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REMOVAL OF DISSOLVED ORGANIC CARBON BY COAGULATION AND ADSORPTION FROM POLLUTED SOURCE WATER IN SOUTHERN TAIWAN

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The removal of dissolved organic carbon from a polluted water source in southern Taiwan by coagulation and powder activated carbon (PAC) adsorption was investigated in light of increasing concern for the production of potentially toxic chlorinated organic products. The results of this study clearly indicated that the effects of coagulation and PAC adsorption on the removal of non-purgeable dissolved organic carbon (NPDOC) from Tungkang River water were complementary. Coagulation by aluminum sulfate (alum) or polydiallyldimethylammonium chloride (PDDAC) alone removed only about 40% NPDOC; this type of NPDOC being preferentially large organic molecules with negatively charged functional groups. On the other hand, at a 20- to 30-min contact time, PAC removed about 60% NPDOC, mostly low molecular weight and uncharged NPDOC. A total 90% removal of NPDOC from this polluted source water was achieved by a combined coagulation and PAC adsorption process. ©1998 Elsevier Science Ltd

INTRODUCTION

The Tungkang River is one of the major drinking water supplies for the second largest metropolitan area in Taiwan, the Greater Kaohsiung area, with a population over two million. However, owing to upstream discharge of swine waste, industrial and domestic wastes, the Tungkang River is heavily polluted. For example, ammonia-nitrogen and non-purgeable dissolved organic carbon (NPDOC) concentrations as high as 10 mg L^{-1} and 8 mg L^{-1}, respectively, have been reported (Yeh and Kao 1993). Although the current treatment strategy (including prechlorination, coagulation, sedimentation, and filtration) employed by the local water treatment facilities is effective for the removal of ammonia-nitrogen, turbidity, color, and bacteria, the removal efficiency for dissolved organic compounds is questionable. Dissolved organic compounds are the precursors of mutagenic halogenated compounds in water formed after chlorination (Rook 1974). An understanding of the efficiency of dissolved organic compounds removal from polluted water sources by coagulation and powder activated carbon (PAC) adsorption processes is needed to improve existing processes and to develop new processes for the removal of dissolved organic compounds from polluted source water.

Semmens and Field (1980) indicated that the removal of natural organic substances from water by aluminum sulfate (alum) coagulation was accomplished via precipitation of soluble organic molecules by soluble aluminum species that were probably cationic aluminum polymers and by adsorption of the organic molecules on precipitated aluminum hydroxide flocs. Glaser and

Edzwald (1979) demonstrated that destabilization of humic acid by cationic polyelectrolytes is highly charge dependent and is based on the neutralization of anionic functional groups by cationic function groups, and that aggregation may occur as humic and polyelectrolyte molecules are randomly cross-linked by electrostatic forces. Reports of removal of dissolved natural organic matter (DNOM, operationally defined as NOM by having passed through a 0.45 μm membrane filter) by coagulation generally cite a removal range of between 10 and 90%, with an average of around 30% (Randtke 1988). The degree of removal achieved depends both on the characteristics of the organic matter present and on the operating conditions. In general, greater removal will be achieved when more highly colored water containing organic matter of higher molecular weight is being treated, and poorer removal will be observed when the organic matter is largely nonhumic in nature.

Historically, PAC has been used primarily for control of seasonal taste and odor problems, and it is generally effective for this purpose. Lee et al. (1981) showed that the adsorption rate of humic substances of a given size correlated with the total pore volume for pores of a given size. The affinity of the adsorbing molecule for water compared to its affinity for the adsorbent is also important (Weber and van Vliet 1981), as is molecular size. PAC has the advantage of being an inexpensive material, and minimal capital expenditure is required for PAC feeding and contacting equipment. Further, PAC can be applied only when required by deteriorating water quality.

The research reported here is a laboratory-scale feasibility study of dissolved organic compounds removal from polluted source water in southern Taiwan by coagulation and PAC adsorption.

EXPERIMENTAL

Water source

Water for coagulation and adsorption tests was taken from the Tungkang River close to the point of extraction for the Kunshe Water Treatment Plant. The water is high in organic content, with dissolved organic carbon concentrations that ranged between 2 and 10 mg L^{-1} during the course of this study. The turbidity ranged between 3 and 8 nephelometric turbidity units (NTU). Water with a higher proportion of humic materials has been reported to exhibit a higher ratio of ultraviolet radiation absorbance at 254 nm (UVA-254) to NPDOC (Edzwald et al. 1985). Figure 1 shows that the specific

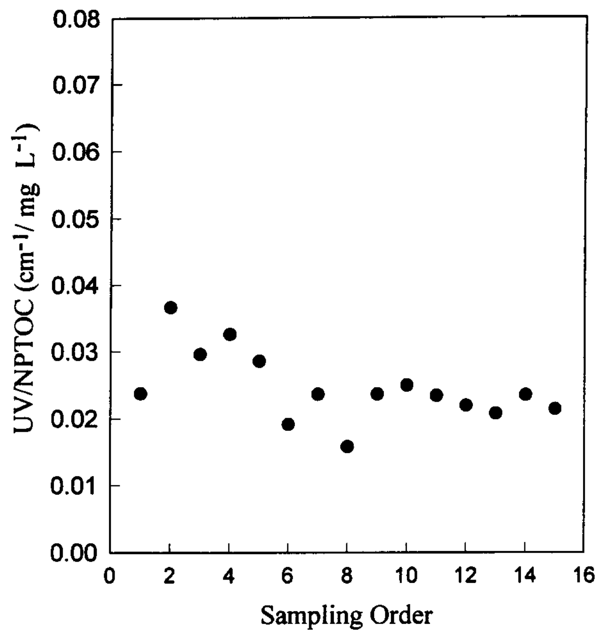

Fig. 1. Variation in specific UV absorbance for Tungkang River water.

UVA-254 of the river water used in this study ranged from 0.036 to 0.015 cm^{-1} per mg/L of NPDOC, which suggests that the DNOM in the Tungkang River is mostly nonhumic. Yeh and Huang (1993) differentiated the DNOM in Tungkang River water into four groups—humic, fulvic acid, hydrophilic, and hydrophilic neutral—according to the hydrophilic/hydrophobic and acid/base properties of the organic compounds. Their results indicate that hydrophilic neutral, which consists of low molecular weight organic compounds from anthropogenic sources, have the largest share of the river water's NPDOC (about 50%).

Reagents

The coagulants used in the coagulation experiments were polydiallyldimethylammonium chloride (PDDAC, high molecular weight, 20% by weight in water), a cationic polyelectrolyte from Aldrich Chemical, and alum from Ferak chemical. The PAC used in the adsorption experiments was -100 mesh Darco G60 from American Norit. The specific surface area and average pore radius of this PAC were determined to be 1053 (m^2 g^{-1}) and 14.2 (Å), respectively.

Test procedure

For coagulation testing, 500 mL samples of river water were used. Rapid mix was simulated by a magnetic stirrer. A measured volume of alum solution was injected into the vortex created by stirring. After 30 s,

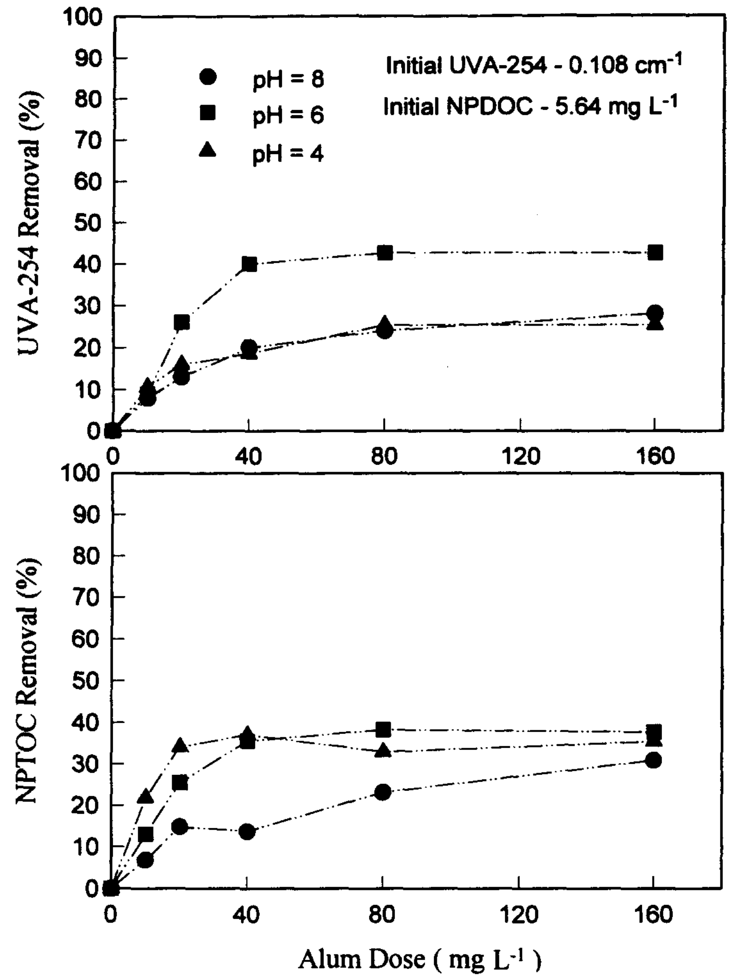

Fig. 2. UVA-254 and NPDOC removal as a function of alum dose at different pH.

the stirrer speed was reduced to slow and the pH was adjusted. The sample was then transferred to a multiple stirring apparatus (Phipps & Bird, Inc.) and flocculated at 60 rpm for 20 min. The sample was filtered through filter paper (0.45 μm) after sedimentation for 1 h. Control samples were subjected to the same procedure without coagulant addition for all pH values tested. Filtered samples were analyzed for UVA-254 and NPDOC. For PAC adsorption testing, 500 mL samples of river water were mixed with a magnetic stirrer and a measured amount of PAC was injected into the vortex. The sample was filtered through filter paper (0.45 μm) after a predetermined contact time and then analyzed for UVA-254 and NPDOC.

Analytical procedure

The UVA-254 measurements were made on a spectrophotometer (Model UV160A, Shimadzu) at a wavelength of 254 nm using a 1-cm quartz cell. The NPDOC measurements were made on a total organic carbon analyzer (Model TOC-5000, Shimadzu). Water samples (15 mL) were acidified to approximately pH 2 with a couple of drops of concentrated HCl and purged with nitrogen. Measured quantities of the purged samples were then injected for directed measurement of organic carbon concentration.

RESULTS AND DISCUSSION

Coagulation

Figure 2 shows the percentage of dissolved organic compounds that absorb UV at 254 nm and NPDOC removal vs. the dosage of alum at different pH conditions. The pattern of removal is characterized by a gradual increase in removal with increasing concentration of coagulant, approaching a maximum of about 40% NPDOC removal, with removal remaining in-

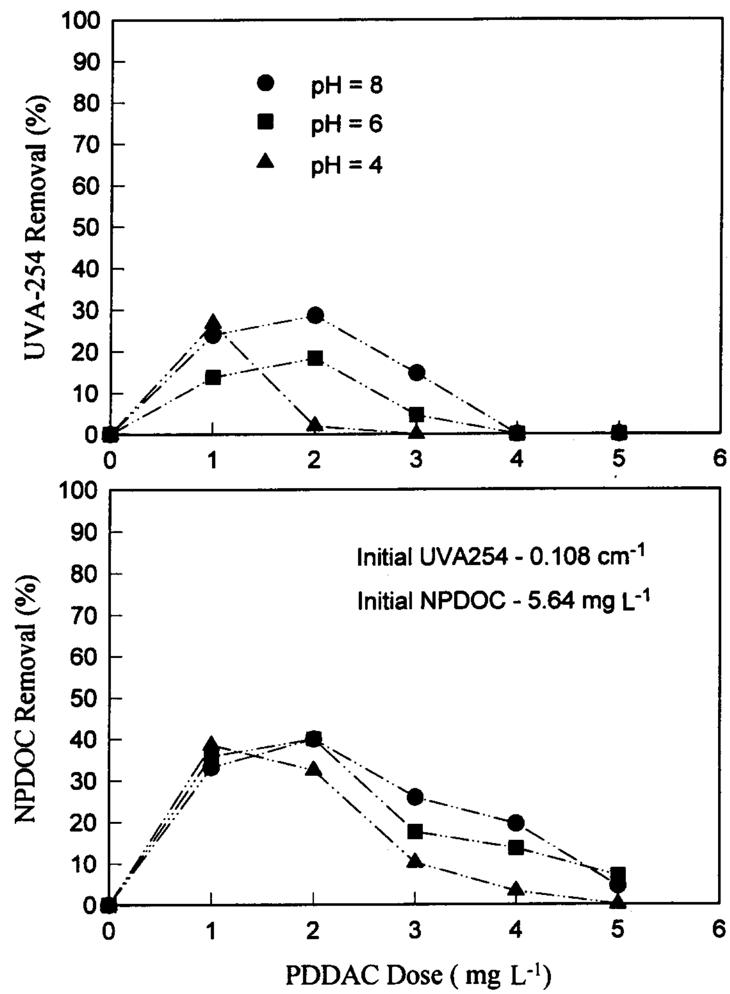

Fig. 3. UVA-254 and NPDOC removal as a function of PDDAC dose at different pH.

complete at high coagulant dosage. The authors hypothesize that alum coagulation removed only those organic molecules such as humic and fulvic acid, molecules with negatively charged functional groups, by precipitation with soluble aluminum specie and adsorption onto aluminum hydroxide precipitate. The remaining 60% NPDOC can be characterized as low molecular weight, neutral, nonhumic compounds. The abundance of these types of compounds, rather than the alum dose, determined the upper limit for NPDOC removal by alum coagulation. In this study, alum was found more effective for NPDOC removal at pH 4 to 6 than pH 8. This is presumably due to the positive charge density of aluminum species decreasing with increasing pH. It is also interesting to note from Fig. 2 that the maximum dissolved organic compounds that absorb UV at 254 nm removal by alum is about 60%. Because it can be assumed on the basis of prior reports that the removal of humic material by alum approaches 100%, it is reasonable to conclude the evidence from these tests indicates that a portion of the neutral nonhumic compounds in the Tungkang River are aromatic or have conjugated double bonds.

Figure 3 shows the percentage of dissolved organic compounds that absorb UV at 254 nm and NPDOC removal vs. the dosage of PDDAC at different pH conditions. The optimum dose of coagulant for NPDOC removal is 1-2 mg L^{-1}. Over- and under-dosing are observed in this case, and the NPDOC removal is about 40% at the optimum dose. In addition, the range of polyelectrolyte dose for effective NPDOC removal decreases with decreasing pH, presumably due to the negative charge of the dissolved organic compounds as a result of dissociation of the carboxyl group decreasing with decreasing pH. These observations clearly indicate that charge neutralization and bridging leading to flocculation are significant for the removal by polyelectrolytes of NPDOC in Tungkang River water. It is

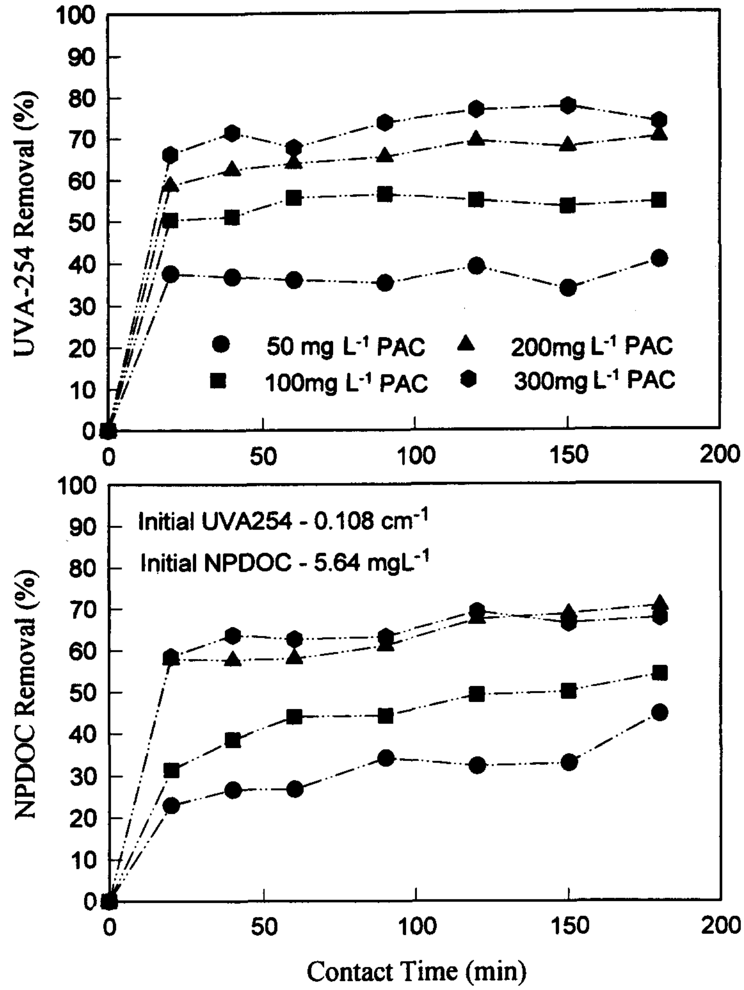

Fig. 4. Kinetics of the removal of UVA-254 and NPDOC by PAC under various doses.

apparent from the coagulation study that alum and polyelectrolyte coagulations remove only dissolved organic molecules such as humic and fulvic acid, those with negatively charged functional groups, which account for about 40% NPDOC in Tungkang River water.

Adsorption

Figure 4 shows the kinetics of adsorption of NPDOC from Tungkang River water on Darco PAC at several different PAC doses. It was found that a contact time of 20 to 30 min was required for the NPDOC to reach adsorption equilibrium under conditions used in this study. In addition, the NPDOC removal efficiency increased with increasing PAC dose until a saturated PAC dosage of 200 mg L^{-1} was reached. Maximum removal efficiencies of 60% for NPDOC and 70% for dissolved organic compounds that absorb UV at 254 nm were obtained in this study.

Coagulation and PAC adsorption removed 40% and 60% NPDOC, respectively, from Tungkang River water at their optimum operating conditions. Thus, it is important to determine whether coagulation preferentially removes the type of NPDOC that PAC does not remove. Figure 5 shows the removal efficiency of NPDOC and dissolved organic compounds that absorb UV at 254 nm, as a function of PAC dosage for samples of raw Tungkang River water without any coagulant pretreatment (alum or PDDAC), and two types of pretreated samples: 1) raw water treated with 160 mg L^{-1} alum, and 2) raw water treated with 1 mg L^{-1} PDDAC. Almost 90% removal of NPDOC and dissolved organic compounds that absorb UV at 254 nm can be obtained for pretreated Tungkang River water at a PAC dosage of 200 mg L^{-1}. This result clearly indicates that the effects of coagulation and PAC adsorption on the removal of NPDOC are complementary. The types of NPDOC most likely to be removed by coagulation are

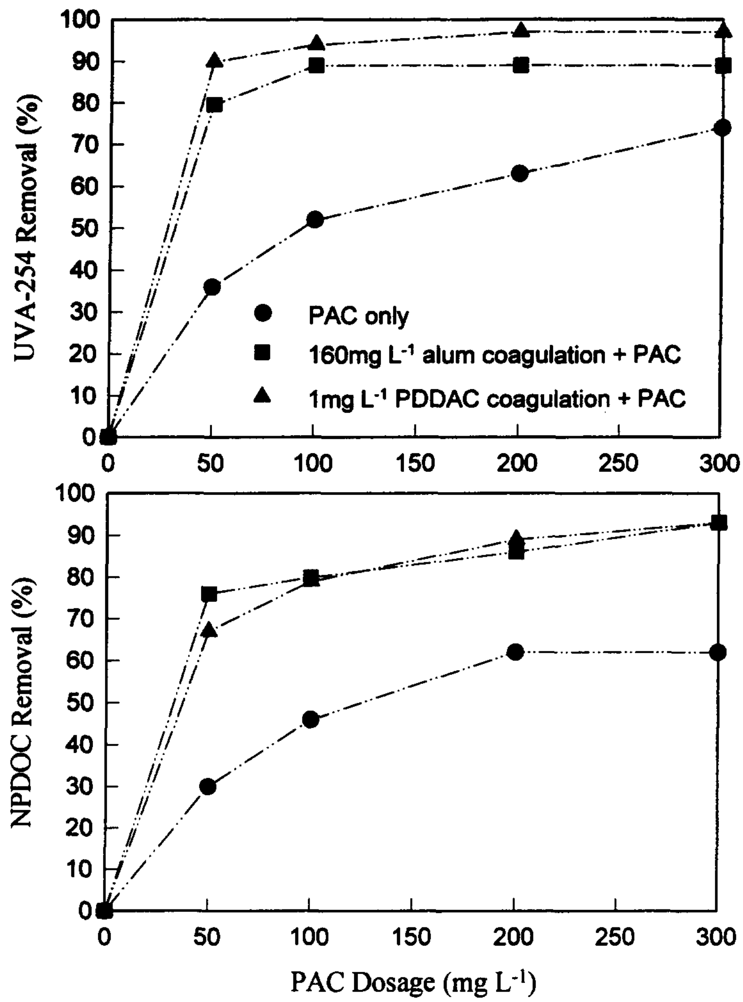

Fig. 5. NPDOC and UVA-254 removal as a function of PAC dose for untreated and pretreated water.

those possessing high molecular weight and negatively charged functional groups able to engage in charge neutralization and adsorption onto floc particles. On the other hand, PAC is more effective for the adsorption of low molecular weight and uncharged NPDOC.

CONCLUSIONS

Laboratory tests of coagulation on Tungkang River water showed that alum or PDDAC could remove about 40% NPDOC, most of which was large organic molecules with negatively charged functional groups. The abundance of this type of NPDOC, rather than the coagulant dose, determined the upper limit for NPDOC removal by coagulation.

In similar tests, PAC was shown capable of removing about 60% NPDOC, most of which was low molecular weight and uncharged, at a 20- to 30-min contact time.

PAC used in conjunction with coagulation proved effective for the removal of NPDOC from Tungkang River water owing to the complementary effect of the two techniques. In addition, PAC has the advantage of being an inexpensive material, with minimal capital expenditure required for PAC feeding and contacting equipment. Further, PAC is easily applied on an as-needed basis, making it particularly useful in situations of deteriorating water quality.

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