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Speciation and coagulation performance of novel coagulant – Aluminium formate

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ABSTRACT

In this study a novel coagulant, aluminium formate, was synthesised and its coagulation performance was evaluated. Aluminium formate can be synthesised from aluminium hydroxide and formic acid at atmospheric pressure and at a temperature of 60 °C. The speciation of the products obtained was studied using electrospray ionisation mass spectrometry. Aluminium formate was found to form mainly small cationic species in water. The coagulation performance was studied in removal of natural organic matter from surface water. Polyaluminium chloride and aluminium sulphate were used as reference coagulants. The results suggest that aluminium formate removes natural organic matter at least as well as the reference coagulants. Raw water characteristics were found to have an impact on the coagulation efficiency of the coagulants studied. Aluminium formate was found to be a potential water treatment chemical for applications where conventionally used coagulants cause problems.

1. Introduction

Coagulation and flocculation are important steps in treating water in different applications. These unit operations can be used in producing potable water for households, or process water for industries, and also in wastewater purification. The purpose of coagulation and flocculation is to transform small colloidal or suspended impurity particles into bigger aggregates and thus make them easier to remove [1].

Most of the colloidal impurities are negatively charged and thus stable due to electrical repulsion. Destabilisation can be achieved by the addition of chemicals that in water generate cations that can neutralise the charge of the particles. Aluminium- and iron-based coagulants are widely used because they produce highly charged cations in water [2]. Although iron chemicals are widely used, aluminium is a more convenient option in many applications. A major drawback in the usage of iron is its yellowish colour. Especially in operating environments in which the colour of the water is an important parameter, aluminium is preferred. For example in the pulp and paper industry iron may deteriorate the quality of the products [3].

The aluminium and iron compounds used in water treatment are mostly chlorides and sulphates. These counter anions may cause various problems in different applications. For example, corrosion due to chloride is a well-known problem. Chloride is not only aggressive to different steel constructions but also even to concrete and aluminium. In addition to chloride, sulphate is also a corrosive agent for various materials [4]. Formate is a less corrosive alternative to these counter anions and thus its salts are used widely in e.g. oil drilling as completion fluids [5]. In such circumstances, chloride salts cause cracking failures of corrosion resistant alloy materials in oil fields [6]. The major advantage of formate over chloride or sulphate is that it decomposes under UV irritation [7]. Thus the accumulation of ions and formation of unwanted precipitates, like gypsum, can be avoided.

Aluminium compounds used in water treatment have been under extensive investigation lately [8–10]. The coagulation efficiency of the most commonly used aluminium salts, namely aluminium sulphate and aluminium chloride, as well as prehydrolysed polyaluminium chlorides and polyaluminium sulphates, have been widely studied in the removal of natural organic matter (NOM) [11]. Beside the most commonly used coagulants, some novel aluminium-based coagulants such as polyaluminium silicate chloride [12] and aluminium–silicate polymer [13] have been studied. Characterisation studies on aluminium compounds have also been conducted to increase the understanding of the coagulation mechanisms [14,15]. Electrospray ionisation mass spectrometry (ESI-MS) has been found to be a useful method in speciation studies of aluminium in water. ESI-MS has also been used to study the speciation of aluminium salts and polymeric prehydrolysed aluminium compounds [16–18].

In this study, the anion of formic acid, formate $[HCOO]^-$, has been used to replace the more harmful counter anions that are commonly used in aluminium chemicals. For this investigation, aluminium formate was synthesised using two different methods.

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The speciation of the obtained products was studied using electrospray ionisation mass spectrometry with a time-of-flight detector (ESI-TOF-MS). The coagulation performance of the synthesised aluminium formates in the removal of NOM was studied by means of jar tests, using surface water as the model raw water.

2. Materials and methods

2.1. Synthesis

Aluminium formate solutions were prepared from aluminium hydroxide by reaction with formic acid. The preparation method used is a modification of the method described in the patent by Bårström et al. [19]. The preparation was carried out using two different methods.

In the first method, aluminium hydroxide (55.6% Al_2O_3 reagent grade, Sigma Aldrich, product no. 23,918-6) was suspended in ultrapure water (18.2 MΩ cm) to generate a sludge containing 5.1% (w/w) of aluminium. Formic acid (98% (w/w), Riedel-deHaën, Reag. Ph. Eur.) was diluted to 80% (w/w) and added to the sludge to reach an Al/HCOOH ratio of 1/3.5. This ratio was selected to ensure that there would be an excess of formic acid for the total reaction of the aluminium. The mixture was stirred with a magnetic stirrer and heated up to 60 °C. The temperature was kept constant at 60 °C and mixing was continued for one hour. After one hour the solution was translucent with very little white precipitate. The product of this method is referred to later in the text as "aluminium formate I".

In the second method, 80% (w/w) formic acid was added directly to the dry aluminium hydroxide powder which caused a vigorous reaction and spontaneous warming of the solution to 62 °C. The mixture was stirred and after the reaction settled down and the temperature started to cool, heating was started to maintain the temperature at 60 °C. After one hour of mixing at 60 °C, a very viscose white solution was attained. Then water was added in the same ratio as in the first method. The mixture obtained with this method was a white suspension. The product of this method is referred to later in the text as "aluminium formate II".

2.2. Coagulation tests

The coagulation performance experiments were undertaken with a six-paddle jar tester (Flocculator 2000, Kemira Kemwater). In addition to the prepared aluminium formates, the coagulation performance of commercial prehydrolysed polyaluminium chloride (Kemira) and aluminium sulphate (VWR BPH Prolabo AnalR Normalpur) were studied in the jar tests.

The raw water used was collected from the river Oulujoki, which is located in Northern Finland and is used as a raw water source for the water treatment plant of the City of Oulu and various industries in the Oulu region. The raw water used was collected on six different days. The total organic carbon (TOC) and UV absorbance were measured, and the results and the calculated specific ultraviolet absorption (SUVA) values are presented in Table 1. There are variations in the raw water from the different sampling days. The water from sampling days 1 to 4 had a significantly lower TOC and thus higher SUVA than the water collected during sampling days 5 or 6. The water with the higher SUVA was used in most of the coagulation tests. The water with the lower SUVA was used to study the raw water characteristics and the effect of ageing.

Table 1
Raw water characteristics.

Sampling day	TOC (mg/L)	UV absorbance	SUVA (L/mg m)
1	7.25	0.330	4.55
2	7.00	0.327	4.67
3	7.50	0.373	4.97
4	7.41	0.340	4.59
5	9.87	0.348	3.53
6	10.60	0.369	3.39

The jar tests were performed with 1000 mL of raw water at room temperature. Firstly, the water was mixed for 1 min at a speed of 400 rpm, during which the coagulant was added and the pH was adjusted. Coagulants were dosed as solutions containing 1 g/L aluminium and the pH was adjusted with a dropwise addition of 0.1 mol/L NaOH (VWR BDH Prolabo, AnalR Normalpur). After rapid mixing, the water was mixed at a speed of 20 rpm for 15 min to achieve floc growth. After the slow mixing, the water was allowed to settle for 30 min. A Metrohm 704 pH meter using a Metrohm 6.0228.000 Ag/AgCl electrode with a Pt 1000 temperature sensor was applied for the pH measurements. The pH meter was calibrated with AVS Titrinorm VWR BPH Prolabo buffer solutions at pH values of 4.00 and 7.00.

Some supernatant was taken from a depth of 10 cm for further analysis. Samples taken from the tests were centrifuged at 1000 rpm (relative centrifugation force being 134 g-units) for 5 min with a Jouan C412 centrifuge and TOC, UV absorbance and the residual aluminium content were analysed from the clear supernatant. Centrifugation was performed to remove particulate matter, which could have interfered with the measurements. Centrifugation was preferred to filtration because in our preliminary tests, filter materials adsorbed residual aluminium from the sample. This resulted in the blocking of the filter membrane and retention of compounds that should have permeated the membrane.

2.3. Analytical methods

2.3.1. Mass spectrometry

Cationic ESI-TOF spectra of aluminium formates were recorded with a mass spectrometer (LCT Micromass) equipped with a Z-spray electrospray interface. The solutions were introduced directly into the spectrometer with a syringe pump (Model 11 Harvard Apparatus). The operating conditions are reported in Table 2. These conditions have been tested earlier for aluminium speciation studies [16]. The spectra were recorded for the aluminium formate samples with an aluminium concentration of 10 mmol/L. The samples were measured at initial pH 4.0 and at pH 5.0 after pH adjustment that was done by adding the required amount of 0.1 mol/L NaOH.

2.3.2. Residual aluminium

Aluminium was analysed with a graphite furnace atomic absorbance spectrometer (AAnalyst 600 Perkin Elmer). The measurement was performed according to standards SFS 5074 and SFS-EN ISO 15586 [20,21]. The wavelength used was 309.3 nm and the slit width was 0.7 nm.

Table 2
Operating parameters of the mass spectrometer used in recording the spectra.

Sample flow-rate	20 μL/min
Capillary voltage	3500 V
Sample cone voltage	70 V
Rf lens	200 V
Extraction cone voltage	5 V
Desolvation temperature	150 °C
Source temperature	120 °C
Resolution	4000
Mass range	80–1000 m/z