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Lignin Removal From Aqueous Solution Using Calcium Lactate: The Effect Of Polymers And Magnesium Hydroxide As A Flocculant Aids

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Palm oil mill effluent (POME) which is mainly associated with lignin has becoming a major concern due to its highly coloured appearance. The main colourant, i.e. lignin particles are difficult to be degraded in oil palm conventional biological ponding system. Coagulation/flocculation could remove the lignin prior to biological treatment and is considered vital to minimize the recalcitrance nature of palm oil mill effluent particles. In this study, the coagulation/flocculation process was investigated to remove lignin particles from aqueous solution. A non-toxic and biodegradable chemical i.e. calcium lactate was utilized as a destabilizer for the removal of lignin with an addition of several flocculants aid i.e. anionic polyacrylamide (APAM), polydimethyldiallylammonium chloride (polyDADMAC) and magnesium hydroxide. The effect of coagulant and flocculant aids dosage was investigated. From this study, it was found that the optimum condition was at 0.7g/L of calcium lactate and 0.5-1.0mg/L of APAM with ~64% of lignin removal. At concentration of 4 mg/L, the removal of lignin for APAM and polyDADMAC is similar. This result shows that the calcium lactate has potential as a coagulant and the efficiency can be enhanced with an addition of polymeric flocculant aids.

Keywords: Calcium lactate, coagulation/flocculation, lignin, zeta potential, polymer, magnesium hydroxide.

INTRODUCTION

Lignin is an important particles that need to be considered for effective treatment of palm oil mill effluent (POME) (Table 1) since it is resistant to biodegradation at high concentration (Ho *et al.*, 1984).

Lignin is a complex aromatic polymer that exist in plant species within ranges

Table 1. The distribution of chemical constituents between the soluble and the particulate fractions of POME (Ho *et al.*, 1984)

	POME[a]	Particulate fraction[a]	Soluble fraction[a]
Total solids	4.24		
Dissolved solids			2.012
Suspended solids		1.942	
'Free' oil drops	0.303		
Extractable oil	1.024	0.673	0.021
Ash			
total	0.602	0.18	0.421
water-insoluble	0.322	0.156	0.169
acid-insoluble	0.110	0.108	0.018
Ethanol/benzene extract	0.376	0.102	0.283
Nitrogen content			
total	0.071	0.045	0.022
extractive-free[b]	0.061	0.038	
Acid-insoluble lignin	0.470	0.412	
Phenolics	0.584	0.246	0.335
Glucode (free)	0.006		0.014
Reducing sugars	0.160		0.145
Starch	0.052	0.008	0.036
Pectin	0.341	0.031	0.328
Total glucose[c]	0.200	0.200	
Total reducing sugars[c]	0.607	0.373	
Total carbohydrates[c]	0.767	0.416	0.390[d]
Pentosans	0.170	0.165	
Holocellulose	0.731	0.574	
α - cellulose	0.591	0.434	
β – cellulose	0.027	0.024	
γ – cellulose	0.113	0.116	

[a] In g/100 ml POME.
[b] Values obtained from extractive-free samples.
[c] Values obtained after acid hydrolysis.
[d] Only the total soluble-carbohydrate concentration, hydrolysis was not necessary.

from (20-40)% of the dry mass of wood (Maximova *et al.*, 2001). Lignin containing wastewater is commonly found in the agricultural industries such as from pulp and paper process (Chang *et al.*, 2004), olive oil processing (Haddadin *et al.*, 2002) and palm oil mill process (Neoh *et al.*, 2014). The presence of lignin in wastewater contribute to the dark brown colour of wastewater and could increase organic pollution load (Betancur *et al.*, 2009). The lignin containing wastewater are of environmental and health concern due to its toxicity and carcinogenic byproduct(Neoh *et al*., 2014).

Since lignin is difficult to be degraded chemically and biologically (Wu *et al*., 2005), a number of treatment methods were investigated in order to remove lignin from wastewater. Methods such as photochemical UV/TiO_2 oxidizing process (Chang *et al*., 2004), adsorption (Maximova *et al*., 2001), electrocoagulation process (Ugurlu *et al*., 2008), filtration/flocculation (Wang *et al*., 2014) and flocculation (Piazza *et al*., 2014). In this study, the physico-chemical method (coagulation/flocculation) was proposed to be employed due to its simplicity, low cost, good removal efficiency and easy onsite implementation (Karthik *et al*., 2008). The addition of suitable polymeric flocculants could enhance the performance of the coagulation/flocculation by producing large flocs and less resistant to shear stress (Zahrim and Hilal, 2011). In recent years, several authors have investigated the roles of calcium lactate and magnesium hydroxide as a coagulant and coagulant aids in a coagulation/flocculation process (Zhao *et al*., 2014, Vandamme *et al*., 2012, Devesa-Rey *et al*., 2011, Devesa-Rey *et al*., 2012). To date, there is no published study that has been carried out for the removal of lignin from wastewater by using calcium lactate-polymer and calcium lactate-magnesium hydroxide.

The aim of this work is to identify the optimum conditions for lignin removal by coagulation/flocculation with the addition of calcium lactate as a coagulant and different types of flocculants aids i.e.APAM, polyDADMAC and magnesium hydroxide as flocculants aid.These flocculants aids have been chosen in this study since it is effective based on previous studies (Zahrim *et al*., 2010, Zahrim *et al*., 2011, Schlesinger *et al*., 2012, Zahrim *et al*., 2014).

METHODOLOGY

Materials

The 2000mg/L lignin solution was prepared by dissolving appropriate amount of lignin (alkali) powder (Sigma-Aldrich, USA) in distilled water. Similarly, the stock solutions of 50g/L calcium lactate (Molecular mass 308.32 g/mol) (Merck, Germany) and 1000mg/L magnesium hydroxide (Molecular mass 58.32 g/mol) (Sigma-Aldrich, USA) also were prepared by dissolving their powder form in distilled water. In addition, the 0.2% polymers solution i.e. polyDADMAC (Tramfloc® 724, 40wt%) and APAM (Tramfloc® 141, 39wt%) were also prepared by dissolving in distilled water and were used within 24 hours.

Jar Test Methods

A standard flocculator apparatus (Phipps & Birds) equipped with stainless steel paddles and stirrer was used for the coagulation/flocculation tests. During the jar tests, the appropriate volume of lignin stock solution was transferred into the round jar. An appropriate dosage of calcium lactate was added to the solution in the jar. The aqueous solution was then rapidly mixed at a paddle speed of 258 rpm for 3 min. Predetermined dosage of APAM, polyDADMAC and magnesium hydroxide were added to the solution in the jar, making the total volume of 500 mL, followed by slow mixing for 10 min at 39 rpm. After allowing settling to occur for 20 min, about 25 mL of the liquid was withdrawn using a pipette from a height of about 3 cm below the liquid surface in each jar(Zahrim *et al.*, 2010).

Analytical Methods

The lignin content was tested by using Biospectrometer (Eppendorf), absorbance at λ_{max}=286 nm. The pH and conductivity was measured by using meter HI 9611-5, Hanna Instrument. The zeta potential was obtained by using Malvern-Zetasizer Nano Series model ZS machine.

Statistical Analysis

Each data point was taken as the average of three measurements with standard deviation (STDEV).

RESULT AND DISCUSSIONS

Effect of Calcium Lactate Dosage

Figure 1, 2, and 3 shows the effect of calcium lactate dosage during coagulation/flocculation of lignin. Various dosages of calcium lactate (0.1g/L, 0.3g/L, 0.5g/L, 0.7g/L, 0.9g/L and 1.2g/L) were used and several parameters including (% lignin removal, zeta potential, pH and conductivity) were tested.

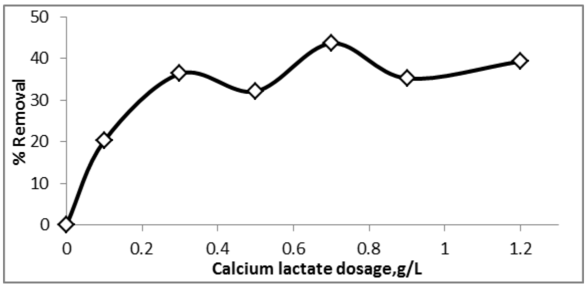

Fig. 1: Effect of calcium lactate dosage on the % removal during coagulation/flocculation of lignin.

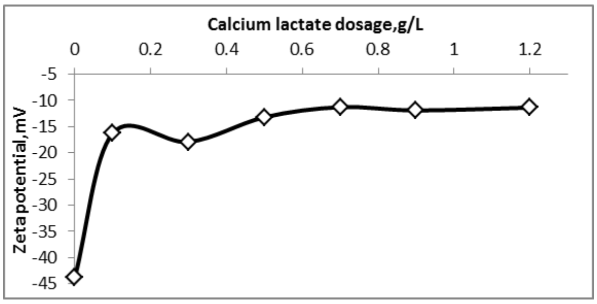

Fig. 2: Effect of calcium lactate dosage on zeta potential during coagulation/flocculation of lignin.

The untreated lignin shows that the lignin particle has negative surface charge i.e. -44 mV (Figure 2). The particles with high negative zeta potential value indicates its superior metal-binding capability, where it has a potential to bind with a positively charged solutes (Betancur *et al.*, 2009). The addition of calcium lactate increase lignin removal and tend to move zeta potential near zero. At near zero zeta potential, the particles tend to agglomerate might be due to the reduction the electrical double layer (Ma *et al.*, 2003).The maximum removal i.e. 44% achieved at 0.7g/L dosage. Generally, at low pHs, metal salts apply a charge neutralization mechanism, while, at higher dosages and pH, precipitation might occur.(Devesa-Rey *et al.*, 2011) had studied on the use of calcium lactate as a coagulant-flocculant at dosage 2-10g/L and pH 5-7 for the reducing of water turbidity. It was reported, the greatest reductions of turbidity were achieved with a moderate concentration of calcium lactate at pH 5. While, (Leentvaar and Rebhun, 1982)had reported the removal of suspended solids from sewage wastewater

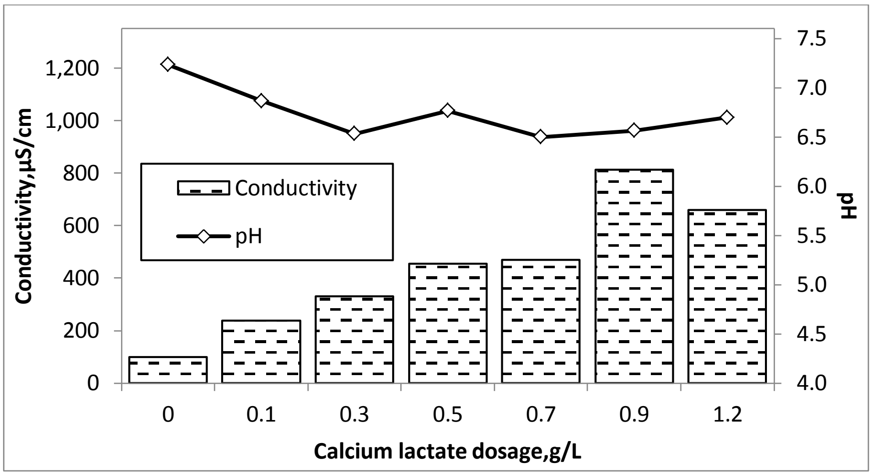

Fig. 3: Effect of calcium lactate dosage on the pH and conductivity during coagulation/flocculation of lignin.

by using precipitated calcium carbonate as coagulant aids at pH 10 and higher was due to the sweep coagulation mechanism. In this study, at final pH range between 6.4-7.0 (Figure 3), the removal of lignin particles using calcium lactate might indicates the combination of charge neutralization-sweep flocculation mechanism.

Figure 3 shows the pH decreased from 7.2 into pH (>6.4 to <7.0), while, the conductivity increased from 100µS/cm to 813µS/cm, at various dosage of calcium lactate. The presence of calcium lactate increased the conductivity due to the presence of salt (Levlin, 2008).

Effect of APAM, polyDADMAC and Magnesium Hydroxide as Flocculants Aid

Figure 4, 5, and 6 shows the effect of flocculants aid dosage during coagulation/flocculation of lignin. Based on the previous finding, the dosage of calcium lactate was fixed at 0.7g/L. Then, different types of flocculants aid (APAM, polyDADMAC and magnesium hydroxide) were applied. For each flocculant aids, various dosages (0.5mg/L, 1mg/L, 2mg/L, 4mg/L and 6mg/L) were used and several parameters (% removal, zeta potential, pH and conductivity) were investigated.

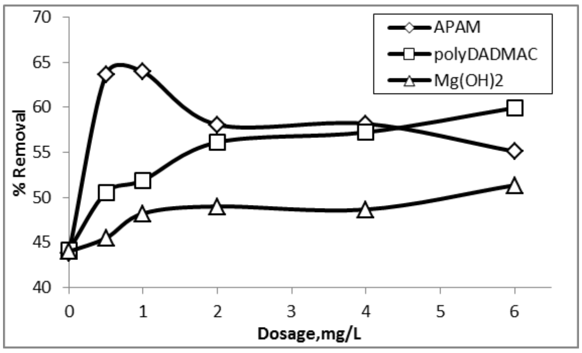

Fig. 4: Effect of flocculants aid dosage on the % removal during coagulation/flocculation of lignin with 0.7g/L calcium lactate.

The graph shows that the addition of polymer as flocculants aid enhanced the removal of lignin compared with the magnesium hydroxide. The application of APAM at as flocculant aids shows highest removal of 64% due to its bridging effect (Peng and Di, 1994) and then causing faster settling rate (Nasser and James, 2007).(Peng and Di, 1994) suggested that

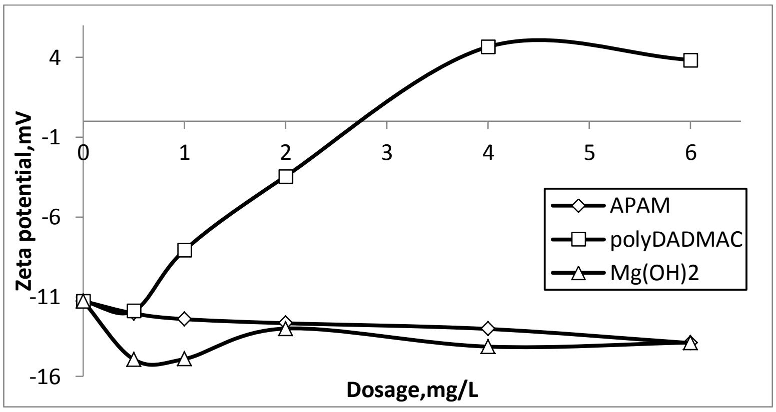

Fig. 5: Effect of flocculants aid dosage on zeta potential during coagulation/flocculation of lignin with 0.7g/L calcium lactate.

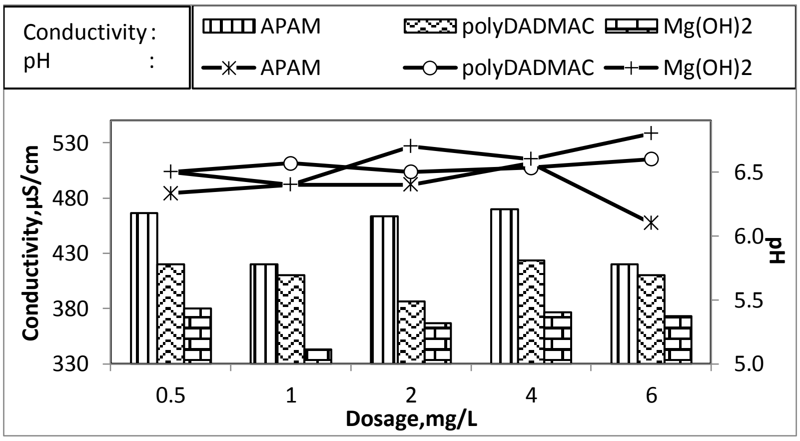

Fig. 6: Effect of flocculants aid dosage on the pH and conductivity during coagulation/flocculation of lignin with 0.7g/L calcium lactate (pH and conductivity without coagulant aids, 6.5 and 470µS/cm).

the APAM able to form larger flocs through a hydrogen bonding with the water surfaces and calcium ions through its amide groups ($-CONH_2$) and carboxylic groups ($-COO^-$).After 1 mg/L of APAM, the percentage removal decreased due to the increases in electrostatic repulsion and consequently restabilisation occurs (Nasser and James, 2007). (Razali *et al.*, 2012) had reported that the flocculation of lignin using polyDADMACis dominated by charge neutralization mechanism. The addition of magnesium hydroxide shows less removal efficiency of lignin since it apply a charge neutralization and adsorptive coagulation mechanism (Gao *et al.*, 2007). At the dosage of 4 mg/L, the removal of lignin particles is similar between APAM and polyDADMAC might be due to the fact that polyDADMAC could act as a bridge to connect the destabilized lignin particles. It can be seen also that the addition of magnesium hydroxide has lower lignin removal than both polymers due to the absence of bridging property.

From Figure 5, the zeta potential value shows greater than zero value at concentration >2.8mg/L of polyDADMAC dosage and keep increasing as the amount of polyDADMAC increased. This trend might be explained by the presence of unreacted polyDADMAC (cationic polymer) during coagulation/flocculation process. There is a small change towards more negatively charged of particle after an addition of APAM might be caused by the free negatively polymer chain molecules (Nasser and James, 2006).

Figure 6 shows the pH and conductivity that was maintainn within the range of 6.3 to 6.8 and 343µS/cm to 470µS/cm after the addition of various flocculants aid dosage. The stable pH is important since several conventional coagulants such as iron and alum based coagulants tend to turn the treated wastewater into acidic conditions at high dosage application.

CONCLUSSION

From this study, it can be concluded that the suitable dosage of calcium lactate with an addition of flocculant aids has potential for the agglomeration of lignin. Maximum lignin removal was achieved at 0.7g/L of calcium lactate and (0.5-1.0)g/L of APAM with ~64% lignin removal. At this optimum condition, pH and conductivity are stable at 6.35 and 443µS/cm, respectively. Zeta potential shows a small change towards more negatively charged of particle after an addition of APAM caused by unreacted negatively molecules.

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