



Effectiveness of humic substance removal during the coagulation process

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Abstract

This study concerns the utility of the coagulation process in removing humic substances and its dependence on the properties of these substances and their concentrations. The coagulation process was performed on model solutions of natural humic acids. Polyaluminum chloride (PAX XL3) and aluminum sulfate were used for this study, which allowed for a comparison of the effectiveness of pre-hydrolyzed and hydrolyzing coagulants. 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 5.51–21.23 gC/m³. The obtained values of reductions in organic carbon concentrations point to a significant process effectiveness (37.2–59.4% and 20.0–41.5% for pre-hydrolyzed and hydrolyzing coagulants, respectively), which increased with increasing molecular mass of the humic substances present in water. These results are analogous to those found for coagulation of surface waters and point to a greater effectiveness of pre-hydrolyzed coagulant in removing humic substances (at the same coagulant dosage). The effectiveness in removing organic substances increased with coagulant dosage and the initial total organic carbon concentration. The coagulation process most effectively removed aromatic substances absorbing UV light. The content of substances absorbing UV light in raw and post-coagulation water was proportional to the dissolved organic carbon content.

Keywords Water treatment · Humic substances · Organic matter properties · Coagulation

1 Introduction

Surface waters are one of the basic drinking water sources, and therefore their treatment is the subject of many studies all over the world. Among all the surface water contamination, the most attention is paid to organic substances [1, 2]. The main group of organic contamination in surface water are humic substances, whose structure is very diverse and has not yet been unambiguously determined [3, 4]. They make up about 90% of all organic substances in surface waters and in general are made up of large-molecule substances, such as humic acid, fulvic acids and humines [3, 5].

Humic substances, being organic substances, may pose a danger to human health. There are no toxic effects on the human body attributed to them; however, they may undergo chemical transformations during water treatment, and therefore, their removal is necessary. They are, in fact, precursors of organochlorides [6–9]. The coagulation process is commonly used for removing humic substances from water [10, 11], and increasing its effectiveness is obtained by the use of electrocoagulation [12–14] or other modifications connected with increasing coagulant effectiveness [15–17]. Satisfactory effects in removing humic substances have been found with the use of natural coagulants, such as powdered added sea bream, or powdered *Moringa oleifera* fruits [18, 19]. Studies have shown

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that aluminum coagulants are more effective in removing humic compounds than iron coagulants [20]. Additional removal of humic substances is ensured by chemical oxidation and advanced oxidative processes [21–23], which results from the mineralization of these substances or a transformation of their structure. Thanks to this, substances are obtained that have a lower potential to react with chlorine.

Unfortunately, depending on the humic substances present in water and the coagulants that are used, a different removal effectiveness is obtained. This means that the chemical properties of chemical compounds in the mixture have an effect on the coagulation process and its effectiveness. Therefore, it is justifiable to perform studies to determine the utility of the coagulation process in removing humic substances as a function of the chemical properties of these substances and their concentration.

2 Object and methods of study

A model solution of concentrated natural humic acids from a mountain river was used for this study. The concentration of organic carbon in the concentrated solution amounted to 1880 gC/m³. Through dilution of the basic solution with demineralized water, four solutions of differing organic carbon concentrations were obtained, with values of approximately 5 gC/m³, 10 gC/m³, 15 gC/m³ and 20 gC/m³. The actual organic carbon concentrations differed slightly from the intended ones, which is due to the natural source of these humic acids and the large-molecule nature of humic substances. The prepared solutions were characterized by a low alkalinity (0.11–0.39 mol/m³), a pH in the range of 6.36–7.46 and an acidity of 0.1 mol/m³.

For studies of the effectiveness of removing humic substances in the coagulation process, pre-hydrolyzed polyaluminum chloride and non-hydrolyzed (hydrolyzing) aluminum sulfate (ALS) were used, whose characteristics are presented in Table 1.

Coagulant dosages were defined in terms of grams aluminum per gram carbon, which allowed for a comparison of process effectiveness with different initial humic substance contents. Five dosages were used: 0.3 gAl/gC, 0.35 gAl/gC, 0.4 gAl/gC, 0.45 gAl/gC and 0.5 gAl/gC. The coagulation process was performed in laboratory conditions (breaker tests), with the use of a VELP Scientifica

flocculator. The tests were performed in 1 dm³ of water. Rapid mixing was performed for 2 min with a speed of 200 rev/min, followed by 20 min. slow mixing at a speed of 15 rev/min. The samples underwent sedimentation for 2 h, after which 700 cm³ of water was decanted for analysis.

For all raw and post-coagulation water samples, pH, general alkalinity and acidity, color at wavelengths of 410 nm and 240 nm, UV₂₅₄ and UV₂₇₂ absorption, total organic carbon (TOC), dissolved organic carbon (DOC) and biodegradable dissolved organic carbon (BDOC) concentrations were determined. Based on the obtained results, the SUVA value was calculated. Raw and chosen post-coagulation water samples also underwent molecular size analysis via Selective Exclusion Chromatography (SEC). The water quality analysis was performed in accordance with norms currently in force in Poland. A list of norms and methods is presented in Table 2.

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 of the peak areas in chromatographs. Calibration was performed with the use of polystyrene sulfonate sodium salts (PSS, American Polymer Standards Corporation) of molecular masses of 891, 1600, 3420, 7420, 15,650 and 29,500 Da.

3 Results and discussion

Water undergoing the coagulation process contained only humic substances, whose organic carbon content was in the range of 5.51–21.23 gC/m³ (Table 3).

The majority of the organic substances in humic substances occurred in dissolved form, whose fraction in TOC was in the range of 96.7–99.5%. Humic present in solutions determined the concentrations of total and dissolved organic carbon, which was proportional to color measured at 410 nm and UV₂₅₄ and UV₂₇₂ absorbance (Fig. 1). Despite the fact that according to Baker [24] humic substances cause the greatest increase in absorbance at a wavelength of 240 nm, no correlation was found between

Table 1 Properties of used coagulants

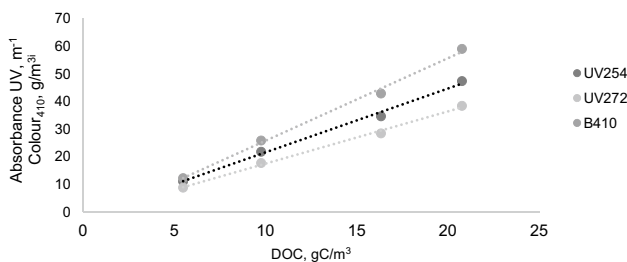
Coagulant	Aluminum (Al ³⁺) %	Chlorides (Cl ⁻) %	Alkalinity %	pH –	Density, 20 °C g/dm ³	Modifiers –
PAX XL3	5.3±0.3	13.0±2	70±5	2.5±0.5	1210±40	Na ⁺ ions
ALS	4.2±0.2	–	–	2.4±0.5	1310±10	–

Table 2 List of norms used for the determination of water quality parameters

Indicator	Unit	Method of determination	Norm
pH		Potentiometric	ISO 5969
Alkalinity	mol/m ³	Titration	PN-EN ISO 9963-1:2001
Acidity	mol/m ³	Titration	PN-C-04540-02:1990
Color at 410 nm	g Pt/m ³	Spectrophotometric	PN-EN ISO 7887:2011
Color at 340 nm	g Pt/m ³	Spectrophotometric	PN-EN ISO 7887:2011
Turbidity	NTU	Nephelometric	PN-EN ISO 7027:2003
UV ₂₅₄	1/m	Spectrophotometric	PN-C-04572:1984
UV ₂₇₂	1/m	Spectrophotometric	PN-C-04572:1984
OWO	g C/m ³	Thermal	PN-ISO 7827:2001
RWO	g C/m ³	Thermal	PN-ISO 7827:2001
BRWO	g C/m ³	Modified van der Kooij	Standard methods
Molecular size distribution		SEC	Standard methods

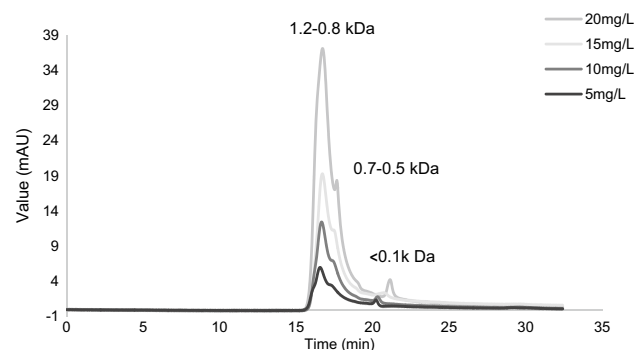
Table 3 Ranges of values of studied water quality indicators

Indicator	Unit	Raw water	PAX	ALS
OWO	gC/m ³	5.51–21.23	3.05–10.4	3.62–13.5
RWO	gC/m ³	5.48–20.77	2.96–10.3	3.33–13.17
BRWO	gC/m ³	1.57–3.17	0.9–2.91	0.16–6.14
C 410	gPt/m ³	12.26–59.1	2.62–15.38	2.74–19.2
C 340	gPt/m ³	9.82–42.99	2.98–14.6	3.48–16.79
Abs 254	1/m	11.08–47.42	3.78–18.5	4.72–22.02
Abs 272	1/m	8.82–38.48	3.0–14.58	3.8–17.44
pH		6.36–7.46	5.21–7.03	4.56–5.45
Alkalinity	mol/m ³	0.11–0.39	0.01–0.16	0–0.1
Acidity	mol/m ³	0.1	0.05–0.25	0.12–1.0
Molecular size 1.2–0.8 kDa	g/m ³	3.298–31.924	0.328–21.521	0.324–13.244
Molecular size 0.7–0.5 kDa	g/m ³	1.22–8.178	0.596–4.774	0.291–5.583
Molecular size > 0.1 kDa	g/m ³	0.07383–0.4383	0.07026–0.3999	0.06834–0.3424

**Fig. 1** Relationship between dissolved organic carbon and absorbance and water color

the amount of these substances (measured as DOC) and the color intensity measured at this wavelength.

A large UV₂₅₄ absorbance value testifies to the presence of chlorinated organic substance precursors [25, 26], which must be removed from water due to the hazard to health that they may present after disinfection with chlorine. On the other hand, a SUVA value of 2.02–2.28 m²/g testifies to the low susceptibility of organic substances to

**Fig. 2** Chromatograms of organic substance content in raw water

removal during the coagulation process [27]. The molecular size of humic substances in raw water was in the range of 0.01–1.2 kDa (Fig. 2). Among humic substances, the large-molecule fraction dominates [28–30]; however, in the studied water the molecular sizes were significantly smaller than found in other studies.

Additionally, it must be noticed that among dissolved organic substances, the biodegradable fraction (substances of a low molecular mass) [31] made up 14.9–31.3% of TOC. The larger participation of biodegradable dissolved organic carbon than that found in natural waters [32] would also indicate a limited potential for these substances to be removed via the coagulation process.

The results that have been obtained indicate a large effectiveness of the coagulation process in removing humic substances, which for TOC was in the range of 37.2–59.4% and 20.0–41.5% for pre-hydrolyzed and hydrolyzing coagulants, respectively.

The effectiveness in reducing total organic carbon content that was found is analogous to that found for coagulation of surface waters [33, 34] and indicates a greater effectiveness of pre-hydrolyzed coagulant in removing humic substances (at a given dosage). In general, the effectiveness in removing organic substances irrespective of the used coagulant increased with increasing coagulant dosage and the initial total organic carbon concentration (Fig. 3).

A consequence of removing total and especially dissolved organic carbon was a decrease in UV_{254} and UV_{272} absorbance and the SUV_a value (Table 4).

For all analyzed indicators, a greater effectiveness of pre-hydrolyzed coagulant was found. This difference was greater with increasing initial organic substance concentrations in raw water and increasing coagulant dosage. Only for raw water with an initial concentration of 5 gC/m³-at a dosage of 0.3 gAl/gC, a greater effectiveness of the ALS coagulant was found. This may be connected to an insufficient pre-hydrolyzed coagulant dosage or may be due to an analysis error. Higher efficacy of pre-hydrolyzed coagulants was confirmed by other studies [25, 35]. It is results of low-sensitivity pre-hydrolyzed coagulants for water temperature changes.

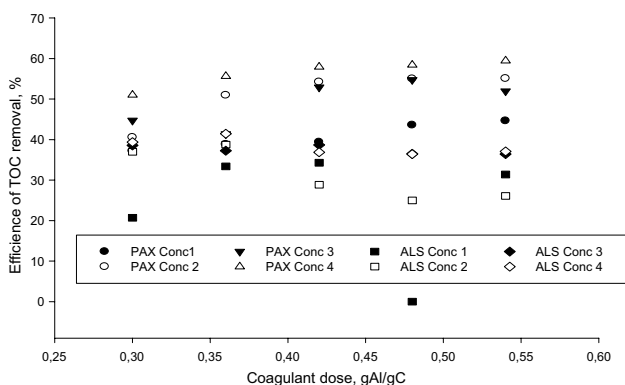


Fig. 3 A comparison of the effectiveness in removing total organic carbon

Table 4 Effectiveness in reducing water quality indicators

Indicator	Unit	Effectiveness of indicator reduction	
		PAX	ALS
TOC	%	37.2–59.4	20.0–41.5
DOC	%	41.1–58.7	30.8–41.9
BDOC	%	0–71.5	0–94.1
Abs 254	%	46.7–70.8	53.0–57.4
Abs 272	%	54.3–71.4	54.3–59.2
SUV	%	8.2–39.1	13.2–34.7
C 410	%	60.2–84.5	67.5–80.0
C 340	%	55.1–82.2	60.9–77.1

For the pre-hydrolyzed coagulant, the effectiveness in reducing UV_{272} and UV_{254} absorbance was found, and color at 340 nm was proportional to the reduction in DOC concentration (Fig. 4). No such relationship was found for color at 410 nm, which corresponds to absorption by humic substances to a much smaller degree [24].

For the hydrolyzing coagulant, no such relationship was found in any of the studied absorbances. Despite this, the values of UV_{254} , UV_{272} absorbances and color at 340 nm and 410 nm after the coagulation process were proportional to the dissolved organic carbon content. Irrespective of the coagulant type, even at dosages of 0.3 gAl/gC, the coagulation process ensured a reduction in organic substances that have an effect on water color and which absorb UV radiation. Regardless of coagulant dosage, no significant reduction of SUV_a values was found, which were in the ranges of: 0.12–0.80 m²/g and 0.43–0.71 m²/g, respectively, for pre-hydrolyzed and hydrolyzing coagulants. No unambiguous effect of coagulant dosage or the initial organic substance concentration on the magnitude of changes of this indicator was found. This confirms the fact that organic substances of low molecular mass are not significantly removed

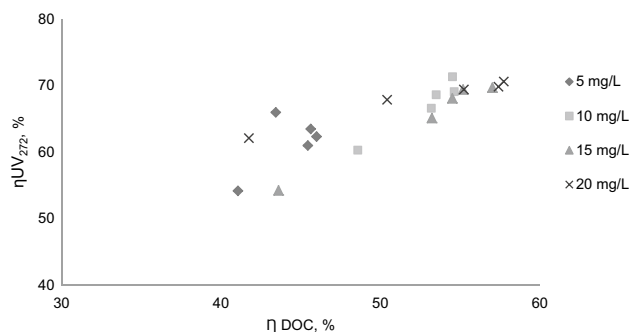


Fig. 4 Relationship between DOC reduction effectiveness and UV_{272} absorbance

during the coagulation process. During the coagulation process, substances of the highest molecular mass were most effectively removed (Table 4). Differences in the effectiveness of the coagulants in reducing organic substances of a given size depended above all on the organic substance concentration in raw water (Fig. 5a, b). Volk et al. [36] have similar conclusion, although they research the molecular size distribution during ultrafiltration process.

For water with a low humic substance content, the effectiveness of removing molecules of sizes 0.8–1.2 kDa and 0.5–0.7 kDa was the same for both coagulants. However, at a TOC initial concentration of 20 mg/L, a greater effectiveness of removing large-molecule organic substances was found for the pre-hydrolyzed coagulant. Irrespective of the coagulant type and dosage, the coagulation process did not have an effect on molecules smaller than 0.1 kDa. This is confirmed by the insignificant reduction in BDOC (Table 4).

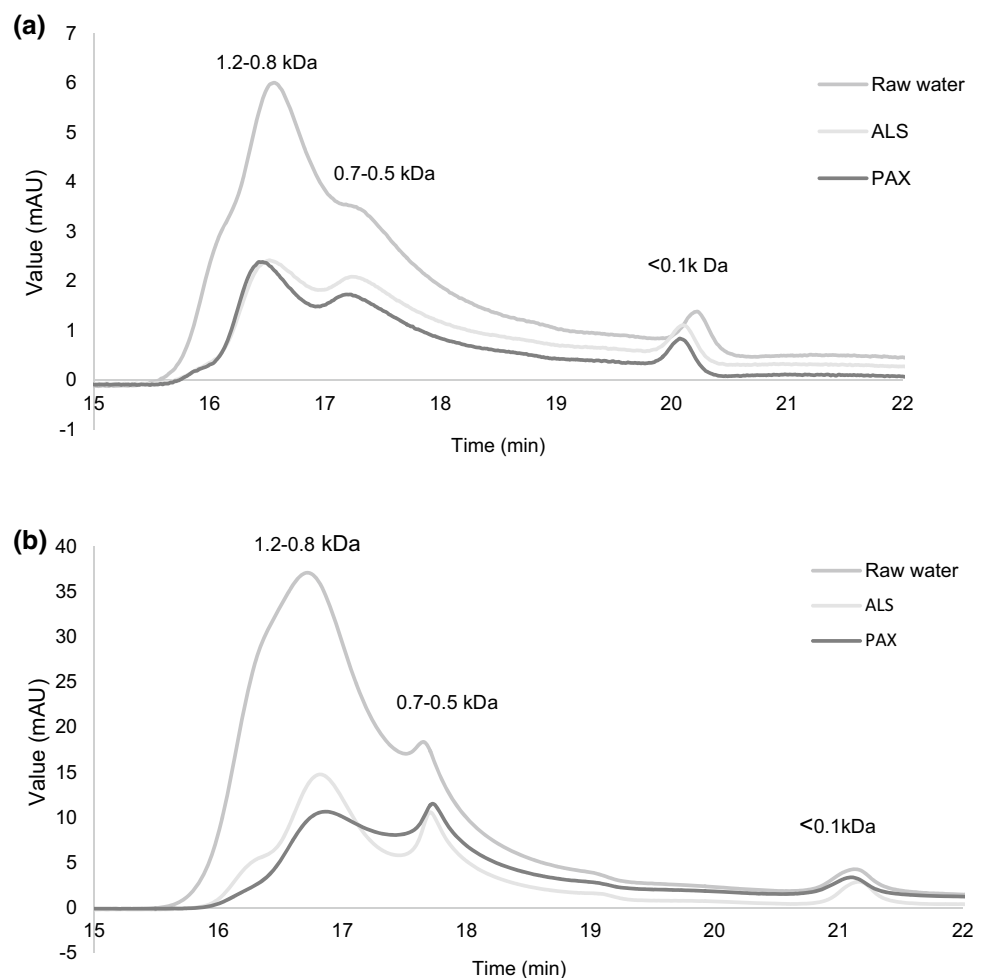
4 Conclusions

Among the humic substances dominated by the color-causing water and substances absorbing UV light. This confirms the established relationship between the values of these parameters and DOC.

The effectiveness in removing organic substances during the coagulation process increases with increased molecular mass of substances present in water and increase in TOC concentration in fresh water. The efficiency of humic substances removal during coagulation with pre-hydrolyzed coagulant was greater than the hydrolysis coagulant one. During the coagulation process, aromatic substances absorbing UV light are most effectively removed.

The absorbance at 340 nm more closely corresponds to removal of humic substances than absorbance at 410 nm. The DOC removal efficiency was proportional to UV_{254} , UV_{272} and color 340 removal efficiency. The UV absorbing substance content in water before and after

Fig. 5 Chromatogram of molecular size distribution for an initial concentration of **a** 5 mg/L **b** 20 mg/L (coagulant dosage of 0.5 gAl/gC)



coagulation is proportional to the dissolved organic carbon concentration.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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