



## Poly(dimethylamine-co-epichlorohydrin) as an alternative to alum for the demulsification of commercial dishwasher wastewater

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### ABSTRACT

The aim of this research was to evaluate the viability of cationic polymers for the treatment of commercial dishwasher wastewater. Commercial dishwashers use large quantities of fresh water during regular use, and produce significant amounts of high-strength oily wastewater in the process. When treating this wastewater, the particles in the dispersed phase often require destabilization to facilitate their separation via gravity. Alum and other metallic salts are generally used for this purpose, though relatively large doses are required. Cationic polymers, which can destabilize colloids at much smaller doses, were herein investigated as a potential alternative to alum. Experimentation was conducted within a single-stage dissolved air flotation column. Out of the eight cationic polymers tested, only one was capable of outperforming alum. This polymer, poly(dimethylamine-co-epichlorohydrin), sold by the product name Superfloc C-572, yielded the greatest removal efficiencies when compared to alum and the seven other cationic polymers tested. Under optimal conditions, a C-572 dose of  $0.10 \text{ mg L}^{-1}$  was able to remove up to 87% of the oil and 90% of the turbidity from the wastewater samples. The removal efficiencies were further increased when the polymer and alum were used together. A C-572 dose of  $0.10 \text{ mg L}^{-1}$  with an alum dose of  $200 \text{ mg L}^{-1}$  yielded removal efficiencies of 95.6%, 94.6%, 73.0%, and 94.4% for oil, turbidity, chemical oxygen demand, and 5-day biochemical oxygen demand, respectively. However, the combined use of alum and polymer produced inconsistent results when treating a range of wastewaters that varied in strength. The C-572 polymer was less sensitive to the effects of dilution and produced more consistent results when treating these wastewaters. The C-572 polymer was also able to operate at a much higher pH range which eliminated the need to adjust the pH of the wastewater prior to treatment. The pH adjustment step was required when using alum. On balance, it was determined that C-572 was a suitable alternative to alum for the demulsification of commercial dishwasher wastewater.

### 1. Introduction

Commercial dishwashers, like those used throughout the restaurant industry, produce significant volumes of high-strength oily wastewater, which are usually discharged directly to the public sewer network. Once in the sewer, some of the oil and grease within this wastewater congeals to form an insoluble deposit within the pipes. These deposits have been shown to consist principally of fatty acid metallic salts, initiating from the reaction of free fatty acids with calcium leached from concrete pipes [1,2]. The accumulation of these deposits constricts the flow of water and eventually clogs the affected sewer lines. The effects of these blockages range from minor sewer flooding to major city wide disruptions due to sanitary sewer overflows [3]. In 2000, 60% of sewer blockages in Hong Kong were attributed to the build-up of oil and grease within the city's sewer pipes [4]. In the United States, this number was estimated to be around 50–75% [5]. Some restaurants may

discharge their wastewater not into public sewer lines, but instead into storm drains, as this is reported to occur in Malaysia [6]. Due to the general lack of stormwater treatment, the resulting discharge directly contaminates receiving waters.

To avoid these problems, emulsified oils can be removed from the wastewater before they are discharged to the sewer. Several methods for this purpose have been recently reviewed, including coagulation/flocculation, dissolved air flotation, electro-coagulation/flotation, and membrane separation [7,8]. Dissolved air flotation (DAF) is a feasible, practical, and well-established method for oily wastewater treatment [9]. As such, it is a widely used treatment method for oil-in-water (o/w) emulsions [10]. A DAF system utilizes dissolved air under pressure, which, when released into the main flotation chamber, produces micro-bubbles in response to the rapid drop in pressure. These bubbles will generally rise 10–100 times faster than oil droplets of similar size [11]. This causes collisions to occur between the rising bubbles and the oil

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**Table 1**  
General polymer information provided by Kemira Oyj.

Product name	Components	CAS number	Classification	Weight
Superfloc C-572	Poly(dimethylamine-co-epichlorohydrin) Water	25988-97-0	Polyamine	Low
Superfloc C-573	Poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) Water	42751-79-1	Polyamine	Low
Superfloc C-577	Poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) Sodium chloride	42751-79-1	Polyamine	Medium
Superfloc C-581	Poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) Water	42751-79-1	Polyamine	High
Superfloc C-587	Poly(diallyldimethylammonium chloride) Water	26062-79-3	PolyDADMAC	Low
Superfloc C-591	Poly(diallyldimethylammonium chloride) Water	26062-79-3	PolyDADMAC	Medium
Superfloc C-592	Poly(diallyldimethylammonium chloride) Water	26062-79-3	PolyDADMAC	Medium
Superfloc C-595	Poly(diallyldimethylammonium chloride) Water	26062-79-3	PolyDADMAC	High

droplets. Three interactions may then occur to facilitate separation: (1) the air bubbles adhere to the oil droplets by electrical attraction, (2) the air bubbles become physically trapped within the structure of the flocculated oil droplets, or (3) the air bubbles chemically adsorb to the surface of the oil droplets [12]. In the latter case, contact alone does not guarantee the successful formation of an air-oil agglomerate; for this to happen, the oil droplet must spread over the air bubble [13], thus requiring the air-water interface surrounding the bubble to be replaced by an air-oil interface. The collision efficiency therefore greatly depends on the surface energies of the air-water, oil-water, and air-oil boundaries [14], highlighting the significant role of interfacial chemistry in the separation of oil via dissolved air flotation. Optimal removal occurs when the surface charges on the interacting droplet and bubble are approximately zero [15].

In the absence of a surfactant, o/w emulsions are thermodynamically unstable due to the high interfacial tension along the oil-water interface. The formation of large oil droplets therefore readily occurs as the two immiscible liquids separate over time. Cleaning agents used in commercial dishwashers are designed specifically to counteract this process, and produce highly stable o/w emulsions. Dishwashing liquids typically contain a mixture of anionic and nonionic surfactants [16], which modify the oil-water interface, reducing the interfacial tension and stabilizing the emulsion.

The droplet size of a stable o/w emulsion is too small to separate by gravity. Therefore it is necessary to enlarge the droplets to a sufficient size so that they may rise within the residence time of the flotation tank. To create large droplets from a stable emulsion, the oil droplets must first be destabilized by means of an emulsion breaker and subsequently flocculated. Metallic salts, such as aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), are often used in this process. The aluminum species, generated upon dissolution, destabilize the o/w emulsion by diminishing the net charge on the oil-water interface, by compressing the diffuse layer surrounding the oil droplets, or by entraining droplets within metallic precipitates.

In place of metallic salts, polymeric coagulants can also be used to generate larger oil droplets. Compared to aluminum sulfate, polymeric coagulants provide a wider operable pH range, lower sludge production, and lower chemical costs [17]. Coagulation of oil droplets using cationic polymers may simply result from the reduction of surface charges which allows van der Waals attraction to overcome the repulsive forces between the particles [18]. Unlike metallic salts, polymers may also facilitate flocculation by means of the electrostatic patch and the inter-particle bridging mechanisms. Both of these mechanisms generally produce stronger floc than those produced by charge neutralization using metallic salts [18]. Under the alkaline conditions commonly found in dishwasher wastewater, it is unclear which

mechanism predominates. Some evidence suggests that adsorption and adhesion through van der Waals forces are the primary drivers of flocculation under these conditions [19]. Nevertheless, when these flocs form and combine with rising air bubbles, they are less dense than the dispersion medium and move upwards, eventually coalescing with other material on the liquid surface to form a scum. Once the separation is completed, the treated water may be extracted.

Previous work has led to the development of a compact single-stage DAF system designed specifically for the treatment of commercial dishwasher wastewater [20]. The effectiveness of the system has thus far been demonstrated using alum as a coagulant [21]. However, the use of alum requires relatively large doses, produces large amounts of sludge, and operates within a relatively narrow pH range. Overcoming these disadvantages would greatly simplify the operation of the DAF system and improve its viability for decentralized treatment. Cationic polymers may be a suitable alternative to alum, but their use in the treatment of dishwasher wastewater has yet to be demonstrated. The objective of this research was to evaluate whether a cationic polymer could be used as an alternative to alum for the demulsification of commercial dishwasher wastewater.

## 2. Experimental methods

### 2.1. Selection of polymers for demulsification

Eight polymeric demulsifiers were provided by Kemira Oyj for examination. Information on each demulsifier is provided in Table 1. Four of the demulsifiers contain polyamines derived from dimethylamine, epichlorohydrin, and ethylenediamine. The remaining four demulsifiers contain polymers derived from diallyldimethylammonium chloride (DADMAC). A description of each polymer's weight, with respect to the other polymers in its classification, is reported in Table 1. Differences in molecular weight are generally due to differences in the length of the polymer chain. The stock solution of each demulsifier was prepared to a concentration of  $0.5 \text{ mg mL}^{-1}$ , as suggested by the supplier. The stock solution of alum was prepared to a concentration of  $100 \text{ mg mL}^{-1}$ . This concentration was selected based on prior research [21].

### 2.2. Experimental setup and DAF operation

The cationic polymers were examined within a bench-scale DAF system. The DAF system was designed and patented specifically for the treatment of dishwasher wastewater [20]. A schematic diagram of the treatment system is shown in Fig. 1. The system consisted of a 1.75 L acrylic flotation column, 3 L pressure tank, air pump, air diffuser, and

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