Optimization of Humic Acids Coagulation with Aluminum and Iron(III) Salts

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Abstract

Humic substances contained in ground and surface waters increase the degree of their pollution, give it a specific colour and contribute to the formation of toxic disinfection by-products in the process of water treatment. Coagulation is an effective method of removing organic compounds, including humic acids (HA), from water and wastewater. The proper selection of coagulants and optimization of such parameters as coagulant dose and the pH of the solution enable improvement of coagulation efficiency.

The objective of the present study was to determine the efficiency of humic acids removal by coagulation, depending on the dose of Al and Fe(III) salts and pH of the analyzed solutions. A model alkaline solution and 0.2 M solutions of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ were used. The experiment was performed with and without pH adjustment, by a standard jar test procedure. COD-Cr [mg $O_2 \cdot dm^{-3}$], colour – PtCo [mg·dm^{-3}], turbidity – FTU [mg·dm^{-3}], suspended solids – SS [mg·dm^{-3}], pH and streaming potential – SP [mV] were determined during coagulation tests.

In the solutions coagulated without pH adjustment and with the optimum doses of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$, COD was at a level of 0.1 to 3% of the initial value and colour was removed almost completely. Iron(III) sulfate was found to be slightly more effective as a coagulant, in respect to COD removal. The results of electrokinetic measurements showed that the charge of molecules of humic colloids depends on the type and concentration of coagulating salt, as well as on the pH of the solution. The analysis of coagulation with pH adjustment revealed that there exists the optimum value of pH for each of the salt doses applied in the experiment. Coagulation with the use of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ proceeded at pH < 5.8 and pH < 4.2, respectively. A decrease in the pH of an HA solution allowed us to considerably (even eight-fold) reduce the dose of coagulants, maintaining high (above 94%) efficiency of humic acid removal by coagulation.

Keywords: coagulation, humic acids, aluminum salts, iron(III) salts.

Introduction

Humic substances are natural components of the aquatic environment and perform a number of important functions in the circulation of organic and inorganic matter [1, 2]. Among the numerous sources of humic substances contained in water, particular attention should be paid to soils in the catchment basins of water bodies and bottom deposits, where biochemical decomposition of organic matter takes place. The proportion of humic substances in the total organic carbon content of ground and surface water may reach even 71.4 to 82.5% [3].

The presence of dissolved organic matter in water often stands in contradiction to economic, sanitary and a esthetic requirements. Organic substances, such as humic acids, lignins or synthetic dyes, dissolved in solutions with a high pH, can be found in the natural environment

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[4], in pulp and paper mill effluents [5] and in textile industry wastewater [6]. Dissolved organic substances affect the values of such parameters as COD, BOD_5, suspended solids and colour, thus deteriorating water quality. Humic substances constitute a potential source of energy and carbon for microbes dwelling in domestic and municipal water as well as in water pipes [7]. They may also be a source of water disinfection by-products, including chlorinated organic compounds like trichloromethane, chloroacetic acids and aldehydes [8, 9], posing a direct health threat to people drinking contaminated water.

Chemical oxidation is one of the methods employed for water and wastewater treatment. Readily assimilable carbon compounds are produced in water during this process. These compounds stimulate the occurrence of such undesirable phenomena as water quality deterioration in drinking water networks and increased corrosiveness of the system [10]. An alternative to chemical oxidation may be physicochemical treatment, i.e. sorption or colloid destabilization by way of chemical coagulation. Those methods have been classified by the US Environmental Protection Agency as the best available techniques (BAT) for the control of disinfection by-products in drinking water [11]. Compared to sorption, coagulation is distinguished by higher simplicity and efficiency [12]. Coagulation, in contrast to sorption with the use of solid phase packing material, can be carried out without the need to rinse and regenerate the adsorbent or dispose of the used adsorbents. The efficiency of treatment by coagulation may be improved through the proper selection of coagulants and optimization of the process parameters, of which the key ones are coagulant dose and the pH of the solution [13]. The above parameters can be optimized based on physicochemical measurements performed on samples of solutions subjected to standard jar tests [14].

The objective of the present study was to optimize the process of coagulation as well as to determine the efficiency of humic acid (HA) removal from a model alkaline solution with aluminum sulfate and iron(III) sulfate, depending on coagulant dose and the pH of the analyzed solutions.

Materials and Methods

A model solution of humic acids was used. 1 dm^3 of the solution contained 500 mg of humic acids (Fluka). The analytical sample of humic acids was dried to constant mass at 50°C, dissolved in 100 cm^3 of 0.1 M NaOH and diluted to 1 dm^3 with redistilled water. The solution was kept in nitrogen atmosphere.

The humic acids solution was coagulated with solutions of aluminum sulfate and iron(III) sulfate at a concentration of 0.2 $mol \cdot dm^{-3}$, prepared from $Al_2(SO_4)_3 \cdot 18 H_2O$ extra pure (Fluka) and $Fe_2(SO_4)_3 \cdot nH_2O$ p.a. (Fluka), respectively.

Coagulation efficiency was determined by a jar test procedure, using 200 cm^3 of humic acids solution. 1 min.

Table 1. Characteristics of a model solution of humic acids.

pH	11.96 ± 0.02
Electrolytic conductivity [$\mu S \cdot cm^{-1}$]	1285 ± 15
Colour – PtCo [$mg \cdot dm^{-3}$]	795 ± 12 (dilution 1:25)
Turbidity – FTU [$mg \cdot dm^{-3}$]	91 ± 5 (dilution 1:25)
Suspended solids – SS [$mg \cdot dm^{-3}$]	289 ± 24
COD [$mgO_2 \cdot dm^{-3}$]	795 ± 10

of rapid mixing (300 rpm) was followed by 10 min. of slow mixing (30 rpm) and 1 h of sedimentation. Indicators of pollution, i.e. COD-Cr [$mg\ O_2 \cdot dm^{-3}$], colour – PtCo [$mg \cdot dm^{-3}$], turbidity – FTU [$mg \cdot dm^{-3}$] and suspended solids – SS [$mg \cdot dm^{-3}$] [15, 16], as well as pH and streaming potential -SP were determined in the coagulated solution. A PCD 03 detector (Mütek Analytic Gmbh) and a HI-9025C pH-meter (Hanna Instruments) were used.

Humic acid solutions with and without pH adjustment were analyzed. The doses of reagents used in the experiment were converted into 1 dm^3 of the model humic acids solution. Coagulation tests without pH adjustment were conducted using increasing doses of coagulants (0.2-2.4 $mmol \cdot dm^{-3}$). Coagulation tests with pH adjustment were carried out using coagulant doses, which did not induce coagulation in tests without pH adjustment. A series of experiments was performed for a specified dosage of coagulant to establish the optimum pH level. In samples of the humic acids solution pH was adjusted with 0.2 M solutions of H_2SO_4 or NaOH. The samples were acidified or alkalized prior to the addition of the coagulant, and final pH was determined after coagulation.

Results and Discussion

The process of humic acid coagulation with aluminum salts and iron(III) salts, without pH adjustment, is presented in Figs. 1 and 2, respectively.
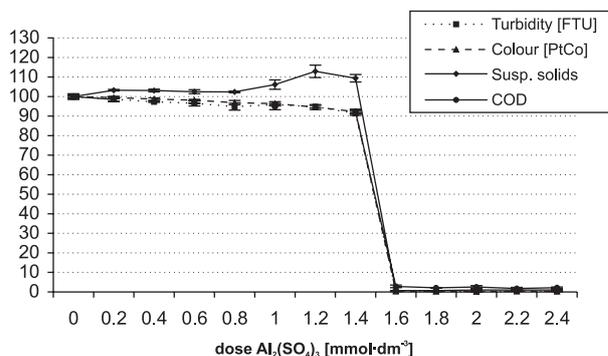

Fig. 1. Changes in the values of pollution indicators for a HA solution, depending on the dose of aluminum sulfate, expressed as a percentage in relation to the initial model HA solution.
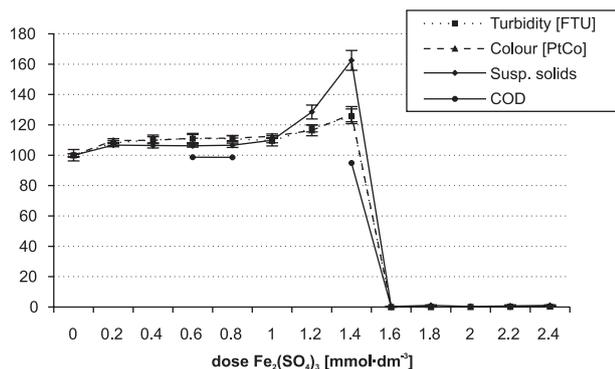
Fig. 2. Changes in the values of pollution indicators for an HA solution, depending on the dose of iron(III) sulfate, expressed as a percentage in relation to the initial model HA solution.

Figs. 1 and 2 show that the doses of both coagulants, ranging from 0.2 to 1 mmol·dm⁻³, had no significant effect on changes of the values of pollution indicators. Doses in a range of 1–1.4 mmol·dm⁻³ caused an increase in the content of suspended solids by around 10% and 60% in the case of aluminum salts and iron(III) salts, respectively. Iron(III) sulfate applied at a dose of 1.4 mmol·dm⁻³ also caused a percentage increase of colour by approximately 25%, compared to the initial value. The dose of both aluminum salt and iron(III) salt equal to 1.6 mmol·dm⁻³ caused precipitation and a rapid decrease of the values of the analyzed indicators.

According to Bryan et al. [17], two doses of metal ions are significant for humic acid coagulation, namely threshold values of aggregation and precipitation. The use of the threshold dose of aluminum salt (1.4 mmol·dm⁻³) for coagulation of humic substances causes an increase in turbidity. This results from the fact that particles enlarge during aggregation, but the size they reach does not permit the sedimentation of suspended solids [18]. This phenomenon affects the values of colour, turbidity and suspended solids. The presence of iron(III) ions contributes also to the formation of coloured organic complexes of iron, and to the intensification of the colour of the solution [19]. The removal of COD and other pollutants is the consequence of precipitation at higher doses of coagulants.

The maximum reduction in colour, to respectively 0.3% and 0.03% of the initial value, was observed following the application of 1.6 mmol·dm⁻³ of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$. The values of the physical characteristics of water (colour, turbidity, suspended solids) decreased to a comparable degree. COD in coagulated samples remained at a somewhat higher level, i.e. 3% for $Al_2(SO_4)_3$ and 0.1% for $Fe_2(SO_4)_3$. Since a further increase in coagulant dose did not significantly improve the overall efficiency of coagulation, 1.6 mmol·dm⁻³ was assumed to be the optimum dose, permitting maximum pollutant removal, as reflected in the values of COD, colour [PtCo], turbidity [FTU] and suspended solids.

High efficiency (approx. 90%) of humic acid coagulation in model solutions with aluminum salts and iron(III)

salts was also confirmed by other authors [20, 21]. Jiang and Graham [22] demonstrated that during coagulation of substances contained in surface water the values of the analyzed parameters decrease in the following order: colour [PtCo] > absorbance (UV_{254}) > dissolved organic carbon (DOC).

Organic matter removal from water depends on several factors, including the nature of dissolved organic substances, the concentration of dissolved organic matter, the type and dose of coagulants, as well as the pH of the solution [13]. Wall and Choppin [23] reported that the efficiency of coagulation increases along with a rise in the concentration of humic acids in treated water. Research results show that iron coagulants are slightly more effective in respect to COD removal than aluminum coagulants. According to Massion et al. [24], iron and aluminum coagulants react differently with organic matter in water. Świderska-Bróż [25] found that Fe^{3+} ions or the hydrolysis products of iron(III) salts interact more strongly with humic acids, compared to Al^{3+} ions. Kaiser [26] demonstrated that the ability to bind organic ligands in surface water increases as follows: $Ca^{2+} < Al^{3+} < Fe^{3+}$.

The process of humic acid coagulation is affected by various reactions such as hydrolysis, formation of complex compounds or adsorption [27]. Those reactions are accompanied by changes in the electric charge of interacting particles, which in turn determines the values of such parameters as zeta potential, electrophoretic mobility and streaming potential (SP) [28]. A fully automated method for measuring streaming potential can also be employed to determine the isoelectric point of the system, and to estimate the amounts of reagents (flocculants, coagulants) required to neutralize the charge of colloids [28, 29].

The curves in Fig. 3 represent changes in the values of streaming potential (SP), accompanied by changes in the pH of the solution, depending on the dose of aluminum sulfate. The initial value of SP was approximately –1270 mV. Coagulant doses in a range of 0-0.8 mmol·dm⁻³ changed the value of SP to approximately -1470 mV. In the case of aluminum salt the changes in SP corresponded
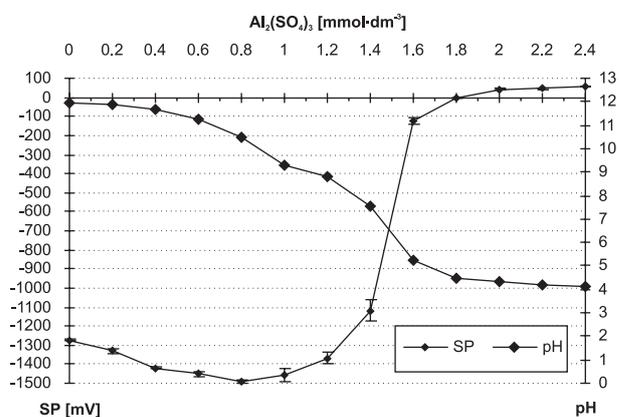

Fig. 3. Changes in the streaming potential and pH of a model HA solution, depending on the dose of aluminum sulfate.

to a decrease in pH from around 12 to 10.45. Salt doses in a range of 1-1.6 mmol dm^{-3} caused a decrease in pH from 9.3 to 5.4 and a significant change in streaming potential, to -126 mV at the dose of 1.6 mmol·dm^{-3}.

The decrease in pH observed as the initial coagulant doses were introduced into the solution resulted from the neutralization of sodium hydroxide. At the same time the reactions of salt hydrolysis proceeded in the solution. The charge of hydrolysis products depends on the degree of salt hydrolysis. At assumption of simplified scheme of reactions of salt hydrolysis, the obtained products may be $Al(OH)_3$ as well as Al^{3+}, $Al(OH)^{2+}$, $AlOH_2^+$ and $Al(OH)_4^-$ ions. The equilibrium state between the concentrations of the above ions depends on the pH of the solution [30]. During the experiment, $Al(OH)_4^-$ ions dominated in the solution at pH of around 12.0-10.0, while pH in the 9.3-5.4 range probably promoted the precipitation of particles of amorphous aluminum hydroxide. According to Rokotonarivo et al. [31], zeta potential (ζ) reaches 0 at pH $\approx$ 8.3, whereas at pH $\approx$ 7.0 molecules of aluminum hydroxides have a high positive electrokinetic potential. Licskó [32] observed greater changes in zeta potential during coagulation with aluminum salts at pH 6.0 – 6.5, compared to pH 4.0–5.0. Dempsey et al. [18] reported that the minimum pH value at which the $Al(OH)_3$ precipitate is formed oscillates around 5.5 for $Al_2(SO_4)_3$. It seems that coagulation of humic acids with the use of aluminum sulfate is the result of adsorption of these substances on amorphous flocs of the aluminum hydroxide precipitate (sweep flocculation).

The zero value of streaming potential (SP) was recorded when $Al_2(SO_4)_3$ was applied at a dose of 1.8 mmol·dm^{-3}. A further increase in coagulant doses caused no distinct changes in SP. In the dose range of 1.8-2.4 mmol·dm^{-3} this potential assumed positive values. The acid reaction of the solution (pH < 5.4) probably contributed to the precipitation of metal-humic complexes in consequence of reactions of aluminum hydroxy cations and Al^{3+} ions with negatively charged HA molecules [33]. Al^{3+} ions present in the solution remained in equilibrium with metal-humic complexes, thus increasing the value of streaming potential.
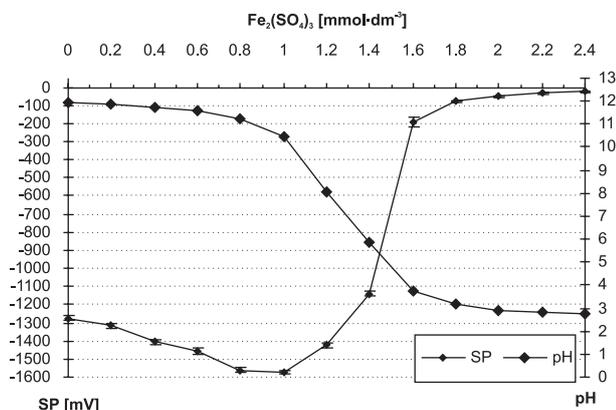
Fig. 4 shows the results of measurements of streaming potential (SP) and pH during coagulation of humic acids with iron(III) sulfate. It was found that an increase in the dose of $Fe_2(SO_4)_3$ from 0 to 1 mmol·dm^{-3} changed the value of SP from approximately -1250 mV at pH $\approx$ 12 to approximately -1570 mV at pH $\approx$ 10.5. Coagulant doses in a range of 1-1.6 mmol·dm^{-3} changed the value of SP to -192 mV and reduced pH to 3.8. At higher doses of $Fe_2(SO_4)_3$ (1.8-2.4 mmol·dm^{-3}) streaming potential was within the -77 mV to -23 mV range. The value of pH for the above doses changed from 3.15 to 2.7.

The hydrolysis of iron(III) salts in alkaline solutions produces ferrates or iron(III) hydroxides. Compared with $Al(OH)_3$, $Fe(OH)_3$ is the dominant component of solutions within a wide pH range of pH 6.0–10.0, and shows lower solubility [34]. According to Jiang and Graham [35], $Fe(OH)_3$ precipitated from a solution of $Fe_2(SO_4)_3$ has its isoelectric point at pH $\approx$ 6. This suggests that below this pH level and at the dose of $Fe_2(SO_4)_3$ > 1.4 mmol·dm^{-3} the surface of precipitated hydroxide molecules was positively charged, which permitted interactions with HA molecules.

During coagulation without pH adjustment the most significant changes in SP were noted when salts were applied at a dose of 1.4-1.6 mmol·dm^{-3}. At the optimum coagulant dose (1.6 mmol·dm^{-3}) pH reached 5.4 for $Al_2(SO_4)_3$ and 3.8 for $Fe_2(SO_4)_3$. Previous studies on coagulation of pulp and paper mill effluents showed that streaming potential changed to the greatest degree at the optimum doses of coagulants, and that its final value was highly dependent on the pH of the solution [5]. Avena et al. [36] confirmed that the electrokinetic potential in an HA solution depends on ionic strength, pH and the type of humic acids. The analysis of humic acid coagulation revealed that the course of the process is determined by the reaction of the solution.

Sulfuric acid was used for the initial adjustment of the reaction of a model HA solution before coagulation. Sulfuric acid is also a product of hydrolysis of the coagulants used in this experiment. Fig. 5 presents changes in pH and streaming potential (SP) caused by the gradual

Fig. 4. Changes in the streaming potential (SP) and pH of a model HA solution, depending on the dose of iron(III) sulfate.
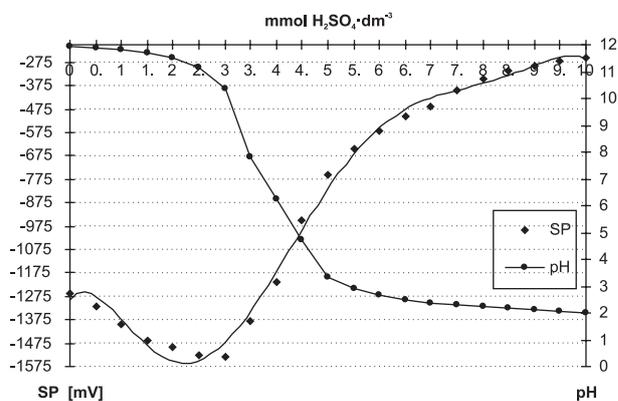

Fig. 5. Changes in the pH and streaming potential (SP) of a model HA solution during acidification with sulfuric acid.

introduction of increasing doses of sulfuric acid into a model HA solution. The curve corresponding to pH illustrates three ranges of changes in this parameter, i.e. pH 12-10.3, pH 10.3-3.3 and pH < 3.3. Those changes resulted from the gradual neutralization of sodium hydroxide, followed by a reaction of acid with sodium humate, and an increase in the concentration of hydrogen ions due to the application of acid at doses exceeding 5 mmol·dm⁻³. During the acidification of a HA solution the value of streaming potential changed from -1265 mV to -1532 mV at a dose of 3 mmol H_2SO_4·dm⁻³. At higher doses of acid a considerable increase in SP was almost linear, reaching -756 mV at 5 mmol H_2SO_4·dm⁻³. Acid doses exceeding 5 mmol·dm⁻³ caused further changes in SP, whose value remained negative even at 10 mmol of H_2SO_4·dm⁻³ and pH ≈ 2. Similar changes in streaming potential along with increasing acidity of an HA solution were reported by Bache et al. [37].

Since humic acids contain carboxyl and hydroxyl (phenolic) groups, they may be classified as organic acids [38]. According to Gustafsson [38], the pK value for carboxyl and hydroxyl (phenolic) groups is 4.1 ± 0.2 and 8.95 ± 0.15 respectively. Dissociation of the above functional groups leads to the formation of negatively charged molecules of humic acids. The degree of ionization of those groups depends on the pH of the solution and affects the value of streaming potential.

In order to determine the efficiency of humic acid coagulation as dependent on the reaction of a HA solution, pH adjustment was carried out. Nine doses of Al and Fe(III) salts were applied. Seven of them did not induce coagulation in tests without pH adjustment, while two corresponded to the already established optimum and higher doses. The results of coagulation tests with pH adjustment are presented in Tables 2 and 3. The doses of H_2SO_4 or NaOH introduced into the solution prior to coagulation as

well as the doses of coagulants are given in the first and second column. Column three shows the optimum pH values, determined experimentally. The other columns show the efficiency of coagulation, reflected in a percentage decrease in the values of the analyzed parameters.

It was found that the optimization of the pH of the solution before the introduction of the coagulant enables humic acid coagulation to achieve high efficiency. During coagulation with aluminum sulfate (Table 2) at a dose of 0.4 to 1.8 mmol·dm⁻³ the optimum pH of the solution increased from 4.2 to 5.8. COD removal efficiency of around 97% was observed already at a dose of 1 mmol·dm⁻³ and pH = 5.2. Higher doses of the aluminum coagulant (1.2 – 1.8 mmol·dm⁻³) enabled almost complete pollutant removal, at the optimum values of pH for each of the applied salt doses.

High efficiency of humic acids coagulation (COD removal efficiency 93.8-99.9%) was also recorded when iron(III) sulfate (Table 3) was applied at a dose of 0.2 to 1.8 mmol·dm⁻³. The optimum pH value for the above doses ranged from 2.3 to 4.1, which indicates a more acidic environment than in the case of aluminum coagulant.

Tables 2 and 3 show that an increase in the doses of salts inducing coagulation was accompanied by an increase in the pH of the solution. This is consistent with the findings of Yu et al. [39], who demonstrated that the optimal conditions of HA coagulation include pH 4.0 for $FeCl_3$ and pH >5 for $Al_2(SO_4)_3$, and that the efficiency of the process decreases along with an increase in pH. Also Cheng [21] noted that humic acid coagulation with increasing coagulant doses is more efficient at higher pH levels.

The dose of acid required to achieve the optimum pH value increased as the dose of salt was reduced. Duan et al. [40] reported that the overall efficiency of HA coagulation with $FeCl_3$ can be improved by about 15 to 20%

Table 2. Efficiency of humic acid coagulation in a model solution, depending on pH and the dose of aluminum sulfate.

Dose [mmol·dm⁻³]		pH_k	Turbidity	Colour	SS	COD
H_2SO_4/NaOH	$Al_2(SO_4)_3$		% removal	% removal	% removal	% removal
1	2	3	4	5	6	7
-	0.2	-	-	-	-	-
4	0.4	4.2	98.3	98.2	99.3	92.3
3.25	0.6	4.7	99.5	99.5	99.3	93.1
2.45	0.8	5.2	99.7	99.7	99.3	95.7
1.9	1	5.2	99.8	99.7	99.7	97.2
1.4	1.2	5.4	99.8	99.8	99.7	99.1
0.55	1.4	5.6	99.7	99.7	99.3	98.6
0.02 NaOH	1.6	5.8	99.8	99.8	99.7	99.9
1.3 NaOH	1.8	5.8	99.5	99.5	98.7	97.7

Table 3. Efficiency of humic acid coagulation in a model solution, depending on pH and the dose of iron(III) sulfate.

Dose [mmol·dm⁻³]		pH$_k$	Turbidity	Colour	SS	COD
H_2SO_4/NaOH	$Fe_2(SO_4)_3$		% removal	% removal	% removal	% removal
1	2	3	4	5	6	7
13.5	0.2	2.3	96.8	96.8	97.2	93.8
4.3	0.4	3.1	99.4	99.3	99.7	98.2
3.15	0.6	3.9	99.6	99.6	99.3	99.1
2.5	0.8	4	99.7	99.7	99.3	99.7
1.85	1	4.1	99.9	99.9	99	99.8
1.2	1.2	4	99.8	99.8	99.6	99.8
0.55	1.4	4	99.8	99.8	100	99.9
0.3 NaOH	1.6	4.2	98	99.8	99.6	99.9
1.3 NaOH	1.8	4.1	96.5	99.8	100	99.8

provided that pH is adjusted with acid before the process. The addition of acid to the solution prior to coagulation probably causes changes in the electric charge of humic acid molecules, and contributes to their easier destabilization with the use of coagulants. The results of the present study confirm that the dose of coagulants may be reduced, maintaining high efficiency of humic acid removal. They may also provide a basis for further investigations into the process of water and wastewater treatment by chemical coagulation.

Conclusions

Coagulation tests without pH adjustment in a model HA solution showed that:
1. Aluminum sulfate and iron(III) sulfate applied at the optimum dose (1.6 mmol·dm⁻³) enabled COD to reduce by 97% and 99.9%, respectively, and to almost completely eliminate colour [PtCo], turbidity [FTU] and suspended solids [SS].
2. Increasing doses of coagulants resulted in characteristic changes in streaming potential. The greatest changes in SP were observed when the optimum doses of salts were used. The analysis of SP versus coagulant dose changes may be used to coagulant dose optimization.
3. During coagulation with the optimum coagulant doses, pH values differed depending on the type of coagulant, and reached 5.4 for $Al_2(SO_4)_3$ and 3.8 for $Fe_2(SO_4)_3$. Coagulation tests with pH adjustment in a model HA solution showed that:
4. There exists the optimum value of pH for each of the coagulant doses applied in the experiment, including those not inducing coagulation in tests without pH adjustment. This value depends on the type of coagulant.

5. $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ applied at a dose of 0.4 mmol·dm⁻³ and 0.2 mmol·dm⁻³, respectively, permitted high (92 – 94%) efficiency of COD removal at pH 4.2 and 2.3, respectively. A further increase in coagulant doses enabled almost 100% pollutant load removal at pH 5.2-5.8 for $Al_2(SO_4)_3$ and at pH ≈ 4.0 for $Fe_2(SO_4)_3$. The efficiency of COD removal was slightly lower (by approx. 2-3%) after coagulation with the majority of doses of aluminum salts, compared with identical doses of iron(III) salts.

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