



## Bench-scale and pilot-scale evaluation of coagulation pre-treatment for wastewater reused by reverse osmosis in a petrochemical circulating cooling water system



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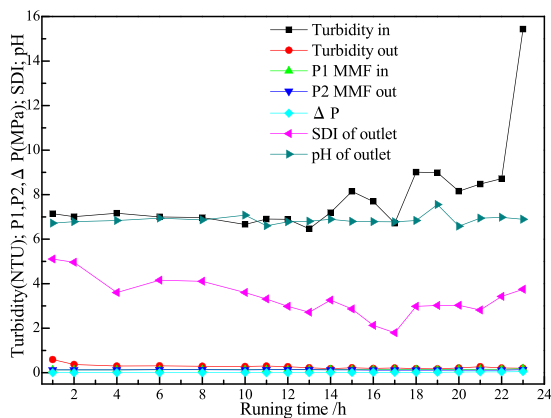
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### HIGHLIGHTS

- Wastewater reused in circulating cooling water system was evaluated in a pilot scale.
- Acrylamide polymers have been optimized by coagulation jar test.
- Running time is 23 h when the dosage of P(DMB-AM) and PAC is 20 mg L<sup>-1</sup> and 15 mg L<sup>-1</sup>.
- PAC and P(DMB-AM) have a good application in wastewater pretreatment for RO process.

### GRAPHICAL ABSTRACT

The water turbidity is less than 0.5 NTU, and the SDI value is less than 5, the pressure difference between the influent and effluent water ( $\Delta p$ ) has been zero, it began to rise slowly after 15 h, and reached 0.05 MPa in 23 h.



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### ABSTRACT

The optimal dosage of four acrylamide polymer coagulants commonly used in industry, namely anionic polyacrylamide P(AA-co-AM), cationic polyacrylamide P(DMB-co-AM), nonionic polyacrylamide P(AM), and hydrophobic polyacrylamide P(OA-co-AM), is explored using coagulation–flocculation jar tests in laboratory. Experimental results show that P(DMB-co-AM) generates a maximum transmittance of 90.8% at 20 mg L<sup>-1</sup>, and therefore has the best coagulation performance. In the second part of this study, the impact of polyaluminum chloride (PACl) and P(DMB-co-AM) concentrations on coagulation–flocculation properties is evaluated using a pilot scale test in a petrochemical plant in Jiangsu, China. Results shows that the running time can reach 23 h when the dosages of P(DMB-AM) and PACl are 20 mg L<sup>-1</sup> and 15 mg L<sup>-1</sup>. The mean diameter of particles (by number) in the feed water, in the water after coagulation, and in the water after the multimedia filter (MMF) was 0.71  $\mu$ m, 0.52  $\mu$ m, and 0.41  $\mu$ m, respectively. Other parameters, including chemical oxygen demand (COD), total dissolved solids (TDS), total Fe, and turbidity, also decreased following the coagulation–flocculation process and MMF. Results of the above tests comprehensively suggest that PACl and P(DMB-AM) can be used successfully in wastewater pre-treatment for the reverse osmosis (RO) process.

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## 1. Introduction

Optimization of industrial wastewater pre-treatment is practically important for recycling, and provides flexibility to satisfy short-term freshwater needs, which contribute to freshwater savings, wastewater reduction and water sustainability [1], as well as to the minimization of environmental disturbance. The process-intensive petrochemical industry in China grows rapidly, challenging the management and protection of natural resources such as water, soils, and atmosphere [2]. With the release of series of environmental policies, the contradiction between the limited water supply and the increasing water demand constrains the sustainable development of petrochemical industry. As one of the major water users, chemical and petrochemical plants consume relatively large quantities of water in processing products, flushing, and disposal of industrial wastewaters, especially in the cooling units. There is an ever increasing demand to minimize this consumption as natural water resources become scarcer [3]. Multiple water conservation technologies have been gradually used in the circulating cooling water system to improve the utilization efficiency of water, especially in the operation of cooling water with a high-concentration circulation water treatment technology [4–7]. Compared with other water resources, wastewater from cooling systems in the petrochemical industry, which only contains scale and corrosion inhibitors, is suitable to reuse as replenishment for recycled cooling water if the particles and colloids stably dispersed in cooling water system have been treated properly. Otherwise, the particles and colloids dispersed could scale, deposit or block the pipe when the wastewater from cooling systems being reused/recycled as cooling water. Filtration such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been used to remove soluble and insoluble organic and inorganic contaminants in wastewater [8–11]. The above techniques are ordinarily combined with rapid filtration, which treats effluents from the filter washed for desalination before wastewater can be recycled.

The blowdown from the circulating cooling water system is characterized by high salinity, high chemical oxygen demand (COD), high turbidity, and high organic and inorganic contaminants. Therefore, the major issue in wastewater recycling is how to reduce COD, turbidity, organic and inorganic contaminants from the cooling system. Before the above filtration processes, wastewater must pass through a pretreatment system to remove COD, turbidity, organic and inorganic contaminants by coagulation and filtration, and to remove divalent and trivalent metal cations prior to the RO process to prevent membrane fouling, or reduce aromatics content and capture oil, grease, and other organics to acceptable levels with an activated carbon system [12]. Hence, the bypass filtration system is a vital part for the recycling water treatment, which makes the recycle water system to work efficiently and economically under the high cycles of concentration [13].

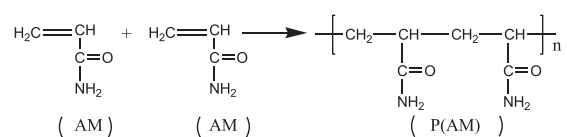
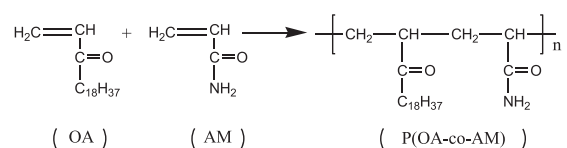
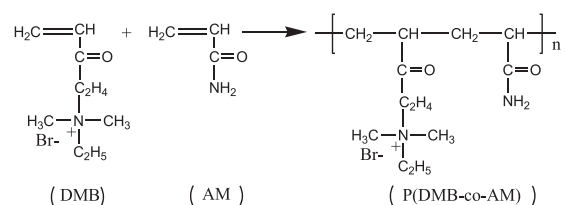
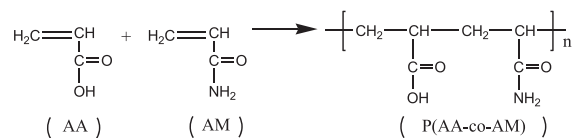
A cooling water reusing project was conducted recently by the coagulation and the filtration-RO process in a petrochemical plant in Jiangsu, China. In the cooling process where the cooling water repeatedly contacts with the external environment, the dust and impurity get into the water cooling system. The suspended solids, calcium and magnesium ions, and the salinity in the circulating water increase, resulting in high turbidity, high hardness, and high electrical conductivity. In addition, the feed water flowing to the reuse system brings the blowdown from the circulating cooling water tower. The wastewater therefore needs to be treated by the coagulation-flocculation-filtration-RO process to remove turbidity, alkalinity, and organic and inorganic contaminants. The permeated water then goes back to the cooling tower for reuse. The designed treatment capacity of feed water and product water is  $250 \text{ m}^3 \text{ h}^{-1}$  and  $190 \text{ m}^3 \text{ h}^{-1}$ , and the designed recovery ratio is more than 75%. The bypass filtration system in this plant uses the conventional sand-filter and the multimedia filter (MMF) system. The silt density index (SDI) of the effluent water after MMF, however, is more than 5, which does not meet the requirement of the RO system.

Organic polymers are widely used as flocculants in pretreatment for microfiltration. However, due to the lack of systematic tests, the operational experience in reclaiming water for the circulating cooling water system is not mature yet. The coagulant performance varied depending on their structure and charge, and it is not very clear how the charge type of the polymers impacts on microfiltration system performance in coagulation pre-treatment for wastewater reused in this cooling water reusing project. In the present study, combination with coagulation of polyaluminum chloride (PACl), the effects of four types of polymer flocculants for wastewater reclamation were systematically investigated and optimized. In the second part of this study, a pilot scale evaluation of pretreatment by coagulation-flocculation was conducted, to explore the reason of inefficiency of the filter, and choose a suitable solution to modify the MMF system, which will provide useful information on optimizing the parameters in the process of industrial wastewater pre-treatment for water recycling and reusing.

## 2. Materials and methods

### 2.1. Materials

Four kinds of acrylamide polymer coagulants with different charge type, namely, anionic polyacrylamide P(AA-co-AM), cationic polyacrylamide P(DMB-co-AM), nonionic polyacrylamide P(AM), and hydrophobic polyacrylamide P(OA-co-AM), were obtained from the Excellent Environmental Technological Co., Ltd, and were prepared by copolymerizing acrylic acid (denoted as AA), cationic monomer dimethylethyl (acryloxyethyl) ammonium bromide (denoted as DMB), hydrophobic monomer octadecyl acrylate (denoted as OA), and acrylamide (denoted as AM), respectively [14]. The molecular weight of the polymers was about  $8.5 \times 10^6$ . The formula and structure of the coagulants generated were shown as follows:



The inorganic coagulant polyaluminum chloride (PACl) was also obtained from the Sanfeng Group Co., Ltd. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and

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