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Potential of oil palm trunk starch as flocculant for contaminant of emerging compound removal

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Abstract. In this preliminary study, a natural flocculant is developed from an oil palm trunk. The flocculant further tested for its ability in turbidity and COD removal with additional of atrazine in wastewater and demineralised water matrix. At the optimum dosage of 20mg/L, the developed cationic OPT starch able to remove around 95% turbidity and 85% COD. In addition, the cationic OPT starch also show the ability to remove spiked atrazine from both water matrixes to the maximum range of 55-85%. In conclusion, the developed oil-palm based flocculant show great potential for real-world application with added cost-effective benefits.

1. Introduction

Today, industry are increasingly interested in developing natural low-cost alternatives to treat water and wastewater [1-8]. The use of natural polymers and synthetic polyelectrolytes is one of the options [2-8]. Recently, many biological products have been proposed and studied as effective coagulants and flocculants to replace the conventional options [9-10]. Some reported products called "bioflocculants" include biopolymers (starch, chitosan, alginate) and microbial materials produced by microorganisms such as bacteria, fungi, and yeast [9-10]. Compared with conventional chemical flocculants, biological flocculants are a safe, biodegradable polymer and will not cause secondary pollution [5].

One of the major biopolymers used as flocculant is starch. Starch exists in numerous plants and product and one of it is the Oil palm (*Elaeis guineensis Jacq.*). Major starch content in the oil palm is the trunk. The starch found in the oil palm trunk (OPT) consist of around 20% its weight (w/w) [11]. With the vast availability of this OPT in Malaysia and Indonesia, OPT starch is one of the untapped resources available for basically free due to its less known potential [11].



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In this study, cationic OPT starch is tested for its potential to act as bioflocculants in the treatment of wastewater. In addition, its ability to removed dissolved contaminant such contaminant of emerging compound eg; atrazine is demonstrated.

2. Material and Methods

2.1. Materials

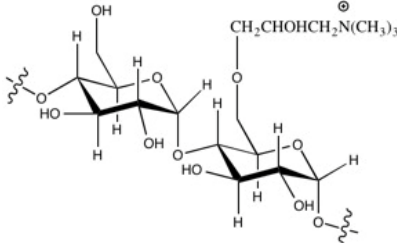
OPT starch was provided by Verdestro Sdn Bhd, Kuantan, Pahang, Malaysia. The cationic etherifying agent (CHPTAC 60% (w/v)), methanol (99.7% analytical grade), isopropanol (99.7% analytical grade), ethanol (95% analytical grade), Atrazine (analytical grade) were purchased from Sigma-Aldrich (M) Sdn. Bhd. Malaysia. The polymer and atrazine properties are shown in Table 1 and 2.

2.2. Preparation of OPT Starch polymer

The cationic OPT starch was prepared based on Heinze et al. [12]. OPT solid which was first dried (20 g, 0.123 mol) suspended in 160 mL isopropanol. Sodium hydroxide (30–70% w/v) was dissolved in 40 mL water before added to the starch suspension. Then, CHPTAC solution (0.615 mol), with molar ratio CHPTAC/SS = 5 was added to the suspension (dropwise)[13]. The mixture then kept at 60°C for 3–5h and let to cooled to ambient temperature. The cooled substance was then washed with 1M hydrochloric acid before being filtered off. The filter product then was and finally rinsed with ethanol.

Table 1. Cationic OPT starch properties (with common structure)

Product	Description	Form	Solubility (in water)	Ionic character	Molecular weight (M)
cationic OPT starch	Modified starch	Flaked solid	Soluble	Cationic	10^6 - 10^8



The chemical structure shows a segment of a starch polymer chain. It consists of two glucose units linked by an alpha-1,4-glycosidic bond. The second glucose unit has a cationic substituent at the C2 position, represented as $CH_2CHOHCH_2N^+(CH_3)_3$. The rest of the glucose rings are shown with their respective hydroxyl and hydrogen groups, and wavy lines indicate the continuation of the polymer chain.

Table 2. Atrazine properties

Charge	Compound	Formula	pKa	MW (g/mol)	Log Kd (pH 7.4)	Log K_{ow} (mean)	Average initial concentration (ng/L)	Recovery %
Neutral	Atrazine	$C_8H_{14}ClN_5$	2.27 (base)	215.7	2.63	2.20	400	91

2.3. Wastewater effluent sample

The wastewater was collected from the sewage treatment plant in Bertam, Penang. The sewage treatment plant treats water from approximately 30,000 residents in the Bertam Perdana. The average daily flow is about 20,000 cubic meters. The characteristics of wastewater are: total suspended solid (TSS), 100-400 mg/L; chemical oxygen demand (COD), 350-500 mg/L; biological oxygen demand, 156.8 mg/L; total nitrogen, 44.5–56 mg/L; total phosphorus, 8.28–9.0 mg/L. The COD (COD test set:

10-150, 50 - 500 mg/l) were analysed using a Merck Reflectoquant® plus analysis kit according to the manufacture's procedures and measured using a Merck Spectroquant NOVA 60.

2.4. Atrazine removal by OPT starch

Atrazine is spike to the wastewater to simulate and evaluate the ability of the OPT starch in removing soluble contaminant that normally found in the wastewater at ng/L concentration. Pyrolyzed Duran brown glass bottle (2000ml) was used throughout this experiment. Demineralised or wastewater effluent is added to the bottle to 1800ml before atrazine is spike into the bottle at concentration of 500 ± 200 ng/L. The working pH is at 7 ± 0.3 . The OPT starch at concentration of 10 to 60 mg/L, mix slowly at 40 rpm for 2 hours, and then let it stand for 1 hour. The collected sample is then filtered using syringe filter (0.45 μ m).

2.5. Analysis of atrazine with gas chromatography

The analysis process is following the procedure established by Mohd Amin et al [5]. Gas chromatography (Agilent's 7890A) is used to analyse the atrazine concentrations and were based on the method by U.S Environmental Protection Agency (USPA) 551.1 (1995). Atrazine in the water was extracted using liquid-liquid micro-extraction method using MTBE as a solvent. 1 mL of the extracted sample was used as injection sample. 2 μ L was injected in splitless mode, and the injector temperature was set at 200°C. Helium was used as the carrier gas (linear velocity was 33 cm/s) at injector temperature of 260°C. The oven temperature was held at 35°C for 9 min, and then raised by 15 °C/min to 225°C. The 225°C was held for 10 min before being raised by 20°C/min to 260°C. The final recovery of atrazine was in the range of 90-110%.

3. Results and Discussion

3.1 Turbidity and COD removal

The initial measured wastewater turbidity value is around 80 ± 0.5 NTU. In this study, the concentration of the polymer dosage is set in range of 0-60 mg/L, as shown in Figure 1. Approximately 20% of the particles settled without adding any flocculant which due to its settling weight. The turbidity is reduced to approximately 4 ± 0.5 NTU at optimum cationic OPT starch dosage of 20 mg/L, which means that the maximum removal rate is approximately 95%. The results obtained are comparable to the study of Van Nieuwenhuijzen [14], which reports that the turbidity removal rate of low-molecular-weight polymers in wastewater is about 65-90%, and the dosage is about 20-30 mg/L. In addition, the optimum removal of turbidity will translate towards higher particle (suspended and non-suspended) removal in the water matrix. This will positively impact the COD removal which universally known to have positive correlation with turbidity removal [2-5]. In this study, the COD removal rate of cationic OPT starch dosage is 50-85% at the optimum application dose of 20 mg/L.

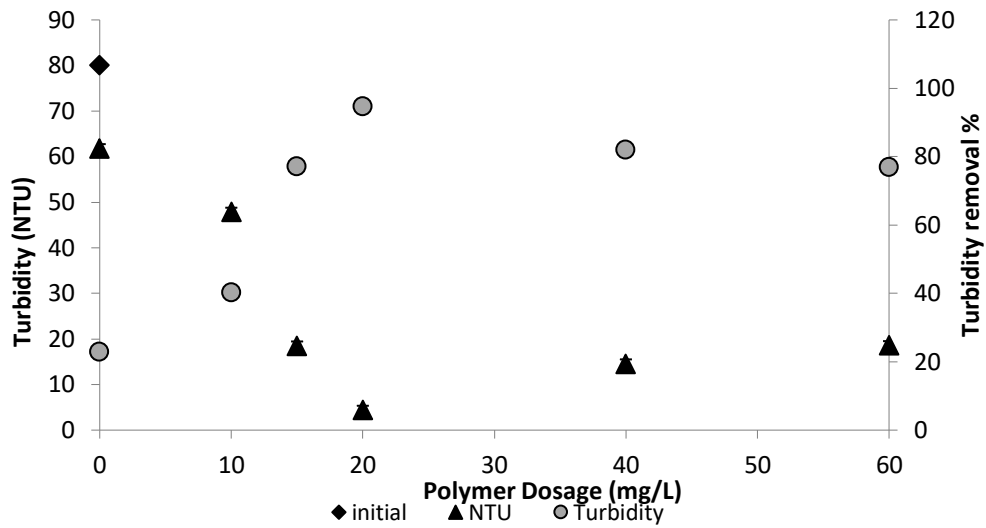


Figure 1. Turbidity removal by cationic OPT starch from raw wastewater.

3.2 Atrazine removal

In this study, OPT starch have demonstrated the ability to removes atrazine from demineralised water and wastewater. The combination of 20 mg/L OPT starch with an atrazine initial concentration of 500 ± 200 ng/L in wastewater (Figure 2). The atrazine removability in the wastewater are around 25-60%. A dose of 20 mg/L OPT starch was considered sufficient to remove atrazine, which was observed in previous studies (in demineralized water) [3]. Compared with wastewater, the atrazine removability in demineralized water are significantly higher at a range of 60-88%. Competition among other organic pollutants for attachment sites on the particle surface will result in a decrease in removal efficiency. In addition, in demineralized water, since the OPT starch covering the entire particle surface adheres during the adsorption of the polymer to the particles, a high removal rate can be predicted, resulting in a diffusion layer that enhances the removal of atrazine [2,3,4].

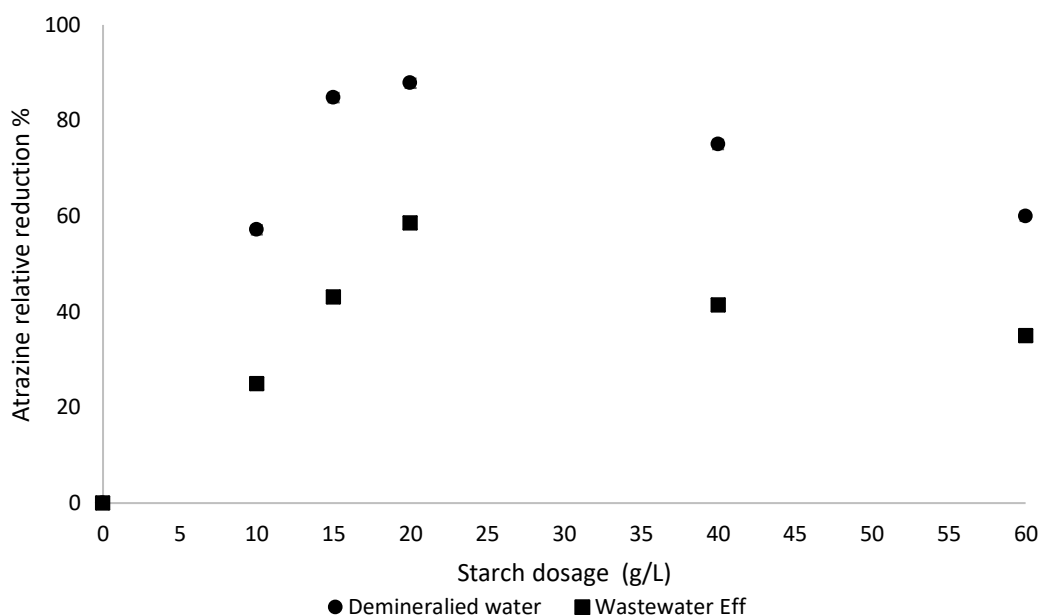


Figure 2. OPT starch atrazine removal ability in wastewater in comparison to demineralised water (500 ± 200 ng/L).

4. Conclusion

This preliminary study shows that the cationic OPT starch have the potential to be use as flocculant for wastewater. In addition, the developed cationic OPT starch also have shown the potential to remove contaminant of emerging concern in this case atrazine from water matrixes. The extent of this removability to other type of contaminant of emerging concern still unknown and require an additional testing.

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