can be seen in Fig. 1(a), the HA rejection is almost independent of transmembrane pressure above 2 MPa with all the membrane used in this research. The rejection through the fouled membrane shows a small curvature, corresponding to an increase in hydraulic resistance with increasing applied pressure, reflecting a slight compressibility of the deposit. The difference between the rejection at $\Delta P = 2$ and $\Delta P = 4$, increases less than 1%. This behavior is completely consistent with predictions of the classical concentration polarization model.

The water flux through the wide porous PBCC 10 kDa and PLGC 10 kDa membranes sharply grows with increase in operating pressure. As a result, the HA concentration in the boundary membrane layer essentially exceeds that in the bulk of solution and leads to a decline in the observed HA rejection. It should be noted that the HA rejection did not exceed 88% even with the relatively narrow-pore PBCC 5kDa and PLGC 5 kDa membranes (NMWCO of 5 kDa). This is obviously due to a broad molecular weight distribution of the HA [29]. Fig. 1(b) shows that the volume flux of PBCC 10kDa and PLGC 10 kDa membranes are practically twice as high in comparison with PBCC 5kDa and PLGC 5 kDa, therefore both groups of membranes were used in further COUF studies on HA removal (Table 1).

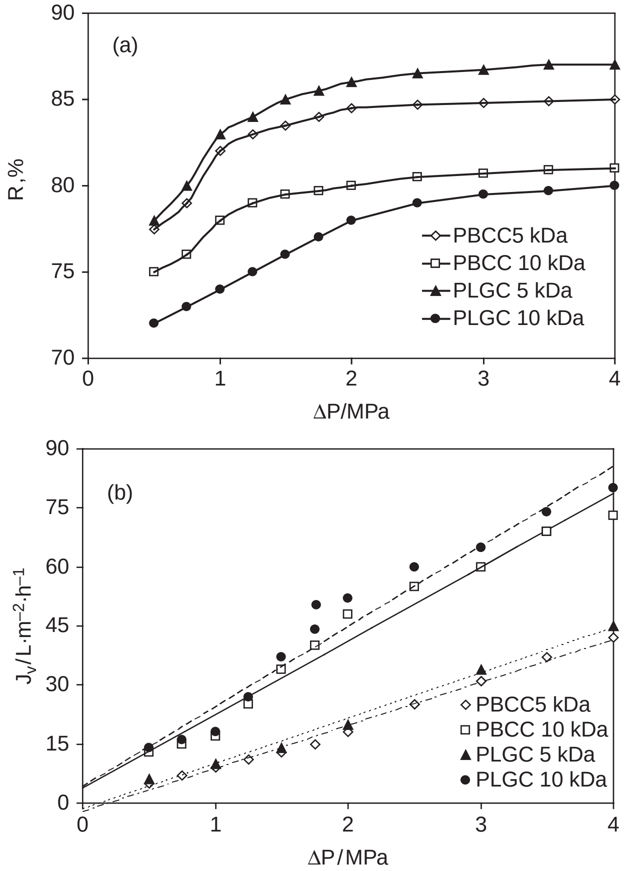

Fig. 1. The rejection of HA (a) and membrane flux (b) versus operating pressure during filtration of HA solution of concentration 20 mg L^{-1} through membranes PBCC 5kDa, PBCC 10kDa, PLGC 5kDa, PLGC 10kDa, pH 7.

Table 1
Values of permeability of the employed membranes

Membrane	Permeability values ΔP/MPa			
	1	2	3	4
PBCC 5	9	9	10.33	10.5
PBCC 10	17	24	20	18.25
PLGC 5	10	10	11.33	11.25
PLGC 10	18	26	21.67	20

The effect of HA to polymer complexants ratio on the HA rejection and volume fluxes is shown in Fig. 2. It is seen that the efficiency of HA removal slightly increases with a HA/polymer ratio, obviously due to an increase in completeness of HA binding at higher polymer concentration. On the other hand, the membrane fluxes somewhat decrease with increase of HA/polymer mass ratio, apparently owing to an increase in viscosity of the

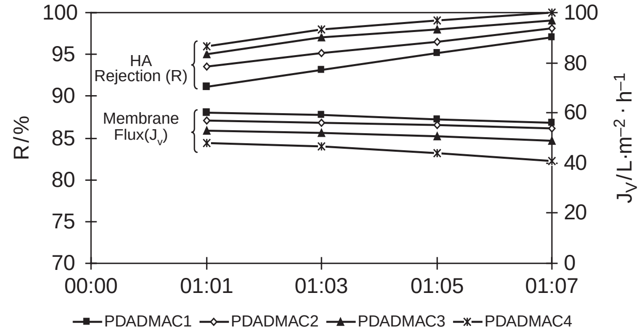

Fig. 2. The HA rejection and membrane fluxes at different HA/PDADMAC mass ratio. The initial HA concentration is 20 mg L^{-1}, Membrane PBCC 5kDa, ΔP = 0.4 MPa, pH 7.

solutions. The volume fluxes of filtration of HA/PDADMAC feed solutions are lower with increasing PDADMAC average molecular weight (Fig. 2). This is because a higher molecular weight of PDADMAC leads to a higher viscosity of HA/PDADMAC solutions.

It was found that high degrees of the HA removal (99 and 100% in the case of 200-350 kDa, average molecular weight, (PDADMAC 3) and 400-500 kDa average molecular weight (PDADMAC 4), respectively, were obtained at a HA/polymer ratio of 1:7 (20:140 mg l^{-1}) (Fig. 2). Obviously at this ratio a number of positively charged sites in polymer macromolecules are excessive for effective binding of HA molecules. The PDADMAC is a polymer whose macromolecules, due to the presence of quaternary amino groups, are capable of strong interaction with negatively charged HA molecules. Table 2 shows the HA rejection (% R), and membrane fluxes (J_v) for the different membranes at different HA/PDAMAC concentration ratios after the systems reaches the higher HA rejection.

Fig. 3 show the dependencies of the HA rejection and membrane flux degree on permeate collection for ultrafiltration of HA/PDADMAC solutions at pH values of 5, 7, and 9, through a PLGC 5kDa membrane. As can be seen, an increase in a pH value of the HA/PDADMAC feed solution from 7 to 9 leads to some decrease in HA rejection (Fig. 3(a)). This is likely because in the presence of the excessive quantity of $^{-}$OH ions the PDADMAC macromolecules gain more rigid conformation, enhancing the passage of macromolecules across the membrane, but also a reduction in HA rejection occurs at higher pH because the quaternary ammonium groups become more hydroxylated and neutralized, decreasing charge double layer thickness and hence their conformational molecular size and allowing easier passage through the membrane [13]. However, the HA rejection increases to some extent with increasing of a degree of permeate collection (Fig. 3(b)). This is obviously, due to possible formation of a self-rejected gel layer of PDADMAC macromolecules on the membrane surface. It can be anticipated that owing to the lack of protonation of the quaternary amino groups of PDADMAC, the HA removal should not change essentially in COUF process with pH alteration.

4. Conclusions

The HA removal from aqueous solutions by COUF using cationic water-soluble polymers such as PDADMAC, with different average molecular weight, was studied.

Table 2
The HA rejection (R/%) and membrane fluxes (J_v) at different HA/PDADMAC mass ratio. The initial HA concentration is 20 mg L^{-1}, ΔP= 0.4 MPa, pH 7

R/%

	PDMAC1				PDMAC2				PDMAC3				PDMAC4			
	1:1	1:3	1:5	1:7	1:1	1:3	1:5	1:7	1:1	1:3	1:5	1:7	1:1	1:3	1:5	1:7
PBCC5	91.1	93.1	95.1	97.1	93.5	95.2	96.5	98.1	95	97	98	99	96	98	99	99.9
PLGC5	89	90	91.5	92	90	92.4	93.5	95	93	948	96.7	98	94.5	95.6	97	97.5
PBCC10	70	72.4	72.5	77	75	75.6	77.1	78	78.9	81.2	83.4	85	84.1	86.2	87.8	89
PLGC10	71	72.9	73.4	76.1	74.5	76.2	78.4	79	79	81.5	84	86	85	86.7	89	90

J_v/L· m$^{-2 \cdot}$ h^{-1}

	PDMAC1				PDMAC2				PDMAC3				PDMAC4			
	1:1	1:3	1:5	1:7	1:1	1:3	1:5	1:7	1:1	1:3	1:5	1:7	1:1	1:3	1:5	1:7
PBCC5	60	59	57.5	56	57	56	55	54	53	52	50.5	49	48	46.5	44	41
PLGC5	61	60	58	57	57.5	56	54.4	53	54	53	51.5	50	49	47	45	42
PBCC10	70	69.5	67	65	68	66.5	64	62	66	64.5	63	62	63	61	58.5	55
PLGC10	80	77.5	75	73	78	76.5	75	73	77.5	74	72.5	71	70.9	68.5	67	66

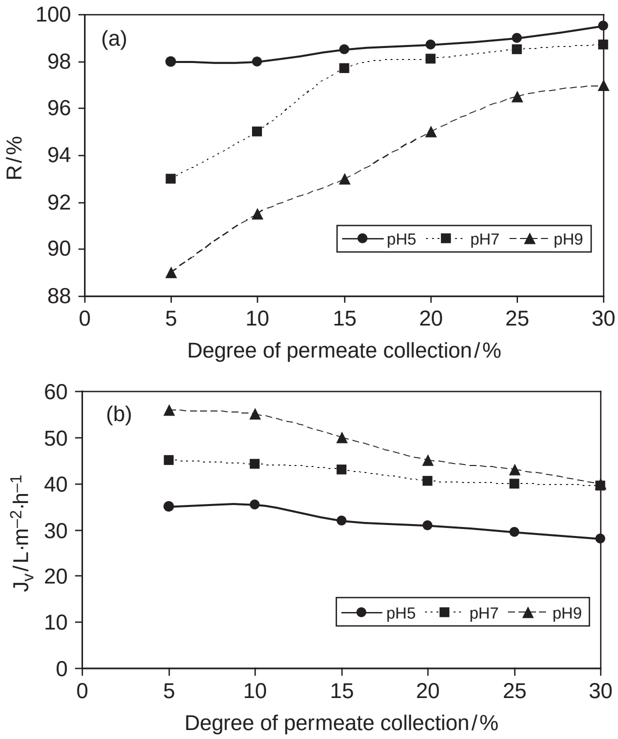

Fig. 3. Rejection of HA (a) and membrane fluxes (b) versus permeate collection at filtration of solution of HA/PDADMAC at ratio of 1:1 (20 mg L^{-1}), at different pH values through membrane PBCC5kDa, ΔP = 0.4 MPa.

The HA rejection enhanced from 71% (PLGC 10 kDa, 1:1 HA/PDADMAC1) to 99.9% (PBCC 5 kDa, 1:7 HA/PDMAC4). It was found that filtration of HA/PDADMAC feed solution the HA rejection increases as pH lowers as a result of the solute binding owing to the protonation of the quaternary amino groups of this polymer. The data obtained show a possibility to obtain a high degree of HA removal from aqueous solutions via HA binding with water soluble cationic polymers such as PDADMAC with ultrafiltration on wide-porous membranes at low (0.1–0.4 MPa) operating pressures.

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