

## Reducing disinfection byproduct precursors through coagulation enhancement as particle weight and size control using potassium permanganate

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### ABSTRACT

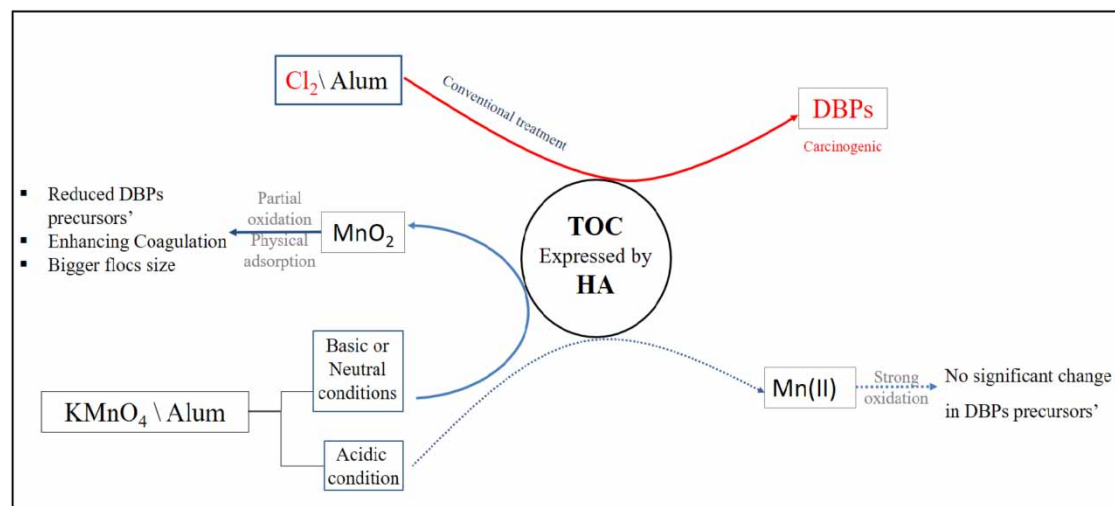
The widespread use of chlorine pre-oxidation in water purification has been limited in several countries owing to the production of carcinogenic byproducts when combined with naturally occurring organic matter. This study investigates the efficient use of potassium permanganate (KMnO<sub>4</sub>) pretreatment and coagulation enhancement as particle size and molecular weight distribution controlling parameters. KMnO<sub>4</sub> pretreatment significantly reduced the apparent molecular weight of humic acid due to KMnO<sub>4</sub> reduction and the continuous generation of manganese dioxide (MnO<sub>2</sub>) formed *in situ* under neutral and alkaline conditions. The MnO<sub>2</sub> formed *in situ* had adsorption characteristics that enabled it to form large and stable flocs with the hydrolysis products of aluminum sulfate. However, under acidic conditions, KMnO<sub>4</sub> pretreatment exhibited strong oxidation characteristics due to Mn(VII) reduction to Mn(II), and the mean particle floc size was the same as without KMnO<sub>4</sub> pretreatment. Overall, KMnO<sub>4</sub> pretreatment is a useful alternative strategy for traditional pre-oxidation using chlorine and a good coagulant enhancement agent in neutral and basic media.

**Key words:** coagulation enhancement, gel permeation chromatography, humic acid reduction, particle size analysis, potassium permanganate

### HIGHLIGHTS

- pH is crucial in the KMnO<sub>4</sub> pretreatment mechanism.
- Under acidic conditions, KMnO<sub>4</sub> pretreatment results in the same mean particle floc size as alum alone.
- The *in situ* formed MnO<sub>2</sub> is incorporated with the alum hydrolysis product, forming larger flocs.
- KMnO<sub>4</sub> pretreatment under optimal conditions results in a significant reduction in the molecular weight distribution of humic acid.

## GRAPHICAL ABSTRACT



## INTRODUCTION

Egypt depends on conventional treatment for surface water purification from the Nile River and its branches. The treatment is a series of processes that include coagulation, flocculation, sedimentation, and filtration and is typically followed by full-scale disinfection (Zouboulis *et al.* 2008). Water treatment plants (WTPs) are often preceded by a pre-oxidation step. Chlorine has been extensively used in developing countries for WTPs to inactivate harmful pathogens and prevent algae accumulation in pipes, tanks, and filters. However, the pre-chlorination step has some limitations because chlorine can react with natural organic matter (NOM) to form various harmful carcinogenic disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Li & Mitch 2018). As a result, several water regulatory agencies have lowered the maximum allowable levels of THMs and HAAs in drinking water (USEPA 2003).

One possible strategy to reduce DBP levels in treated water is for WTP operators to perform the chlorination step after coagulation, sedimentation, and filtration, which significantly reduces THM formation, sometimes by more than 50% (García & Moreno 2009). However, eliminating the pre-chlorination step may not be a viable option, as it has been used for controlling biological growth, taste, and odor during water treatment processes (Lapsongpon *et al.* 2017).

The use of alternative pre-oxidants, such as ozone, chlorine dioxide, UV, and potassium permanganate (KMnO<sub>4</sub>), instead of chlorine has been investigated in many studies (Xie *et al.* 2016). KMnO<sub>4</sub> has long been used for removing iron and manganese by oxidation and precipitation. Recently, KMnO<sub>4</sub> has received much attention for its use in treating NOM and removing algae. KMnO<sub>4</sub> utilization has the advantage of lower installation costs, easy application, and production of nonhazardous byproducts (Yu *et al.* 2011; Tian *et al.* 2013; Phatai *et al.* 2014).

Many researchers have discussed the efficiency of KMnO<sub>4</sub> in removing DBP precursors. While some authors attributed its enhancement to the chemical oxidation reaction, others believed it was physical adsorption on the *in situ* formed manganese dioxide (MnO<sub>2</sub>).

Hidayah & Yeh (2018) reported that KMnO<sub>4</sub> pre-oxidation caused the breakdown of high-molecular-weight organics into low-molecular-weight organics. They also revealed that increasing KMnO<sub>4</sub> dosage could decrease aromatic matter, as evidenced by 23 and 28% reductions in UVA<sub>254</sub> and SUVA<sub>254</sub> values, respectively. Moreover, DBP formation potential in terms of THM formation potential and HAA formation potential decreased by approximately 15 and 23%, respectively.

Another approach was studied by Ma *et al.* (2001), who performed pre-oxidation with KMnO<sub>4</sub> to improve surface water coagulation using high organic content. They found that the MnO<sub>2</sub> formed *in situ* during KMnO<sub>4</sub> reduction significantly improved the coagulation and sedimentation processes. Manganese dioxide can adsorb naturally occurring organic materials through surface binding to form larger particles, increase the floc density, and improve the particle settling velocity (Liu *et al.* 2012; Lin *et al.* 2013; Cui *et al.* 2020).

Previous studies have discussed NOM removal by  $\text{KMnO}_4$  pre-oxidation at specific pH values (Zhang *et al.* 2009; Liu *et al.* 2012; Xie *et al.* 2016) without analyzing particle size and precursors' molecular weight distribution and their relationship to  $\text{KMnO}_4$  efficiency in coagulation enhancement. Therefore, the current study tries to fill the knowledge gap and complete the picture of using  $\text{KMnO}_4$  as an alternative pre-oxidant to enhance the removal of DBP precursors by determining the reaction pathway at different pH values using floc particle size and molecular weight distribution. Different modes of action are identified (oxidation or adsorption), and detailed analyses for controlling parameters are presented.

## MATERIALS AND METHODS

### Chemicals

Humic acid (HA): A stock solution was prepared by dissolving 1 g HA (Fluka) in 1,000 ml of 0.1 M NaOH, which was then filtered through a 0.45  $\mu\text{m}$  filter membrane and stored at  $-4^\circ\text{C}$  in the dark. The stock solution was diluted, and the total organic carbon (TOC) was measured and recorded.

The stock solutions used in this study included  $\text{KMnO}_4$  solution (0.5 g/L),  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  coagulant (0.5 g/L), and kaolin (50 g/L). All chemicals were of reagent grade, and all solutions were made using deionized water.

### Synthetic water preparation

The synthetic water samples comprised HA, kaolin, and tap water from Shoubra El-Kheima WTP and were used to simulate actual surface water contaminants. Table 1 lists the properties of the synthetic water.

### Preliminary determination of alum and $\text{KMnO}_4$ dosage

The alum working dose was predetermined using a standard jar testing apparatus (Hach) with a six-paddle stirrer in 2-L square plexiglass beakers. It was determined based on the turbidity removal efficiency of the artificial samples. The working  $\text{KMnO}_4$  dose was estimated based on the turbidity removal efficiency and the permissible residual Mn(II) according to Egyptian drinking water quality regulations.

### Experimental setup

The jar test experiments were conducted on the synthetic samples at room temperature of  $25^\circ\text{C} \pm 1^\circ\text{C}$ . The predetermined  $\text{KMnO}_4$  dose was mixed at 225 rpm for 5 min, followed by the addition of the determined alum dose at the same rate for 2 min, and then the mixing speed was lowered to 35 rpm for 15 min. The solution was allowed to settle for 15 min. All samples were analyzed for turbidity using a Hach 2100 N turbidimeter (USA).

### Size exclusion chromatography

The variation in HA concentration and molecular weight distributions were analyzed by gel permeation chromatography (PL-GPC 50 with integrated RI, Agilent Technologies, USA) during the jar test experiment after  $\text{KMnO}_4$  pretreatment, flocculation, and sedimentation. The samples for GPC analyses were filtered through glass fiber filter paper with a pore size of 0.45  $\mu\text{m}$  before analysis.

### Floc size distributions

The development of floc size distributions during the jar test experiments were continuously monitored using a laser particle size analyzer (Mastersizer 2000, Malvern Instruments, UK) by drawing water through the optical unit of the instrument and back into the jar test beaker again with a peristaltic pump on the return tube. The inflow and outflow tubes were positioned in

**Table 1** | Synthetic water properties

No.	Parameter	Value
1	TOC content	5 mg/L
2	$\text{UV}_{254}$ absorbance	$0.700 \pm 0.002$
3	pH	$8.25 \pm 0.10$
4	Turbidity	$30.0 \pm 0.5$ NTU

the jar opposite one another at a depth just below the surface by 4 cm. Mean floc size measurements were taken every 30 s during the jar test experiments and logged onto a computer (Xu *et al.* 2016).

## RESULTS AND DISCUSSION

### Determination of the optimal doses of alum and $\text{KMnO}_4$

Figure 1 shows the turbidity removal efficiency during the jar test experiments of different alum doses, where the optimal alum dose was 2.5 mg/L. As shown in Figure 2,  $\text{KMnO}_4$  pre-oxidation had an obvious effect on the alum coagulation and turbidity removal efficiency of the artificial samples. The turbidity removal from the pretreated samples with  $\text{KMnO}_4$  exceeded that without  $\text{KMnO}_4$  pretreatment (Ma *et al.* 2001; Zhang *et al.* 2008). The turbidity removal efficiency did not increase significantly with further  $\text{KMnO}_4$  increase, where it achieved a plateau and then decreased, which may be attributed to  $\text{KMnO}_4$  color or the suspended colloidal  $\text{MnO}_2$  formed *in situ*.

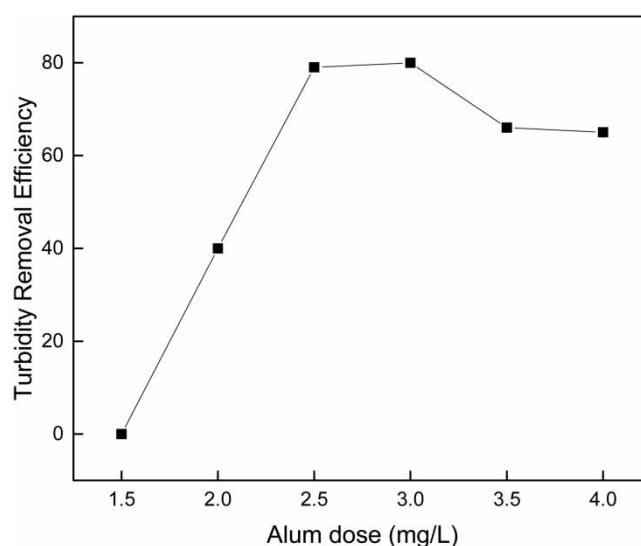


Figure 1 | Alum dose determination of the artificial sample.

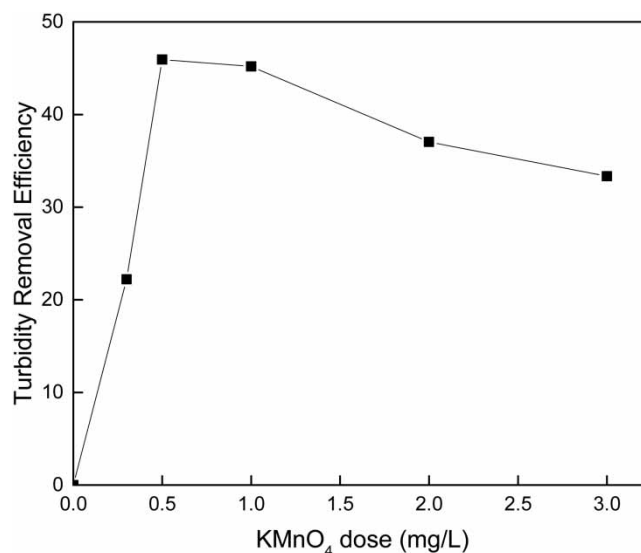


Figure 2 | Permanganate dose determination of the artificial sample.

KMnO<sub>4</sub> has oxidation characteristics that might degrade HA into low-molecular-weight fragments, which may be removed by subsequent coagulation. In addition, the MnO<sub>2</sub> formed *in situ* has adsorption characteristics that may be the factor responsible for HA removal, or perhaps both mechanisms are working together (Zhang *et al.* 2009; Liu *et al.* 2012).

### Dynamic analysis of floc size during alum coagulation jar test with KMnO<sub>4</sub> pretreatment

Figure 3 shows the growth of the mean floc particle size during the alum coagulation jar test with and without KMnO<sub>4</sub> pretreatment at different pH values. The order of aggregation and floc formation time is pH 5.5 > pH 7.0 > pH 8.5. This could be possible because the optimal pH of the alum working dose is between 5.5 and 6 (Nowacka *et al.* 2014; Pivokonsky *et al.* 2015).

Under acidic conditions, the mean floc diameter increased rapidly at 2 min, reaching a maximum with a mean floc diameter of approximately 100 µm and remained constant after 5 min flocculation for both with and without KMnO<sub>4</sub> pretreatment. This effect occurred because of KMnO<sub>4</sub>'s strong oxidation properties and Mn(VII) reduction to Mn(II) (Kao *et al.* 2008; Li *et al.* 2012), which has no effect on the mean floc diameter size.

The largest mean floc diameter was formed at pH 7.0 with KMnO<sub>4</sub> pretreatment, which started at 4 min of flocculation and gradually increased because of the continuous generation of colloidal MnO<sub>2</sub>, which combined with the hydrolysis products of alum and aggregated into larger flocs. After 15 min of flocculation, the maximum steady value was reached at approximately 105 µm, compared to 63 µm in the case without KMnO<sub>4</sub> pretreatment.

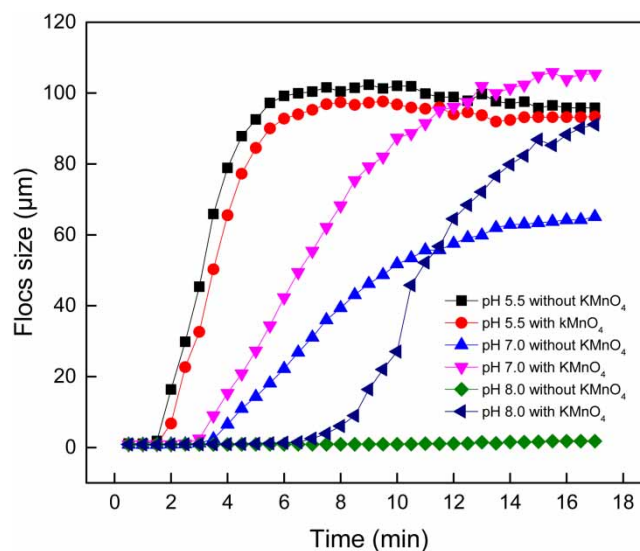
The coagulation jar test with the selected alum dose at pH 8.5 did not produce flocs. However, KMnO<sub>4</sub> pretreatment induced floc formation after 8 min, and the mean floc particle size increased continuously owing to the continuous formation of colloidal MnO<sub>2</sub> during KMnO<sub>4</sub> reduction, reaching 100 µm after 18 min.

### Characterization by GPC

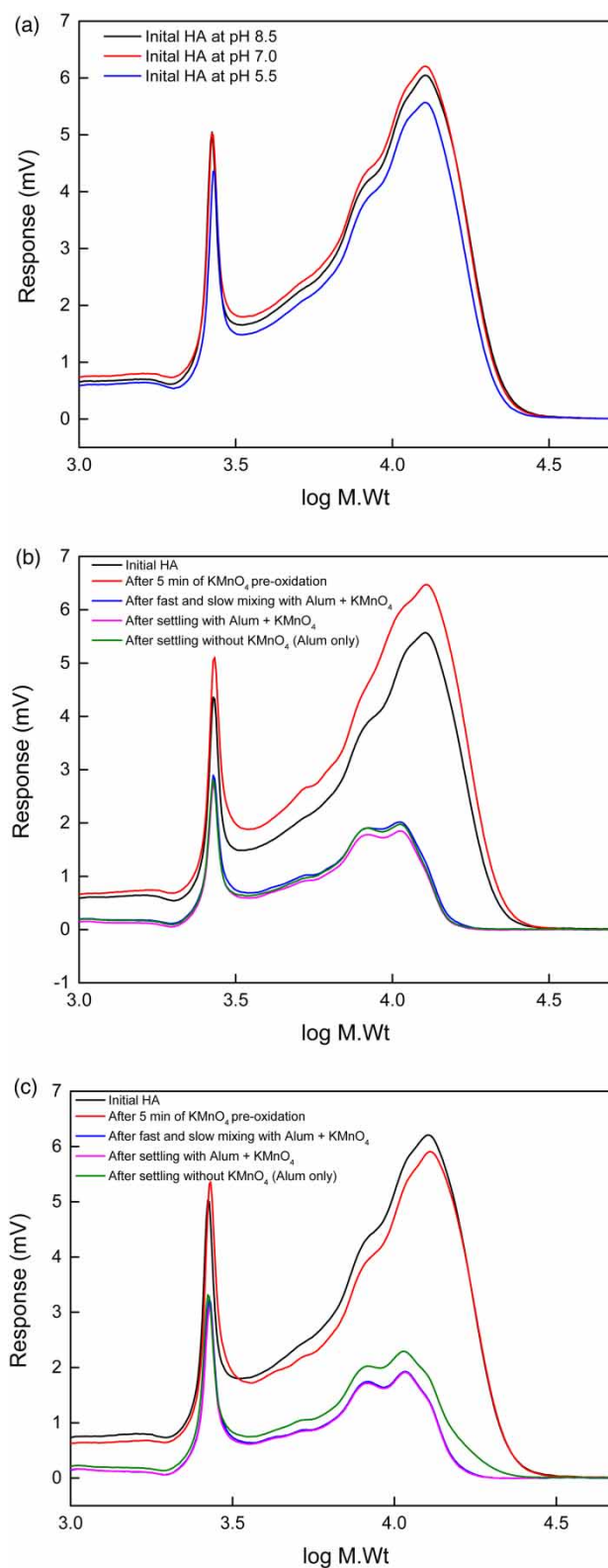
Figure 4 shows the molecular weight distribution of the original HA solution and the improved alum coagulation process of HA by KMnO<sub>4</sub> pretreatment at different pH values. Larger molecules elute faster than smaller molecules in size exclusion chromatography (SEC). Therefore, the broad peaks in the SEC chromatogram with the shortest elution time were assigned to large molecules.

The artificial HA comprised two main bands with different molecular size fractions at all selected pH values. As shown in Figure 4, the percentages of the two peaks decrease with lowering the pH of the original HA because HA with a few negative charges was removed more by self-aggregation at lower pH values (Hakim *et al.* 2019).

Before the addition of alum, the chromatogram of HA after 5 min of KMnO<sub>4</sub> pre-oxidation showed a decrease in the organic matter content under neutral and basic conditions (Figure 4(c) and 4(d)). This is because the MnO<sub>2</sub> formed

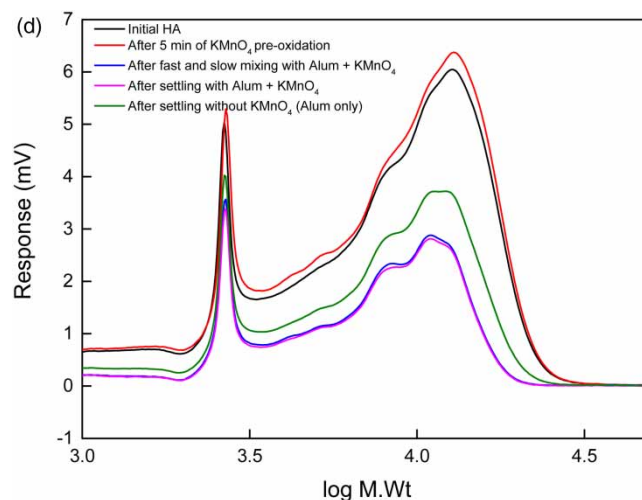


**Figure 3** | Time course of mean floc size development with and without permanganate pretreatment under different pH values.



**Figure 4** | Molecular weight (MW) distributions of (a) untreated original artificial HA samples at different pH values and treated HA using the  $KMnO_4$ /alum coagulation process, (b) pH 5.5, (c) pH 7.0, and (d) pH 8.5. (*continued.*).





**Figure 4** | Continued.

*in situ* has adsorption ability and may adsorb HA fractions (Xie *et al.* 2013). In contrast, the organic contents increase under acidic conditions because HA organic compounds are degraded to low-molecular-weight compounds during  $\text{KMnO}_4$  reduction to  $\text{Mn(II)}$ , proving that the oxidation mechanism prevails (Figure 4(b)).

Furthermore, under the same alum dosage of 1.0 mg/L as  $\text{Al(III)}$ , the apparent molecular weight was reduced, and the high-molecular-weight compounds were more easily removed by the subsequent alum coagulation process than the low-molecular-weight ones. Notably, coagulation with  $\text{KMnO}_4$  pre-oxidation caused a greater reduction in peak height and area for all types of molecular weight organic compounds than coagulation without  $\text{KMnO}_4$  pretreatment, especially under basic and neutral conditions. This effect occurred because the  $\text{MnO}_2$  formed *in situ* can adsorb HA and then interact with the hydrolysis product of alum to form large flocs with higher specific gravity and higher settling velocity, resulting in improved HA removal (Ma *et al.* 2001).

## CONCLUSION

This study investigates  $\text{KMnO}_4$  as a feasible alternative pre-oxidant and coagulant enhancement agent. pH is a critical factor affecting  $\text{KMnO}_4$  behavior in the entire mechanism and process, which could be either only strong oxidation under acidic conditions or mild oxidation and adsorption through the *in situ* formed  $\text{MnO}_2$  at neutral and basic media in proportion. The molecular weight distribution was significantly reduced using  $\text{KMnO}_4$  under neutral and basic conditions, indicating that HA was broken down into lower-molecular-weight fragments that could be easily adsorbed by coagulant hydrolysis products and *in situ* formed  $\text{MnO}_2$ . Furthermore, particle size analysis revealed that the continuous formation of colloidal  $\text{MnO}_2$  under neutral and basic conditions allows it to combine with alum hydrolysis products and aggregate into larger flocs, enhancing the coagulation process.

Overall,  $\text{KMnO}_4$  is an excellent strategy and alternative to pre-oxidation, particularly in areas prone to organic loads, to overcome the issue of DBP formation. After evaluating its performance on natural surface water samples, we recommend using  $\text{KMnO}_4$  pre-oxidants on WTPs with a high organic load.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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