

Effects of hydrophobe contents of amphiphilic polyelectrolytes on flocs size and removal efficiency of NOM from waters

R. Alnaizy, M. Sayem Mozumder, B. F. Abu-Sharkh and Sk. A. Ali

ABSTRACT

Polymer-based coagulants, such as amphiphilic polyelectrolytes, are used for water treatment in two distinct ways, as coagulant aids and as primary coagulants. In the latter role, polymers have a number of advantages over inorganic coagulants, notably the smaller volume of sludge produced and reduced sludge management costs. This study examines the impact of molecular structure of novel amphiphilic polyelectrolytes on floc size and size distribution determined by dynamic light scattering. These parameters are related to hydrophobe contents and charge of the polyelectrolyte. These characteristics are also related to the removal efficiency of natural organic matter (NOM). It is expected that a much lower amount of polymer is sufficient when amphiphilic polyelectrolytes are used as primary coagulants/flocculants in treating waters contaminated with NOM. The smaller polymer amount may result in lesser treatment costs as well as yielding a much lower sludge volume. Dynamic light scattering and UV absorbance results confirmed an optimum polymer dose of 0.3 ppm with up to 5% hydrophobe contents. The polymer hydrophobe contents were directly related to the system performance and NOM removal efficiency. The pH of the solution was virtually unaffected.

Key words | amphiphilic, coagulation, flocculation, hydrophobe, NOM, polyelectrolytes

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INTRODUCTION

NOM is ubiquitous in natural aquatic systems (river water and groundwater). Although many researchers have tried to define NOM, it has been concluded that NOM cannot be simply defined as particular chemical structures but can only be broadly characterized into generic groupings. The character of the NOM is dependent on the source from which it is derived and the chemical and biological degradation to which it has been subjected. In general, NOM may include humic acids (HAs) (comprising approximately 60 ~ 90% of dissolved organic carbon in natural waters), hydrophilic acids, proteins, lipids, amino acids, and hydrocarbons (Thiruvengkatachari *et al.* 2002). NOM is believed to be the major precursor to the formation of disinfection byproducts (DBPs), such as trihalomethanes (THMs) (Bellar *et al.* 1974; Rook 1974) and haloacetic acids

(HAAs) (Krasner *et al.* 1989) by reacting with chlorine in water treatment systems (Stevens *et al.* 1976; Babcock & Singer 1979; Christman *et al.* 1983; Singer 1994; Andersen *et al.* 2001). It also may react with other chemicals used in the water treatment process. Consequently, it is very important to remove NOM from natural waters to some appreciable extent. Optimization of coagulation performance for the removal of NOM was investigated using various real surface waters, by evaluating a range of variables such as mechanical conditions for coagulation/flocculation, sequence of chemical additions, coagulant type and doses, coagulation pH, restabilization zones, zeta potential on colloidal particles in a suspension, and water quality characteristics (Ueda & Harada 1968; Singh *et al.* 1999; Jia-Qian 2001; Yu *et al.* 2003). Conventionally

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aluminum-based coagulants are used in water treatment. Recently there has been a shift towards using iron or polymer-based coagulants in water treatment. The advantages of using polymer-based coagulants such as amphiphilic polyelectrolytes over inorganic coagulants are: 1) produce no additional solids; 2) reduce the volume of waste sludge; 3) increase clarifier throughput by producing larger flocs; and 4) work over a wide range of pH without altering the system pH, resulting in eliminating the need for chemicals to adjust the pH (Ueda & Harada 1968).

The removal of NOM from natural waters can be achieved with amphiphilic polyelectrolytes. Many investigators have reported that a cationic polyacrylamide (CPAM) of high charge was effective in removing UV absorbing compounds (used as a measure of trihalomethanes precursors) in various groundwaters (Andersen *et al.* 2001). Others have reported that a low charge and low molecular weight (M_w) polymer performed only reasonably well (Glaser & Edzwald 1979). Weakly basic polymers may flocculate NOM via hydrogen bonding to free amino groups. Organic polymers generally did nearly as well as alum for groundwater, eliminating 86–100% of the color that alum does, and performing even better when other particulates were present (Singh *et al.* 1999). On fractionated waters, alum was best for removal of HAs and fulvic acids (FAs) as measured by UV absorbance (Edzwald *et al.* 1985; Colby *et al.* 1997). Humic substances are a series of relatively high molecular weight, brown to black-colored substances formed by secondary synthesis reactions. The term is used as a generic name to describe the colored material or its fractions obtained based on solubility characteristics such as HA and FA. They include both hydrophilic and hydrophobic moieties, so that they may be adsorbed on the surfaces of many particles (Buffle 1990). Other researchers found that humic material, e.g. hydrophobic organic carbon, is more vulnerable to coagulation than hydrophilic organic carbon (Collins *et al.* 1986; Semmens & Staples 1986; Singer & Harrington 1993). Narkis & Rebhun (1975) studied the mechanism of flocculation of clay suspensions in various conditions of interaction with humic and fulvic acids by using a radioactively labeled cationic polyelectrolyte. They concluded that large doses of flocculant were required to ensure the reaction environments are favorable for complete reaction. Therefore, it is essential to develop alternatives to optimize the flocculant dose.

Glaser & Edzwald (1979) used cationic polyethylenimine (PEI) of varying M_w from 600 to 50,000–100,000 to observe their interaction with humic substances and concluded that low M_w PEI/HA aggregates are not strongly bonded compared to high M_w . Consecutively, higher M_w polyelectrolytes (10–1,000 times higher than Glaser and Edzwald's PEI) are expected to exhibit more interaction with humic substances leading to a better removal efficiency of NOM from contaminated waters. Kam & Gregory (2001) reported that optimum flocculation of humic substances occurred with less cationic charge in case of low-charge polyelectrolytes than those with higher charge density; however the degree of removal was considerably better in the latter case.

Amphiphilic polyelectrolytes with varying percentage of hydrophobes are believed to be a good candidate in NOM removal from contaminated water. They exhibit self-assembling phenomena in aqueous solution preceded by hydrophobic interactions. The physics behind hydrophobic self-associations in amphiphilic polyelectrolytes is that hydrophobic interaction competes with electrostatic repulsion within the same polymer chain and/or between different polymer chains. Thus, the balance of hydrophobic interaction and electrostatic repulsion determines whether the polymer undergoes hydrophobic self-association. Primarily, this balance is a function of the numbers of charges and hydrophobes in the polymer as well as the size of the hydrophobe (Tripathy *et al.* 2002).

The objective of this study was to investigate a novel class of hydrophobically modified amphiphilic polyelectrolyte in treating waters contaminated with NOMs. The study also examined the effect of hydrophobe contents and molecular structure of amphiphilic polyelectrolyte on the flocs size. Dynamic light scattering technique was used in characterizing the contaminated water, polymers and floc properties.

MATERIALS AND METHODS

HA sodium salt 50–60% supplied by ACROS ORGANICS, New Jersey, USA was used in distilled water with a conductivity of $<5 \mu\text{S cm}^{-1}$. HA contaminated water was prepared in 10 and 20 ppm. The apparent M_w of 10 ppm humic acid solution measured by static light scattering was

found to be 4.0×10^6 . The pH, UV absorbance (at 254 nm) and particle size of the contaminated waters were then measured before the jar-test experiments. Before treatment, the pH of the 10 ppm HA solution was 6.0 ± 0.2 , UV absorbance of filtered samples were $0.26\text{--}0.27$ (cm^{-1}) at 254 nm and the particle size of unfiltered and filtered samples were 225 nm and 75 nm, respectively. Millipore disposable filters of pore size $0.45 \mu\text{m}$ and $0.20 \mu\text{m}$ was used to filter the samples before the size characterization and UV absorbance measurements, respectively. Conventional jar tests were then performed. The variation between duplicate jar tests was normally less than 2%. Turbidity of untreated water was measured as 1.0 NTU (lies within the acceptable range). Hence, the turbidity of the waters was not observed later. UV absorbance was measured to characterize the sample solutions before and after jar tests. The optimum dose of the polymer, which corresponds to the greatest removal of NOM, was calculated using the UV_{254} absorbance data (Bolto *et al.* 2001).

Novel amphiphilic polyelectrolytes of very high M_w were tested in the coagulation/flocculation experiments. Polymers were synthesized by cyclocopolymerization of sulfur dioxide, *N,N*-diallyl-*N*-carboethoxymethylammonium chloride, and the hydrophobic monomer *N,N*-diallyl-*N*-octadecylammonium chloride, shown in Figure 1. Polymers were synthesized in the chemistry department laboratories of KFUPM (Hussein *et al.* 2005; Mozumder *et al.* 2005). This novel class of amphiphilic polyelectrolytes was cationic in nature. Hydrophobe contents were varied from 0% to 5%. Polymers were characterized for M_w , radius of gyration (R_g) and hydrodynamic radius (R_h) by using both static and dynamic light scattering techniques.

Jar tests and sample analyses

Coagulation/flocculation of NOM-contaminated synthetic water was performed by using a stirrer device consisting

of 6 removable stainless steel paddles together with 6 Jars (1.3 litre, square, graduated to 1 litre). Each run was performed on one litre of contaminated water. The experiments were initiated by adding a predetermined amount of amphiphilic polyelectrolytes (0.1 wt.%) dropwise. Afterward the solution was stirred rapidly at 100 rpm for 2 minutes. The solution was slowly flocculated at 40 rpm for 40 minutes. Following the flocculation step, aggregates/flocs were allowed to settle for 30 minutes without mixing. A 100 ml sample (supernatant) was collected from each jar and filtered through a Whatman No. 1 filter paper, which effectively simulates a sand filter. Finally, the pH, UV_{254} absorbance and floc sizes were measured from each sample. For each polymer sample, two to three replicates were conducted to check the reproducibility of the results and the averages of the replicates were taken. The pH of the untreated and treated samples was measured with the Orion pH meter, model 720A. The pH meter was calibrated with two standard buffer solutions with pH of 4.0 and 10.0. After using the pH meter, the electrode was stored in neutral solution. Ultra violet absorbance at 254 nm is directly related to the aromatic fraction of NOM (Edzwald *et al.* 1985; Korshin *et al.* 1997; Dilling & Kaiser 2002). One cm quartz cell was used for absorbance at the short wavelength (254 nm). Sample solutions were pre-filtered through a $0.2 \mu\text{m}$ filter. The pH was not adjusted and measurements were obtained at room temperature. Shimadzu UV-1601PC UV-visible spectrophotometer was used for the measurements.

Size characterization

Flocs size characterization was performed by static and dynamic light scattering techniques. Light scattering experiments were conducted using DAWN EOS (a trademark of Wyatt Technology Corporation) light-scattering instrument (ASTRA for Windows User's Guide for the DAWN DSP &

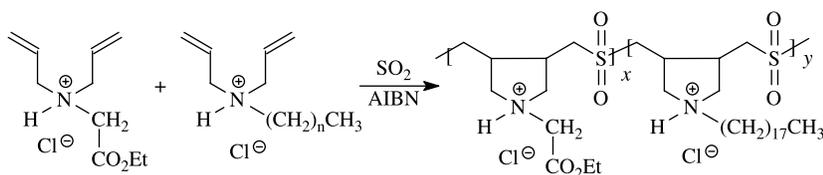


Figure 1 | Synthesis of amphiphilic Polyelectrolyte.

miniDAWN, Light Scattering Equipment, version 4.70, May 1998). Static laser light scattering was used to determine the M_w and R_g of the polyelectrolytes and the humic substances. The Berry fit method (User's manual of Wyatt Technology Corporation's Light Scattering Instrument 1998 version 4.70, May 1998) was used to analyze the scattered light data. Three to five ml samples, contained in small transparent bottles, were placed into the light scattering cuvette to measure the intensity scattered by the samples. No mixing or vibration was required during the measurement.

The apparent M_w of NOM and amphiphilic polyelectrolytes was determined in solutions containing 0.5 N sodium chloride to eliminate charge repulsions and to allow accurate determination of M_w . Copolymers containing no hydrophobe were prepared and characterized for use as control. The average M_w of the polymer with no hydrophobe was $9.03 \times 10^5 \text{ g mol}^{-1}$. It was expected that the true M_w of the amphiphilic polyelectrolytes would be close to the unmodified one because all polymers were prepared under exactly the same conditions. Dynamic light scattering was used to determine the hydrodynamic radius of the amphiphilic polyelectrolytes and to characterize the size of the flocs collected as supernatant from each testing jar. The CONTIN and Dynals algorithms (User's Manual of Wyatt Technology Corporation's Light Scattering Instrument, version 4.70, May 1998) were used to determine the size distribution of polymers and flocs. Dynamic light scattering was also used to investigate interaction of the copolymers with NOMs and determine the onset of flocculation and precipitation.

RESULTS AND DISCUSSION

Amphiphilic polyelectrolytes which are often referred to as hydrophobically modified polyelectrolytes possess charges as well as hydrophobes along with or pendant to the polymer backbone. This novel class of polyelectrolytes exhibits self-assembling phenomena in aqueous solution (Tripathy *et al.* 2002). Noncovalent forces, such as electrostatic, hydrogen bonding, van der Waals, and hydrophobic interaction, are responsible for self-association behavior

which makes amphiphilic polyelectrolytes promising in water treatment.

Hydrophobic association of tested amphiphilic polyelectrolytes directly affected the R_g and R_h of polymer molecules as well as their apparent M_w . As shown in Figures 2 and 3, all three parameters for size characterization (R_g , R_h , and M_w) increased with the increase of the polyelectrolytes' hydrophobe contents. Results indicated a remarkable increase in the R_g , R_h and M_w (greater than four times) when the hydrophobe content was increased from 2.5% to 5%. The increase in polymer size and apparent M_w that was observed in the 5% hydrophobe sample was mainly due to significant self-association.

Effects of amphiphilic polyelectrolytes hydrophobe contents on hydrodynamic radius of the formed flocs

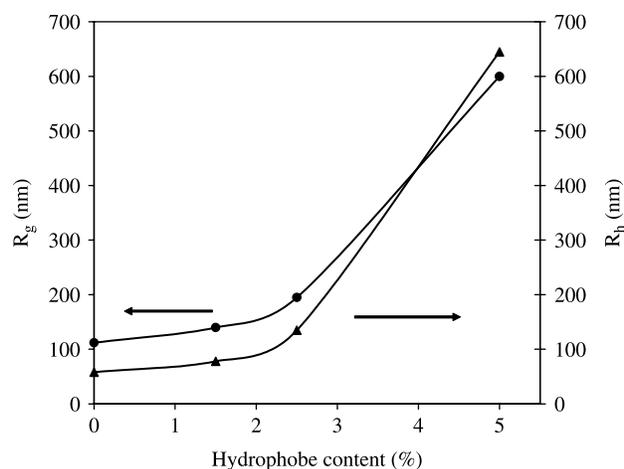


Figure 2 | Radius of gyration (R_g) and hydrodynamic radius (R_h) of amphiphilic polyelectrolytes as a function of hydrophobe contents.

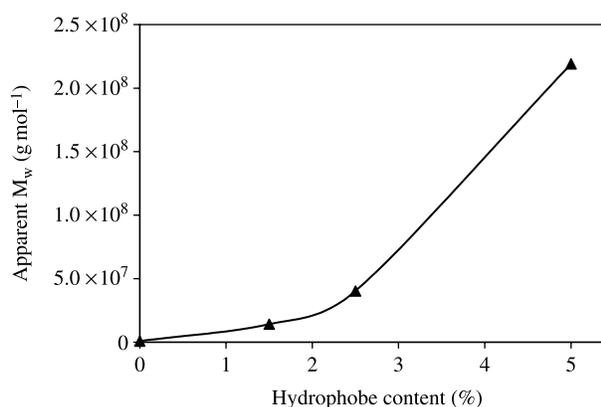


Figure 3 | Apparent M_w of amphiphilic polyelectrolytes as a function of hydrophobe contents.

which were collected as supernatant are shown in Figures 4 and 5. Results displayed a considerable increase in floc size with the increase of polyelectrolytes hydrophobe contents and confirmed the self-association phenomenon of the polyelectrolyte that was described earlier in this section. Figure 5 confirms that larger flocs were formed and removed by filtration as described in the methods section. This may indicate that polymers with higher hydrophobe percentage had a higher efficiency in removing NOMs from waters. Figure 4 shows the changes in size of the unfiltered polymer and floc aggregates with the change of hydrophobe contents. The maximum aggregate size with 0% hydrophobe contents was 850 nm which was found at a polymer

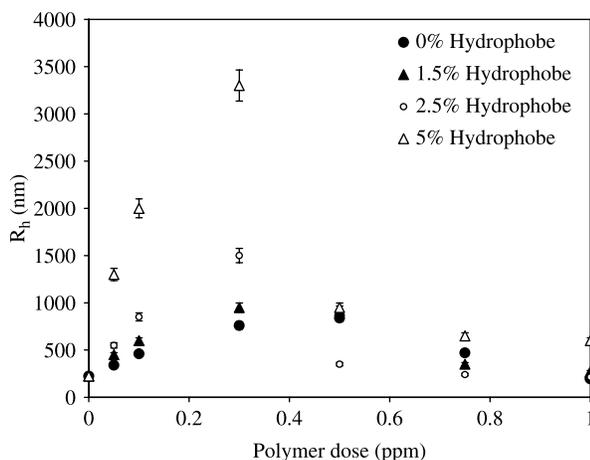


Figure 4 | Effect of hydrophobe contents on the R_h of flocs (unfiltered sample).

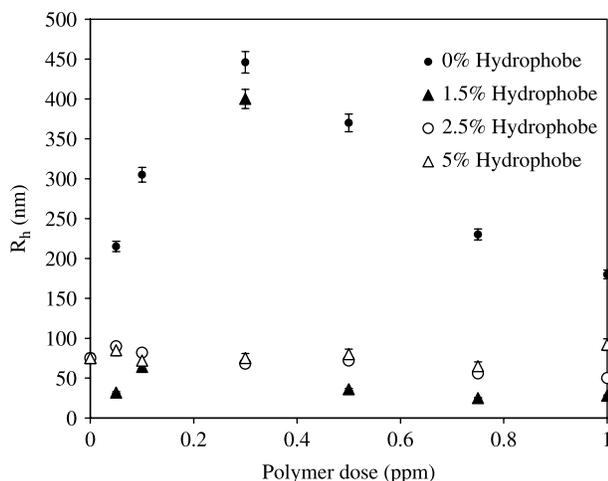


Figure 5 | Effect of hydrophobe contents on the R_h of flocs (filtered sample).

dose slightly exceeding 0.5 ppm. Filtration did not change the size distribution substantially because of the relatively small size of the aggregates formed during flocculation with 0% hydrophobe containing polymers. Increasing the hydrophobe contents of the polymer to 1.5% increased the maximum aggregate size to 950 nm, as shown in Figure 4. However, the largest flocs were found slightly above a polymer dose of 0.4 ppm. Also at this dose, filtration was not efficient because flocs were not large enough to be retained by the filter. Further increment of hydrophobe contents in the polyelectrolyte up to 2.5% substantially increased the size of the aggregates. The maximum aggregate size with this run was in the region of 1,500 nm (Figure 4). This enhanced the removal efficiency by filtration as all large aggregates were removed by filtration (Figure 5). Moreover, the optimum dose was lower, approximately 0.3 ppm.

Coagulation/flocculation experiments with copolymer containing 5% hydrophobe resulted in the largest size aggregates. Aggregates as large as 3,300 nm were formed at a polymer dose of 0.3 ppm as shown in Figure 4. Similar to the 2.5% hydrophobe copolymer, filtration retained all large size aggregates (Figure 5). Figure 4 also depicts the effects of the polymer amount (dose) on the floc size. In all experiments with the polyelectrolytes containing 2.5% to 5% hydrophobe, the aggregate size increased with increasing polymer dose up to 0.3 ppm. If the polyelectrolyte amount was further increased, the R_h of the formed aggregates reduced substantially. For polyelectrolytes with less than 1.5% hydrophobe contents, the decrease in the R_h of the formed flocs was observed at polymer concentrations above 0.5 ppm. It may be due to the cationic nature of amphiphilic polyelectrolytes. Flocculation occurred when the cationic polyelectrolytes attracted the negatively charged humic substances and neutralized the charges and thereby formed aggregates. The addition of a large amount of polymers caused the destabilization of flocs yielding smaller aggregates. The presence of more polyelectrolytes brought the same charges closer to each other, which caused repulsion rather than attraction; and hence, it promoted the destabilization of aggregates. As the polymer-bound hydrophobes undergo interchain, intrachain and intra-plus-interchain association (Tripathy *et al.* 2002), the higher the hydrophobe content until reaching a critical

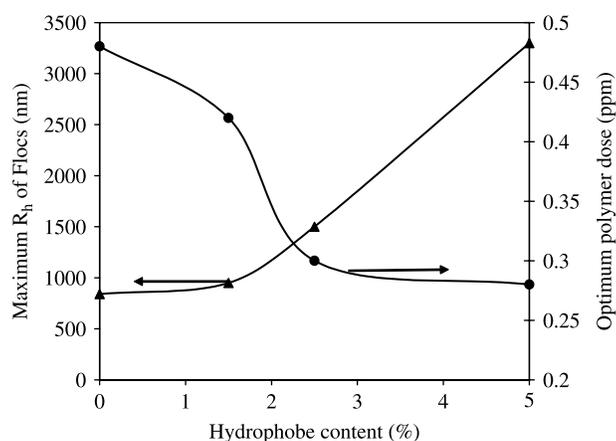


Figure 6 | Influence of hydrophobe contents on maximum floc size and optimum polymer dose.

value (5%) the better would be the association leading to the formation of larger aggregates.

Polyelectrolytes containing 0% and 1.5% hydrophobe produced comparatively smaller aggregates, many of which passed the 0.45 (m filter and were not removed completely by filtering (Figure 5). On the other hand, due to possessing higher self-assembling ability, polyelectrolytes containing 2.5% and 5% hydrophobe formed relatively larger aggregates and almost all of the aggregates were removed by filtration (Figure 5). As shown in Figure 6, as hydrophobe contents increased, the R_h of flocs increased but the optimum polymer dose decreased. It was evident that higher hydrophobe contents ensured higher interaction

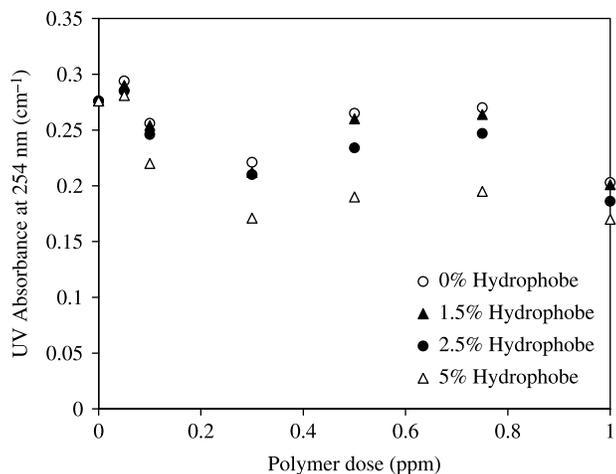


Figure 7 | Effect of hydrophobe contents of the tested polyelectrolytes on UV_{254} absorbance.

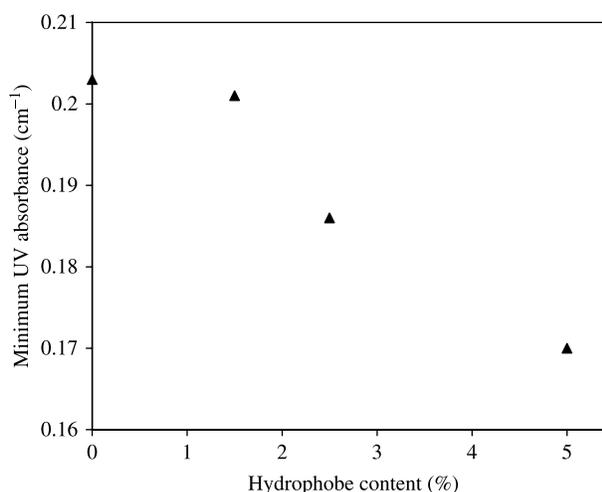


Figure 8 | Effect of hydrophobe contents on minimum UV absorbance of the treated samples.

with humic substances. Figure 6 shows diverse decreasing pattern of optimum polymer dose with increasing hydrophobe contents in different region of the curve as the slopes were not the same. Although the decrement of polymer dose was significant in the range of 1.5% to 2.5% hydrophobe contents, it was not considerable in the range of 2.5% to 5% hydrophobe contents. It appeared that the critical self-association of the polymers occurred at 2.5% hydrophobe contents. Therefore, beyond this point, the effect was not very noticeable.

To estimate NOM removal efficiency, UV absorbance analyses were performed for all the samples. Figure 7 shows

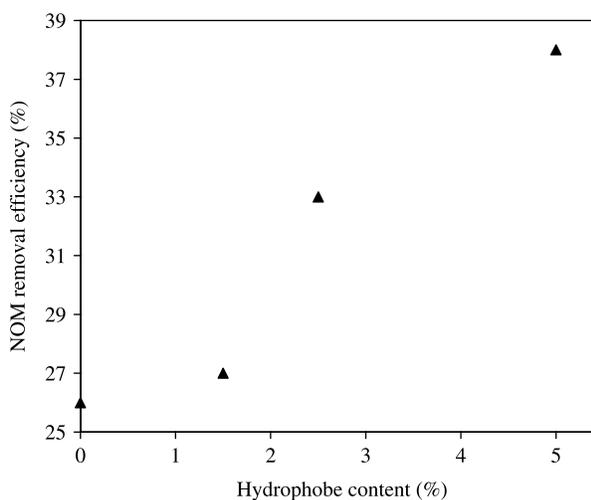


Figure 9 | Effect of hydrophobe contents on NOM removal efficiency (UV absorbance is used in efficiency calculation).

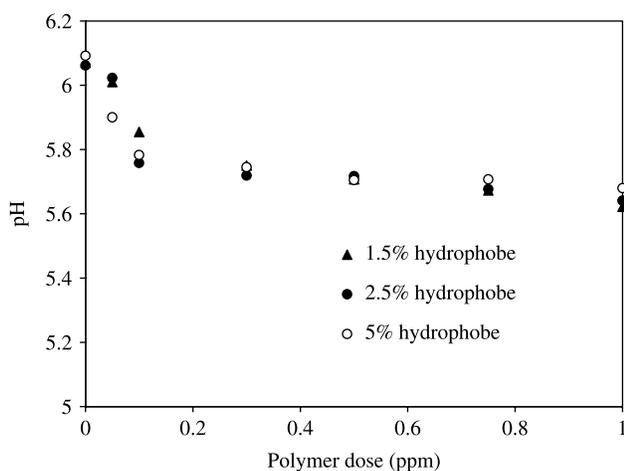


Figure 10 | Effect of polymer dose on pH of the system.

that the greatest removal of NOM was found at polymer dose of 0.3 ppm for all utilized polymers containing diverse percentage of hydrophobe. However, the polyelectrolyte with lower hydrophobe contents had lower removal efficiency than the polyelectrolyte with higher hydrophobe contents. In general, the removal efficiency increased as hydrophobe contents increased (Figures 8 and 9). The slight increase at polymer dose of 0.05 ppm was a result of the addition of the polymer because no coagulation/flocculation was observed at this low polymer dose. The results indicated that coagulation/flocculation started at polymer dose higher than 0.05 ppm up to 0.3 ppm. The UV absorbance results were in total agreement with the dynamic light scattering results yielding the same optimum polymer dose. As it is shown in Figure 8, the optimum polymer dose was found to be around 0.3 ppm. The pH of the solution was virtually unaffected (Figure 10).

CONCLUSIONS

The study demonstrated that smaller amounts of coagulants/flocculants were needed when amphiphilic polyelectrolytes were used as primary coagulants/flocculants in treating NOM- contaminated waters. The appreciably lower polymer amount than the amount of any conventional coagulants/flocculants may reduce the cost of treating as well as yield a much lower sludge volume. Both dynamic light scattering and UV absorbance analyses

confirmed an optimum polymer dose of 0.3 ppm with up to 5% hydrophobe contents to treat waters contaminated with 10 ppm of HA. Degree of hydrophobic association was directly related to the coagulation performance and NOM removal efficiency. Improved water treatment system may be anticipated with hydrophobe contents higher than 5%. However, increasing the hydrophobe contents further reduced solubility of the polyelectrolytes. The pH of the solution was virtually unaffected. Future studies will focus on the use of amphiphilic polyelectrolytes to treat NOM contaminated waters in the presence of other impurities and suspended matters.

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