



Experimental investigation and modeling of dissolved organic carbon removal by coagulation from seawater



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HIGHLIGHTS

- Coagulation by FeCl₃ with seawater was carried out.
- DOC removal modeling was made with detailed organic fractionation.
- DOC removal in seawater by coagulation improved marginally with increased pH.
- Hydrophobic and hydrophilic fractions showed completely different removal behaviors.
- DOC removal model is beneficial in coagulation design for desalination plants.

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ABSTRACT

Coagulation removes colloidal matters and dissolved organic carbon (DOC) which can cause irreversible membrane fouling. However, how DOC is removed by coagulant is not well-known. Jar test was used to study the removal of hydrophobic and hydrophilic DOC fractions at various doses (0.5–8.0 mg-Fe⁺³ L⁻¹) of ferric chloride (FeCl₃) and pH (5.0–9.0). Natural organic matter (NOM) in seawater and treated seawater were fractionated by liquid chromatography-organic carbon detector (LC-OCD). Compared to surface water, the removal of DOC in seawater by coagulation was remarkably different. Majority of DOC could be easily removed with very low coagulant dose (<5.0 mg-Fe⁺³ L⁻¹) and the removal efficiency did not vary with pH, but the DOC composition in treated water had significantly changed. Hydrophobic fraction (HB) was better removed at high pH while hydrophilic fraction (HF) was better removed at low pH. A modified model of Kastl et al. (2004) which assumed that the removal occurred by adsorption of un-dissociated compounds onto ferric hydroxide was formulated and successfully validated against the jar test data.

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1. Introduction

The concentrations and types of natural organic matter (NOM) in seawater vary with time and location. Dissolved organic carbon (DOC) is a collective (surrogate) parameter expressed in mg of all carbon in organic molecules in unit volume and it is most widely used to represent the concentration of NOM (Emelko et al., 2011). The DOC of seawater is typically 2–5 mg L⁻¹. This dissolved organic matter from algae and humic substances in seawater NOM

causes severe fouling of reverse osmosis (RO) membranes by organic adsorption or biofilm growth (Shon et al., 2009). Therefore, pretreatment for removal of NOM is essential in seawater RO plant.

Coagulation/flocculation is one of the available chemical pretreatment options for the removal of colloidal particles and NOM (Duan et al., 2002). NOM molecules are complex mixtures of aromatic and aliphatic molecules with organic acid groups, the majority of which are negatively charged at neutral pH. Some of these compounds possess hydrophobic character while some attain it when pH changes. This negative charge and hydrophobic character can be reacted and removed by coagulation and separation of precipitated solids. Thus, metal coagulants such as Al and Fe are used commonly in water treatment under appropriate dose and pH condition to form precipitates of Al- or Fe-hydroxides (Edzwald and Haarhoff, 2011).

Abbreviations: CDOC, chromatographic DOC; DOC, dissolved organic carbon; HB, hydrophobic; HF, hydrophilic; LC-OCD, liquid chromatography-organic carbon detector; LMW, low molecular weight; NOM, natural organic matter; RO, reverse osmosis.

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The modeling and prediction of DOC will be beneficial for optimization of the treatment process (i.e. coagulant dose and coagulation pH) through limited number of experiments, if the impacts of various fractions on the membrane fouling are known. Furthermore, applicable conceptually valid models would provide further understanding of the process and would aid in better control (Kastl et al., 2004).

Several empirical and semi-empirical models have been proposed and used in prediction of DOC removal during coagulation (van Leeuwen et al., 2005; Edwards, 1997; Harrington et al., 1992; Moomaw, 1992). Tseng and Edwards (1999) showed that the accurate predictions of final DOC by enhanced coagulation was possible using the model developed by Edwards (1997). Kastl et al. (2004) improved the model by Edwards (1997) by conceptually separating the DOC into three fractions: Non-sorbable fraction – hydrophilic compounds which cannot be removed at any pH by a given coagulant; non-polar fraction – compounds that can be removed at any pH as it possess neutral charge irrespective of pH; and humic acid fraction – compounds that is capable of dissociating like a weak acid and is assumed that only the neutral form can be removed by adsorption. Similar to Edwards (1997), Kastl et al. (2004) assumed that the removal follows Langmuir adsorption theory. They successfully validated their model against 17 different water sources in Australia and United States (US) Kastl et al., 2004. Aryal et al. (2011) applied the model of Kastl et al. (2004) to quantitatively prove that biologically activated carbon enhances the removal of DOC by converting the non-sorbable organic fraction into sorbable organic fractions.

To date, however, little works have been reported on the DOC removal by coagulation from seawater or saline water or its modeling. The general factors that influence the DOC removals in seawater following coagulation are now well understood and studied, but formulation of a quantitative model has been hindered due to complex interplay between seawater organic matters. In addition to the difference in NOM character, the salinity and ion product (on the seawater chemistry of significant parameters) can also affect chemical hydrolysis and metal-hydroxide solubility reactions during coagulation (Edzwald and Haarhoff, 2011). Thus, seawater could show a different coagulation performance from freshwater.

In the pretreatment of seawater, ferric salts, particularly ferric chloride (FeCl_3), are recommended because the equilibrium solubility of Fe with amorphous ferric hydroxide in seawater is low over a wide range of pH and temperature conditions. $\text{Fe}(\text{OH})_3$ is highly insoluble, leaving less residual dissolved Fe in the water after pretreatment and hence it causes only minor scaling effect on RO membrane. Assuming raw seawater pH is about 8 and Fe dose is low, the buffer intensity is fairly low at pH 7.5–8.0 (Edzwald and Haarhoff, 2011). Thus it requires only a small addition of strong acids in coagulation step.

In this study, a standard coagulation jar test was carried out using FeCl_3 as coagulant at a wide concentration of 0.5–8.0 $\text{mg-Fe}^{+3} \text{L}^{-1}$. The liquid chromatography-organic carbon detector (LC-OCD) was used to quantify the DOC concentration in seawater following coagulation. The use of LC-OCD enabled a more detailed fractionation of DOC compounds in seawater as well as that remained after coagulation. LC-OCD is the combination of a size exclusion chromatography with a continuous ultra-violet (UV) detector which enables quantification of DOC (Huber and Frimmel, 1994; Huber et al., 2011). Depending on the size of the molecules, the different fractions of the organic matter can be identified and quantified. DOC can be divided into two fractions (hydrophobic and hydrophilic) by LC-OCD. The hydrophobic (HB) DOC is calculated from the difference of DOC and chromatographic DOC (CDOC or hydrophilic (HF) DOC). All organic matter retained in the column is defined as HB DOC. This can be either dissolved hydrocarbons or

micro particulates including humics. CDOC is calculated from the area enclosed by the total chromatogram (Huber and Frimmel, 1994). The HF DOC compositions are classified as biopolymers, humics, building blocks, and low molecular weight (LMW) neutrals and acids.

The aim of this study was to develop a quantitative mathematical model of the residual (remaining) DOC in seawater after coagulation treatment with FeCl_3 at different pHs and coagulant doses. The model described was used to fit the experimental data for removal of HB and HF DOC fractions by coagulation. It is expected that the data would reduce the number of experiments necessary and enable prediction of benefits achievable by coagulant dose and pH change.

2. Model development

Kastl et al. (2004) described removal of DOC by enhanced coagulation with aluminum and iron salts for various doses and pHs. They used a Langmuir adsorption theory to model DOC removal onto the metal hydroxide surface. They hypothetically divided DOC into three fractions:

- (1) Humic acid fraction which adsorbs in associated form and therefore its adsorption is pH dependent as humic acid is defined as a weak acid with a dissociation constant of K_a .
- (2) Neutral component which is adsorbed by metal hydroxides and the adsorption is pH independent.
- (3) Non-sorbable fraction (inert organic fraction) the removal by metal hydroxides can be neglected.

In this study, it was intended to describe the removal of DOC in the form of HB and HF fractions arising from measurements using LC-OCD and hence modification to the model was needed. Within HB and HF fractions, there are multiple compounds each behaving differently to coagulation treatment. A complicated model with many parameters is needed to account for all the compounds measured by LC-OCD. Such model would not justify its practical or theoretical utility. Hence, a simple approach to the modeling was adopted. This was done by replacing the conceptual non-polar fraction in Kastl et al. (2004) with two fractions: a hydrophobic fraction which behaves as a weak base (BOH) and a non-polar hydrophobic fraction (HB_{np}). In addition, the humic acid conceptually assumed in the Kastl et al. (2004) is replaced with a dissociable hydrophilic fraction in an acidic form (HA), of which the neutral form could only be removed. Non-sorbable fractions in Kastl et al. (2004), which are mostly low molecular hydrophilic compounds, are renamed as inert hydrophilic fraction (HF_i). The conceptual representation of fractions and their removal is presented in Fig. 1 and the explanation is given below.

DOC is therefore the sum of both fractions:

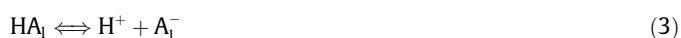
$$\text{DOC} = \text{HB} + \text{HF} \quad (1)$$

Hydrophilic compounds are, for the purpose of modeling, divided into dissociating acidic and inert fraction in terms of coagulation or non-sorbable fraction:

$$\text{HF} = \text{HA} + \text{HF}_i \quad (2)$$

where HA is dissociating HF compounds, which are adsorbed onto ferric hydroxide in their associated form.

Dissociation of HA in liquid form is assumed to progress according to the reaction:



This is an equilibrium reaction, when in dissolved form it would be controlled by the equilibrium constant:

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