Effect of natural organic compounds on the removal of organic carbon in coagulation and flocculation processes

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Abstract Natural organic matter (NOM) in water contains organic compounds that are both hydrophobic and hydrophilic with a wide range of molecular weights. It is composed of non-homogeneous organic compounds such as humic substances, amino acids, sugars, aliphatic and aromatic acids, and other chemical synthetic organic matters. NOM in water is a major concern not only because of its contribution to the formation of disinfection by-products (DBPs) and taste and odor, but also its influence on the demand for coagulants and disinfectants, the removal efficiency of water treatment processes, etc.

This research aims at identifying the influence of NOM in coagulation and flocculation processes in order to optimize the coagulation and flocculation conditions. In this study, pretreated pond water was used as the source water. It was observed from the experimental results that:

(1) The optimum pH for coagulation to remove NOM is around 7.

(2) The optimum alum dose at this pH can vary from 125–1,225 mgl^{-1} when the TOC is increased from 4 to 25 mgl^{-1}.

(3) The presence of secondary compounds such as Ca^{2+}, Mg^{2+} divalent cations had no significant effect on the removal of organic matter.

(4) The presence of clay increased the organic removal by 15%.

(5) The organic compound with higher molecular weight has higher removal affinity in coagulation process.

(6) Floc size and settling velocity of floc and sludge production all increased with the increase in NOM concentration. From the results of Capillary Suction Time (CST) tests, the floc formed with lower TOC readily released the water to make the dewatering process easier.

(7) The organic removal efficiency was significantly different for natural water containing non-homogeneous organic compounds compared to the synthetic water containing humic acid only (homogeneous organic matter).

For example, the NOM removal efficiency was 80% for the synthetic water containing humic acid with TOC of 7 mgl^{-1} at pH 7; but the NOM removal for the pretreated pond water was 60%.

Keywords Coagulation; flocculation; natural organic matter (NOM); total organic carbon (TOC)

Introduction

Removal of organic contaminants from surface water becomes one of great importance in water treatment process because of health, aesthetic and operational problems. Types of organic contaminants that are present in natural water are shown in Figure 1. The three major components are natural organic matter (NOM), synthetic organic chemicals and others. The NOM is divided into four subgroups namely: humic substances, microbial exudates and dissolved organics from plant tissues and animal wastes. The higher molecular weight fractions of NOM such as hydrophobic acids (HPOA – e.g. humic acids and fulvic acids) and hydrophobic neutrals (HPON) can be extracted by XAD-8 resins and the lower molecular weight fractions such as transphilic acids (TPHA) and transphilic neutrals (TPHN) can be extracted by XAD-4 resins. The filtrate from these two resins will be of hydrophilic NOM (HPI).

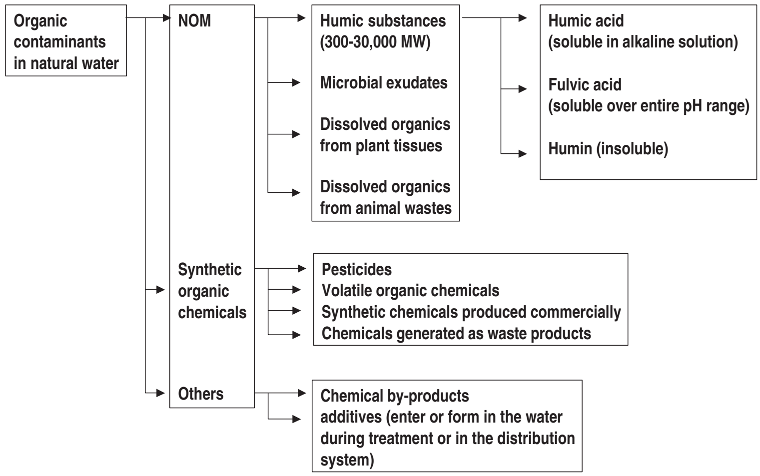

Figure 1 Types of organic substances present in water (adapted from Jegatheesan and Vigneswaran, 1997)

Research have been conducted to study the influence of organic substances using synthetic water (with humic acid) in water treatment processes and to evaluate their relationship with pH, total organic carbon (TOC) removal and the demand of coagulant dosage (Choudhary, 1993; Cho, 1995). This study examines the removal of organic substances from drinking water by coagulation and flocculation processes and identifies the influence of NOM on the operating parameters such as pH, TOC and coagulant dose.

Methodology

Natural water was obtained from the canal that runs close to the Asian Institute of Technology (AIT) in Bangkok, and pretreated by using 5 and 0.2 μm cartridge filters. The filtrate from 0.2 μm cartridge filter was passed through a reverse osmosis (RO) membrane to concentrate the NOM present in the water. This concentrate was used in subsequent coagulation/flocculation experiments (using jar tests) at different dilutions. Synthetic water was prepared by dissolving humic acid in distilled water. Experiments were conducted in this study to find the following:

1. Optimum operating conditions of pH and alum dose:
   - for natural water at different TOC (4, 7, 10, 19 and 25 mgl^{-1});
   - for natural water (TOC = 7 mgl^{-1}) with secondary compounds such as Ca^{2+} and Mg^{2+};
   - for natural water (TOC = 7 mgl^{-1}) with clay.
2. Floc characteristics:
   - floc size;
   - settling velocity;
   - molecular weight distribution;
   - capillary suction time (CST) test.
3. NOM removal efficiency in natural and synthetic waters.

Results and discussion

Optimum alum dose

Figure 2 shows the removal of NOM from natural water by coagulation and flocculation in terms of percentage TOC removal. The natural water used in the experiments contained a TOC of 7 mgl^{-1}. At optimum alum dose, the lowest TOC removal of 15.8% was achieved at pH 4. With the increase of pH up to 7, the TOC removal increased up to 60%. However, at

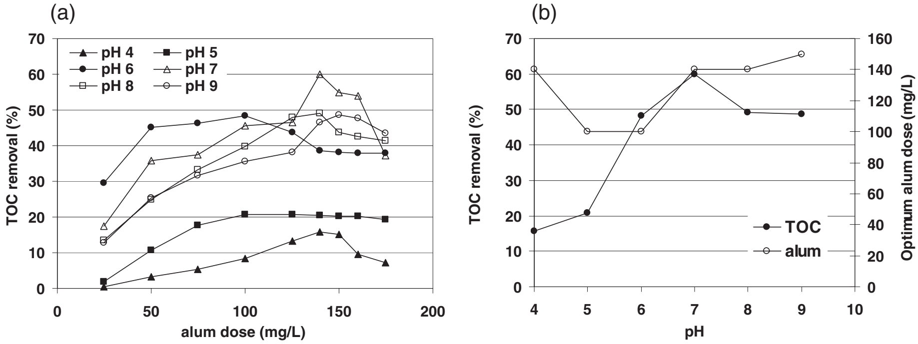

Figure 2 (a) Jar test results for TOC removal from natural water (TOC = 7 mgl^{-1}) at different pH values. (b) Optimum alum dose required and corresponding TOC removal from natural water (TOC = 7 mgl^{-1}) at different pH values

pH 9 the TOC removal decreased to 48.6%. Thus, optimum pH for maximum organic removal was around 7. These characteristics of NOM removal at different pH can be explained on the basis of the behavior exhibited by alum at different pH. At higher pH, chemical functional groups associated with NOM ionized and resulted in the increase of negative charge. At lower pH there is no ionization of any functional groups of NOM and the NOM removal is achieved mainly due to adsorption. Figure 3 illustrates the stability diagram of natural water for an initial TOC concentration of 7 mgl^{-1}. More than 50% of TOC removal was achieved using alum coagulant doses of 75 to 150 mgl^{-1} near pH 7. Coagulation process is achieved by removing NOM through the precipitation of $Al(OH)_3$. Here the regions 5 and 6 show higher TOC removal referred to as sweep coagulation.

Table 1 also shows the optimum alum dose and corresponding pH for the NOM removal in natural water with initial TOC values of 10, 14,19 and 25 mgl^{-1}. When the TOC of the natural water increased from 4 to 25 mgl^{-1} at pH 7, the optimum alum dose required NOM removal increased from 125 to 1,225 mgl^{-1}.

Effect of secondary compounds in NOM removal

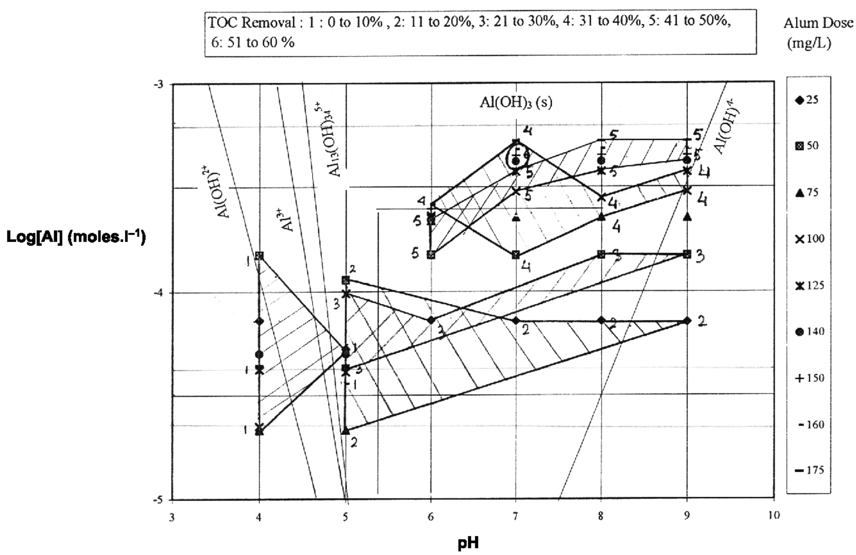

Figure 3 Log[Al] moles/L of natural water (with TOC = 7 mgl^{-1}) as a function of pH at different alum doses

Table 1 Optimum alum dose and corresponding TOC removal for natural water with different initial TOC values

Initial TOC (mgl^{-1})	pH	Optimum alum dose (mgl^{-1})	TOC removal (%)
4	7	125	
10	7	450	64.6
14	6	225	58.7
14	7	550	63.1
14	8	575	60.0
14	9	600	60.3
19	7	950	63.8
25	7	1,225	63.2

Table 2 Effect of Ca^{2+} and Mg^{2+} on NOM removal

Secondary component (mgl^{-1})		Optimum alum dose (mgl^{-1})	TOC removal (%)	Residual Al (mgl^{-1})
Ca^{2+}	48.3	300	58.6	23.0
	68.3	225	58.9	0.1
	88.3	225	58.6	0.2
	108.3	225	59.5	0.08
Mg^{2+}	43.0	325	55.4	0.06
	63.0	225	58.1	0.6
	83.0	225	61.5	not measured
	103.0	225	58.6	0.2
	123.0	300	62.5	0.1

The effect of secondary components such as the Ca^{2+} and Mg^{2+} divalent cations in the water on NOM removal was studied as they are responsible for exerting hardness in wide range. As shown in Table 2, the presence of secondary compounds does not have a profound effect on the NOM removal. The TOC removal varied from 58% to 60% when the Ca^{2+} concentration increased from 48.3 to 108.3 mgl^{-1}. Similarly, the TOC removal varied from 55% to 62% when the Mg^{2+} concentration increased from 43.0 to 123.0 mgl^{-1}.

Effect of clay in NOM removal

Table 3 compares the TOC removal with and without the addition of clay. For natural water with 7 mgl^{-1} of TOC, the NOM removal was 60% (at pH 7) in the absence of clay. The NOM removal increased to 75% (at pH 7) with the addition of 100 mgl^{-1} of clay. However, the required optimum alum dose increased from 140 mgl^{-1} to 300 mgl^{-1} when clay is added to natural water. It can also be seen from Table 3, that the removal of TOC in the natural

Table 3 Effect of clay in optimum alum dose, TOC removal and residual aluminium at different pH

pH	Without clay		With clay (100 mgl^{-1})		Residual aluminum (mgl^{-1})	
	Optimum alum dose (mgl^{-1})	TOC removal (%)	Optimum alum dose (mgl^{-1})	TOC removal (%)	Without clay	With clay (100 mgl^{-1})
4	140	15.8	250	17.7	10.0	18.0
5	100	20.6	250	46.9	7.5	18.0
6	100	48.3	250	48.4	2.0	16.0
7	140	60.0	300	75.0	0.07	6.0
8	140	49.1	325	69.6	0.06	1.4
9	150	48.6	350	57.7	0.06	0.08

water that contained clay increased with the increase in pH up to 7 and then decreased when the pH further increased up to 9. Thus, the optimum pH for maximum NOM removal is around 7 and independent of turbidity (caused by clay) but the alum dose requirement will increase with an increase in turbidity or the NOM contents of the water.

From the above data, a relationship between the optimum alum dose and the operating parameters such as pH, TOC and turbidity has been derived:

$$\text{Optimum alum dose} = (7.34 \times \text{pH}) + (47.73 \times \text{TOC}) + (55.95 \times \text{turbidity}) - 362.07$$

This equation can be used to provide economic operational management of treatment plants mainly using the sedimentation unit. The equation explains the nonlinear relationship between the optimum alum dose and the concentration of NOM in the water as the optimum value of alum dose depends not only on organic concentration but also on the pH and turbidity of the water.

Floc characteristics

The floc formed in coagulation and flocculation processes was observed under a microscope and found to be transparent. This made the floc measurement a difficult task. However, the settling velocities of floc formed under different operating conditions were measured using a settling column (Table 4).

Although the organic substances and clay both are negatively charged, the organic substances get adsorbed onto clay particles due to the bridging action of metallic hydroxide. It promotes the floc growth and settling velocity of floc as shown in Table 4. The higher concentration of clay, the larger will be the floc size and higher the settling velocity. Also, the floc formed with clay will be dense and of small size.

Figure 4 shows the molecular weight distribution of natural water with TOC 14 mgl^{-1}, before and after the coagulation/flocculation processes. From the figure it can be seen that the coagulation/flocculation process is effective in removing NOM with higher molecular weight components. From this study, it was found that about 64% of higher molecular weight organic compounds (> 2,200 dalton) present in raw water was reduced to 6.6% by coagulation, whereas 36% of lower molecular weight organic compounds (< 2,200 dalton) were reduced to 26% by coagulation.

Study on dewatering characteristics of floc was carried out in order to evaluate the floc characteristics by using the capillary suction time (CST) method. The CST method determines the rate at which water is released from sludge. It provides a quantitative measure of how readily the sludge releases its water. The result can be used to assist in sludge

Table 4 Settling velocity of flocs formed by coagulation and flocculation of natural water (with and without clay) at pH 7

TOC (mgl^{-1})	Optimum alum dose (mgl^{-1})	Settling velocity ($cm\ s^{-1}$)
Natural water without clay		
7	140	0.115
10	450	0.248
14	550	0.342
19	950	0.496
25	1,225	0.536
Natural water with clay		
7 (clay = 50 mgl^{-1})	300	0.121
7 (clay = 100 mgl^{-1})	300	0.137
7 (clay = 150 mgl^{-1})	300	0.136
7 (clay = 200 mgl^{-1})	300	0.237

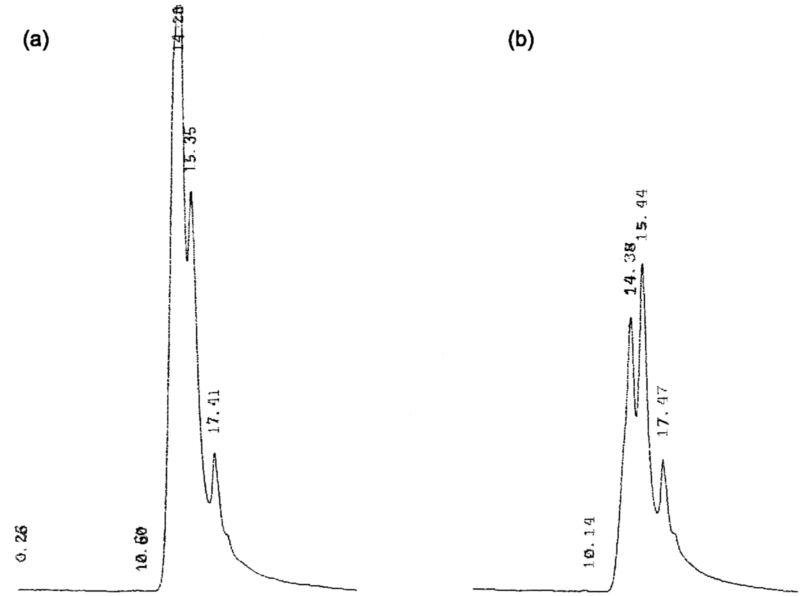

Figure 4 Molecular weight distribution of natural water (TOC = 14 mgl^{-1}): (a) before coagulation; (b) after coagulation

dewatering process to evaluate sludge conditioning aids and dosages; also when used in conjunction with jar tests it can be used to evaluate coagulation effects on the rate of release of water from sludge. The CST results obtained in this study are shown in Table 5.

From Table 5 it can be seen that the release of water from sludge decrease with the increase in NOM concentration of the water. The sludge produced at low TOC concentrations is fluffier and has a high amount of free water than bound water, which makes sludge dewatering an easy task.

NOM removal in synthetic and natural waters

NOM removal from synthetic water containing humic acid was observed in this study and compared with the NOM removal from natural water (7 mgl^{-1} TOC and pH 7). Figure 5 shows the results and from the figure it can be seen that the NOM removal from synthetic water is higher (82%) than from the natural water (60%). The optimum coagulant dose required for synthetic water (125 mgl^{-1}) was less than that required for natural water (140 mgl^{-1}). The presence of non-homogeneous organic compounds in the natural water reduces the removal efficiency of NOM.

Conclusion

From this study it can be concluded that the optimum pH for coagulation to remove NOM is around 7. The optimum alum dose at this pH can vary from 125–1,225 mgl^{-1} when the TOC is increased from 4 to 25 mgl^{-1}. However, the presence of secondary compounds such as Ca^{2+}, Mg^{2+} divalent cations had no significant effect on the removal of organic matter; the presence of clay increased the organic removal by 15%; the organic compound with higher molecular weight has higher removal affinity in coagulation process. The results also

Table 5 Floc characteristics of natural water as a function of CST at optimum pH and alum dose

Initial TOC (mgl^{-1})	4	7	10	14	19	25
Solids produced (kgm^{-3})	0.79	1.43	1.65	3.46	3.48	6.11
CST (seconds)	0.9	18.7	19.2	25.1	30.1	33.5

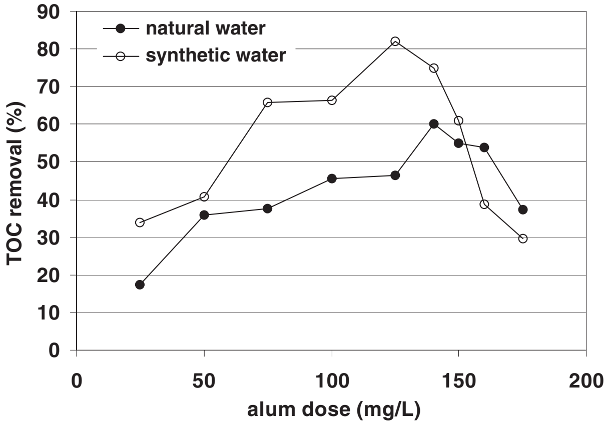

Figure 5 Comparison of TOC removal in natural water and synthetic water prepared using humic acids (both waters contained 7 mgl^{-1} of TOC at pH 7)

showed that the optimum coagulant dose, floc size and settling velocity of floc and sludge production all increased with the increase in NOM concentration. When the TOC concentration was increased from 4–25 mgl^{-1}, the floc size and settling velocity were increased by more than 350% and the sludge production was increased by 6.02 kg m^{-3}. From the results of capillary suction time (CST) tests, the floc formed with lower TOC readily released the water to make the dewatering process easier. The organic removal efficiency was significantly different for natural water containing non-homogeneous organic compounds compared to the synthetic water containing humic acid only (homogeneous organic matter). For example, the NOM removal efficiency was 80% for the synthetic water containing humic acid with TOC of 7 mgl^{-1} at pH 7; but the NOM removal for the pre-treated pond water was 60%.

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