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Synthesis of Magnetic Cellulose as Flocculant for Pre-Treatment of Anaerobically Treated Palm Oil Mill Effluent

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Recently, more attentions have been paid to natural polymer-based flocculants in wastewater treatment, since they are believed to be low-cost, nontoxic, and environmentally friendly materials. In present work, a hybrid flocculant namely magnetic cellulose (Magcell) was successfully synthesised through simple crosslinking method. As preliminary study, effect of ratio between magnetite powder and cellulose and also volume of glutaraldehyde as crosslinking agent were selected in this research. Meanwhile, the effectiveness of flocculant was determined by performing a jar test to treat an anaerobically treated palm oil mill effluent (AnPOME). The best ratio cellulose to magnetite powder and volume of closslinker was chose based on optimum removal of turbidity, total suspended solid (TSS), colour and chemical oxygen demand (COD) from sample wastewater. Result shows that the best combination cellulose to magnetite powder are 1 : 1 (g/g) with glutaraldehyde volume of 1.5 mL. This optimum parameters show about 74.60 %, 63.90 %, 77.20 %, and 55.80 % reduction in turbidity, colour, TSS, and COD. Overall, approach to produce magnetic cellulose as newly hybrid flocculant has potential to substitute existence flocculants due to the better performance.

1. Introduction

Water pollution remains to be an important issue in palm oil in that requires constant monitoring and control to reduce the environmental impacts. Liquid waste in this industry, commonly as palm oil mill effluent (POME) contributes to a total of 58.4 % of waste generated per ton of fresh fruit bunch processed (Mohtar et al., 2017). Some conventional treatment methods are used to handle such wastewater, including biological oxidation (ponding system) and physical-chemical treatment (e.g activated carbon, adsorption, coagulation/flocculation, membrane technology etc.) (Ali Amat et al., 2015). Among these methods, coagulation/flocculation the most widely used solid-liquid separation process in removal of suspended and dissolved solids, colloids as well as organic matter present in industrial wastewater (Wolf et al., 2015).

Inorganic salts containing multivalent metals such as alum, polyaluminium chloride, ferric chloride etc. have been widely used as coagulant due to lower price as compared to other chemicals (Bhatia et al., 2007). However major environmental impacts associated with the usage of these chemicals are reported, including production of metal hydroxide (toxic) sludge in large quantity which creates disposal problem and an increase in metal (e.g aluminium) concentration in treated water which affects human well-being (Lee et al., 2014). It is necessary to develop environmentally-friendly coagulant and bio-flocculants appears to be a promising material in treatment of wastewater continues to increase; and bio-flocculants have emerged to be promising alternative material (Oladoja, 2015).

Cellulose is a naturally occurring polymer that is cheap and easily available (Olivera et al., 2016). High performance of cellulose as a coagulant in drinking water and municipal wastewater treatment is widely reported (Shanmugarajah et al., 2015). However, natural polymers like cellulose suffers short shelf life due to biodegradation over time, which leads to lower flocs stability and strength during coagulation-flocculation process (Lee et al., 2012).

Following rapid development of nanotechnology, application of magnetic nanoparticles in water treatment is being studied by numerous research teams. It is believed that magnetic nanoparticles (Fe_3O_4) show the finite-size impact and high proportion of surface-to-volume, resulting a higher adsorption capacity (Mohammed et al., 2017). Speedy settling and following separation of stacked magnetic nanoparticles from solution and

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speedy settling speed can be easily achieved using an external magnetic field (Chiavola et al., 2017). Application of magnetic nanoparticles alone as flocculant is less viable as the flocs formed are fragile and possess low density compared to wastewater, thus longer settling time is required (Lu et al., 2016).

Crosslinking is a plausible solution to the mentioned disadvantage. It is a surface modification technique commonly used to overcome problems hold by both natural polymer and inorganic material in wastewater treatment application (Ambashta and Sillanpaa, 2010). Among the available chemicals used for polymer crosslinking, glutaraldehyde has been extensively studied as a polymer crosslinking agent for food, textile and industrial applications (Bhattacharya, 2004). It is believed that glutaraldehyde as crosslinker is believed can improves the mechanical properties and water stability of the crosslinked materials (Deng and Ting, 2005). It is necessary to study on crosslinking of both materials to overcome the shortcomings related to applications of cellulose and magnetic nanoparticles in wastewater treatment.

The main aim of the present investigation is to identify appropriate combination between cellulose and magnetite powder as well as of glutaraldehyde required during synthesis of magnetic cellulose flocculant. The optimum parameters were chosen based on performance of pollutants reduction in AnPOME wastewater during flocculation

2. Materials and methods

2.1 Materials

AnPOME was collected from Kilang Kelapa Sawit Adela, Johor. The sample was preserved in refrigerator below that 4 °C and above the freezing point. Cellulose and magnetite powder were purchased from Qingdao Unionchem Co., Ltd. and Inoxia Ltd.. Glutaraldehyde (25 % purity) was purchased from Acros Organic. Ethanol (C_2H_5OH) with 95 % purity was purchased from HmbG, Malaysia. COD reagents were prepared according to ASTM D1252 method.

2.2 Preparation of Magnetic Cellulose

The magnetic cellulose synthesis procedure was adapted from the work by Sajab et al., (2013). Briefly, a pre-weighed amount of cellulose was mixed with 100 mL distilled water containing desired amount of magnetite powder suspension. All combinations of cellulose and magnetite powder are shown in Table 1.

The mixture was then heated at 65 °C using water bath shaker for 6 h, followed by cooling to room temperature. Then, 1 mL of glutaraldehyde (25 % purity) was added dropwise into the mixture followed by stirring for one hour at room temperature to allow crosslinking. The solution was then filtered, rinsed with ethanol and distilled water before drying in an oven at 50 °C until constant weight was achieved.

The best ratio was determined based on the highest removal of turbidity, colour, TSS and COD via jar test (See Section 2.3). Once the best ratio was determined, the same procedure was repeated by varying volume of glutaraldehyde (0.5, 1.5, 2.0 mL).

Table 1: Mass ratio used during magnetic cellulose synthesis

Grade	Weight of cellulose (g)	Weight of magnetite powder (g)
Magcell 1	1	2
Magcell 2	1	1
Magcell 3	2	1

2.3 Coagulation-flocculation Process

Characteristics of untreated AnPOME (initial turbidity, colour, TSS and COD) were analysed and then the average values were used for evaluation of flocculation performance. The coagulation-flocculation process was performed via jar test (Thrusoft Jar Tester SJ-10). For each test sample, 1 L of AnPOME was mixed with desired ratio of cellulose to magnetite powder and also volume of glutaraldehyde in a 2 L beaker. Then the mixture was stirred for 3 min at 200 rpm. During mixing, flocculant with ratios shown in Table 1 were added into each beaker. After that, the mixture were stirred for 15 min at 30 rpm. Finally, the system was left undisturbed for 30 min to permit the flocs settling. Supernatants were collected using syringe for subsequent analyses.

The optimum ratio of cellulose and magnetite powder was obtained from the analyses result and the same procedure was repeated to study on the effect of crosslinker volume.

2.4 Analytical Analysis

The removal efficiencies of all pollutants were calculated using the following Eq(1);

$$\text{Percentage Removal (\%)} = \frac{C_O - C_f}{C_O} \text{ x } 100 \text{ \%Percentage Removal (\%)} = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

where,
C_0 = Initial concentration of parameters, mg/L, and
C_f = Final concentration of parameters, mg/L

Turbidity of wastewater was measured using HACH Ratio/XR turbidimeter. To determine the TSS, a gravimetric analysis was used with the aid of vacuum filtration apparatus. The weight of solid retained on the filter paper was determined after drying for 1 hour at 103 - 105 °C. Concentration of colour was measured by using HANNA COD Meter and Multiparameter Photometer (HI 83099) based on calorimetric method. COD of the samples before and after treatment was determined by ASTM D1252 method, whereby 2.5 mL of sample was added to prepared reagent followed by heating HANNA COD Reactor (HI 839800) at 150 °C for 2 h. The reagent with sample was then cooled to room temperature prior to titration with ferrous ammonium sulphate.

3. Results and discussion

3.1 Characteristic of Untreated AnPOME

Table 2 lists the values for the tested parameters of AnPOME sample prior to coagulation pre-treatment. The recorded values are the mean values before each jar test was performed.

Table 2: Values of selected parameters of AnPOME

Parameters	Unit	Mean values
Turbidity	NTU	492
TSS	mg/L	10,290
COD	mg/L	12,553
Colour	PtCo	2,040
pH	-	8.1

3.2 Effect Ratio of Cellulose to Magnetite powder

The percentage removals of all pollutants (turbidity, colour, TSS, and COD) are presented in Figure 1.
It is observed that excess amount of cellulose and magnetite powder reduced the removal of organic matter and colour present in AnPOME wastewater. Magcell 2 produced the highest removal for all pollutants studied. Turbidity removal for this grade of flocculant was about 74.60 %, while only 36.20 % and 59.10 % turbidity removal were recorded for Magcell 1 and Magcell 3. Similar trend is also observed for TSS removal where 42 % was recorded.
For Magcell 1 while Magcell 2 and Magcell 3 were able to remove 71.10 % and 50.30 % of TSS. Highest colour removal was also recorded for Magcell 2 (~51 %) compared to Magcell 1 (17.20 %) and Magcell 3 (33 %).
Lastly, evaluation from COD removal shows that the highest percentage was observed for Magcell 2 during flocculation process. About 52 % COD reduction was obtained compared to only 30 % and 40.70 % when Magcell 1 and Magcell 3 were used.
From the result obtained, it is concluded that excessive amount of cellulose or magnetite powder reduced the effectiveness of synthesised flocculant and later affected the coagulation-flocculation performance. In this case, cellulose only acted as a coagulant aid which aided the attachment of particles from wastewater to attach to the polymer chain of cellulose (Mohtar et al., 2016).
Charge destabilisation process was incomplete due to insufficient amount of coagulant, and less destabilised particles tend to attach to available sites on cellulose. Low removal efficiencies of organic matters were recorded despite large amount of cellulose used (Jawaid and Abdul Khalil, 2011).

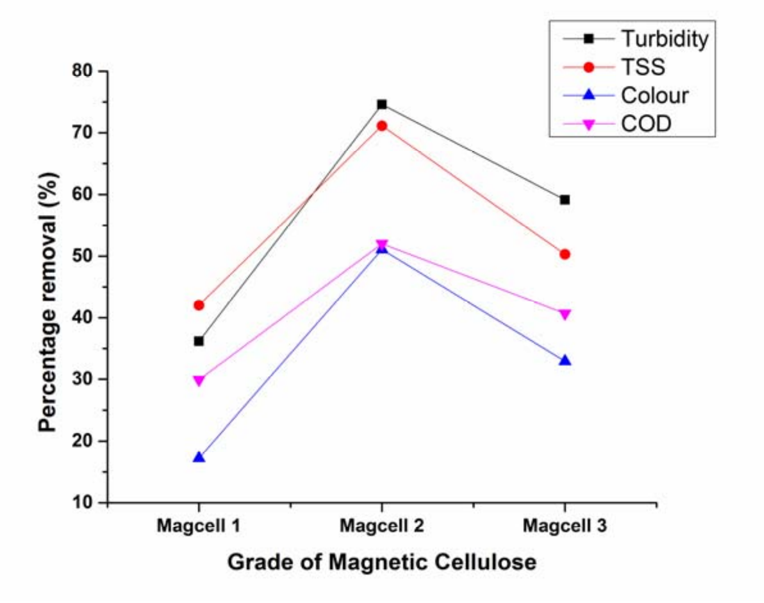

Figure 1: Percentage removal of all responses with different grade of magnetic cellulose

Higher amount of magnetite powder compared to cellulose also reduced the flocculation efficiency. Low degree of protonation occurred on magnetite under basic condition, ability of Fe^{2+} to destabilise negatively charged particles present in wastewater was reduced when excessive magnetite powder were applied (Saifuddin and Dinara, 2011), leading to reduction in colloidal particles removal.

3.3 Effect Volume of Glutaraldehyde

Removal percentage of turbidity, TSS, colour, and COD in AnPOME sample by Magcell 2 as a function of volume of glutaraldehyde is shown in Figure 2. It was found that the removal efficiencies increased remarkably with the increment of glutaraldehyde volume until optimum condition was observed followed by decrement beyond that point.

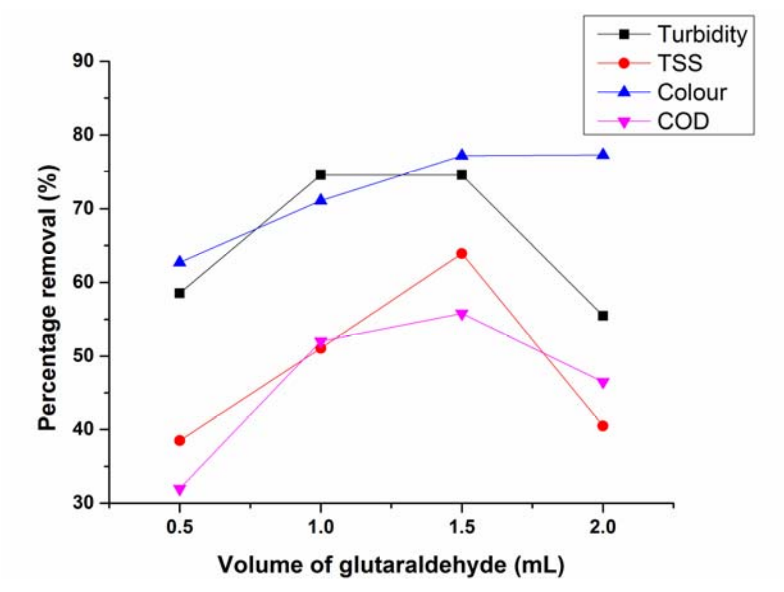

Figure 2: Percentage removal of all responses with various volume of glutaraldehyde

The highest turbidity removal (74.5 %) was achieved when 1.5 mL of crosslinker was used. The result also not very significant when 1 mL of glutaraldehyde were used. The result is comparable when 0.5 mL and 2.0 mL were used in this study which were 58.5 % and 55.5 % turbidity reduction.
Meanwhile, volume of glutaraldehyde had less influence on TSS removal. The highest TSS removal (77.2 %) was achieved with 1.5 mL glutaraldehyde as compared to 62.7 %, 71 % and 77 % when 0.5, 1.0 and 2.0 mL of glutaraldehyde were used.
Significant difference in term of COD removal was observed for magnetic cellulose synthesised with different volume of crosslinker. In this case, 55.7 % reduction of COD was obtained when 1.5 mL of glutaraldehyde was used. Meanwhile, only 32 %, 52 %, and 46 % COD removal were achieved when 0.5, 1.0 and 2.0 mL of glutaraldehyde were used in this study.
From the result obtained, it can be rationalised that attachment between cellulose and magnetite is limited by amount of glutaraldehyde available during crosslinking, and low glutaraldehyde amount results in decreased efficiency of magnetic cellulose during flocculation process (Deng and Ting, 2005).
Excessive amount of glutaraldehyde also reduces the flocculant performance due to the reaction between excessive glutaraldehyde molecules with magnetite after completion of crosslinking under influence of polarity attraction. Such reaction reduces of available active site for adsorption of destabilised charge from wastewater during flocculation (Lü et al., 2017). This resulting the flocculation process when magnetic cellulose were applied.

3.4 Comparison of Flocculation Performance

The flocculation efficiency of magnetic cellulose grade 2 (Magcell 2) was compared with cellulose as tabulated in Table 3. It is clearly shown that Magcell 2 possesses higher performance in pollutants removal compared to cellulose due to the ability of nano-sized magnetite to attract more colloidal particles (Chiavola et al., 2017).

Table 3: Comparison flocculation performance of Magcell 2 and cellulose

Flocculant	Percentage Removal (%)			
	Turbidity	TSS	Colour	COD
Magcell 2	74.5	77.2	63.9	55.7
Cellulose (1 g)	52.85	48.90	13.14	12.55

4. Conclusions

The preliminary study in preparation and application of magnetic cellulose was presented in this article. The optimum synthesis conditions were determined and discussed. It was found that the flocculant produced from equivalent amount between cellulose and magnetite powder (1 : 1 (g/g)) together with 1.5 mL of glutaraldehyde as crosslinker yielded an optimum result AnPOME treatment due to its capability to destabilise the charge while providing adequate active sites for adsorption of organic matter and colour pigment onto magnetic cellulose flocculant.
For future works, detailed studies will be performed on the application of magnetic- based bio-flocculant in palm oil wastewater treatment.

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