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Removal of Phthalate Esters with PDA through Enhanced Coagulation Technology

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ABSTRACT

The removal of environmental hormone phthalate esters (PAEs) by enhanced coagulation was studied. Copolymer of dimethyl diallyl ammonium chloride and acrylamide(PDA) was employed to removal dimethyl phthalate(DMP), diethyl phthalate(DEP), di-butyl phthalate(DBP). During the coagulation/ flocculation process, parameters such as the dosage of PDA, pH value, string time on the second stage and settling time was investigated in order to determine the condition of enhanced coagulation treatment. The results showed that the maximum removal rate of DMP, DEP and DBP were reached 89.7 %, 91.8 % and 92.4 % respectively when the solution of DMP, DEP and DBP initial concentration all were 0.5 mg/L, the dosage of PDA was 8.0 mg/L, pH value was 10.0, the characteristic viscosity is 7.12 dL/g, the time of second stage was 4.0 min and the settling time was 2.0 h. Based on the enhanced coagulation, the maximum removal rate of total organic carbon(TOC) was reached 20.1%.

Keywords: Enhanced coagulation; PDA; phthalic acid ester; removal efficiency.

INTRODUCTION

Phthalates (PAEs), also known as phthalate esters, is a class of synthetic organic compounds. It is widely used in toys, food packaging materials, rubber, fertilizer, pesticides and other industries and has serious harm on the human health. More than 80 % of the PAEs are used as plasticizers for plastics [1-4]. As plasticizer, PAEs has no real aggregate reaction but only connected to the polymer molecules through the hydrogen bond and van der Waals force. With the passage of time, PAEs can be migrated from plastic to the external environment thereby damaging environments [5-6]. In addition, PAEs has carcinogenic, teratogenic, mutagenic and reproductive toxicity hazards. It also may produce cross-generation effects through lactation and placenta, and even interfere with normal hormone secretion and disrupts biological function [7-11]. Due to its properties of low water solubility and low volatility, PAEs tends to attached to solid particles, exhibiting strong adsorption affinity and are commonly found in the atmospheric dust, rivers and soils of the environment through biological concentration in food chain. At present, China's surface water source is generally polluted by PAEs, and PAEs are detected in the water of the Jialing River and the Yangtze River as the source water [12,13]. PAEs even can be detected in the tap water [14]. Therefore, it is imminent to study the routine process of PAEs.

At present, numerous studies have been done on the treatment of PAEs at home and abroad, such as adsorption method [15,16], biodegradation method [17,18], advanced oxidation method [19], but how to reduce the cost to improve the treatment effect is still a big problem. For the current water supply plant, the technology which can achieve a specific treatment effect with a low processing cost, or a slight increase in processing costs is the study trend. Flocculation method, as a commonly used water treatment method, is widely used for the advantages of good treatment effect, simple operation, being easy to control cost and other advantages [20-22].

In this study, the flocculant was used as self-made PDA in the laboratory, which was applied to the removal of DMP, DEP, DBP in water and discussed the influence of the amount of the flocculant PDA, the pH value of the water sample, the viscosity of the PDA, the mixing time of coagulation, the settlement time of coagulation, and the total TOC removal rate.

MATERIALS AND METHODS

Material and Instruments: The analytical grade materials such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), used in this study was purchased from Chongqing Oriental reagent factory. Copolymer of dimethyl diallyl ammonium chloride and acrylamide (PDA) in this study was made in laboratory. The instruments used in this study were as follows: ZR4-6 Flocculation Test Mixer (Zhongrun Water Industry Technology Development Co. Ltd. China); LiquiTOC Analyzer (Elementar Analysensystem GmbH); AL104 Precision Electronic Balance (Mettler Toledo Instruments Co. Ltd.); Delta 320 Desktop pH meter (Mettler Toledo Instruments Co. Ltd.）LC-10AT High performance liquid chromatography (SHIMADZU); DHG-9070A Heating and Drying Oven (Gongyi Yuhua Instrument Co., Ltd. China).

Coagulation test: The coagulation test was carried out in a 250mL beaker. 100 mL mixed solution with concentration of 0.50 mg L^{-1} of DMP, DBP and DEP was putted in a beaker and adding laboratory self-made flocculant PDA to experimented flocculation stirring according to the set procedures. See references for specific parameters [23]. Settling for 2.0 h after flocculation stirring, and then the supernatant was taken to determine the concentration of DMP, DBP and DEP after filtering (0.45 um).

RESULTS AND DISCUSSION

The effect of PDA dosage on the removal rate: The effects of the amount of PDA on the removal rate of DMP, DEP and DBP in the simulated water samples were studied according to the flocculation test method without adjusting the initial pH value of the simulated water samples.

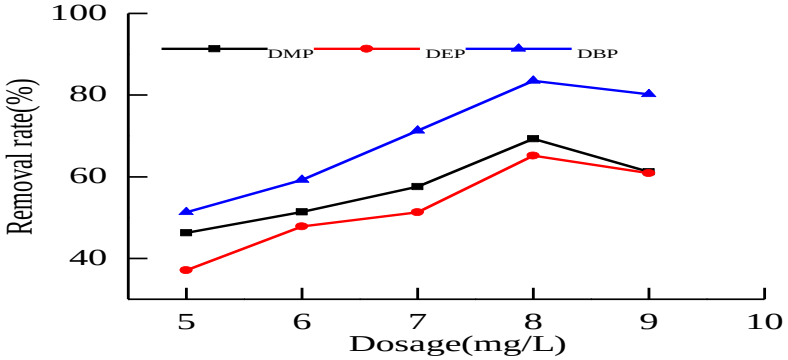

Figure 1. The effect of PDA dosage on the removal rate

It can be seen from figure 1, in the dosage range of 5 ~ 9 (mg L^{-1}), with the increasing of flocculant PDA dosage, the removal rates of DMP, DEP and DBP are gradually increased. When the dosage is 8.0 mg L^{-1},

the removal rate reached the maximum values, which were 69.3 %, 65.2 % and 83.5 % respectively. And the removal rate was decreased when continue to increase the dosage. It can be seen that organic flocculant PDA has obvious removal effect on characteristic organics DMP, DEP and DBP in water. This was because the PDA is a cationic flocculant, its molecular chain has a positive charge, while DMP, DEP and DBP in the aqueous solution showed an electronegativity, the flocculant PDA would play charge neutralization and inter attracted with DMP, DEP and DBP in the water [23-24]. When the dosage of flocculant PDA was relatively small, the positive charge of flocculant could not attract the pollutant molecules in the water to achieve the purpose of removal. With the increase of flocculant dosage, positive charge of flocculant was also increased, then the ability of the DMP, DEP and DBP removing was stronger. When the dosage was more than the optimal dosage, the flocculant molecules were attracted and wound with each other, so the removal rate is decreasing.

The effect of initial pH on the removal rate: The initial pH value of simulated water samples was controlled in the range of 2.0 ~ 10.0 and PDA was used to remove organic matter DMP, DEP and DBP. Take the dosage of PDA as 8.0 mg L^{-1} to research the effect of initial pH value of simulated water samples on the removal rate of DMP, DEP and DBP.

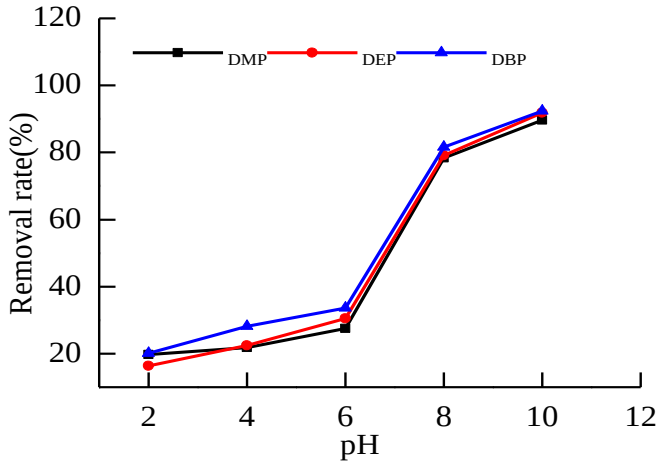

Figure 2. The effect of pH value on the removal rate

Figure 2 showed that the change of pH value has a significant effect on the removal of DMP, DEP and DBP from flocculant PDA, indicating that each flocculant has its most suitable pH value in flocculation test. When the pH value of the simulated water samples was between 2.0 and 10.0, the effect of flocculant PDA on the removal rate of organics had been increasing. When the pH value was 10, the removal rate of DMP, DEP and DBP reached 89.7 %, 91.8 % and 92.4 % respectively.

The effect of intrinsic viscosity on the removal rate: Without adjusting the initial pH value of simulated water samples, PDA was used to remove organic matter DMP, DEP and DBP, and the dosage of PDA was controlled to 8.0 mg L^{-1}. The effect of intrinsic viscosity on the removal rate of DMP, DEP and DBP were studied by adding different intrinsic viscosity of PDA to water.

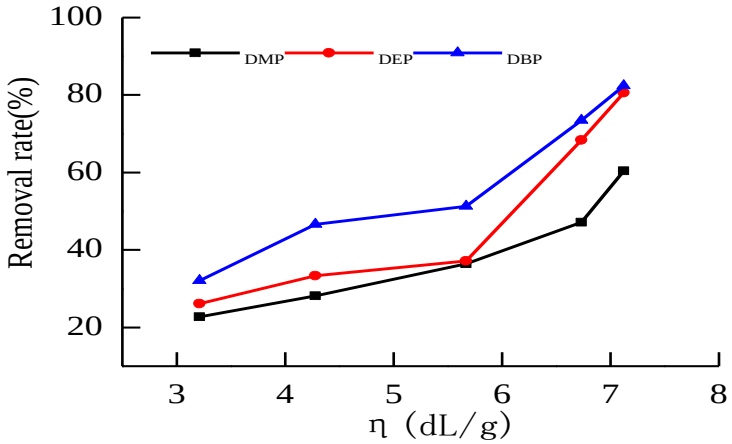

Figure 3. The effect of PDA intrinsic viscosity on the removal rate

As shown in figure 3, the removal rate of organics DMP, DEP and DBP was increasing gradually with the increase of the intrinsic viscosity value. When the intrinsic viscosity was 7.12 dL g^{-1}, the removal rate of DMP, DEP and DBP reached the maximum, which were 60.4%, 80.6% and 82.4% respectively. This was because when the specific viscosity of the flocculant was higher, the more positive charge in the aqueous solution was, the stronger the charge neutralization was. If the intrinsic viscosity of the flocculant was greater, the molecular chain was longer, the ability to bridge was stronger, the removal of the target molecules DMP, DEP and DBP in the water was better.

The effect of stirring time on the removal rate: Without adjusting the initial pH value of simulated water samples, PDA was used to remove organics DMP, DEP and DBP, and the dosage of PDA was controlled to 8.0 mg L^{-1}. Through changing the stirring time in medium speed stage during the flocculation stirring process to research the effects of the stirring time on the removal rate of DMP, DEP and DBP.

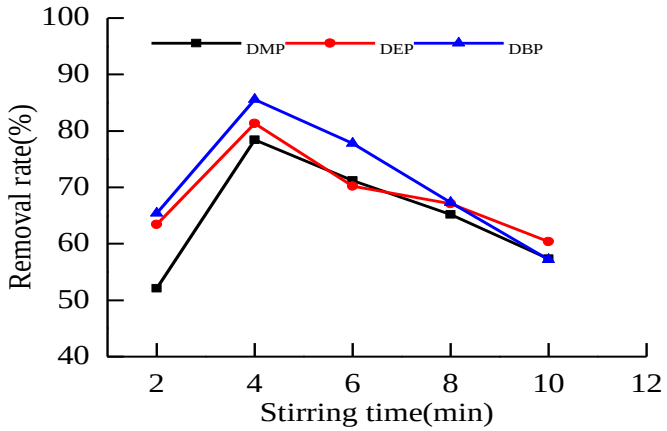

Figure 4. The effect of stirring time on removal rate

It can be seen from figure 4 that the removal rate of DMP, DEP and DBP by flocculant PDA showed a tendency of increase firstly and then decrease with the prolongation of stirring time in medium speed stage. When the stirring time was 4.0 min, the removal rates of organics DMP, DEP and DBP reached the maximum, which were 78.4 %, 81.3 % and 85.6 % respectively. This was due to the PDA removed the organic matter DMP, DEP and DBP in the simulated water sample to achieved water purification was mainly by the action of the cationic flocculant's charge neutralization and the adsorption bridging [22]. On the one hand, the formed floccules would be destroyed under the action of external forces, and resulting

the organics DMP, DEP, and DBP in flocs be re-released When the mixing time was too long. On the other hand, long time mixing may make the molecular chain of organic high molecular flocculant fractured, reduced its bridging capacity and decreased removal rate.

The effect of settling time on the removal rate: Without adjusting the initial pH value of simulated water samples, PDA was used to remove organics DMP, DEP and DBP, and the dosage of PDA was controlled to 8.0 mg L^{-1}. Through changing the settling time to research the effects of it on the removal rate of DMP, DEP and DBP.

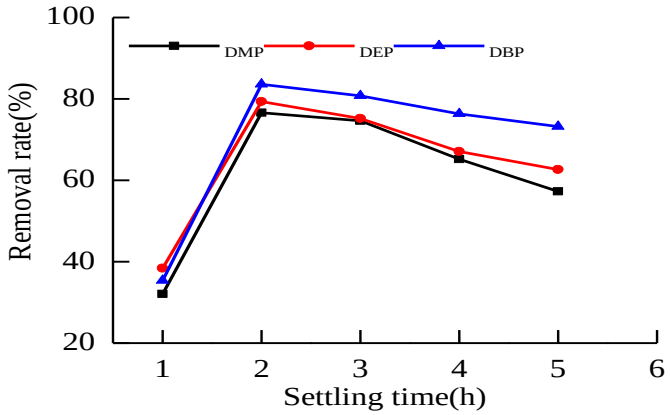

Figure 5. The effect of settling time on removal rate

The figure 5 above shows that the removal rate of organics DMP, DEP and DBP showed a tendency of increase firstly and then decrease with the prolongation of settling time. When the settling time was 2.0 h, the removal rates of DMP, DEP and DBP reaching the maximum, which were 76.6 %、79.3 % and 83.6 % respectively. This was because before 2.0 h, the PDA, carrying organic DMP, DEP and DBP molecules, form tiny floc which settling in the bottom of the beaker slowly under the action of gravity to achieve the purpose of removal. With the extension of time, the molecular thermal movement in the system played a leading role, and the formed flocs was small. It was easy to make organic DMP, DEP and DBP re-spread to the solution, and resulting in decreased removal rate [23].

The relationship between PDA dosing and TOC: The flocculant PDA was used as a flocculant to remove the organics DMP, DEP, DBP and the effect of PDA dosage on the removal rate of TOC in the condition of not adjusting the initial pH value of the simulated water sample.

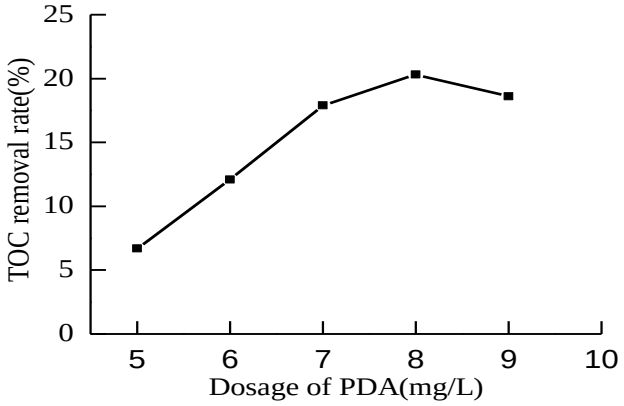

Figure 6. The effect of PDA dosage on TOC removal rate

The results were shown in figure 6. The removal rate of TOC showed a tendency of increase firstly and then decrease with the increase of PDA dosage. And the removal rate of TOC reached 20.1 % when PDA dosage is 8.0 mg/L. This was same as the tendency of PDA dosage on TOC removal rate. It indicated that the DMP, DEP and DBP were the important sources of TOC, and the level of TOC was proportional to the concentration of DMP, DEP and DBP in the solution.

APPLICATIONS

The results indicate that if PDA was useful to remove the organics, because of its electrical neutralization and bridging effect, the maximum TOC removal rate is reached.

CONCLUSIONS

(1) It can achieve better results when adopting the enhanced coagulation method to remove the DMP, DEP and DBP in water by using the self-made PDA. When the initial concentration of DMP, DEP and DBP were all 0.5 mg L^{-1}, the dosage of PDA was 8.0 mg L^{-1}, pH was 10.0, the intrinsic viscosity was 7.12 dL g^{-1}, the stirring time of second stage was 4.0 min and the settling time was 2.0 h, the maximum removal rates of DMP, DEP and DBP were 89.7 %, 91.8 % and 92.4 % respectively.

(2) When the PDA was used to remove the organics DMP, DEP and DBP in the water, the PDA achieved the purpose of removing the organics by playing its electrical neutralization and bridging effect, and the maximum removal rate of TOC reached 20.1%.

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