



Understanding the coagulant activity of zirconium oxychloride to control THMs formation using response surface methodology

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ABSTRACT

In the present study, impact of coagulant activity of zirconium oxychloride and aluminium sulphate on the kinetics of chlorine consumption and trihalomethanes (THMs) formation has been delineated. Zirconium Oxychloride showed rapid chlorine decay within the first 30 min, which further achieved steady rate after 60 min, but in case of aluminium sulphate chlorine consumption has been increased drastically throughout the chlorine decay. Zirconium oxychloride has effectively reduced significant amount of slow reducing agents (SRA) as well as fast reducing agents (FRA), which correspond to the rate of reduction in phenolic groups from water enriched with Natural Organic Matter (NOM) which eventually decreased trihalomethane mediated cancer risk by ~ 2.3 times among adults as compared to aluminium sulphate. Result depicts the outstanding coagulant activity of zirconium oxychloride as it tends to surpass aluminium sulphate in reducing NOM “measured as Absorbance Slope Index (ASI)” and phenol by 57.98% and 49.02% respectively from NOM enriched chlorinated water, which also resembles the THMs removal trend observed during cancer risk assessment.

1. Introduction

Over the past years, the chlorine-based disinfection process has been the most effective public measure for the control of microbial contaminants in drinking water across the world (Xie, 2016; How et al., 2017; Priya and Mishra, 2017). However, the reactivity of chlorine towards aromatic moieties of NOM has elicited deleterious environmental impact due to the formation of carcinogenic chlorinated by products such as THMs and their associated cancer risks (Priya and Mishra, 2017).

In surface water, THMs is the most dominant chlorinated by product formed due to abundance of NOM deposited through various anthropogenic activities (Chu and Li, 2002). Chloroform, Dibromochloromethane (DBCM), Bromodichloromethane (BDCM) and Bromoform are four components of THMs group but chloroform is the most dominant species formed in surface water (Uyak and Toroz, 2005). USEPA (1999) has classified chloroform, BDCM and bromoform as probable human carcinogen group, which has also been validated by several researchers. Literature suggests that THMs mediated cancer risk has surpassed USEPA reference limit by 10–100 times in many South East Asian countries (Priya and Mishra, 2017).

During disinfection, chlorine exists either as acids like hypochlorous acid (HOCl) or anions (OCl⁻), which tend to react with aromatic moieties of NOM to form THMs. However, the second order reaction

between chlorine and NOM gets catalysed in the presence of stronger nucleophiles such as hydroxyl and amino groups (Minear and Amy, 1996; Cowman and Singer, 1996).

During chlorination, chlorine gets hydrolysed to form HOCl (Eq. (1)) which further dissociates to form hydrogen and hypochlorite ions (Eq. (2)):



Several researchers have demonstrated the role of substitutions reaction and oxidation (carbon bonds) while delineating the reaction pathway between halogens and NOM (Westerhoff et al., 2004). The kinetics of chlorine consumption by aromatic moieties of NOM to form THMs depend upon the availability of FRA and SRA in surface water (Zhan et al., 2010). A chlorine decay model depicted occurrence of two prominent phenomena, namely *Initial Rapid Decay* and *Slow Continuing Decay* due to the presence of FRA and SRA respectively during chlorine consumption by reactive sites of NOM in water as shown in (Eqs. (3) and (4)) (Zhan et al., 2010).



Where Cl₂ and SRA represent free chlorine available in water.

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The intense impact of stronger electron donating functional groups such as hydroxyl (OH⁻) groups on higher halogen consumption had also been reported while phenolic groups are prominent constituents of NOM, which makes significant contribution in formation of THMs in drinking water (Westerhoff et al., 2004; Rook, 1976). Phenolic groups are one of the SRA which provokes higher degree of chlorine consumption during Slow Continuing Decay process after chlorination (Norwood et al., 1987; Gallard and Von Gunten, 2002).

During Phenol-chlorine reaction, phenol undergoes oxidation via Electrophilic Aromatic Substitution (EAS) and Electron Transfer (ET) reactions with hypophalous acid (chlorine) to form mono-, di-, 2, 4, 6 trichlorophenol for phenol (as shown in Eqs. (5)–(7)) depending upon the degree of substitution pattern on aromatic rings (Rook, 1976; Gallard and Von Gunten, 2002). Literature has reported that aromatic rings undergoes bonding cleavage during the formation of chlorinated by products, when two “OH” groups” are in the *meta* position to each other (Boyce and Hornig, 1983) The mechanism of phenol chlorination as a function of pH was delineated based on speciation of chlorine (Eq. (2)) and phenol (Eq. (5)), the acid-catalysed reaction of HOCl with nondissociated phenol (Eq. (6)) and phenolate anions has been shown in (Eq. (7)).



The second order kinetics of chlorination of phenols and resorcinol are highly depended on pH, while slightly alkaline or neutral pH accelerates the rate of chlorine consumption by phenolic groups in NOM (Faust and Hunter, 1967).

The Differential Spectroscopy (ΔA_{272}) is the rapid and reliable approach to understand the dynamics of chlorine decay as (“Chlorine consumption”) by aromatic fraction of NOM. (Korshin et al., 2009).

$$\Delta A_{272} = A_{272}^{\text{Cl}} - A_{272}^{\circ} \quad (8)$$

Where A_{272}^{Cl} and A_{272}° represents absorbance at the wavelength of 272 nm before and after chlorination respectively. However, variation in NOM characteristic upon chlorination has been measured as ASI, which has shown linear (positive) correlation with rate of chloroform formation (Correlation factor ~0.9) in chlorinated water, which tend to decrease upon chlorine dosing which might be due to reduction in aromatic chromophores (Korshin et al., 2009).

Coagulation is a substantial remediation approach to disrupt the tenacity of widely distributed contaminants in source water and its distribution system. Basically, coagulants destabilize the negatively charged colloidal particles through the mechanism of charge neutralization, sweep flocculation and adsorption and allow them to form macro particles which eventually settle down. However, the prominent mechanistic approach would depend upon the specification of coagulants used in the process. According to Hardy-Schultz rule, the critical

coagulant dose for lyophobic sol is sensitive to the availability of counter ions for the efficient coagulant performance (Hussain et al., 2013). But, hydrolysed metallic precipitates play a crucial role for the destabilization of NOM fractions in case of hydrolysing salts such as chemical coagulant. Aluminium sulphate is the most preferred chemical coagulant used in the water treatment, but it has not been considered choice for the treatment of NOM enriched raw water (Priya et al., 2017; Jarvis et al., 2012). However, Jarvis et al. (2012) reported that zirconium oxychloride has shown better flocculating property and coagulant activity which might be due to higher cationic charges and faster rate of hydrolysis than traditional coagulant (Hussain et al., 2013; Priya et al., 2017; Jarvis et al., 2012). It has been reported that zirconium oxychloride elicited non-toxicity effect on health while higher aluminium residuals in water might induce neuro degenerative diseases (Arezoo, 2002; Freitas et al., 2016).

In the present study, the kinetics of chlorine consumption by zirconium oxychloride has been assessed and compared with aluminium sulphate. Impact of coagulant behaviour in the dynamics of FRA and SRA during chlorine decay and variation in mechanistic approach of both coagulants have also been elucidated. The optimization of coagulation process has been carried out using 2³ full-factorial central composite design and Response Surface Modelling method to elaborate the interaction between factors (such as pH and coagulant dose) and their subsequent effect on coagulant activity with respect to removal of NOM concentration (as ASI), phenol and turbidity. The concept of the ASI and Differential Spectroscopy have been employed to understand the effects of coagulants on the dynamics of NOM reactivity towards chlorine.

2. Material and methods

2.1. Chemicals

Aluminium sulphate octadecahydrate [Al₂(SO₄)₃·18H₂O] and zirconium oxychloride (ZrOCl₂·8H₂O) were procured from Merck (India) and Universal Laboratories (India) respectively. Humic acid and kaolin were purchased from Loba Chemie, Mumbai, India. Coagulant solution was prepared in Millipore water (Merck, Germany). Analytical grade chemicals were used.

2.2. Preparation of coagulant solution

The coagulant solution of aluminium sulphate and zirconium oxychloride were prepared by dissolving 1 g of coagulant salt in 1 L of deionized water to prepare respective solution. Both coagulant solutions were further stored at 4 °C.

2.3. Preparation of synthetic water

Synthetic water was prepared using kaolin and humic acid to

Table 1
ANOVA Analysis for coagulant activity of zirconium oxychloride.

	Turbidity reduction				ASI reduction				Phenol reduction			
	Sum of squares	df	Mean square	F value	Sum of squares	df	Mean square	F value	Sum of squares	df	Mean square	F value
Quadratic model	3516.54	5	703.25	435.23	4512.31	5	902.46	36.89	3559.12	5	711.82	56.01
A-pH	54.09	1	54.09	33.48	199.541	1	199.54	8.16	395.42	1	395.42	31.12
B-Doses	1252.09	1	1252.09	774.90	137.001	1	137.00	5.60	272.30	1	272.30	21.43
AB	98.27	1	98.27	60.82	171.581	1	171.58	7.01	90.47	1	90.47	7.12
A ²	348.84	1	348.84	215.89	2034.90	1	2034.90	83.18	1258.09	1	1258.09	99.00
B ²	626.14	1	626.14	387.51	308.061	1	308.06	12.59	411.53	1	411.53	32.38
Residuals	11.31	7	1.62	–	171.257	7	24.46	–	88.96	7	12.71	–
Lack of fit	11.28	3	3.76	483.90	170.433	3	56.81	278.03	88.95	3	29.65	10,153.63
Pure Error	0.031	4	7.770-E-003	–	0.82	4	0.20	–	0.012	4	2.920E-003	–
Total	3527.54	12	–	–	4683.56	12	–	–	3648.08	12	–	–

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