Chemical Engineering Journal 254 (2014) 635–646

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Comparison of the coagulation performance of tetravalent titanium and zirconium salts with alum

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HIGHLIGHTS

- $ZrCl_4$ achieved better DOC removal near to its isoelectric point than alum and $TiCl_4$.
- For $TiCl_4$, DOC removal at pH 4.5 was dominantly due to adsorption-enmeshment mechanisms.
- $ZrCl_4$ is more efficient for the removal of low molecular weight organics than alum.
- $TiCl_4$ produced relatively larger, faster initial growth and heterogeneous size flocs.
- The composite of Ti and Zr salts with alum could be a good option for improved removal.

ARTICLE INFO

Article history:
Received 7 April 2014
Received in revised form 4 June 2014
Accepted 7 June 2014
Available online 16 June 2014

Keywords:
Charge neutralization
Dissolved organic carbon
Fluorescence spectroscopy
Titanium tetrachloride
Zirconium tetrachloride
Zeta potential

ABSTRACT

With occurrences of high concentrations of dissolved organic carbon (DOC) in drinking water supplies and consequential increased health risks from halogenated disinfection by-products following chlorine disinfection, there is need to develop improved cost effective methods that lead to low residuals of organics in drinking waters. In conventional treatment of drinking waters, alum and ferric based salts are generally used removing low to moderate percentages of the organics present. Where raw waters are high in DOC, the residuals may also then be at comparatively high levels. Performances of titanium tetrachloride ($TiCl_4$) and zirconium tetrachloride ($ZrCl_4$) for drinking water treatment were studied and compared with alum. Jar test experiments were performed at various coagulant doses and pH levels to determine the optimum conditions based on removal efficiencies of organic content (DOC), zeta potential for assessing the destabilization mechanism and the kinetics of coagulation. The Ti(IV) and Zr(IV)-based coagulants showed greater capacity for DOC removal at near their isoelectric points, with $ZrCl_4$ providing the highest DOC removal. Negative zeta potentials of Ti flocs at pH 4.5, indicated that dominant destabilization of organics occurred by adsorption-enmeshment mechanisms, whereas, charge neutralization was the dominant mechanism at pH between 3 and 3.5. Fluorescence spectroscopy and HPSEC showed that $ZrCl_4$ was more efficient for the removal of low to medium MW range organic compounds (<2000 Da) than $TiCl_4$ or alum. $TiCl_4$ produced relatively larger flocs with faster initial growth and with more heterogeneous sizes, than alum and $ZrCl_4$. The results indicate that these Ti and Zr salts could be used as alternative coagulants in water treatment processes with some capacities exceeding that of alum, providing there are no health risks from their application.

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1. Introduction

Water for drinking purposes needs to be safe and aesthetically acceptable for human consumption. Surface waters used for drinking water supplies can vary significantly in concentration and character of natural organic matter (NOM), color, turbidity as well as inorganic constituents such as carbonate and divalent cation concentrations. These constituents influence water quality when they are transported into receiving waters via surface and sub-surface runoff [1]. For potable supply, water treatment can include physical, chemical and biological processes designed to

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http://dx.doi.org/10.1016/j.cej.2014.06.014
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reduce treated water constituents to levels that comply with relevant guidelines or regulatory levels. One of the most widely used physico-chemical processes for removal of water contaminants is coagulation. Al(III) and Fe(III)-based salts are the most commonly used coagulants in water and wastewater treatment due to their low cost and abundant availability [2]. Application of high doses of alum and ferric coagulants for enhanced removal of organics from drinking water is based on a need to minimize concentrations of residual organics that act as precursors in the formation of halogenated disinfection by-products that are of health concern. The US EPA, under the Safe Drinking Water Act (Stage 1 Disinfectant and Disinfection Byproducts Rule), details enhanced coagulation requirements for total organic carbon (TOC) removals of between 15% and 50%, based on raw water TOC and alkalinity levels. In Australia, raw surface waters used for potable supply can have high concentrations of dissolved organic matter with DOC concentrations exceeding 10 mg/L [3–5]. DOC concentrations in major waterways used for potable supply can vary markedly in response to climate cycling, from extended dry (such as in an El Niño period) to very wet climate conditions (such as in a La Niña period) in Australia. In the La Niña cycle that occurred in 2010–2011, DOC concentrations up to 15.9 mg/L were recorded in a major Australian river (River Murray) used for potable supplies [5]. With such high concentrations of DOC in source waters used for potable supply and where chlorination is practised for disinfection, there is a need for highly efficient treatment methods to minimize residual DOC concentrations in drinking water supplies. Where conventional coagulation processes are applied with aluminum or ferric based coagulants for high DOC waters, and removal rates are at about 50% then residual organics can high in treated water. Under warm climate conditions as experienced in Australia and where chlorine is used for disinfection purposes, an increased risk from formation of halogenated disinfection by products can occur. To address this risk, investigations have been conducted in an attempt to identify coagulants of greater efficiencies such as HPAC (a composite of aluminum chloride, activated silicates and PolyDADMAC; [6] than those conventionally used, such as alum [7].

In the pursuit of improved treatment processing for dealing with challenging water qualities, other metal-based coagulants have and are still being considered. Coagulation efficiencies of titanium (Ti) based-salts were first reported by Upton and Buswell [8] and subsequently other studies have been reported [9–11]. Titanium and zirconium compounds (for use in coagulation) have been reported to be non-toxic and to not pose known risks to health and the environment [12,13]. Zhao et al. reported the removal of fulvic acid spiked into synthetic water by titanium tetrachloride at a low pH around 4–5 where the zeta potential of Ti flocs was near to the isoelectric point; this indicating potential application for waters and wastewaters with low pH. They also stated that DOC removal occurs through a combination of adsorption and charge neutralization mechanisms [14]. A potential advantage of Ti coagulants is the capacity for their reuse, such as in the recycling of waste sludge, as titanium dioxide (TiO_2), [9,15,16]. Jarvis et al. recently reported that zirconium oxychloride showed optimum DOC removal at pH 4–5 with greater positive zeta potential of their flocs than Al^{3+} or Fe^{3+} based coagulants [17]. The potential application of tetravalent Ti(IV) and Zr(IV) coagulants has attracted attention of the water industry, likely due to their reported attributes as well as low cost and commercial availability [17,18]. The Schulze-Hardy rule refers to a generalization that the critical coagulation concentration for a typical lyophobic sol is extremely sensitive to the valence of the counter-ions [19]. From the Schulze-Hardy rule, higher valency metal based counter-ions lead to more efficient destabilization of colloidal particles; however, for hydrolyzing metal salts, hydrolysis products or precipitates are more important than the simple ions for coagulating both particulates and dissolved NOM in water. The high coagulating power of multivalent ions is caused by their propensity to form hydrolysed products that have specific adsorption; the higher the valence, the higher the contribution of specific adsorption in the coagulation process [20–22]. For drinking water application, the relative effectiveness of charge neutralization by Na^+, Ca^{2+} and Al^{3+} ions is in the ratio of 1:60:700, respectively [23].

In this paper, we report results of investigations conducted on the coagulation performances of tetravalent titanium and zirconium salts, in comparison with the conventional coagulant, alum. Destabilization mechanisms (adsorption, charge neutralization, enmeshment or sweep) of organic matter were assessed with correlation of DOC removals with changes in zeta potentials of flocs formed at various treatment conditions.

2. Materials and methods

2.1. Surface water and analyses

Water samples were collected from a drinking water reservoir (Myponga Reservoir, located approximately 80 km south of Adelaide, South Australia) that has water of quality characterized by high color and dissolved organic matter (DOC > 10 mg/L). In this work, reservoir water samples were collected from the inlet point to Water Treatment Plant. For analyses of DOC, UV absorbance (UV_{254nm}) and color, raw and treated water samples were filtered through 0.45 μm membrane filters, pre-rinsed with high purity water. DOC was determined using a TOC analyzer (Model 820, Sievers Instruments, USA). UV_{254nm} and color were measured at 254 nm with 1 cm quartz cuvette and at 456 nm with 5 cm glass cuvette, respectively using a UV–vis spectrophotometer (UV-120 spectrophotometer, MIOSTECH Pty Ltd., Australia). Turbidity was determined using a 2100 N HACH turbidimeter. Zeta potentials (ZP) of flocs formed at various pH levels and coagulant doses were determined at 25 °C using a Zetasizer Nano ZS instrument, Malvern Instruments Ltd., UK, with the detection range of 3.8 nm to 100 μm (diameter) size particles.

2.2. Preparation of coagulants

The coagulants used in the jar test experiments were alum ($Al_2(SO_4)_3 \cdot 18H_2O$), titanium tetrachloride ($TiCl_4$) and zirconium tetrachloride ($ZrCl_4$). Alum was obtained from Incitec Pivot Ltd. – Port Adelaide, South Australia. The $TiCl_4$ (M = 189.68 g/mol; assay ⩾ 99%) and $ZrCl_4$ (M = 233.04 g/mol; assay ⩾ 98%) for synthesis were supplied by Merck Schuchardt OHG, Germany. The stock solutions (1.6 g/L as metal concentration) of $TiCl_4$ and $ZrCl_4$ were prepared by dissolving 3.71 mL of $TiCl_4$ (0.2 M HCl solution) and 4.14 g of $ZrCl_4$ in high purity Milli-Q® water. The same concentration of alum stock solution was prepared as detailed previously by Hussain et al. [24]. Newly prepared $ZrCl_4$ and $TiCl_4$ solutions were stored overnight for approximately 14 h at room temperature to dissolve the metal salts and subsequently stored at 4 °C prior to their use. The concentrations of Al, Ti and Zr in stock solutions were verified using inductively coupled plasma mass spectrometry (ICP-MS).

2.3. Coagulation–flocculation experiments

Evaluation of coagulants was carried out using a standard jar-test apparatus (Model FMS6V, SEM Pty, Brisbane, Australia) equipped with six paddle gang stirrers and Gator jars, each of 2 L water capacity. Coagulant doses (designated X_1) were varied between 3.5 and 18.4 mg/L (as metal concentration) and the coagulation pH (designated X_2) controlled at target levels ranging between 4.5 and 8 (Table A.1 in Appendix A, as Supplementary

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