

Effectiveness of removing humic substances from surface water in coagulation and ion exchange on MIEX-Doc resin

Katarzyna Rucka^a, Anna Solipiwko-Pieścik^a, Małgorzata Wolska^{a,b,*}

^aFaculty of Environmental Engineering, Wrocław University of Science and Technology, 27 Wybrzeże Wyspiańskiego st., 50-370 Wrocław, Poland, emails: malgorzata.wolska@pwr.edu.pl (M. Wolska), katarzyna.rucka@pwr.edu.pl (K. Rucka), anna.solipiwko-piescik@pwr.edu.pl (A.S.-Pieścik)

^bWrocław Municipal Water and Sewage Company, New Technologies Centre, Na Grobli 14/16, 50-421 Wrocław, Poland

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ABSTRACT

This study concerns the utility of the coagulation process and ion exchange on MIEX-Doc resin in removing humic substances from surface water. The coagulation process was carried out for two aluminum coagulants, that is, hydrolyzing aluminum sulfate and pre-hydrolyzed polyaluminium chloride. The coagulant dosages were determined as gram aluminum per gram carbon, thanks to which it was possible to compare the process effectiveness for different initial organic carbon concentrations, whose values were in the range of 5.9–21.51 gC/m³. The ion exchange of MIEX-Doc resin was conducted for three different dosages of 1, 2.5, and 5 cm³/L. The studies were conducted in laboratory conditions on model solutions prepared on the base of natural humus dissolved in deionized water. Humic substances were effectively removed in both process types (41.0%–62.1%, 35.2%–49.0%, and 40.2%–82.1% for pre-hydrolyzed coagulant, hydrolyzing coagulant, and MIEX-Doc resin respectively). The biodegradable fraction was mainly removed during ion exchange. During the ion exchange, substances with particle sizes of 0.5–1.2 kDa were removed, while this range for the coagulation process was 0.8–1.2 kDa. Ion exchange is an effective method of removing humic substances even at high concentrations in raw water and ensures their elimination to the level required for drinking water.

Keywords: Water treatment; Humic substances; Organic matter properties; Coagulation; Ion exchange; MIEX-Doc resin

1. Introduction

Humic substances are the main constituent of natural organic matter present in surface waters. They are characterized by a very diverse structure and particle size. However, their structure and properties have not been fully understood, and therefore they are still a subject of studies worldwide [1,2]. It has been found that they are precursors of organic chlorine disinfection products [3–6]. Studies [7] have shown that disinfection by-products generation is determined by dissolved organic carbon (DOC) content and UV₂₅₄ values as a measure of aromatic substance content. UV absorbance

measurements are used to evaluate chlorinated organic substance precursor content [8]. According to Korshin et al. [9], these precursors exhibit a much greater correlation with absorbance at a wavelength of 272 nm than at 254 nm. Previous studies have shown the effectiveness of the coagulation process in removing humic substances [10–12] where the use of pre-hydrolyzed coagulants ensures greater effectiveness of their elimination [12]. Furthermore, it was shown that depending on the properties of these substances, they may be better removed at different pH values [13]. Apart from coagulation, adsorption [14] is commonly used to remove humic substances, which ensures the removal of substances with lower molecular masses than during the coagulation process [15]. The effectiveness of adsorption depends on, above all,

* Corresponding author.

on the pore size distribution [16] and the specific surface area of the adsorption material.

Increased efficiency in the removal of low molecular weight organic substances is found in GWA beds with developed biofilm. In that situation the mechanism of pollutant removal occurs by not only adsorption but also biodegradation.

On the other hand, the use of ion exchange for removing humic substances is limited, as mainly mineral ions are removed during this process [17,18]. There are several resins, mainly anion exchange resins, dedicated to removing ionic organic substances. Resins from the MIEX group are most commonly used [19]. The use of this resin allows for the removal of organic substances of medium and small molecular mass [20], and therefore the size of removed particles coincides to a major degree with the effectiveness of the coagulation process. Due to this, the MIEX-Doc ion exchange process is sometimes used for supporting the coagulation process [21], which allows for decreasing the coagulant dosage and increasing the effectiveness of removing dissolved organic compounds. It should be noticed that the efficiency of eliminating organic substances during ion exchange depends on the type of resin used. In general, it has been shown [22], that MIEX-GOLD resin is more effective as compared to MIEX-Doc. However, the effectiveness in removing humic substances during the MIEX process has not been unambiguously determined.

Therefore, it is reasonable to compare the effectiveness of coagulation and ion exchange processes on MIEX resin in the removal of humic substances. Especially in terms of changes in the concentration of different molecular weight substances. There is little information in the literature on the effectiveness of these processes in removing humic substances of specific particle sizes. The research is important because the presence of low molecular weight substances in tap water can create risk for human health.

Therefore, it was justified to carry out studies comparing the effectiveness of these two processes concerning this main type of surface water pollution.

2. Methodology and study process

The studies were conducted in laboratory conditions on model solutions prepared on the base of a mixture of natural humus dissolved in deionized water. The mixture characterized different properties of molecular weight and structure of organic substances. In practice the content of organic carbon is different. The model solutions were prepared so that the initial organic substance content was around 5, 10, 15, and 20 mgC/dm³. Both processes were carried out on a six-station coagulator dedicated to jar tests. The processes were carried

out in 1 dm³ of water. Each test was repeated three times, with the presented results being the average values. Coagulation and ion exchange tests were carried out in parallel so that the obtained results were reliable and comparable.

By conducting the studies in laboratory conditions and on model solutions, allowing for a relatively stable room temperature for conducting the processes.

The coagulation process was carried out for two aluminum coagulants, that is, hydrolyzing aluminum sulfate (ALS) and pre-hydrolyzed polyaluminium chloride from the PAX commercial product group. In both cases, the same coagulant dosage was used, ranging from 0.3–0.5 gAl/gC (1.6–10.6 gAl/m³).

The mixing of water with the coagulant lasted for 2 min followed by a 20 min flocculation, with the rotational speed for these stages being 120 and 20 rpm respectively, followed by a 2 h long sedimentation.

The coagulant properties were presented in Table 1.

On the other hand, high selectivity for organic compounds removal of strong base resins anion exchange (MIEX-Doc resin) produced by IXOM company in Australia for organic components removal, was conducted for three different dosages of 1, 2.5, and 5 cm³/L, with a suspended resin-water contact time in the range of 5–60 min. Water samples were taken while mixing, except for the last sample. After sampling, the resin was removed from the samples with the use of a magnet. The samples were then filtered to remove the residual resin. A portion of fresh non-regenerated resin was used for each test.

For all water, the DOC concentration, UV₂₅₄ and UV₂₇₂ absorbance and watercolor at wavelengths of 340 and 410 nm were determined, after filtration by membrane filter with 0.45 μm pore size. For raw water and chosen post-process samples, pH, alkalinity, acidity, biodegradable organic carbon (BDOC) and the organic molecular size distribution were also determined. Additionally, for samples undergoing ion exchange, chloride concentrations were determined both before and after the process to assess the water salinity increase. For raw and post-coagulation water, the total organic carbon concentrations were determined. All samples after ion exchange were filtered to separate the resin.

All analysis were performed by the applicable standards and standard methods. Chromatographic analysis was performed with the use of an UltiMate 3000 Dionex liquid chromatograph, equipped with a DAD detector. The results were obtained with detection at 254 nm. A Shodex OHpak SB-803 HQ polymer column with a molecule size of 13 μm and dimensions of 8 × 300 mm was used, along with a Shodex OHpak SB-G 6B, 10 μm, 6 × 50 mm pre-column. An analysis of concentrations of molecules of a given size was performed based on changes in the peak areas in chromatographs.

Table 1
Properties of used coagulants

Coagulant	Aluminum (Al ⁺)	Chlorides (Cl ⁻)	Alkalinity	pH	Density, 20°C	Modifiers
	%	%	%	–	g/dm ³	–
PAX XL3	5.3 ± 0.3	13.0 ± 2	70 ± 5	2.5 ± 0.5	1,210 ± 40	Na ⁺ ions
ALS	4.2 ± 0.2	–	–	2.4 ± 0.5	1,310 ± 10	–

Calibration was performed with the use of polystyrene sulfonate sodium salts (PSS, American Polymer Standards Corporation) of molecular masses of 891; 1,600; 3,420; 7,420; 15,650; and 29,500 Da.

3. Results and discussion

The natural humic substances used in the study were characterized by a relatively small molecular mass as compared to those found in the literature [23], up to 1.2 kDa (Fig. 1), which significantly influenced the studied processes and their effectiveness [24].

These substances had a refractory character, as evidenced by the values of UV_{254} and UV_{272} (Table 2). The model solutions were characterized by a high color intensity, which increased with increasing humic substance concentration. In contrast to a study by Madsen-Østerbye et al. [25] a higher color intensity was found for a wavelength of 410 nm than for 340 nm. This is probably related to the low molecular mass of these substances.

An important property, which determined the low susceptibility of humic substances to being removed in water

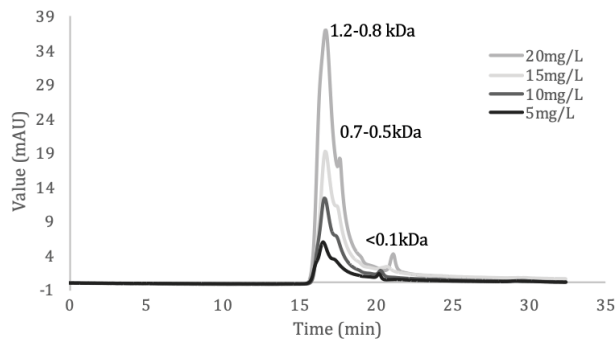


Fig. 1. Chromatograms of particle size distribution in model solutions.

treatment processes, especially coagulation [26], was a low specific absorbance in the UV light (SUVA), or specific UV absorbance value, whose value was in the range of 1.91–2.19 m^2/g .

Additionally, it should be noted that the water treatment processes are affected by the degree of biodegradability of organic substances contained in water. Among humic substances, the biodegradable fraction of dissolved organic carbon amounted to 26.3%–39.9%, or slightly higher than found in other studies [27].

Humic substances were effectively removed in both process types, and the ranges of reductions in each studied water quality indicator are presented in Table 3. The order of effectiveness in removing dissolved organic carbon in the analyzed processes is as follows: $\eta_{PAX} > \eta_{ALS}$.

The ion exchange process was more effective than coagulation in eliminating substances absorbing UV light at wavelengths of 254 nm and 272 nm, and in removing colored compounds (for color intensity determined at 340 nm).

The results that have been obtained confirm the relationships obtained by Madsen-Østerbye et al. [25]. On the other hand, with respect to color at 410 nm, very similar efficiencies were found in both processes and for both coagulants. A significant difference in the obtained effectiveness concerned specific UV absorbance. Specifically, during the coagulation process a reduction in this indicator was found in all water samples, which confirms that larger molecules are removed during this process [27]. On the other hand, during the ion exchange on MIEX resin, for the lowest resin dosage, an increase in SUVA values was found. That relation did not depend on the initial humic substance concentration and the contact time. This may testify to the significant removal of low molecular mass humic substances. With the use of larger resin dosages, this mechanism was not noticed, and the reduction in SUVA found for the majority of water samples was in the range of 0.8%–65.5%. The lack of one

Table 2
Ranges of values of studied water quality indicators

Indicator	Raw water	PAX	ALS	MIEX-Doc
TOC, g C/m ³	5.9–21.51	3.05–10.4	3.62–13.5	–
DOC, g C/m ³	5.67–21.02	2.96–10.3	3.33–13.17	1.65–19.3
BDOC, g C/m ³	2.32–6.22	0.39–2.91	0.16–2.87	1.24–5.07
Abs 254, 1/m	11.71–46.02	3.78–18.5	4.72–22.02	1.14–42.38
Abs 272, 1/m	9.56–37.59	3.0–14.58	3.8–17.44	0.98–34.86
C 410, g Pt/m ³	20.85–60.75	2.63–15.38	2.59–19.2	4.65–58.76
C 340, g Pt/m ³	11.18–42.67	2.98–14.6	3.49–16.79	1.43–40.33
SUVA, m ² /gC	1.91–2.19	1.22–2.01	1.31–1.79	0.69–2.25
pH	6.6–7.65	5.21–7.46	4.56–5.45	6.65–8.22
Alkalinity, mol/m ³	0.125–0.35	0.01–0.16	0–0.1	0.11–0.34
Acidity, mol/m ³	0.06–0.09	0.05–0.25	0.12–1.0	0.025–0.06
Chloride, g Cl/m ³	100–412	–	–	103.5–448
Molecular size 1.2–0.8 kDa, g/m ³	3.2984–31.92	0.328–21.521	0.324–13.244	0.004–6.6923
Molecular size 0.7–0.5 kDa, g/m ³	1.2205–8.178	0.596–4.774	0.291–5.583	0.017–5.5635
Molecular size > 0.1 kDa, g/m ³	0.0738–0.438	0.07026–0.399	0.06834–0.342	0.052–0.171

Table 3
Ranges of effectiveness in improving water quality indicators in coagulation and ion exchange processes

Indicator	Effectiveness of indicator reduction		
	PAX	ALS	MIEX-Doc
TOC, %	38.83–62.12	25.87–48.33	–
DOC, %	41.0–62.1	35.2–49.0	40.2–82.1
BDOC, %	0–77.2	0–96.1	18.3–65.9
Abs 254, %	45.9–71.4	52.2–59.7	38.4–91.1
Abs 272, %	53.7–72.0	53.6–60.4	38.7–91.1
C 410, %	68.2–87.4	68.4–87.6	37.9–84.9
C 340, %	59.1–82.1	60.7–74.1	38.2–91.4
SUVA, %	8.2–39.1	13.2–34.7	–27.5*–65.5

* increase in value

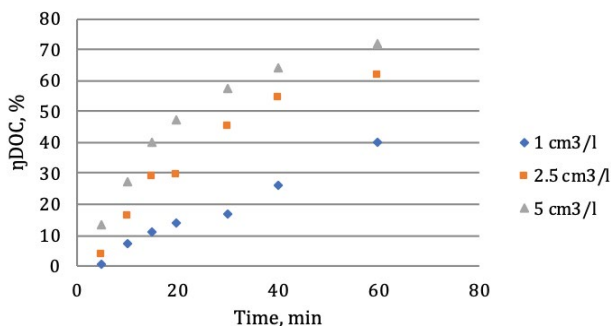


Fig. 2. Effectiveness of DOC removal with respect to resin dosage and resin-water contact time (for an initial concentration of 5 gC/m³).

unambiguous direction of change testifies to the removal of molecules of various sizes.

During the ion removal process, an increase in the effectiveness in removing dissolved organic carbon with increasing resin dosage and resin-water contact time was found (Fig. 2). This relationship was found for each of the initial concentrations.

However, such a relationship was not found for the coagulation process, which resulted from insufficiently effective sedimentation of post-coagulation suspensions.

Changes in the BDOC concentrations during the coagulation process were ambiguous. This confirms the results of another study [28], which found that during coagulation, substances of the lowest molecular mass are not removed or removed to an insignificant degree. On the other hand, during the ion exchange process, an increase in the removal of BDOC was found with increasing contact time (Fig. 3). However, only increasing the resin dosage from 2.5 to 5.0 cm³/L increased the removal effectiveness of the biodegradable fraction.

During the ion exchange process, non-biodegradable substances were also removed with greater effectiveness, which is characterized most often by a larger molecular mass and absorbs UV light. During the coagulation process, the non-biodegradable fraction was also removed with large effectiveness (Table 2). This means that ion exchange

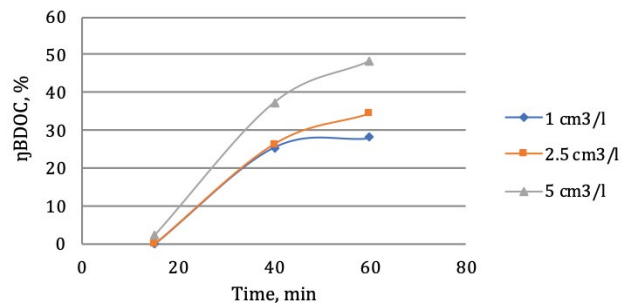


Fig. 3. Effectiveness of removing BDOC during the ion exchange process (for an initial concentration of 15 gC/m³).

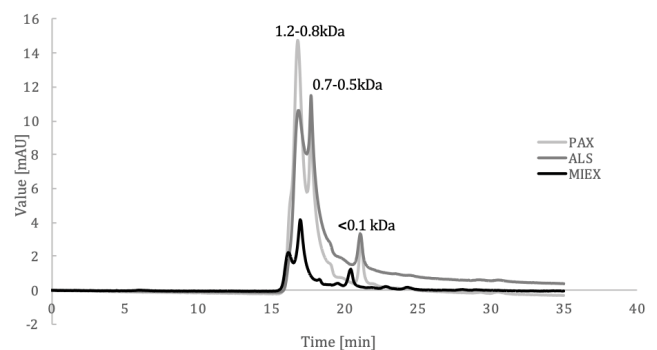


Fig. 4. Chromatograms of molecular mass distribution in water after coagulation (dosage of 0.5 gAl/gC) and ion exchange (dosage 5 cm³/L 60 min contact time).

provides greater effectiveness in removing the humic substance of varied molecular masses, allowing for the simultaneous removal of both biodegradable and non-biodegradable substances [19]. A consequence of this was a significant decrease in the number of substances of molecular masses in the range of 0.5–0.7 kDa and 0.8–1.2 kDa. However, the coagulation process mainly removed substances with molecular masses of 0.8–1.2 kDa (Fig. 4).

A consequence of removing humic substances of mainly a large molecular mass in both processes was the increase in the biodegradable fraction in dissolved organic carbon in 94.4%, 45% and 65% of samples for ion exchange, coagulation with pre-hydrolyzed coagulant and coagulation with ALS respectively. Differences in the percentages of this fraction result from differences in removing dissolved organic carbon (Table 2).

For both processes, colored substances dominated among the removed humic substances, which is confirmed by the relationship between DOC removal effectiveness and water-color measured at a wavelength of 340 nm (Fig. 5).

The fact that irrespective of the initial humic substance content, it was possible to decrease their concentrations to acceptable values in the studied range of dosages and contact times testifies to the utility of the ion exchange process as compared to the coagulation process (irrespective of the coagulant used). On the other, obtaining acceptable values of DOC (lower than 4 gC/m³) required the use of coagulant dosages much greater than those used in practice. This

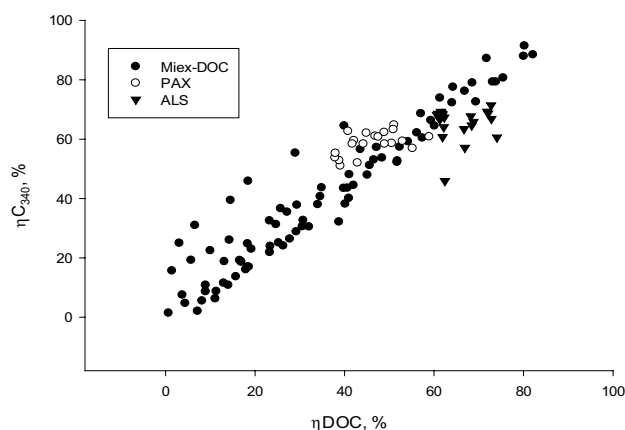


Fig. 5. Relationship between the effectiveness of removing dissolved organic carbon and color intensity.

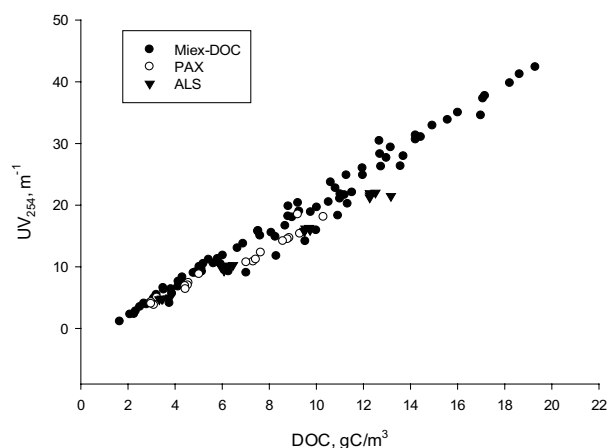


Fig. 6. Relationship between dissolved organic carbon content and UV_{254} absorbance in water subjected to coagulation and the ion exchange processes.

may be unachievable effectiveness increases insignificantly. Furthermore, the use of high dosages of aluminum coagulants carries a risk of a significant increase in residual aluminum concentrations [29].

Among the dissolved organic substances present in treated water, refractive compounds dominated irrespective of the process used, as shown by the relationship between DOC and UV_{254} (Fig. 6). An analogous relationship was found for color measured at a wavelength of 340 nm, which corresponds to the maximum absorbance of large molecular mass humic substances [30].

The relationships that were found only confirm that despite the lowering of humic substance concentrations, colored refractive compounds still dominate.

4. Conclusions

- Both coagulation and ion exchange allows the removal of humic substances, but ion exchange on MIEX-DOC resin is more effective.

- The effectiveness of removing humic substances increased with increasing resin dosage, contact time and the initial humic substance concentration. During the coagulation process, an increase in process effectiveness was found with increasing coagulant dosage but not with increasing initial concentrations of humic substances.
- Among the removed humic substances, refractive and colored compounds were most effectively removed, being the largest percentage of all organic compounds.
- The biodegradable fraction was mainly removed during ion exchange.
- Irrespective of the process used, the effectiveness of removing organic compounds was directly proportional to the decrease in the color intensity of the solution.
- During the ion exchange, substances with particle sizes of 0.5–1.2 kDa were removed, while this range for the coagulation process was 0.8–1.2 kDa.
- Ion exchange is an effective method of removing humic substances even at high concentrations in raw water and ensures their elimination to the level required for drinking water.

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