Feasibility of humic substances removal by enhanced coagulation process in surface water

Mohammad Mehdi Amin, Mahdi Safari[1], Afshin Maleki[1], Mohammad Ghasemian[2], Reza Rezaee[1], Hassan Hashemi

Environment Research Center, Isfahan University of Medical Sciences, Isfahan, Iran, [1]School of Health, Kordestan University of Medical Sciences, Sanandaj, Iran, [2]Tehran Wastewater Company, Power Ministry, Tehran, Iran

Address for correspondence:
Eng. Mahdi Safari,
School of Health, Kordestan University of Medical Sciences, Sanandaj, Iran.
E-mail: safari.m.eng@gmail.com

ABSTRACT

Aims: This study evaluates the effectiveness of polyaluminium chloride (PACl) as a coagulant for enhanced coagulation (EC) of humic substances (HS) in surface water.

Materials and Methods: Dissolved organic carbon (DOC), ultraviolet absorbance (UV_{254}), specific ultraviolet absorbance (SUVA), and humic acid (HA) were determined as the HS indices. HS was extracted by Amberlit XAD-7HP from water and HA was analyzed by high performance liquid chromatography (HPLC). The HS index was determined in raw water and after clarification and filtration in all seasons. The efficiency of PACl for removal of HS, both in the jar test and pilot scale were determined.

Results: The average extraction efficiency for XAD-7HP was 77%, and the HA concentration was determined in all seasons ranging from 0.15 to 0.29 mg/ L in raw water. The DOC in raw water was in the range of 1.5 to 4mg/L, in all seasons. The average removal efficiency of PACl for EC was 52% for HA in the pilot scale. Also the average removal efficiencies of PACl EC for DOC and UV_{254} were 43 and 57% on the pilot scale and 38 and 41% in the jar test, respectively. The optimum pH for removal of HS was 7.5 ± 0.2 and the optimum PACl dose was 12 ± 0.5 mg/L.

Conclusions: After EC, the aluminum concentration was lower than the maximum concentration level (MCL) of aluminum in drinking water (< 0.05 mg/L). The efficiency of PACl EC was more effective in the high molecular weight fraction of HS and UV_{254}. In addition, PACl EC was more affected by the increasing coagulant dose than the pH decrease. The removal efficiency of PACl EC at high pH > 8.5 was very poor for the HS index and turbidity.

Key words: Dissolved organic carbon, enhanced coagulation, high performance liquid chromatography, humic acid

INTRODUCTION

Humic substances (HSs) are very complex and heterogeneous organic matter with a high molecular weight and various functional groups, which are produced from the chemical and biological degradation of plants and animal tissues.[1-3] HS constitutes an important fraction of soil organic matter and the largest fraction of natural organic matter (NOM) in the water systems (60% of the dissolved organic carbon).[4]

Humic substances are generally classified into humic acids (HAs), fulvic acids (FAs), and humins according to their solubility in aquatic water. The fraction of HSs that is not soluble in water under acid conditions (pH below 2), but becomes soluble at higher pH values is defined as the HAs fraction, and the fraction of HSs that is soluble under all pH conditions is called the FA fraction. It is not soluble in water under acid conditions (pH below 2), but becomes soluble at higher pH values.[5] HA constitutes the higher molecular weight fraction (1500 to 50000 Da) in streams, and FA constitutes the moderate molecular weight substances (from 600 to 1000 Da) in streams.[5,6]

A humic substance can cause, color, odor, and taste problems in drinking water, biological growth in the distribution systems, formation of disinfection by-products after disinfection processes, can increase chlorine demand for disinfection,[2,7,8] heavy metal and insecticide mobility,[9] poor oxidation of iron and manganese, and membrane fouling.[2] The most common disinfection by-products (DBPs) observed after the disinfection process in water are Trihalomethanes (THMs), which are a cause of concern as probable carcinogens in laboratory animals and may cause adverse health effects in humans.[8-10]

The United States of America (USA) has set maximum contaminant levels for trihalomethanes (THM) and haloacetic acids (HAA) of 80 and $60\,\mu g/L$, respectively. On the other hand, the EU-regulated THM limit is at a $100\,\mu g/L$.[11] Therefore, determination and the removal of HS is necessary to reduce these problems.

In recent times, instrument analysis methods, such as high performance liquid chromatography (HPLC) and gas chromatography (GC) have been popular for the determination of small amounts of humic substances in natural waters.[6,12] HPLC has been the most employed to determine aquatic humic substances, especially based on molecular weight distribution (MWD).[13,14] The molecular weights of HSs play an important role in the behavior of HSs, such as, adsorption, metal binding, and hydrophobic partitioning, in the environment.[6]

Humic sunstances can be removed from raw water by several processes: By activated carbon,[15] advanced oxidation process,[16] electro-microfiltration (EMF),[17] ion-exchange resin,[18] ultrafiltration,[19] conventional coagulation,[13] and enhanced coagulation.[7,20]

The US environmental protection agency (USEPA) identifies enhanced coagulation as the best available technology (BAT) for TOC removal from water.[7] The enhanced coagulation process is suggested by numerous literature reports for increasing DBP precursor removals.[11,20-26] Therefore, the EC technique is able to meet the EPA and EU THM limits of 80 and 100_g / l, respectively[11] Generally, increasing the dosage of the coagulant, and adjusting the pH are two main

methods to achieve the EC aim.[7] The most important mechanisms by which NOM can be removed by coagulation are precipitation (formation of an aluminum or iron humates or fulvates), charge neutralization of colloidal NOM, and coprecipitation by adsorption on the metal hydroxide.[11,20] The major adsorption phenomenon involved in the enhanced coagulation process is coprecipitation. During coprecipitation, the soluble organic material is adsorbed onto the reactive sites on the surfaces of the growing hydrous metal oxide crystals. The site-specificity, pH dependence, and surface of the hydrous metal oxide are the most important factors affecting the efficiency of coprecipitation.[27] The effects of higher dosage are providing more metal for complex formation and achieving sweep-floc coagulation. A lower pH reduces the charge density of the NOM and makes it more hydrophobic (absorbable), therefore, adsorption becomes more favorable and the required coagulant dosage decreases.[11,27] The practical definition of EC is that it provides treatment conditions that still sustain effective turbidity removal, while also increasing NOM removal.[11]

The objective of this study was to survey the removal efficiency of humic substances by PACl via jar tests and the pilot scale, at the Isfahan water treatment plant. The study has established the optimal pH of coagulation and concentration of PACl dosage for HS removal both in the jar and pilot scale experiments.

MATERIALS AND METHODS

Water source and sampling
The natural water source used in this study was raw water from the Isfahan water treatment plant, which came from the Zayandehrood river. After sampling, the raw and processed water samples for HS analyses were transported within one hour to the laboratory and were kept in the dark at 4°C to retard the biological activity prior to use.

Chemicals and materials
Humic acid sodium salt (50–60%) (Sigma-Aldrich Corporation) was used as the humic acid standard. Polyaluminium chloride (PACl) was used as the coagulant (already used in the Isfahan water treatment plant). Sodium hydroxide (NaOH) and hydrochloric acid (HCL) were used to increase and decrease the pH value, respectively. Methanol and Milli-Q water (0.05 μs/cm, Millipore) were used in all HPLC and DOC experiments.

Extraction of humic substances
Preparation the resin column: Among various fraction methods for HSs isolation, the XAD method was selected by the international humic substance society (IHSS) and was suggested by the standard method for water and wastewater examination as an effective method. Many researchers had used XAD resin adsorption methods for fractionation of humic substances in aquatics.[28-34]

Amberlites XAD-7HP resin was used to isolate the HS from the water in this study. A plexiglass column with 3 cm diameter and 40 cm length was filled with XAD-7HP resin according to Kim and Yu 2006.[35,36] After packing, the column had to be cleaned with methanol, 0.1N NaOH, 0.1N HCl, and distilled water,[36] to remove the remaining impurities. The same cleaning procedure was employed after each isolation.

Sample preparation: A volume of 15 L of water was used for the preparation of each sample. The samples were filtrated first through a 0.45 μm membrane (Whatman No.1), the pH of samples were adjusted to 2 by hydrochloric acid, and then the filtrated samples were passed through XAD-7HP resin column, at flow rates of 10 – 15 mL/min, for 20 hours, by using the peristaltic pump. The hydrophobic fraction was adsorbed in the resin bed, and then the adsorbed material was washed by 0.1N NaOH (300 mL) and isolated. Following that, by using cationic exchange resin (H$^+$ type) (Amberlit IRC-50, MERCK, Germany), the Na$^+$ ions in the solution were substituted with H$^+$.

Analytical methods

High-performance liquid chromatography

HPLC separations were performed using a Waters HPLC system (model 746) equipped with a Waters 515 Pump, a Waters 486-UV / VIS detector and a 50 μL manual injector. A commercial, pre-packed, analytical HPLC BIO SUIT 5 μm HR SEC column (7.8 × 300 mm) was purchased from the Waters corporation (USA). Silica with a 5 μm particle size and 125 Å pore size was chosen as the stationary phase. The BIO SUIT GUARD SEC column (7.5 × 75 mm) contained the same packing material as the analytical column. HPLC with size-exclusion chromatography (SEC) was identified as a useful fractionation method for HS in water treatment.[37-40] The relative standard error was 3% in HPLC.

The mobile phases were prepared by mixing of phosphate buffer (PB) 0.1 mol / L, sodium sulfate (Na$_2$SO$_4$) 0.1 mol/L, and sodium azid (NaN$_3$) 0.05% in Milli-Q water. The flow rate was 1 mL/min and the injection volume was 50 μL.

Dissolved organic carbon

DOC was defined as the fraction of TOC that passed through the membrane filter and was measured with the same TOC measurement. The DOC concentration was measured by using a Shimadzu TOC-5000 analyzer according to the combustion-infrared method.[41] The method detection limit (MDL) was 0.13 mg/L (as DOC).

Ultraviolet absorbance

Ultraviolet (UV) absorbance at 254 nm detection was a rapid and reliable method to measure HS in water. The UV$_{254}$ (l/m) was measured using a DR-5000 UV/VIS spectrophotometer after it was filtrated through a 0.45 mm membrane (RSE

5%). The machine was calibrated using the Milli-Q water as a blank.

Specific ultraviolet absorbance

Specific UV absorbance (SUVA) (l/mg-m) is a useful indicator of HS character in water. SUVA is calculated as the ratio of UV absorbance at 254 nm (l/m) to DOC (mg/L).

Residual aluminum

Residual aluminum is defined as the dissolved and particulate species of aluminum that leaves the treatment plant in treated water and enters into the distribution system. Residual aluminum in treated and raw water is measured using a DR-5000 spectrophotometer according to the HACH corporation method (RSE 5%).

Enhanced coagulation process

In this study enhanced coagulation was investigated both in the jar test and on the pilot scale. Already in the Isfahan water treatment plant (IWTP), PACl was used as a coagulant, so we selected it for this study. This investigation was an applicant study, thus all the changes were employed based on the natural calculation condition, and based on the pH decrease, and the dose was increased as suggested by the USEPA.

Selection of the optimal pH value

To determine the optimum pH for a selected coagulant dose, jar tests were conducted by using a constant coagulant dose and varying the pH of the coagulation by using sulfuric acid. The optimum pH of coagulation was identified as the highest pH, at which there was maximum DOC and HA removal.

Selection of the optimal PACl dosage

To determine the optimum coagulant dosage at the selected pH, the coagulant concentrations were varied in each jar, while the optimum pH value was maintained as a constant.

RESULTS

Raw water characteristics

The characteristics of the entire raw water in the Isfahan water treatment plant, which was selected for all raw water samples, are summarized in Table 1 (annual average). These parameters were analyzed during the different seasons of the study year. In this study XAD-7HP resin efficiency was investigated by the humic acid standard solution and the average extraction efficiency was 77%. DOC and HA were the two major indices of the dissolved humic substances in aquatic water. The concentration of HA as a high molecular weight HS fraction was determined in all seasons ranging from 0.15 to 0.29 mg/L in raw water. Also the DOC concentration had a range of 1.5 to 4 mg/L in raw water, during all the seasons. Table 1 shows that the UV$_{254}$ and SUVA values of IWTP range from 8.3 to 18.37 and 2.89 to 4.72, respectively.

Table 1: Main parameters of the water source in Isfahan water treatment plants			
Parameter	Value		
	Maximum	Average	Minimum
Turbidity (NTU)	47	25	16
DOC (mg/L)	4.00	2.363	1.50
Humic acid (mg/L)	0.29	0.24	0.15
UV_{254} (1/m)	18.37	11.06	8.3
SUVA (1/mg-m)	4.72	4.23	2.89
Aluminum ($\mu g/L$)	25	15	5
Alkalinity (mg/L $CaCO_3$)	160	145	135
Temperature (°C)	22	18	15
EC ($\mu S/cm$)	365	357	354
pH	8.35	8.25	8

The residual aluminum concentration was in the range of 5 to 25 $\mu g/L$ in raw water. After conservational coagulation, the average residual aluminum was 30 $\mu g/L$.

Humic substance removal by enhanced coagulation

Optimum PACl for Turbidity removal: Before the enhanced coagulation proceeds, the coagulant dose in the conventional coagulation for turbidity removal must be selected. Several runs of jar tests were done to achieve this aim. A wide range of PACl dosages were added to the raw water to remove the turbidity. The optimum turbidity removal amount was achieved at 9 mg/L PACl dosage. At a pH value of 8.25 (natural water pH) and at this coagulant dose, the removal efficiency for turbidity was achieved at 85% in conventional coagulation.

Optimum pH value for enhanced coagulation by PACl

In this study the pH of the raw water was above neutral (8.25). Jar tests and pilot scales with three and more batches of raw water were conducted at a fixed PACl dosage of 9 mg/L, and at different pH solution. The effect of pH on the removals of DOC, HA, and turbidity is shown in Figure 1. It shows that a decrease in the pH value from 9 to 4.5 causes approximately 40% removal efficiency of DOC and HA. Also as shown in Figure 2, by decreasing the pH, a UV_{254} removal efficiency of up to 45% is achieved. The results suggest that the optimal pH for removal of the HS index in IWTP is 7.5 ± 0.2.

Optimum PACl dosage for enhanced coagulation by PACl

Jar tests and pilot scales with three more batches of raw water were conducted at different PACl dosages, and at a fixed coagulation pH of 7.5. Figures 3 and 4 indicate the effect of PACl dosage concentration on the residual DOC, HA, UV_{254}, and turbidity in the jar test and pilot scale test. These figures show that increasing the PACl dosage from 2 to 20 mg/L causes approximately 60% removal efficiency for the HS index.

Comparison of conventional and enhanced coagulation by PACl

The removal efficiency for conventional and enhanced coagulation by PACl is shown in Figure 5. As shown in this figure the removal efficiency of turbidity and the HS index in enhanced coagulation is significantly increased, as compared to conventional coagulation. The average removal efficiency of PACl for EC is 52% for HA in the pilot scale. Also the average removal efficiency of PACl EC for DOC, and UV_{254} is 43 and 66% in the pilot scale and 38 and 40% in the jar test, respectively.

Residual Aluminum

The concentration of residual aluminum after enhanced coagulation is shown in Figure 6. It shows that an increase in both the pH value and coagulant dosage in the jar test and pilot scale enhanced coagulation, cause an increase in the residual aluminum.

DISCUSSION

According to this result the HS concentration at IWTP was moderate, but for prevention of the concerned problem, this material must be removed. The XAD-7HP shows good efficiency for HSs fractionation of water with the characteristics given a little earlier in the text. As shown in Figure 5, the conventional coagulation removal efficiency for UV_{254} is more than the other HS index. High SUVA samples are correlated with high molecular weight HS, such as humic acid.

Figure 1 shows the effect of pH on the removal of DOC, HA, and turbidity, in the jar and pilot scales, respectively. It
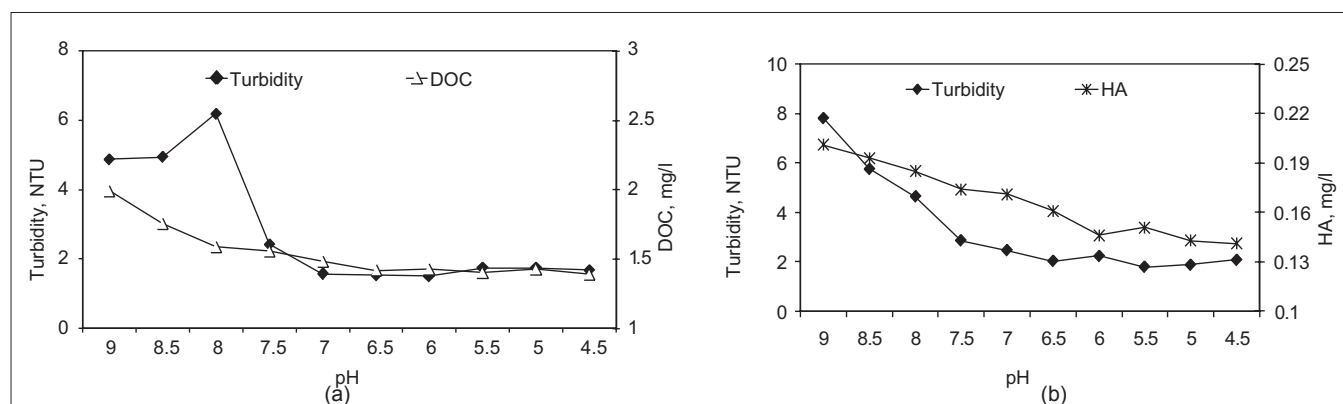
Figure 1: Effect of pH on the removal of DOC, HA, and turbidity: (a) in jar test and (b) in pilot scale
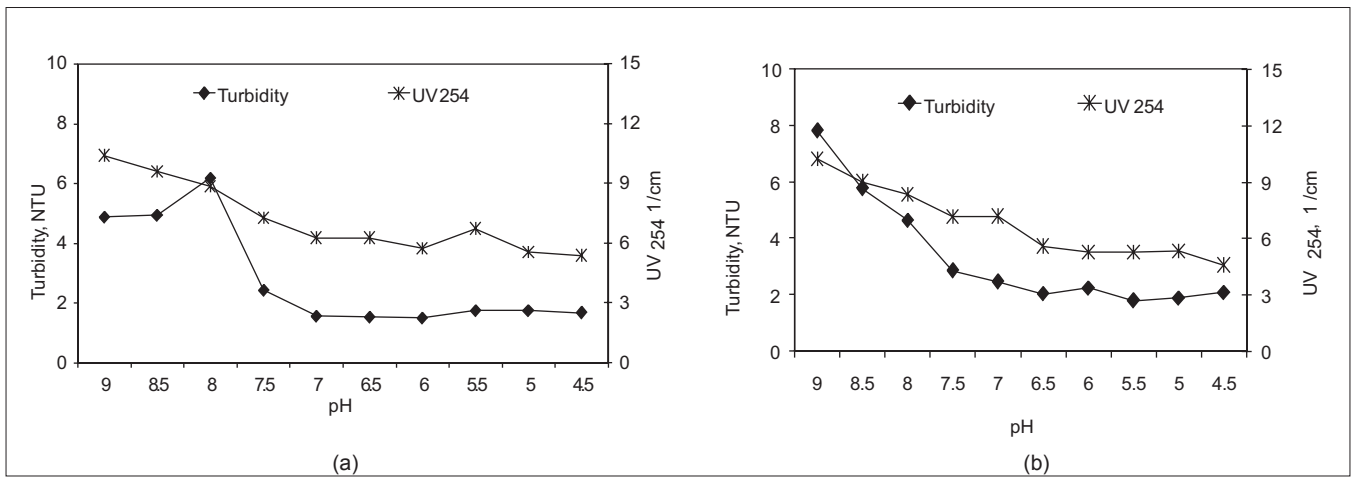
Figure 2: Effect of pH on removal of UV_{254} and turbidity: (b) in jar test and (b) in pilot scale
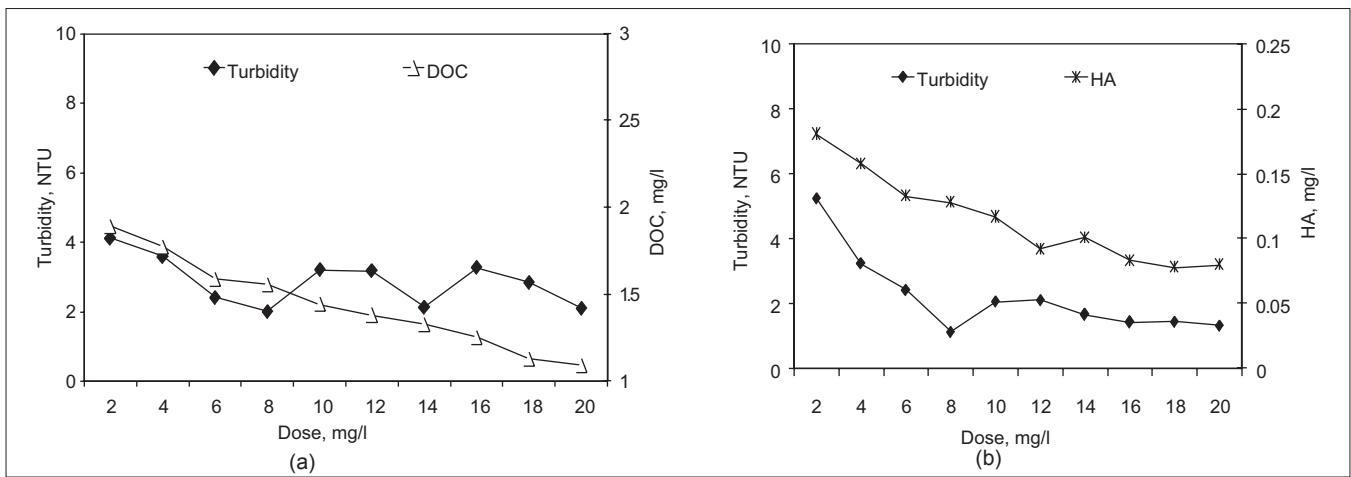

Figure 3: Effect of PACl dosage concentration on residual DOC, HA, and turbidity in: (a) jar test and (b) pilot scale
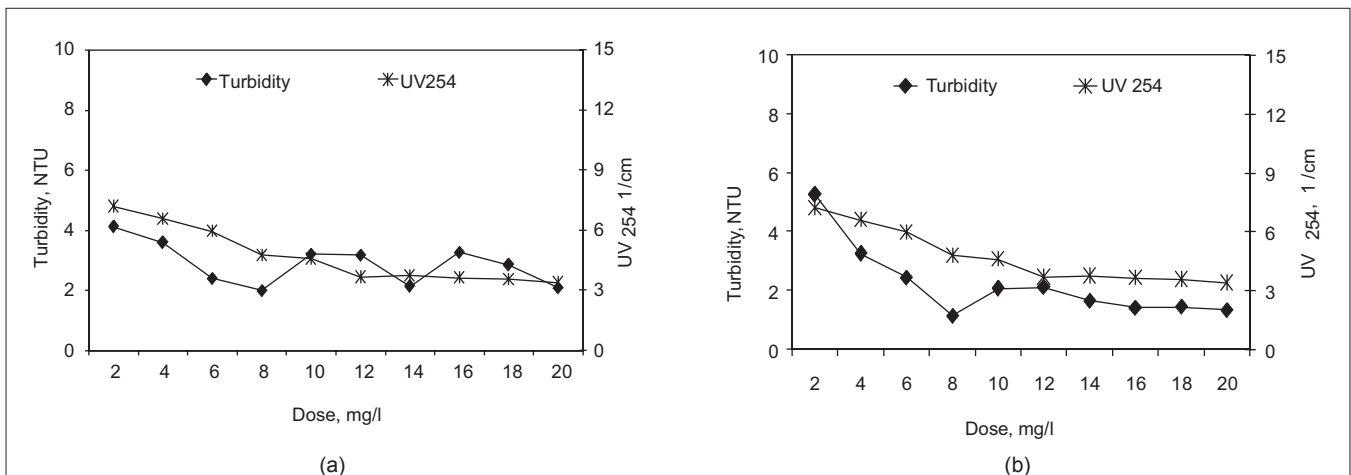

Figure 4: Effect of PACl dosage concentration on residual UV_{254} and turbidity in: (a) jar test and (b) pilot scale

appears that with increasing coagulation, the pH, DOC, HA, and turbidity removal decreases. However, decreasing the coagulation pH is not more effective in these removals. For a further reduction of the concentration of residual DOC in the water, treatment by using either higher doses of alum or

reduction to pHs between 5 and 6 will be necessary.[42]

Also as shown in Figure 2, decreasing coagulation pH was not more effective in UV_{254} removal. Yan *et al.*[43] reported that the PACl contained significant amounts of highly charged and

stable polynuclear aluminum hydrolysis products, which were less affected by the pH of the raw water than the traditional coagulants (alum and ferric salts).

As shown in Figures 3 and 4, increasing the PACl coagulant dosage was more effective for removal of the HS index than decreasing the pH value in IWTP. Yan *et al.*[44] showed that increasing the dosage of PACl could increase the DOC removal performance. Figure 5 showed that the PACl removal efficiency of HA was higher than that of DOC for a given jar test. In a compared traditional coagulant, PACl had that highest performance for DOC removal.[43] The reason for the good efficiency of PACl for DOC removal could be because of the high neutralization ability of this coagulant.[45] In general, the coagulation process had a poor capability to eliminate the low molecular weight of HS in raw water.[8,11] This observation was also consistent with the findings in this study. Considering both factors of the HS removal efficiency and the PACl cost, an optimal PACl dosage concentration of 12 ± 0.5 mg/L was chosen.

As shown in Figure 6, the residual aluminum concentration after EC in the jar and pilot scale was lower than $50\,\mu g/L$. This concentration was lower than the low limit of the secondary drinking water standard (50 to 200 $\mu g/L$). The use of PACl in EC increased the concentration of the total aluminum to a much higher level in the water. Most of the aluminum was in the form of flocs, which could be easily removed by sedimentation, flotation, and sand filtration.[43]

CONCLUSIONS

The conclusions from this study may be summarized as follows:
- Using XAD-7HP resin HSs fractionation and the HPLC instrument with a Bio Suit SEC Column was a simple method for HA analyses and supposed for other fractions of NOM in the environment.
- Decreasing the pH in enhanced coagulation with PACl did not play a satisfactory role in HS removal. Increasing the coagulant dose was found to be more effective for enhanced coagulation with PACl. The enhanced coagulation efficiency by PACl for HA, DOC, and UV_{254} removal gained 52, 38, and 66%, respectively.
- Optimum pH for removal of HS was 7.5 ± 0.2 and the optimum PACl dose was 12 ± 0.5 mg/L.
- The SUVA index in raw water was high, and the average concentration was 4.23 for this water.
- Residual aluminum in row water and in processed water was lower than the standard ($50 - 200\,\mu g/L$).

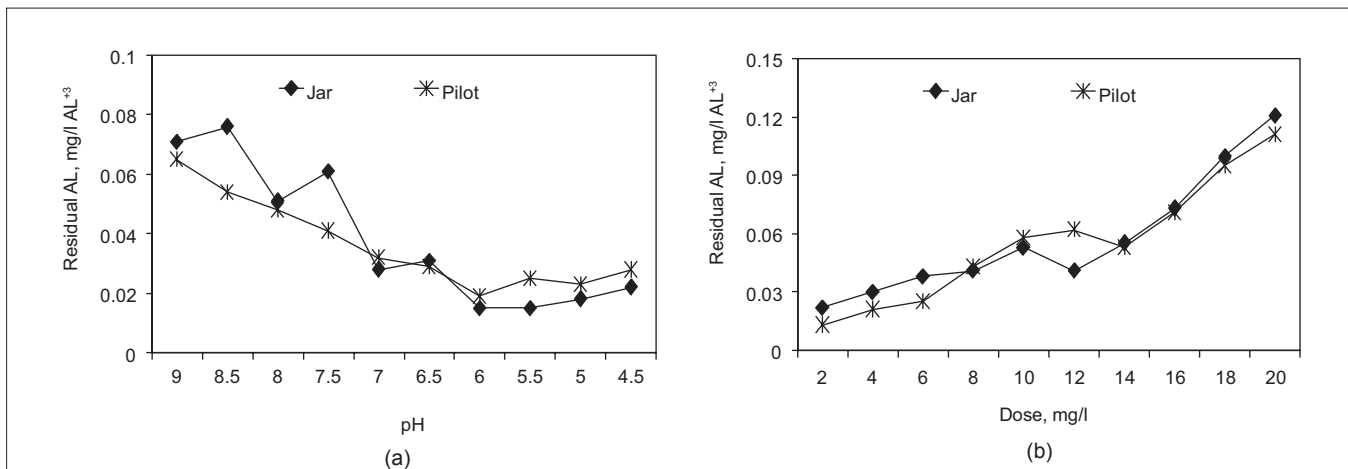## ACKNOWLEDGMENTS
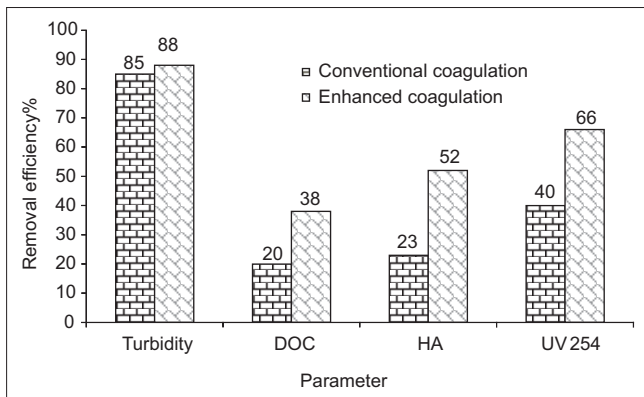
Figure 5: Removal efficiency for conventional and enhanced coagulation by PACl in pilot scale

Figure 6: Concentration of residual Aluminum in jar test and pilot scales in coagulant dose increase (b) and pH decrease (a)

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