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Characteristics of BPA removal from water by PACl-Al_{13} in coagulation process

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ABSTRACT

This paper discussed the coagulation characteristics of BPA with polyaluminum chloride (PACl-Al_{13}) as coagulant, examined the impact of coagulation pH, PACl-Al_{13} dosage, TOC (total organic carbon) and turbidity on BPA removal, and analyzed the possible dominant mechanisms in water coagulation process. Formation and performance of flocs during coagulation processes were monitored using photometric dispersion analyzer (PDA). When the concentration of humic acid matters and turbidity was low in the solution, the experimental results showed that the removal of BPA experienced increase and subsequently decrease with the PACl-Al_{13} dosage increasing. The optimal PACl-Al_{13} dosage was found at BPA/PACl-Al_{13} = 1:2.6(M/M) under our experiment conditions. Results show that the maximum BPA removal efficiency occurred at pH 9.0 due to the adsorption by Al_{13} aggregates onto BPA rather than charge neutralization mechanism by polynuclear aluminous salts in the solution. The humic acid matters and kaolin in the solution have significant effect on BPA removal with PACl-Al_{13} in the coagulation. The BPA removal will be weakened at high humic matters. The removal rate of BPA increased and subsequently decreased with the turbidity increasing.

1. Introduction

Bisphenol A [BPA;2,2-(4,4-dihydroxydiphenyl)propane; CAS # 80-05-7; made by combining acetone and phenol; $\log K_{ow}$, 3.4; pK_a, 9.6–11.3; vapour pressure (25 °C), 5.3×10^{-9} kPa; water solubility, 120–300 mg L^{-1}] is an important organic chemical as an intermediate in the manufacture of polycarbonate plastic, epoxy resin, flame retardants and other special products [1–3], widely employed in the packaging of foods, in the preparation of domestic bottles and envelopes, etc.

Unfortunately, BPA is also a well-known endocrine disruptor agent that contaminates surface waters through wastewaters of industries producing BPA or BPA-containing products, or by leaching or dissolution of discarded final products [4]. It has been reported that BPA has estrogenic activity [5–7] and acute toxicity to rats and mice fed at high-doses, with particularly strong effects in fetuses [8–11]. Human exposure to BPA eventually released from these materials is of increasing concern due to its endocrine disrupting potential. Schonfelder et al. [12] measured BPA in the blood of pregnant women, in umbilical blood at birth and in placental tissue, and all samples examined were found to contain BPA at levels within the range shown to alter development. Collectively, these results suggest that it is necessary to prevent BPA from discharging and to purge effectively from the environment.

Chemical coagulation followed by sedimentation is a proven technique for the treatment of wastewater containing high suspended solids especially those formed by the colloidal matters. Research and practical applications have shown that coagulation will lower the pollution load and could generate an adequate water recovery [13–16]. The mechanisms to explain the coagulation of humic substances include charge neutralization, precipitation, bridge-aggregation, adsorption and sweep flocculation [17,18]. Under different conditions, the different mechanism or their combination may be dominant. The relative importance of these mechanisms depends on factors such as pH, coagulant dosage, turbidity and TOC. But much less has been understood on the mechanisms of BPA removal by coagulation.

Polyaluminum chloride (PACl) has been commonly applied to remove colloidal particles and organic matters in water and wastewater treatments. Effective coagulation by PACl depends on the interaction between the aluminum hydrolysis species and particles as well as organic matters. However, poor performance of PACl has been blamed on its low content of critical hydrolysis products, especially polycationic aluminum (Al_{13}). Al_{13} is a highly charged polymeric aluminium species, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$, which is

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an effective agent for charge neutralization [19]. Studies have also confirmed that Al_{13} is the key to efficient coagulation of particulates and natural organic matter (NOM) by PACl [20–23].

Recently, considerable interest has been shown in removal of bisphenol A from wastewaters, Zeng et al. [24] investigated adsorption behaviors of BPA on sediment, Barbieri [25] studied photodegradation of BPA, and various research on biodegradation of BPA were also presented [26,27]. However, few mentioned the adsorbing, moving and transforming behavior of BPA by PACl-Al_{13} as coagulant in coagulation process. The main objective of this research was to understand the impact of coagulation pH, coagulant dosage, turbidity and TOC on floc formation kinetics and examine the coagulation behaviors and mechanisms of BPA. Understanding this process can strongly contribute to risk assessment and fate modeling of BPA in water treatment process. We put more emphasis on investigating the mechanisms and effect of the BPA removal by coagulant PACl-Al13 rather than simulating a treatment process of natural water, thus we fixed a relatively higher concentration of BPA in water so as to observe a clearer process of coagulation. Simultaneously, the relatively higher BPA concentration is in agreement with the concentration in special incidents such as occurrence of environmental pollution accidents when BPA concentration encounters a sudden rise, the data detected in the experiments will provide a risk forecasting for water pollution accidents.

2. Materials and methods

2.1. Materials

BPA, with purity of 99%, was purchased from TCI Corp., (Tokyo, Japan). Acetonitrile (HPLC grade), sodium humate, kaolin were obtained from the Second Regent Ltd. Co. of Shanghai in China. All other chemicals and solvents used in the study were of analytical grade and HPLC grade purchased from standard manufacturers. In order to avoid the interference of some cations and anions in natural water, synthetic test water was prepared to conduct the investigation. All glassware had been pre-cleaned and acid-washed before use.

3. Bench-scale experiments

3.1. Chemical coagulation parameters

In this study, the parameters carried out in Chemical coagulation experiments were pH 4.0–10.0, TOC concentration 1.4–11.2 mg L^{-1}, PACl-Al_{13} dosage 5–17.5 mg L^{-1} and turbidity 2.5–30.3 NTU.

3.2. Chemical coagulation experiments

For the coagulation tests, a jar test procedure was applied by using a DC506 six-paddle stirrer (Shanghai Laboratory Instrument Works Co., Ltd.). Synthetic test water was prepared by adding sodium humate stock solution and kaolin into BPA solution (5.0 mg L^{-1}). A PACl product of high Al_{13} content was separated from preformed PACl by sulfate precipitation and nitrate metathesis [28]. This PACl was named PACl-Al_{13} here. The *B* value of PACl was 2.0. Meanwhile, the pH of test water was adjusted by 0.1 M HCl and 0.1 M NaOH. The sodium humate solution was made with TOC concentrations of 5 g L^{-1}.

A total of 800 mL of the aforesaid test solution was transferred to a 1 L beaker. A certain amount of kaolin was mixed in test water. The suspension was vigorously stirred for 0.5 h in order to avoid ageing phenomena and to reproduce the same behavior in each batch [29]. Turbidity was measured using a Hach 2100N Turbidimeter. The coagulant was injected directly above the liquid surface. After being dosed, 5 min of rapid mixing at 200 rpm was applied, followed by 20 min of slow stirring at 40 rpm. The flocs were allowed to settle for 30 min. Formation of flocs was detected with the implement PDA (photometric disperse analyzer, iPDA-100, Econovel Co., South Korea). The output from the PDA, the flocculation index (FI) was recorded from 30 s before the beginning of rapid mixing to settlement period. A small sample was taken immediately after the 1 min rapid mix period for zeta Potential (Zeta-Meter, Macrotech Nichion Co., Japan). At last, sample was collected from 2 cm below the surface for pH measurements (Model PHS-3C pH Meter Manual, Shanghai Precision & Scientific Instrument Co., China); at the same time, collected samples were filtered through quantitative filter paper to measure residual BPA concentration and TOC. Three replicates of experiments were carried out and data obtained in the experiments were the average values. The coagulation experiments were conducted at temperature 25 °C.

3.3. BPA analysis

The amount of BPA in subsample was determined by high performance liquid chromatography (HPLC) system equipped with fluorescent detector (Agilent 1100-FLD, USA) and a Zorbax SB-C18 column (HP, 4.6 × 150 mm, USA). The mobile phase was acetonitrile–water solution (50:50, v/v), and the flow rate was 1 mL min^{-1}. The temperature of the column was 40 °C. The excitation wavelength was 226 nm and the emission wavelength was 310 nm. The injection volume was 10 μL. The retention time of BPA was 3.14 min. The calibration cure equation for BPA detection was peak area = $204.86C_{BPA}$ ($R^2 = 0.999$), where C_{BPA} was the BPA concentration (within the range of 0–10.0 mg L^{-1}). The limit of detection for BPA analysis was 0.013 mg L^{-1}. High concentration samples were measured after diluting to the above range with 0.01 M $NaNO_3$.

3.4. Flocculation kinetics

The flocculation kinetics after coagulant addition was monitored by using a photometric dispersion analyzer. The principle of this monitoring technique was described in literature [20,30]. The output from the PDA, or flocculation index (FI), is sensitive to particle size and can be effectively utilized to describe the aggregation progress of fine particles, such as the initial aggregation, breakage, and re-aggregation behaviors of particles. The most practical use of the FI is that it shows a significant increase as particles aggregate, thus allowing a dynamic assessment of coagulation mechanisms [29].

4. Results and discussion

4.1. Effect of coagulant dosage

The general experimental approach was to first characterize the relationship between the coagulation dosage and settling performance (turbidity/TOC removal) for optimized PACl-Al_{13} dosage, and then to correlate these results with PDA experiments in which floc formation rates were measured vs time. These experiments were performed at bench scale using synthetic water in order to precisely control water quality variables, using solution containing BPA of 5.0 mg L^{-1}. The effect of coagulant dosage on the BPA removal was examined at 5, 7, 9, 10, 11, 13, 15, 17.5 and 3.37 mg L^{-1} of TOC and temperature of solution of 25 °C were kept constant, and pH value was taken at 7.0 ± 0.05 in experiments.

As shown in Fig. 1, when PACl-Al$_{13}$ dosage ranged from 1 to 13 mg L^{-1}, increasing PACl-Al$_{13}$ dosage improved BPA removal in the settling process. While the maximum BPA removal efficiency occurred at 26.8%, zeta potential of 0.36 mV approaching isoelectric point was obtained. The results indicate that the dominant removal mechanism at the pH of 7.0 is by charge neutralization which promoted agglomeration of destabilized colloids. A majority of the evidence suggests that, under water treatment conditions, the positively charged, insoluble aluminum hydroxide sols are the most realistic species responsible for particle destabilization during coagulation by adsorbing to the surface of the oppositely charged, much larger natural colloids and entering into an electrical bond [31,32]. As the coagulant dissolves, the cations serve to neutralize the negative charge on the colloids. This occurs before visible flock formation, and mixing rapid is effective in this phase. At lower PACl-Al$_{13}$ dosages, the physical enmeshment mechanism is less significant and smaller, lighter flocs develop. While at higher PACl-Al$_{13}$ dosage, this interaction between voluminous aluminum hydroxide precipitates and natural colloids is known as sweep coagulation. Eangregory and Carlson [33] demonstrated that in this mode particles are destabilized by adsorption of aluminum hydroxide sols and are enmeshed in sol aggregates, promoting the formation of relatively large, settleable flocs. Thus BPA not initially adsorbed are removed by enmeshment in the flocs.

Several studies emphasized the importance of optimizing particle zeta potential (or electrophoretic mobility) to produce favorable conditions for particle removal. Elimelech and O'Melia, for example, clearly showed that the removal efficiency of 0.75 μm particles increased as zeta potential decreased (i.e., approached zero) [34]. Because zeta potential is an indicator of the effective surface charge and therefore the degree of destabilization of particles [33]. Amirtharaja and Tambo [35] reported that the zeta potential range of properly destabilized particles is usually in the range of −4 to +3 mV. For these reasons, in the research presented here, optimum PACl-Al$_{13}$ dosage, were considered to be those that achieved a zeta potential of approximately 0.0 ± 2 mV. As shown in Fig. 1, the BPA removal increased with the increase of coagulant dosages before reaching the optimal dosage, which was found at BPA/PACl-Al$_{13}$ = 1:2.6(M/M) under our experiment conditions, and zeta potential remained negative but gradually approached zero. When zeta potential was reversed, the BPA removal decreased due to the re-stabilization of particles.

It has long been recognized that zeta potential is a very good index of the magnitude of the repulsive interaction between colloidal particles [36]. When the zeta potential reverses from negative to positive and further increases, the repulsive forces increase gradually. The attractive van der Waals forces are not enough to agglomerate the colloidal particles, allowing the repulsive forces associated with compressed electric double layer to dominate, which reduced the probability of successful particle–particle grain collisions, thus BPA was not able to get removed.

For the data presented in Fig. 2, floc formation kinetics clearly increased as PACl-Al$_{13}$ dosage increased from 5 to 13 mg L^{-1}. When the time was approximately 1000 s, the rate of FI (flocculation index) increase was greatest for the PACl-Al$_{13}$ dosage (13 mg L^{-1}) that was optimum for coagulant, from then on, FI value remained steady ranged from 0.45 to 0.54. Higher dosage did not significantly increase the rate of floc formation. As we can see, floc growth follows a classical pattern composed of a short induction period followed by a rapid growth phase until the steady state floc size is reached. Comparison of the steady state floc size revealed that the dosage of 13 mg L^{-1} produced flocs of a significantly larger size compared to the other dosages. These data appear to correlate with the results presented in Fig. 1, which indicates that the mechanism might be re-stabilization of colloidal particles when over dosed of coagulant was added.

4.2. Effect of pH

Experiments were conducted to study the effect of pH on the BPA removal, a series of experiments were performed using solution containing BPA of 5 mg L^{-1}. The effect of pH on the BPA removal was examined at 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0, 3.37 mg L^{-1}of TOC and temperature of solution of 25 °C were kept constant, and PACl-Al$_{13}$ dosages were taken 2, 6, 12 mg L^{-1} in experiments.

The experimental results for BPA removal efficiency with pH changing are reported in Fig. 3. BPA removal efficiency increased with increasing the pH up to 9.0, and then decreased for each treatment processes. The changes of zeta potential with pH are shown in Fig. 3. For all three coagulant dosages, the efficient BPA removal occurs in the alkaline pH region at 9.0 and zeta potential approached isoelectric point when pH value was approximately 7.0, accordingly BPA removal efficiencies were 23.6%, 28.3% and 32.2% for 2, 6, 12 mg L^{-1} of PACl-Al$_{13}$ dosages, respectively.

At low pH values, coagulation speed and the particle size of coagulant formed were in a low value. Eangregory and Carlson discovered that because of the adsorption of H$^+$, particles are destabilized by fewer but more highly charged sols, which may result in

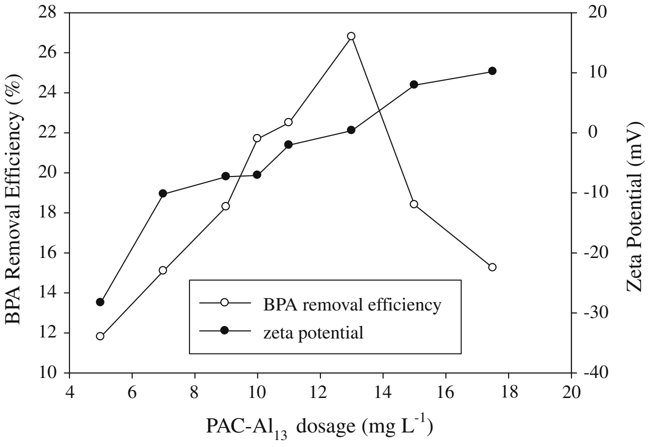

Fig. 1. Effect of PAC-Al$_{13}$ dosage on BPA removal efficiency and zeta potential of 5.0 mg L^{-1} BPA solution (TOC = 3.37 mg L^{-1}; pH = 7.0).

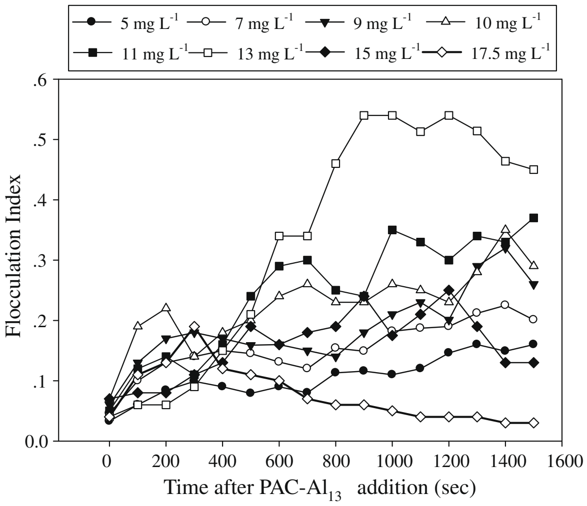

Fig. 2. Flocculation index vs time for eight PAC-Al$_{13}$ dosages.

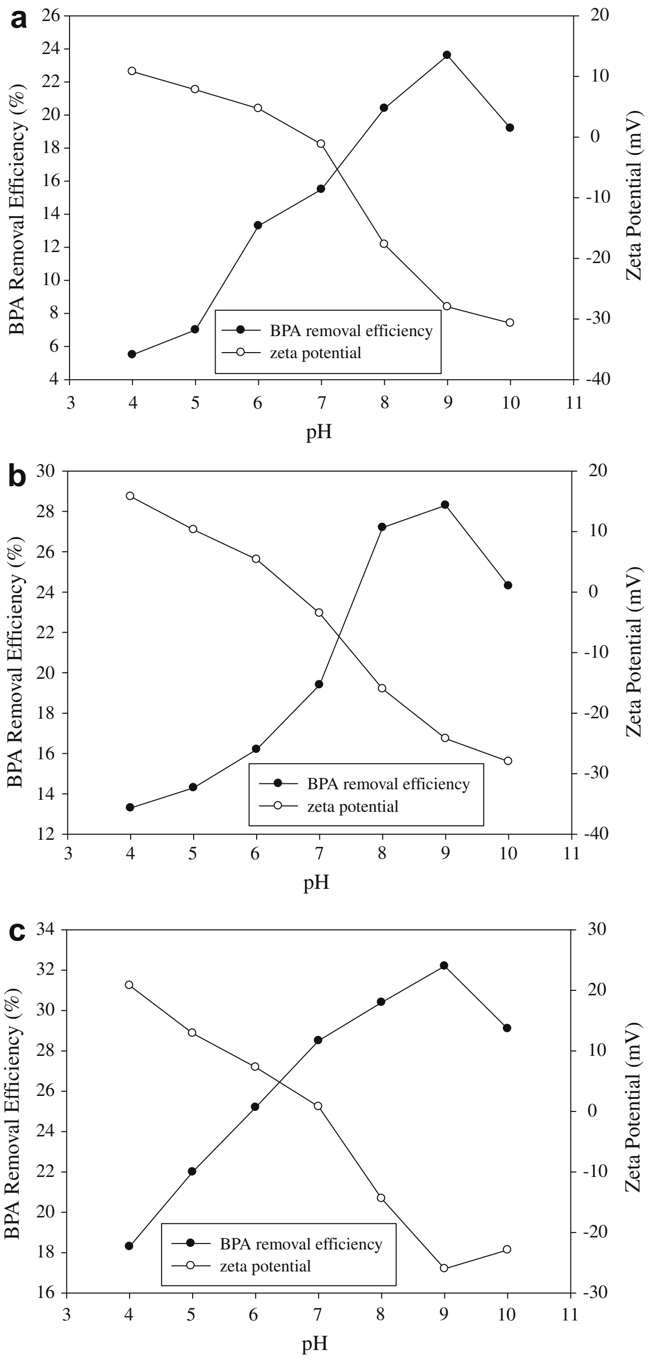

Fig. 3. Effect of pH on BPA removal efficiency and zeta potential of 5.0 mg L^{-1} BPA solution. PAC-Al_{13} dosages were as follows: (a) 2; (b) 6; (c) 12 mg L^{-1}. TOC = 3.37 mg L^{-1}.

an uneven surface charge distribution and a reduced probability of successful particle collisions [33].

BPA removal improves significantly as coagulation pH increases because hydrolysis products of PACl-Al_{13} possess high positive charge which have a strong charge neutralization ability on humic acid and colloids, whereafter large flocs are generated. At least two mechanisms might be involved in the removal of BPA: adsorption of BPA to the surface of destabilized colloids which subsequently formed voluminous agglomeration of precipitates as well as enmeshment of BPA in the flocs.

The maximum BPA removal efficiency was obtained at pH 9.0, the same results were also found in the research of Lin and Chin [37]. The effect on the coagulation of BPA could be interpreted from two aspects. First, with the increase of pH, the carboxylic and phenolic groups on the humic acid molecular chain will become more negatively charged due to protonation reactions, therefore, not enough coagulant will be available to achieve neutralization or form insoluble complexes. Second, Al_{13}, which possesses a +7 valence, could be decomposed by deprotonation reactions that release the protons in pairs to yield the Al_{13} with less positive charges such as Al_{13}^{5+}, Al_{13}^{3+} and Al_{13}^{+} when the pH was raised [38]. As a result, the Al_{13} aggregates can be more easily generated during coagulation process at high pH, and the size of them increases with increasing pH values [37]. Chen et al. [39] has indicated that Al_{13} aggregates result in efficient coagulation at alkaline pH. Compared with the two mechanisms, the adsorption by Al_{13} onto BPA is of primary importance, whereas the loss of charge neutralization is of secondary or little importance.

4.3. Effect of TOC

In previous bench-scale experiments, PACl-Al_{13} dosage was optimized based on zeta potential (for two TOC concentrations) over a pH range of 4.0–10.0 at 13 mg L^{-1}. TOC on the BPA removal was adjusted to 1.4, 3.8, 5.5, 7.0, 9.3, 11.2 mg L^{-1}, with initial BPA of 5.0 mg L^{-1}, pH of 9.0 ± 0.05 and temperature 25 °C of solution keeping constant.

Based on the information contained in Fig. 4, with TOC increasing, BPA removal efficiency increased, the maximum removal of 25% was obtained while the TOC reached 3.8 mg L^{-1} at +2.3 mV of zeta potential approaching to isoelectric point. The PDA results are reported in Fig. 5. It can be observed that a mass of relatively larger size aggregates formed. Subsequently, FI value obtained steady state at the range of 1.16–1.31 after 1000 s at TOC of 3.8 mg L^{-1}, relatively higher than that of 0.65–0.73 at TOC of 1.4 mg L^{-1}. Natural organic material (NOM) is widespread in natural water, and might affect the removal efficiency of BPA through different ways. In our experiment, sodium humate was chosen as a representative NOM to assess its influence on BPA removal in coagulation process. Sharp et al. [40] characterized NOM into its components as hydrophobic and hydrophilic fractions, the hydrophobic fractions were then separated further to humic acid fraction (HAF) and fulvic acid fraction (FAF). Coagulating FAF resulted in the production of small more compact flocs, less susceptible to shear. McKnight et al. [41] found out that FAF is removed mainly through an adsorption pathway, as well as BPA. Whereas the flocs produced by HAF were larger and more open and more susceptible to increased shear. Huang and Shiu [42] found out that HAF is thought to be removed through a combination of

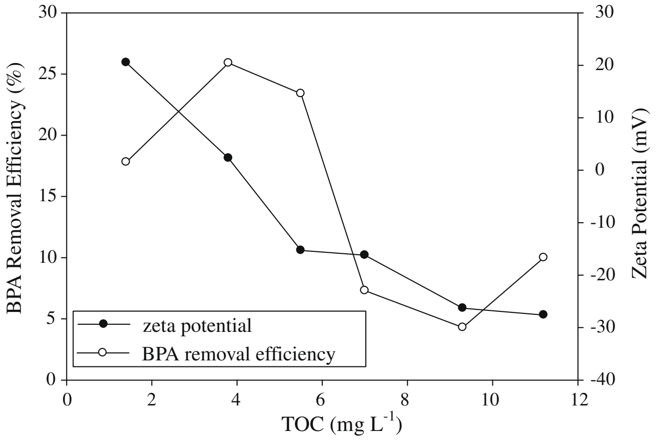

Fig. 4. Effect of TOC on zeta potential and BPA removal efficiency of 5.0 mg L^{-1} BPA solution (PAC-Al_{13} dosage was 13 mg L^{-1}; pH = 9.0).

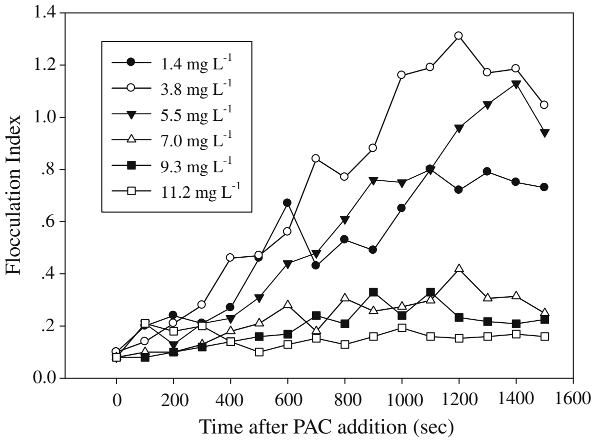

Fig. 5. Flocculation index vs time at six TOC levels.

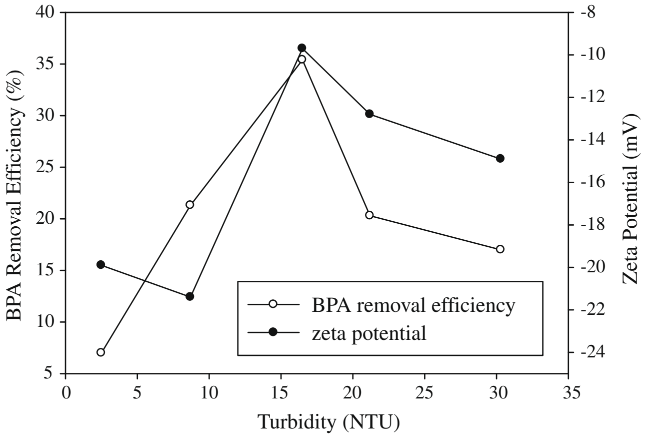

Fig. 6. Effect of turbidity on zeta potential and BPA removal efficiency of 5.0 mg L^{-1} BPA solution (PAC-Al_{13} dosage was 13 mg L^{-1}; pH=9.0; TOC = 3.37 mg L^{-1}).

charge neutralization (for colloids), complexation/precipitation and ligand exchange adsorption, therefore the removal mechanism of BPA is further complicated. However, the synergistic effects of isolated NOM fractions are to be further studied, as a result the synergistic effects of isolated NOM fractions on BPA removal is to be studied in our future work.

As TOC subsequently increased, there was a tendency of decrease for BPA removal. The removal efficiency reduced to 4.3% at TOC of 9.3 mg L^{-1}, charge reversal from positive to negative and finally reaching 26.3 mV was observed. FI value kept a steady state ranging from 0.23 to 0.33 after 1000 s, indicating that fewer and smaller flocs formed. Previous studies have found out that the organic material of NOM is predominantly phenolic and carboxylic in nature, but also contains alcohol, purine, amine and ketone groups and is often described as a weak anionic polymer with complex structure [40]. Over dose of this sort of macromolecular compound depressed the possibility of flocs aggregation by adsorption to the surface of suspended particles thus coating more negative charge on colloidal particles which consequently attained re-stabilization. In addition, Avnea and Koopal [43] researched that adsorption follows a two stage sequence of fast followed by slow adsorption during which competitive displacement occurs where high absorption affinity compounds replace low affinity ones. Therefore when large concentration of NOM exist in solution, the inhibition on BPA plays an important role.

Attention should be paid to a finding of this investigation that with increasing TOC to 11.2 mg L^{-1}, BPA removal efficiency reached approximately 10% at −27.6 mV of zeta potential, and accordingly FI remained steady at the range of 0.15–0.19. The results indicate that at higher TOC levels, more colloids increased the probability of sweep flocculation onto organic matters.

4.4. Effect of turbidity

Experiments were conducted to study the effect of turbidity on BPA removal. The turbidity of test water was adjusted to 2.5, 8.7, 16.5, 21.2, 30.3 NTU by stock kaolin solution, 13 mg L^{-1} of PACl-Al_{13} dosage, 9.0–0.05 of pH, 3.37 mg L^{-1} of TOC and solution temperature of 25 °C were hold in constant for coagulation processes.

The changes of zeta potential and BPA removal efficiency with turbidity are shown in Fig. 6. With the increase of turbidity from 2.5 NTU to 16.5 NTU, removal efficiency of BPA and zeta potential increased from 7% to 35.4%, −19.9 to −9.7 mV, respectively. Simultaneously, FI value went up with turbidity increasing, while going with an augmentation of FI values range in the steady state. The observed data suggest that in the case of low turbidity, due to the cationic hydrolysis products of PACl-Al_{13}, the adsorption rate increases with surface charge. Because the electrostatic attraction between the positively Al_{13} aggregates and negatively kaolinite surface increases with surface charge, more colloidal particles generate arise from charge neutralization and adsorption mechanism and subsequently, more flocs formed with an increase of attachments points number leading to an significant increase in the amount and size of flocs, accordingly an increase of adsorption to BPA.

With the turbidity further increased from 16.5 to 30.3 NTU, removal efficiency of BPA reduced accordingly. When the turbidity reached 30 NTU, BPA removal efficiency reached 17%, with zeta potential reducing to −14.9 mV, and FI value kept steady between 1.02 and 1.24 after 1000 s (Fig. 7). On the one hand, it can be concluded that in the case of relatively high turbidity the colloidal particles grow to an overwhelmingly large number, thus there exists a lot more attachment points which generate large size of compact flocs than those in low turbidity, and consequently the effect of trapping and adsorption to BPA reduce compared with that of low turbidity.

5. Summary

1. Bench-scale experiments were performed to investigate the removal efficiency of BPA and the coagulating properties in water coagulation process with PACl-Al_{13} as coagulant. When

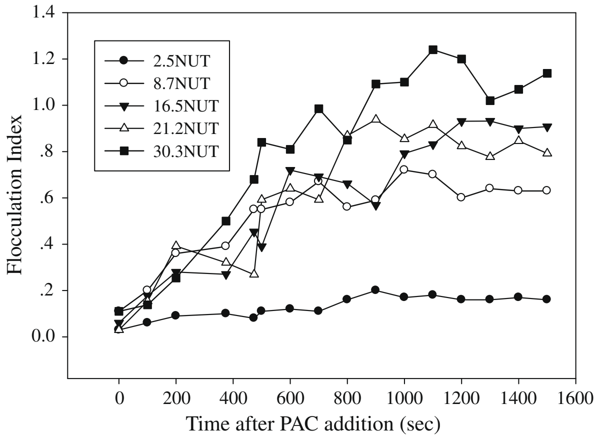

Fig. 7. Flocculation index vs time at five turbidities.

the concentration of organic matter and turbidity was low in the solution, the experimental results showed that the removal of BPA experienced increase and subsequently decreased with the PACl-Al_{13} dosage increasing. The optimal PACl-Al_{13} dosage is found at BPA/PACl-Al_{13} = 1:2.6(M/M) under our experiment conditions.

2. It is found that the maximum BPA removal efficiency occurred at pH 9.0 due to the adsorption by Al_{13} aggregates onto BPA rather than charge neutralization mechanism by polynuclear aluminous salts in the solution.
3. The humic matters and the turbidity matters in the solution have significant effect on BPA removal by PACl-Al_{13} coagulation. The BPA removal will be weakened at high concentration of humic matters.
4. The removal rate of BPA increased firstly and subsequently decreased with the turbidity increasing. The removal efficiency of BPA will be weakened at high turbidity.

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