

Short Communication

Changes in Iron(II) and Iron(III) Content in a Solution of Humic Acids During Coagulation by Means of Monomeric Iron(III) Salts

Bartosz Libecki*, Jerzy Dziejowski

Department of Chemistry, University of Warmia and Mazury in Olsztyn,
Plac Łódzki 4, 10-757 Olsztyn, Poland

Received: 28 September 2009

Accepted: 15 March 2010

Abstract

This study discusses the results of laboratory analyses investigating the chemical coagulation of a model of humic acid solution with the use of monomeric iron(III) salts – chloride and sulfate – in a standard coagulation test environment. The objective of the study was to determine changes in iron compound concentrations in the tested solution as a result of coagulation. The following parameters were analyzed in solution samples: changes in COD, colour, turbidity, suspended solids, pH, and streaming potential in relation to the applied coagulant dose. The content of total iron (Fe_{total}) and iron(II) was determined in solution samples after coagulation. The lowest Fe_{total} concentrations were observed following the use of optimal coagulant doses, and higher doses led to a repeated increase in total iron levels. In purified solution samples, iron(III) was partially reduced to iron(II) with an 8-42% share of Fe_{total} , depending on salt type and the applied dose.

Keywords: coagulation, iron concentration, humic acids, iron(III) salts

Introduction

Humic and fulvic acids, heterogeneous mixtures of anionic organic polyelectrolytes, have a high share of organic matter in soil and the natural environment [1]. Humic substances react with iron compounds as part of, for example, complex formation and redox reactions, and they are responsible for the various forms of iron found in the natural environment [2]. Iron may occur in the form of organic complexes of iron(II) and iron(III), simple ionic forms, and colloidal forms, as well as in the form of amorphous and crystalline oxides and hydroxides [3, 4]. Iron compounds found in water are in a state of chemical balance that is determined by the pH of the reactive environment, the type of organic compounds, level of oxidation and light penetration [2, 4]. Soil leaching is the natural

source of water-borne iron. In consequence of this process, the iron content of underground water at the point of intake may reach from several to several dozen $mg \cdot dm^{-3}$ [5]. Secondary contamination of water with iron(III) compounds may be due to the water treatment process and the corrosion of metal components of systems for the purification, storage and distribution of water.

Chemical coagulation is one of the stages of the water treatment process. The coagulation method is used to remove organic compounds that intensify water colour and turbidity, as well as the precursors of toxic disinfection by-products (DBP), including humic acids [6]. During chemical coagulation, colloidal organic molecules bind as a result of electrostatic interactions, complexing, aggregation, and sorption processes with the involvement of hydrolysis products of Al and Fe(III) salts [7]. Monomeric and polymeric iron(III) salts are popularly used coagulants. Water and wastewater treatment by chemical coagulation should

*e-mail: bmd@uwm.edu.pl

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

| | |
|--|----------------------|
| pH | 11.96±0.02 |
| Conductivity [$\text{mS}\cdot\text{cm}^{-1}$] | 1325±5 |
| Colour PtCo [$\text{mg}\cdot\text{dm}^{-3}$] | dilution 1:25 795±12 |
| Turbidity FTU [$\text{mg}\cdot\text{dm}^{-3}$] | dilution 1:25 91±5 |
| Suspended solids – SS [$\text{mg}\cdot\text{dm}^{-3}$] | 289±24 |
| COD [$\text{mg}\cdot\text{dm}^{-3}$] | 795±10 |
| DOC* [$\text{mg}\cdot\text{dm}^{-3}$] | 246.5 |

*Counted on the basis of the following assumptions: 53% C_{org} content of humic acids molecules (Fluka) [11], residue after ignition at 7% HA dry matter.

ensure the effective removal of organic impurities and the minimal level of metal compounds in the purified solution. Laboratory tests of chemical coagulation involving the standard coagulation method (jar test) are a highly useful tool for determining optimal process conditions in industrial applications [8, 9].

The objective of this study was to determine the effect of iron(III) salt dose on total iron, iron(II) and iron(III) concentrations in the analyzed solution following humic acid coagulation in a standard coagulation test environment.

Materials and Methods

The model humic acids (HA) solution was prepared directly before the test in accordance with the methodology described in the author's previous study [10]. The solution contained 500 mg HA (Fluka) in 1 dm^3 . The parameters of the HA solution are presented in Table 1.

Coagulant solutions with concentrations of $0.2 \text{ mol}\cdot\text{dm}^{-3}$ were prepared using analytically pure $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ salts and analytically pure $\text{Fe}_2(\text{SO}_4)_3\cdot 7\text{H}_2\text{O}$ salts dissolved in double-distilled water.

Coagulation effectiveness was determined with the use of the coagulation test performed in glass beakers filled with solution samples of 200 cm^3 . The applied procedure involved 1 minute rapid mixing at 300 rpm, followed by 10 minutes slow mixing at 30 rpm and 1 h of sedimentation. The following parameters were determined after coagulation: pH, Chemical Oxygen Demand (COD) Cr-method [$\text{mg O}_2\cdot\text{dm}^{-3}$], PtCo colour [$\text{mg}\cdot\text{dm}^{-3}$], turbidity-Formazin Turbidity Unit (FTU) [$\text{mg}\cdot\text{dm}^{-3}$] and suspended solids (SS) [$\text{mg}\cdot\text{dm}^{-3}$] [12].

The total iron (Fe_{total}) content was determined in the tested solutions. For the purpose of mineralization, the samples were acidified to $\text{pH}<2$, concentrated HNO_3 and HCl (1:1) was added, and the samples were heated. After mineralization, pH of the solutions was adjusted to $\text{pH } 3.5\pm 0.2$ with the use of 5.0 M NaOH , and then the solutions were diluted to 100 ml with double-distilled water. Fe_{total} concentrations were determined by colorimetry (510 nm) using 1,10 phenanthroline (HACH – method No. 8008) [12-14].

The content of iron(II) was analyzed in sample solutions after coagulation using the optimal dose and higher doses of the coagulant. A colorimetric analysis was carried out directly after pH, adjusting to $\text{pH } 3.5\pm 0.2$ without preliminary mineralization of samples (HACH – method No. 8146). The content of $\text{Fe(III)} = \text{Fe}_{\text{total}} - \text{Fe(II)}$.

The pH of the investigated solutions was determined with an HI-9025C (Hanna Instruments) pH-meter. Colour, turbidity, COD, suspended solids, Fe(II), and Fe_{total} concentrations were determined using a Dr 2000 (HACH) spectrophotometer. The streaming potential (SP) of the analyzed solutions was determined with an SPD-03 meter (Mütek Analytic).

Results and Discussion

A preliminary analysis of humic acid coagulation was carried out to determine the optimal coagulant dose. The optimal dose was set at a level, which supported the elimination of a minimum of 90% of impurities measured in terms of COD, colour (PtCo), turbidity (FTU), and suspended solids (SS). The results of the iron(III) chloride test are presented in Figs. 1a and 1b.

The addition of $3.2 \text{ mmol Fe}^{3+}\cdot\text{dm}^{-3}$ (FeCl_3) resulted in a significant decrease in color and turbidity values to around

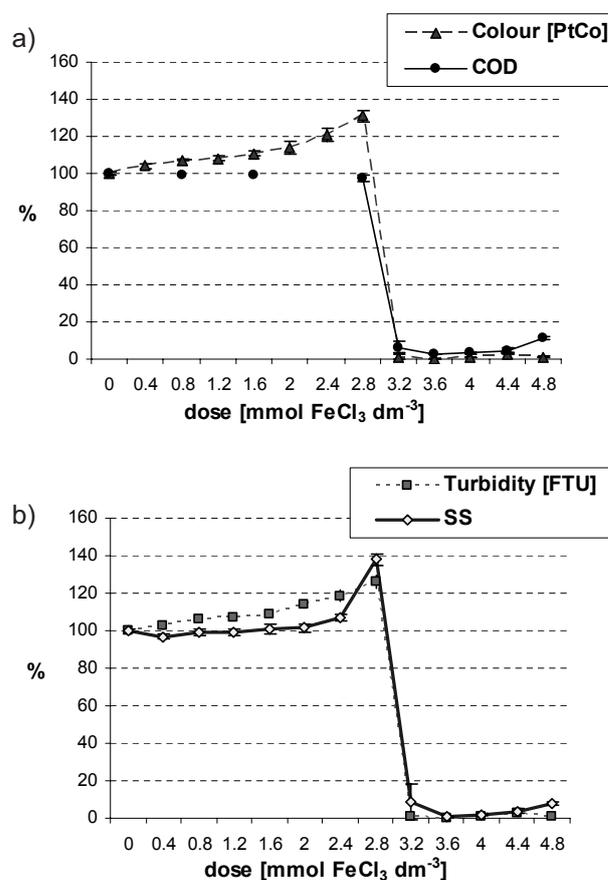


Fig. 1. Changes in values of parameters: colour and COD (a), turbidity and suspended solids (b), for a model solution of humic acids with respect to FeCl_3 dosage.

1% initial value, and COD to around 3.6%. The 3.2 mmol·dm⁻³ dose was set as the optimal dose. Three ranges of the applied salt doses led to characteristic changes in the analyzed parameters, i.e.: threshold doses of 2.0-2.8, optimal dose of 3.2, and higher doses of 3.6-4.8 mmol Fe³⁺·dm⁻³. Similar changes in the investigated values were determined following the use of the Fe₂(SO₄)₃ coagulant. The relevant results are presented in the authors' previous work [10].

The curves illustrating changes in pH of the samples after coagulant dosing are presented in Fig. 2, and changes of the streaming potential (SP) in samples subjected to coagulation tests with coagulant doses of 2.0 to 4.8 mmol Fe³⁺·dm⁻³ are presented in Fig. 3.

An increase in the tested salt doses led to a gradual drop in pH of the analyzed solutions, and the course of the noted changes was similar for both studied salts. The solutions had an alkaline pH at salt doses in the range of 0.4-2.4 mmol Fe³⁺·dm⁻³ (Fig. 2). Characteristic changes in SP values were noted following the application of FeCl₃ at 3.2 mmol Fe³⁺·dm⁻³ and higher doses (Fig. 3). A clear change in SP

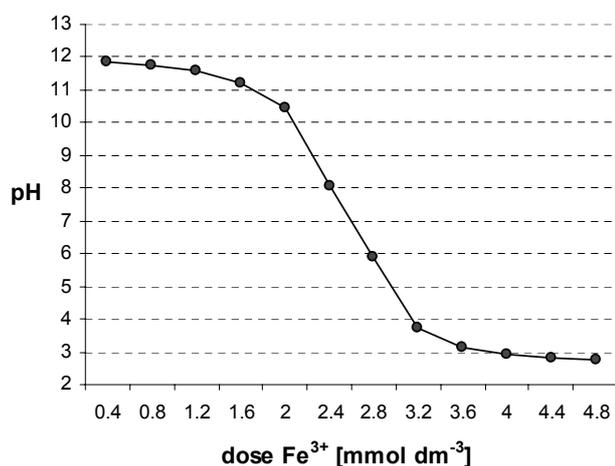


Fig. 2. Changes in values of pH of a humic acids model solution with respect to Fe(III) salts dosage.

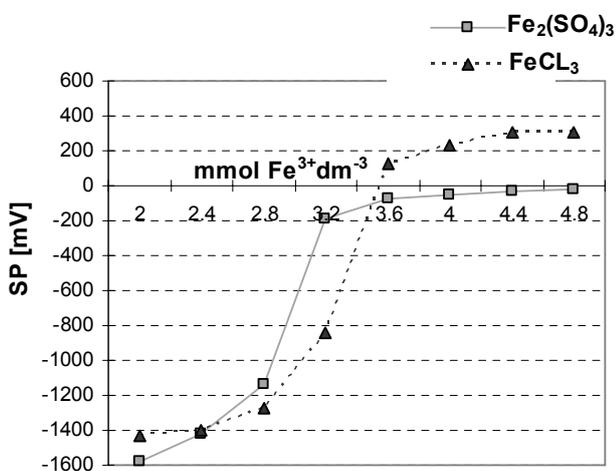


Fig. 3. Changes in the streaming potential for jar-tested samples of a humic acids solution where Fe³⁺ ion content is within the range of 2.0-4.8 mmol·dm⁻³.

parameters from -840 to 122 mV was observed in the dose range of 3.2-3.6 mmol Fe³⁺, and it was accompanied by a change in the pH of the solution from around 4.0 to 3.0 as noted in Fig. 2. Positive SP values were noted beginning with the dose of 3.6 mmol Fe³⁺·dm⁻³. As regards Fe₂(SO₄)₃, a significant increase in SP from -1,140 to -190 mV was reported in the dose range of 2.8-3.2 mmol Fe³⁺·dm⁻³, with a pH change from 6.0 to around 4.0. SP values increased insignificantly and remained negative at successive coagulant doses.

The solution's pH is one of the key determinants of Fe(III) salt hydrolysis, which produces charged ferrate molecules at pH>10, Fe(OH)₃ in a neutral environment and positively charged oxyhydroxides at pH<4 [15]. It is believed that interactions between dissociated humic acids molecules and cationic products of Fe(III) salt hydrolysis have the form of ionic reactions neutralizing the electrical charge [16-18].

Table 2 presents changes in total iron and iron(II) concentrations, and the percentage content of iron(II) in total iron in the HA solution, with respect to the applied coagulant dose.

As regards both analyzed coagulants, an increase in Fe_{total} levels was proportional to the applied doses in the range of 0.4 to 2.8 Fe³⁺·dm⁻³. The optimal dose of 3.2 mmol Fe³⁺·dm⁻³ produced minimal concentrations of Fe(III) ions in the solution at 2.5 and 4.07 mg Fe·dm⁻³ for Fe₂(SO₄)₃ and FeCl₃, respectively. A further dose increase from 3.6 to 4.8 mmol Fe³⁺·dm⁻³ did not enhance solution quality, and total iron concentrations rose to around 70 mg Fe·dm⁻³ at the dose of 4.8 mmol Fe³⁺·dm⁻³.

The Fe(II) content was determined in HA solution samples after coagulation with Fe(III) doses of 3.2 to 4.8 mmol Fe³⁺·dm⁻³. The above eliminated the effect of organic residues in the solution on the results of spectrophotometric measurements. The salt dose of 3.2 mmol Fe³⁺·dm⁻³ produced the lowest Fe(II) content of 0.3 mg Fe²⁺·dm⁻³ for FeCl₃ and 1.3 mg Fe²⁺·dm⁻³ for Fe₂(SO₄)₃. At higher doses, Fe²⁺ concentrations increased to 5.2 mg and 6.7 mg Fe²⁺·dm⁻³ for Fe₂(SO₄)₃ and FeCl₃, respectively. The percentage share of Fe²⁺ in total iron content varied subject to the applied salt dose. A clear decrease from 42% to 9% was observed following the application of FeCl₃, and a drop from 28% to 7.6% was noted after the use of Fe₂(SO₄)₃ within the dose range of 3.6-4.8 mmol Fe³⁺·dm⁻³.

The use of coagulants did not fully eliminate COD and colour (Fig. 1a), turbidity and suspended solids (Fig. 1b). The above suggests the presence of dissolved organic substances in the form of organic ferric complexes that increase solution colouring [19]. The application of coagulant doses higher than the optimal dose led to a decrease in the solution's pH<3.8 (Fig. 2). According to Weber et al. [20], the share of organic ferric complexes in the total content of dissolved iron decreases at pH<3.5.

The presence of iron(II) in the samples results from oxidation and reduction processes that accompany the reaction between dissolved organic matter and iron(III) ions [21]. Humic Fe(III) complexes participate in the transfer of elec-

Table 2. The concentration of Fe_{total}, Fe(II), and the percentage of Fe(II) in Fe_{total} in analyzed coagulation test samples.

| Dose of coagulant [mmol Fe ³⁺ ·dm ⁻³] | Fe _{total} [mg Fe·dm ⁻³] | | Fe ²⁺ [mg Fe ²⁺ ·dm ⁻³] | | Fe ²⁺ /Fe _{total} [%] | |
|---|--|---|--|---|--|---|
| | FeCl ₃ | Fe ₂ (SO ₄) ₃ | FeCl ₃ | Fe ₂ (SO ₄) ₃ | FeCl ₃ | Fe ₂ (SO ₄) ₃ |
| 0.4 | 22.83 | 24 | - | - | - | - |
| 0.8 | 44.33 | 45.5 | - | - | - | - |
| 1.2 | 67.15 | 66.67 | - | - | - | - |
| 1.6 | 89.17 | 88.33 | - | - | - | - |
| 2.0 | 108.6 | 108.17 | - | - | - | - |
| 2.4 | 132.88 | 130.33 | - | - | - | - |
| 2.8 | 148.67 | 149.17 | - | - | - | - |
| 3.2 | 2.5 | 4.07 | 0.31 | 1.33 | 12 | 31.7 |
| 3.6 | 8.13 | 10.42 | 3.38 | 2.9 | 42 | 27.9 |
| 4.0 | 24.87 | 26.47 | 4.98 | 4.1 | 20.1 | 15.5 |
| 4.4 | 47.33 | 45.87 | 6.02 | 4.72 | 12.7 | 10.2 |
| 4.8 | 73.33 | 68 | 6.72 | 5.25 | 9.1 | 7.6 |

trons during abiotic Fe(III) reduction [22], and the quantity of reduced Fe(III) increases dramatically with a pH decrease in the range of 4.0-3.0 [23].

The results presented in Table 2 indicate that Fe(II) concentrations and the share of Fe(II) in the total iron content were higher for iron chloride. Various iron(III) salt anions may affect redox reactions of dissolved organic substances in the presence of light [4]. According to Chen et al. [24], anions inhibit the photooxidation of organic substances in the following series: NO₃⁻<Cl⁻<CO₃²⁻<SO₄²⁻<PO₄³⁻.

Redox reactions taking place in a standard coagulation test environment may be affected by the following factors: organic substance type and organic concentrations in the solution, access to light and oxygen, and solution mixing conditions [23, 25]. However, a full explanation of the processes observed during coagulation with iron(III) salts requires research with the use of speciation analysis methods. For practical purposes, the results obtained from the present study using Fluka HA would require the verification in an experiment with aquatic natural organic matter, collected from real water samples.

Conclusions

The following conclusions have been drawn from the study of humic acid coagulation involving monomeric Fe(III) salts in a standard coagulation test environment:

1. More than 95% COD reduction efficiency and 99% color [PtCo], turbidity [FTU], and suspended solid [SS] reduction efficiency was observed after the application of the optimal dose of 3.2 mmol Fe³⁺·dm⁻³ of both FeCl₃ and Fe(SO₄)₃. Changes in the streaming potential of the

solution pointed to the neutralization of the negative electrical charge of colloidal organic molecules.

2. The lowest Fe_{total} concentrations of 2.5 and 4.07 mg Fe·dm⁻³ were noted after the use of optimal Fe₂(SO₄)₃ and FeCl₃ doses, respectively. Higher doses resulted in a repeated increase in the total iron content of the studied solution.
3. Fe²⁺ concentrations increased in successive samples after coagulation as a result of redox reactions running in lowered pH conditions. The percentage share of Fe²⁺ in total iron content carried out from about 8 to 42%, depending on salt type and applied dose.

References

1. PEFFERKORN E. Structure and stability of natural organic matter/soil complexes and related synthetic and mixed analogues. *Adv. Colloid Interface Sci.*, **73**, 127, **1997**.
2. PULLIN J.M., CABANISS S. The effects of pH, ionic strength, and iron-fulvic acid interactions on the kinetics of nonphotochemical iron transformations. I. Iron(II) oxidation and iron(III) colloid formation. *Geochim. Cosmochim. Ac.* **67**, (21), 4067, **2003**.
3. KUNG K.-H., MCBRIDGE M.B. Coordination complexes of p-hydroxybenzoate on Fe oxides. *Clay. Clay. Miner.* **37**, (4), 333, **1989**.
4. FENG W., NANSHENG D. Photochemistry of hydrolytic iron (III) species and photoinduced degradation of organic compounds. A mini review. *Chemosphere.* **41**, 1137, **2000**.
5. ŁOMOTOWSKI J. Theoretical background to the problem of iron-compound washout from the aquifer. *Ochrona Środowiska.* **4**, (59), 9, **1995** [In Polish].
6. WATT B. E., MALCOLM R.L., HAYES M. H. B., CLARK N. W. E, CHIPMAN J. K. Chemistry and potential muta-

- genicity of humic substances in waters from different watersheds in Britain and Ireland. *Water Res.* **30**, (6), 1502, **1996**.
7. AMIRTHARAJAH A., O'MELIA Ch. R. Coagulation processes: destabilization, mixing and flocculation. Guide to selection of water treatment processes. *Water Quality and Treatment*. AWWA- 4th ed., pp. 269-365, **1990**.
 8. HAHN H. H., EPPLER B., KLUTE R. Comparison of wastewater flocculation in jar test experiments, continuous-flow reactors and large-scale plants. In: *Chemistry of Wastewater Technology*. Editor- Allan J. Rubin. Ann Arbor Science., pp. 245-261, **1980**.
 9. JUNG A.V., CHANUDET V., GHANBAJA J., LARTIGES B.S., BERSILLON J.L. Coagulation of humic substances and dissolved organic matter with a ferric salt: An electron energy loss spectroscopy investigation. *Water Res.* **39**, 3849, **2005**.
 10. LIBECKI B., DZIEJOWSKI J. Optimization of Humic Acids Coagulation with Aluminum and Iron(III) Salts. *Polish J. Environ. Stud.* **17**, (3), 397, **2008**.
 11. PALLADINO G., FERRI D., MANFREDI C., VASCA E. Potentiometric determination of the total acidity of humic acids by constant-current coulometry, *Anal. Chim. Acta* **582**, 164, **2007**.
 12. APHA, AWWA and WEF Standard methods for examination of water and wastewater, 19th ed. Washington, **1995**.
 13. HACH Dr/2000 Spectrophotometer Handbook, Manual Procedures, **1993**.
 14. SCHILT A. S. Analytical Applications of 1,10-Phenanthroline and Related Compounds. Oxford: Pergamon Press, **1969**.
 15. FLYNN M. CH. Hydrolysis of inorganic iron(III) salts. *Chem. Rev.* **84**, (1), 31, **1984**.
 16. CHENG W. P. Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution. *Chemosphere* **47**, 963, **2002**.
 17. DUAN J., GREGORY J. Coagulation by hydrolyzing metal salts. *Adv. Colloid Interface.* **100-102**, 475, **2003**.
 18. LIBECKI B., DZIEJOWSKI J. Interactions of aluminum and iron(III) salts with humic acids in a model alkaline solution. *Polish J. Natur. Sc.* **23**, 681, **2008**.
 19. KOWALSKI T. On the chemical parameters of water pollutants and their effect on the choice of coagulants. *Ochrona Środowiska* **4**, (59), 3, **1995**.
 20. WEBER T., ALLARD T., BENEDETTI M. F. Iron speciation in interaction with organic matter: Modelling and experimental approach. *J. Geochem. Explor.* **88**, 166, **2006**.
 21. NIEROP K. G. J., JANSEN B., VERSTRATEN J. M. Dissolved organic matter, aluminium and iron interactions: precipitation induced by metal/carbon ratio, pH and competition. *Sci. Total Environ.* **300**, 201, **2002**.
 22. STRUYK Z., SPOSITO G. Redox properties of standard humic acids. *Geoderma* **102**, 329, **2001**.
 23. CHEN J., GU B., ROYER R. A., BURGOS W. D. The roles of natural organic matter in chemical and microbial reduction of ferric iron. *Sci. Total Environ.* **307**, 167, **2003**.
 24. CHEN Y., ZAHRAA O., BOUCHY M. Inhibition of the adsorption and photocatalytic degradation of an organic contaminant in an aqueous suspension of TiO₂ by inorganic ions. *J. Photoch. Photobio. A* **108**, 37, **1997**.
 25. FUKUSHIMA M., TATSUMI K. Light acceleration of iron(III) reduction by humic acid in the aqueous solution. *Colloid. Surface. A* **155**, 249, **1999**.

