EVALUATION OF SELECTED COMMERCIAL FLOCCULANTS FOR REMOVAL OF ORGANIC AND INORGANIC WOOD PRESERVATIVES FROM PROCESS WATER.

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INTRODUCTION

A large amount and variety of flocculants and coagulants are consumed by industries such as pulp and paper, and mining for wastewater treatments every year. Coagulants/flocculants also remove suspended substances from water at drinking water and municipal wastewater treatment facilities. Coagulants can destabilize fine, stable colloidal suspensions and induce precipitation. Flocculants induce individual particles to combine into larger sizes and speed up the settling out process. Inorganic materials like alum (aluminum sulfate), aluminum chloride, ferric sulfate and ferric chloride, and organic polymers such as polyamines and polyacrylamides have been widely utilized for such purposes (Ouellette 1996). While alum is still the most common coagulant/flocculant, the application of organic polymeric materials such as polyacrylamides is increasing. The main reason for this, in addition to treatment efficiency, is the large amount of sludges produced from the alum treatment process and the cost associated with it for further processing, such as dehydration and disposal of the sludges.

Many studies have been done on the application, cost, and effectiveness of polymeric coagulants/flocculants in the past decade. Cathalifaud et al. (1993) reported that the suspension of kaolinite and ferric chloride could improve the coagulation-flocculation process, and de Velasquez et al. (1998) demonstrated 87% turbidity removal and 87% total suspended solid elimination by treating wastewater effluent from biological and chemical treatment systems with anionic and zwitterionic polymers in combination with metallic hydroxide. Boneva et. al. (1994) and Bolto (1995) enhanced the treatment of wastewater with water-soluble polymers. New cationic flocculants of high charge densities and high molecular weights were introduced for the removal of oil & grease (Sang et al. 1995). To reduce the cost of treatment process, the application of synthetic organic polymers such as poly(diallyldimethylammonium chloride) was evaluated. Addition of this polymer reduced the usage of poly(aluminum chloride) in the treatment by 50% (Lee et al. 1998). Working on alternative procedures for the treatment of secondary effluents from the pulp and paper industry with solid residues of the process (*e.g.* dreg, grit, heavy ash) and activated carbon, an appreciable reduction of color, halogenated compounds, as well as significant savings on the amount of flocculants used was observed (Frizzo et al. 1996).

The wood-preserving industry has a variety of chemicals such as creosote, pentachlorophenol (PCP) and chromated copper arsenate (CCA) in their treatment process. A large volume of contaminated wastewater containing these chemicals are generated that should be cleaned up. Creosote is a complex mixture of chemical constituents, including various polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, and heterocyclic compounds. PCP is another common organic wood-preservative that is used in a 5-8% concentration in the pressure treatment of wood with number two diesel oil. Technical grade PCP also contains of the lower chlorinated phenols along with minute amounts of chlorobenzodioxins, chlorobenzofurans and chlorobenzenes. CCA is the most utilized waterborne wood-preservative for pressure-treatment of wood, that resist attack by termites and the fungi that cause decay. These chemical substances are introduced to the process wastewater from several different sources, such as pressure treatment, steaming of wood, vapor drying or oil seasoning. Treatment of such wastewater will be difficult because the wastewater contains various chemical compounds with different chemical and physical properties, which require certain conditions and chemicals for treatment. No major prior studies have been done on the removal efficiency of commercial flocculants/coagulants for the treatments of process water from wood treating facilities.

This study evaluated different commercial polymeric flocculants that are currently being used by industry for the treatment of wood-preserving process wastewater containing a high concentration of oil & grease, polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol (PCP), petroleum hydrocarbons, suspended solids, and traces of other inorganic chemicals.

MATERIALS AND METHODS

The wastewater for this research was obtained from two different wood treatment sites in Mississippi. One contained PCP and CCA, and the other creosote; both had high levels of oil and grease and suspended solids. The wastewater was mixed vigorously with an industrial stainless steel blender to form a 1/1 (v/v) mixture. The flocculants in this study were kindly provided from five different wood treatment plants, and the amount for the treatments were adjusted to the same concentration of flocculants that are currently at each plant, as shown in Table I. One liter amber bottles were used for the jar test of the wastewater treatments, and three replicates were made for each treatment. After the bottles were allowed to settle overnight, three 250 ml portions of the treated water was taken from each jar for continuous liquid-liquid extraction, total suspended solid analysis, and metal analysis. Continuous liquid-to-liquid extraction with dichloromethane (EPA Method 3520; U.S. EPA 1992) was accomplished with 250 ml of the treated water, concentrated to 5 ml by Kuderna-Danish apparatus, and analyzed by gas chromatography (GC) for selected PAHs (2-ring PAHs; naphthalene, 1 and 2-methylnaphthalene, biphenyl, 3-ring PAHs; anthracene, phenanthrene, acenaphthene, acenaphtylene, fluorene, carbazole, dibenzofuran, 4, 5 and 6-ring PAHs; fluoranthane, 1,2-benzanthracene, chrysene, pyrene, benzo(a)pyrene, benzo(ghi)perylene), PCP (EPA methods 8040 and 8100; U.S. EPA 1992) and total petroleum hydrocarbons (MS method). The analysis of total suspended solids (TSS) and oil & grease were performed according to methods 2540D and 5520B, respectively, of "Standard methods for the examination of water and wastewater" (Clesceri et al. 1989). The content of arsenic, chromium and copper were analyzed by inductively coupled plasma (ICP) atomic absorption according to methods 200.9, 218.1 and 220.1, respectively, of "Methods for Chemical Analysis of Water and Wastes" (U.S. EPA 1983).

Statistical analysis of the data obtained was done with the completely random design (CRD) method, with the S.A.S. software (Release 6.12, Statistical Analysis System Institute).

RESULTS AND DISCUSSION

Data for the concentration of PAHs obtained by GC analysis are shown in Figure 1. These data show that total selected PAHs decreased from an initial concentration of approximately 760 mg/L to under 100 mg/L for each treatment. This represents a reduction of over 85% for the PAHs, in which treatments I, III and IV gave the best results.

Figure 2 depicts the decrease of PCP concentration as a result of the treatments. The average initial concentration of 45 mg/L was reduced to 1 - 5 mg/L after treatment. Treatments IV, I and III were the most effective on the removal of PCP, and concentrations were reduced to 2.5, 1.3 and 0.8 mg/L, respectively, representing 95, 97 and 98% reduction, respectively.

Total petroleum hydrocarbons (unbranched C10~C25) data are summarized in Figure 3. Approximately 96% of total petroleum hydrocarbons were removed from the treatments, except for treatment V where only 85% of the total petroleum hydrocarbons were removed.

The data obtained from oil and grease analysis are shown in Figure 4. The oil and grease analysis reflects not only the PAHs, PCP, and TPH, but also many other organic compounds that are not individually identified. The initial concentration of 1900 mg/L was reduced to approximately 300 mg/L, an 85% reduction of oil and grease. No significant differences between the five treatments was observed.

Figure 5 summarizes the analysis of total suspended solids (TSS). Treatments I and III reduced the initial concentration of 590 mg/L of TSS to less than 10 mg/L, that is more than 98% reduction of TSS, while treatments II and V removed only 75% and 70%, respectively. Unlike oil and grease that did not show significant differences between the treatments, these results for TSS show significant differences between the treatments. These removal efficiencies of TSS resemble the results for selected PAHs, PCP and TPH. This suggests that the compounds analyzed here, form a suspended solid or are being adsorbed on suspended solid particles that can be filtered. Therefore, in the treatment of wastewater generated from wood treatment plants, the

reduction of total suspended solids involves essentially the removal of PAHs, PCP and TPH.
ICP atomic absorption analysis of inorganic elements revealed that the treatments reduced arsenic, chromium and copper from the initial concentration of 13, 50, and 150 ppb to less than 5, 10, and 30 ppb respectively. Although the treatments reduced the concentration of metals, no significant difference was observed between the five treatments in treating. The concentration of the metals after treatment were very close to the detection limit of the analyses. The initial concentration level of copper, chromium and arsenic in the wastewater used in this study turned out to be very low, further studies need to be conducted to measure and evaluate the efficiency of these flocculants for wastewater treatment containing high levels of CCA.

In all treatments, a significant decrease in concentration of chemicals in the treated water was observed, and compared to other treatments; treatments I and III seemed to be more effective in the removal of various chemicals included in process wastewater from wood treatment plants. The polymer or resin described as, "Melamine, Polymer with Formaldehyde" in treatment I and, "Formaldehyde Resin" in treatment III seems to be the key component in the treatments. Since the polyacrylamide in treatments I and V were the same polymer provided by the same manufacturer, and treatment V seemed to be the least effective of the five treatments. Although not clear how these polymer resins function in the treatments, they definitely enhanced the elimination of total suspended solids from the treated water, which is the essential factor to be monitored, resulting in the most effective removal of chemicals such as PAHs, PCP and TPH found in process wastewater generated from wood preserving treatment sites.

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Table I. Polymeric Flocculants and Coagulants.

Treatment	Description of polymer*	Amount used
I	Acrylamide, Polymer with Acrylic Acid Melamine, Polymer with Formaldehyde	100 ppm 250 ppm
II	Tannin Based, Cationic Coagulant	100 ppm 75 ppm
III	Anionic Polyacrylamide Cationic Polyacrylamide Formaldehyde Resin	5 ppm 5 ppm 250 ppm
IV	Aminomethylated Tannin Polymer	70 ppm
V	Acrylamide, Polymer with Acrylic Acid	100 ppm

* Information from the material safety data sheet (MSDS), provided by the manufacturer of the polymers.

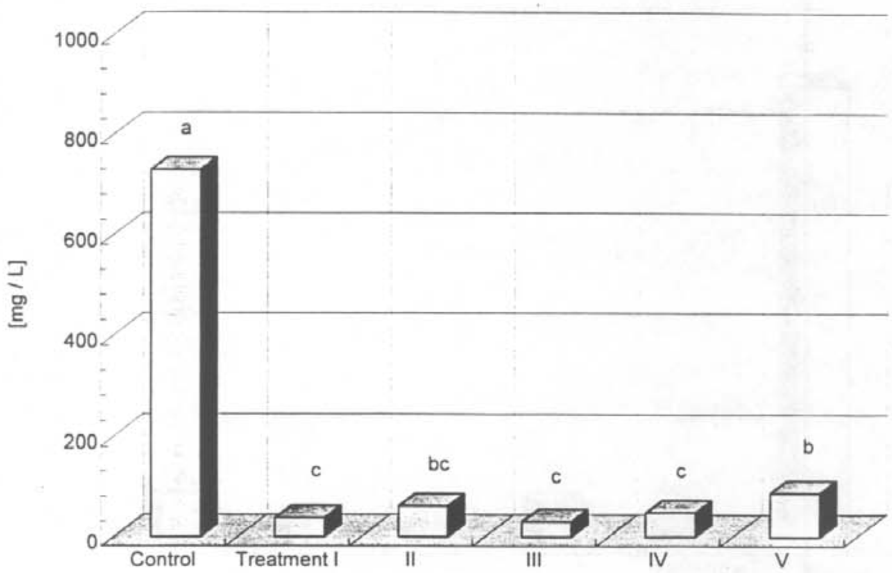

Figure 1. Gas chromatographic analysis of total selected polycyclic aromatic hydrocarbons (PAHs) in process water after treatment with flocculants. Each bar represents an average of three replicates.

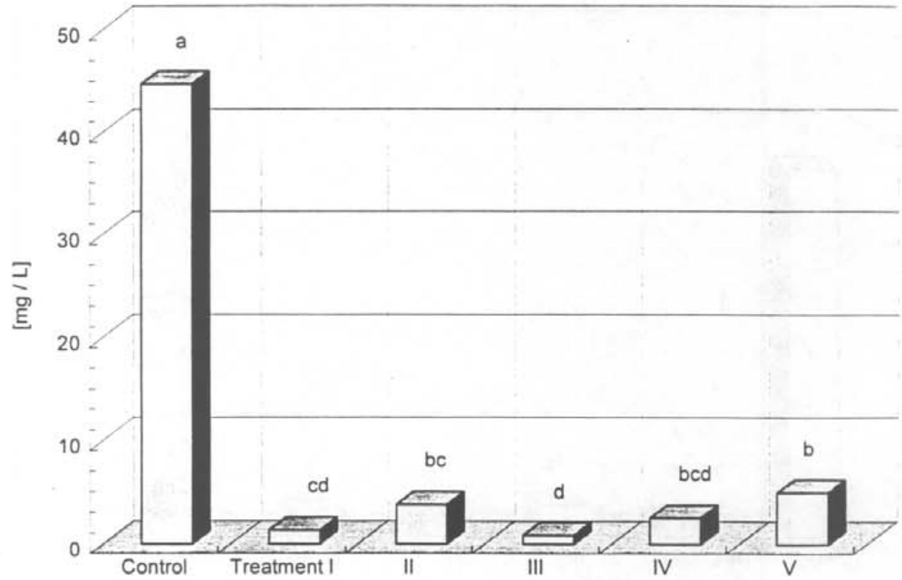

Figure 2. Gas chromatographic analysis of pentachlorophenol (PCP) in process water after treatment with flocculants. Each bar represents an average of three replicates.

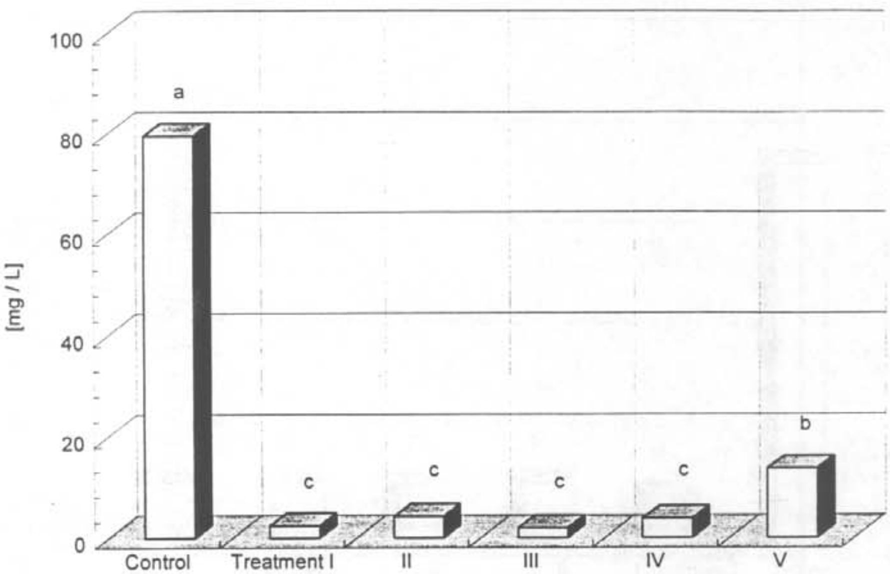

Figure 3. Gas chromatographic analysis of total petroleum hydrocarbons (unbranched C10~C25) in process water after treatment with flocculants. Each bar represents an average of three replicates.

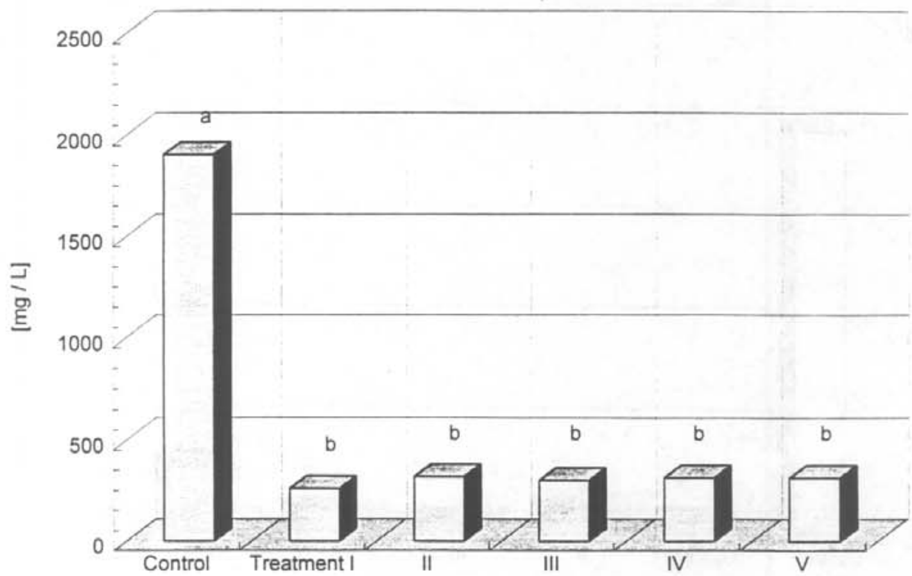

Figure 4. Oil and grease analysis of process water after treatment with flocculants. Each bar represents an average of three replicates.

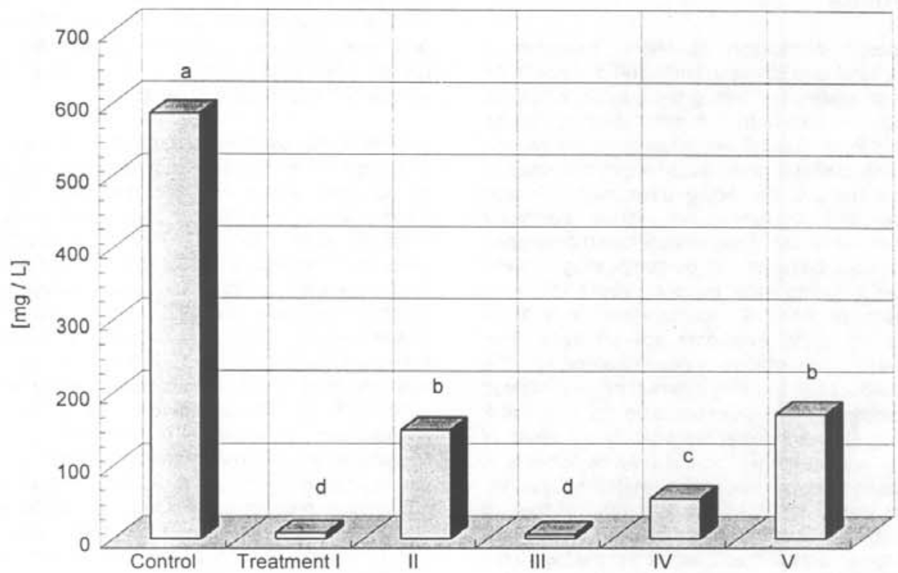

Figure 5. Total suspended solids (TSS) analysis of process water after treatment with flocculants. Each bar represents an average of three replicates.