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COAGULATION/FLOCCULATION OF LIGNIN AQUEOUS SOLUTION IN SINGLE STAGE MIXING TANK SYSTEM: MODELLING AND OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Lignin particles contribute to color pollution in river water and treating this type of pollution biologically is difficult. In this study, the treatment of a model solution containing lignin using a single mixing tank system approach with poly-diallyldimethyl ammonium chloride (polyDADMAC) as destabiliser was carried out. The effect of various flocculants i.e. calcium lactate, magnesium hydroxide and anionic polyacrylamide (APAM) were investigated. Calcium lactate performed better than magnesium hydroxide and anionic polyacrylamide as flocculants. The coagulation/flocculation with polyDADMAC-calcium lactate removed lignin through a complex mechanism: the adsorptive-charge neutralization-precipitation-bridging mechanism. Response surface methodology (RSM) study indicated that strong interaction in the coagulation/flocculation of lignin occurred between the initial pH-polyDADMAC dosage, initial pH-calcium lactate dosage and polyDADMAC-calcium lactate dosage. The highest lignin removal achieved was between 50-68%. The removal behavior depended on the initial lignin concentration in the solution. The results showed that lignin removal from aqueous solution is possible in a single stage mixing tank by utilizing polyDADMAC-calcium lactate as a dual coagulant. The method mentioned here will potentially be useful for the treatment of lignin containing wastewater from several industrial processes such as palm oil mill, pulp and paper, olive mill etc.

Keywords: coagulation, lignin, polyDADMAC, single tank system, calcium lactate

1. Introduction

Lignin is the second most abundant biopolymer in nature (Kansal et al., 2008) and the most abundant in terms of aromatic biopolymers (Huijgen et al., 2014). In an agro-based industry, dissolved lignin, its degradation products, hemicellulose, resin acids and phenols contribute to the dark brown colour of the wastewater (Zahrim et al., 2014a). Although most of the organic compounds are removed, the wastewater still remains colored even after biological treatment (Mohammed and Chong, 2014). In addition, the lignin compounds may cause fouling on membrane filtration systems (Chen et al., 2014). The treatment of lignin containing wastewater is challenging and has attracted the attention of several researchers for lignin removal/recovery from wastewater (Haddadin et al., 2002, Kansal et al., 2008, Wang et al., 2014, Zahrim et al., 2014a). The recovered lignin can be used as a flocculating agent (Fang et al., 2010, Rong et al., 2014) and fuel (Pinto et al., 2015).

In a wastewater treatment process, coagulation/flocculation is widely used as a pre-treatment in the removal of natural organic matter, since it has low capital cost, is efficient and is simple to operate (Teh et al., 2014). Since coagulation/flocculation is usually conducted in a two stage mixing process which involves a rapid stirring and slow stirring, this present study intends to investigate the combination of coagulant and flocculants into one single stirring scheme. The single stirring scheme will allow the coagulation and flocculation process to take place together in a simpler process (Liang et al., 2014).

Inorganic coagulants, such as alum and ferric chloride, have been widely used due to their efficiency (Fang et al., 2010). However, these conventional coagulants cannot keep up with the increasing demands for organic matter removal and due to this, the researchers were motivated to investigate and develop natural and modified natural polymers as coagulant (Rong et al., 2014).

This paper investigates the removal of lignin particles by a coagulation/flocculation process in a single tank system using polyDADMAC as a coagulant. In addition, we also study the effect of different flocculants: calcium lactate, magnesium hydroxide and anionic polyacrylamide (APAM). Previously,

Zahrim *et al* reported that the calcium lactate alone and calcium lactate-APAM can remove 44 % and ~50 % of lignin-tannin from palm oil mill effluent respectively (Zahrim et al., 2014a). In another study, Zahrim *et al* found that the lignin removal from synthetic solution for calcium lactate alone, calcium lactate-polyDADMAC, calcium lactate-magnesium hydroxide and calcium lactate-APAM is 44, 60, 50, and 64%, respectively (Zahrim et al., 2014b). Both of these processes were conducted using a conventional coagulation method i.e. rapid mixing followed by slow mixing. To the best of our knowledge, there is no published study on utilizing polyDADMAC-calcium lactate in a single mixing tank. Finally, the central composite design (CCD) method was applied to optimize four operating variables of the coagulation/flocculation process including initial pH, mixing speed, coagulant dosage and flocculants dosage.

2. Methodology

2.1 Coagulation/flocculation of lignin aqueous solution

2.1.1 Materials

The lignin solution was prepared by dissolving the appropriate amount of lignin (alkali) powder (Sigma-Aldrich, USA) in distilled water. The pH adjustment was made by adding a few drops of 1% NaOH and 1% HCl solution. Similarly, the stock solutions of 1000 mg/L calcium lactate (Molecular mass 308.32 g/mol) (Merck, Germany) and 1000 mg/L magnesium hydroxide (Molecular mass 58.32 g/mol) (Sigma-Aldrich, USA) also were prepared by dissolving their powder form in distilled water. Polymers were supplied by Tramfloc, Inc., Houston, Texas.The polymer solutions, i.e. polyDADMAC (Tramfloc® 724, 40 wt %) and APAM (Tramfloc® 141, 39wt %), were also prepared by dissolving in distilled water and were used within 24 hours. The concentration of both diluted polymers were 0.4% wt %. According to the supplier, the Tramfloc® 724 is a high molecular weight, highly charged, and liquid cationic polyDADMAC polymer. Moreover, Tramfloc® 724 is completely water soluble. Tramfloc® 141 is an anionic polyacrylamide of medium molecular weight and moderate charge density. Tramfloc 141 is supplied as a stable, high density dispersion. Tramfloc® 141 is completely water soluble and produces high viscosity solutions at very low concentrations. Details of the polymers is shown in Table 1.

Table 1: Physical and chemical properties of polymers

	Tramfloc 724	Tramfloc 141
Physical state, color and odor	Straw colored, viscous liquid with amine odor	White or off-white liquid. slight mild odor
pH	5.0 - 8.0	NA
Boiling point/range, ^{0}C	>100	NA
Water solubility	Completely soluble	Completely soluble
Melting point/range, ^{0}C	-2.8 – 0	NA
Flash point, ^{0}C	>100	>93
Freeze point, ^{0}C	NA	1.7
Vapor pressure, mm @ 25 ^{0}C	20-30	NA
Specific gravity	1.08 - 1.09	1.08-1.20
Octanol/water partition coefficient	Kow <10	NA
Viscosity, cps	~1000	NA
VOC content, % volatile	NA	~50

NA = not available

2.1.2 Jar test methods

A standard flocculator apparatus (Phipps & Bird, Inc.) equipped with stainless steel paddles and stirrer was used for the flocculation tests. During the jar tests, the appropriate volume of lignin stock solution was transferred into the round jar. An appropriate dosage of polyDADMAC was added to the solution in the jar. The aqueous solution (polyDADMAC + lignin) was then mixed at a paddle speed of 76 rpm for 3 min. Following that, the predetermined dosage of APAM/calcium lactate/magnesium hydroxide were added to the solution in the jar, making the total volume up to 500 mL, followed by 10 min of mixing with the same paddle speed. 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., 2010b, Zahrim et al., 2014a).

2.2 Experimental design

In order to determine the relationship between factors that affecting the output response of the process, the statistical design of experiments (DoE) was conducted. Process optimization based on a statistical method called response surface methodology (RSM) is a powerful experimental design tool to recognize the performance of composite systems (Khayet et al., 2011). In this study, the DoE and RSM were investigated using a commercial statistical package, Design-Expert Version 8.0.7.1 (Stat-Ease Inc.). The effects of factors on the response was found by employing the quadratic CCD with 4 factors and 3 levels. The 4 factors that had been considered as controllable variables in the design of the experiment, namely, initial pH, concentration of polyDADMAC, concentration of calcium lactate and mixing speed. Table 2 shows the levels in coded and actual values of the controllable variables. The output response is the absorbance and a total of 30 experiments were performed (Table 3).

Table 2: Actual and coded values of independent variables used for experimental design.

Variable	Symbol	Real value of coded levels		
		-1	0	+1
Initial pH, pH	x_1	6.25	7.75	9.25
Mixing rate (rpm), MS	x_2	25	75	125
polyDADMAC dosage (mg/L), C_p	x_3	0.5	4.75	9
Calcium lactate dosage (mg/L), C_c	x_4	0.03	3.52	7.0

Table 3: CCD experimental design (DoE) for absorbance by coagulation/flocculation.

Run no. (N)	polyDADMAC (mg/L) x_1^a	Calcium lactate (mg/L) x_2^a	pH x_3^a	Mixing rpm x_4^a	Absorbance, λ_{max286}
1	0	0	0	0	0.052

2	0	0	0	-1	0.086
3	+1	-1	+1	+1	0.474
4	+1	+1	+1	+1	0.500
5	0	0	0	+1	0.300
6	-1	0	0	0	0.084
7	0	0	0	0	0.052
8	+1	-1	-1	+1	0.361
9	0	+1	0	0	0.050
10	0	0	0	0	0.052
11	0	0	+1	0	0.102
12	0	0	0	0	0.051
13	+1	+1	-1	-1	0.073
14	+1	0	0	0	0.048
15	0	-1	0	0	0.081
16	-1	+1	+1	-1	0.369
17	+1	+1	+1	-1	0.363
18	-1	-1	-1	+1	0.347
19	+1	-1	+1	-1	0.244
20	-1	+1	+1	+1	0.465
21	+1	-1	-1	-1	0.080
22	-1	+1	-1	+1	0.370
23	-1	+1	-1	-1	0.086
24	-1	-1	+1	-1	0.279
25	0	0	-1	0	0.053
26	-1	-1	+1	+1	0.223
27	+1	+1	-1	+1	0.369
28	0	0	0	0	0.051
29	0	0	0	0	0.051
30	-1	-1	-1	-1	0.092

[a] -1=low value, 0=center value, +1=high value

2.3 Analytical methods

The lignin content was tested by using a Biospectrometer (Eppendorf), monitoring absorbance at λ_{max}=286 nm (Zahrim et al., 2014b). 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. Each data point was taken as the average of three measurements with standard deviation (STDEV).

3.0 Result and discussion

3.1 The effect of polyDADMAC dosage as a destabilizer

The coagulation/flocculation of lignin was conducted with various dosages of polyDADMAC (5, 10, 15, 20, 30 and 50 mg/L). Several parameters including lignin removal, zeta potential, pH and conductivity were analysed (Figure 1- 3).

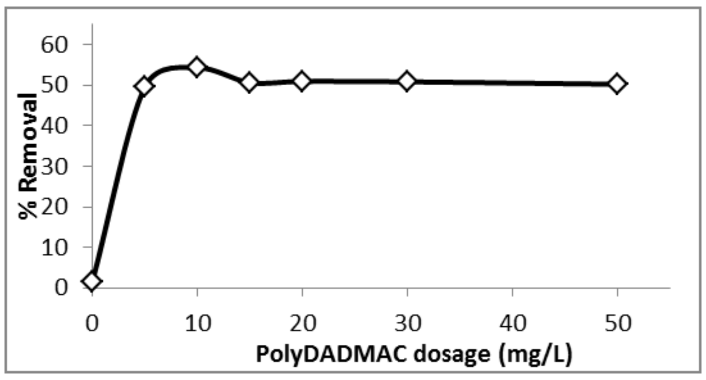

Figure 1: Effect of polyDADMAC dosage on the % removal during coagulation/flocculation of 2000 mg/L of lignin.

Based on Figure 1, the lignin removal increased with increasing dosage of polyDADMAC up to 8 mg/L with a maximum of 55% lignin removal achieved. However, the lignin removal was slightly decreased regardless of polyDADMAC dose from >8-13 mg/L. Beyond the optimal dosage of polyDADMAC, the charge reversal occurs on the particle surfaces due to an excess of polyDADMAC molecules (Ariffin et al., 2012). From Figure 1, it can be seen that there is no improvement in the lignin removal after the addition of 13 mg/L of polyDADMAC dosage, as the particles are further away from each other (Ariffin et al., 2012).

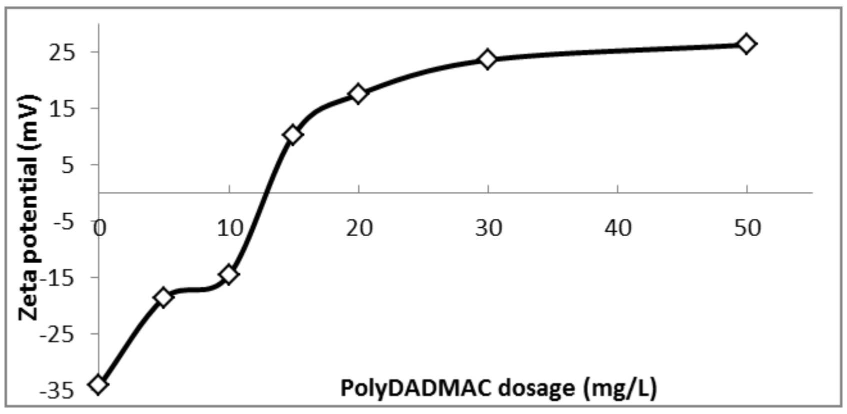

Figure 2: Effect of polyDADMAC dosage on zeta potential during coagulation/flocculation 2000 mg/L of lignin.

As shown in Figure 2, initially, the surface charge for lignin particles is -35 mV, indicating the presence of negatively charged particles suspended in solution. Considering the lignin solution charges, the separation which occurs during the coagulation/flocculation process requires the addition of a positive polymer to neutralize the negatively charged particles. Figure 2 shows that there is an increase of zeta potential towards zero after the addition of polyDADMAC, which might be due to a charge neutralization mechanism (Lee and Westerhoff, 2006). The mechanisms of alteration of lignin particle zeta potential by polyDADMAC can be classified as (John, 2008, Bolto and Gregory, 2007):

- Charge neutralization including by electrostatic patch effects – Lignin particles are negatively charged and it is believe that electrostatic interaction gives strong adsorption in these polyDADMAC-lignin particle systems. Consequently, neutralisation of the particle surface and even charge reversal can occur. Therefore, it is possible that that the lignin removal could occur simply as a result of the reduced surface charge of the particles and therefore a decreased electrical repulsion between them (Bolto and Gregory, 2007).
- Charge neutralization-precipitation - PolyDADMAC is used to neutralize the charge of the lignin particles. Precipitates of the lignin particles-polyDADMAC are formed by cross-linking between the negatively charged lignin particles and the polyDADMAC.

- Inter-particle bridging – PolyDADMAC will adsorb on lignin particles while its loops and tails extend some way into solution (Tian et al., 2006). This gives the possibility of attachment of the loops and tails of polyDADMAC segments to other lignin particles, thus 'bridging' particles together.

The zeta potential value shows a greater than zero value at >13 mg/L of polyDADMAC dosage and keeps increasing as the amount of polyDADMAC was increased. This occurs after complete neutralization phenomenon (Ariffin et al., 2012) that might be explained by the presence of excess polyDADMAC (cationic polymer) during coagulation/flocculation process. The positive charged zeta potential is caused by chains of polyDADMAC which carry N^+ that attach or are absorbed by the neutralized particles (Ariffin et al., 2012).

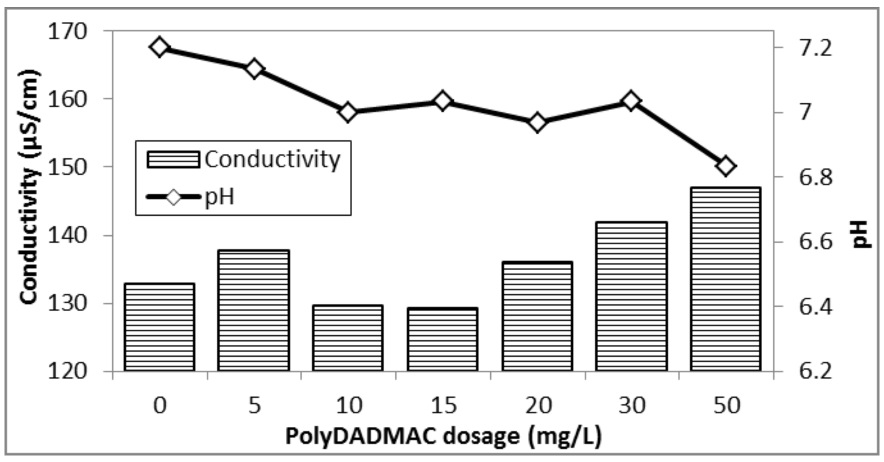

Figure 3: Effect of polyDADMAC dosage on the pH and conductivity during coagulation/flocculation of 2000 mg/L of lignin.

Figure 3 shows the pH and conductivity of lignin solution after treatment with various dosages of polyDADMAC. As the polyDADMAC dosage increases, the treated solution pH decreases might be due to hydrolysis phenomenon (SNF-Floerger, 2015). However, the pHs for all polyDADMAC dosages are within the acceptable range (i.e. not acidic) although the pH is slightly decreased from 7.2 into pH (>6.8

to 7.1). It should be noted that conventional inorganic coagulant i.e. iron and aluminium based coagulant tend to turn treated water pH into acidic solutions (Zahrim et al., 2010b) and hence a neutralization step is required before the treated water can be discharged into rivers. The conductivity of treated lignin solution is slightly increased as the polyDADMAC dosage increases. It is believed that it is due to the increase in the concentration of the unreacted polyDADMAC (John, 2008). Interestingly, at polyDADMAC optimum dosage i.e. 10 mg/L, the conductivity is similar to the control one i.e. zero polyDADMAC. This observation indicates that the application of optimum polyDADMAC dosage may result in zero or minimum conductivity increment in the treated solution.

3.2 The effect of calcium lactate, magnesium hydroxide and APAM dosage as flocculants

Based on the previous studies, the flocculation of lignin was conducted with various types of flocculants i.e. calcium lactate, magnesium hydroxide and APAM. Various dosages (0.5, 1, 2, 4 and 6 mg/L) of each flocculant were used and several parameters including lignin removal, zeta potential, pH and conductivity were analysed as shown in the Figure 4-6. From Figure 4, it can be seen that the maximum lignin removal were 68, 65, and 65% for calcium lactate, APAM and magnesium hydroxide, respectively. It should be noted that calcium lactate achieved 65% lignin removal at lower dosage i.e. 0.5 mg/L. Adsorption-precipitation-sweep coagulation could be the agglomeration mechanism for calcium lactate-lignin particles (Zahrim et al., 2014a).

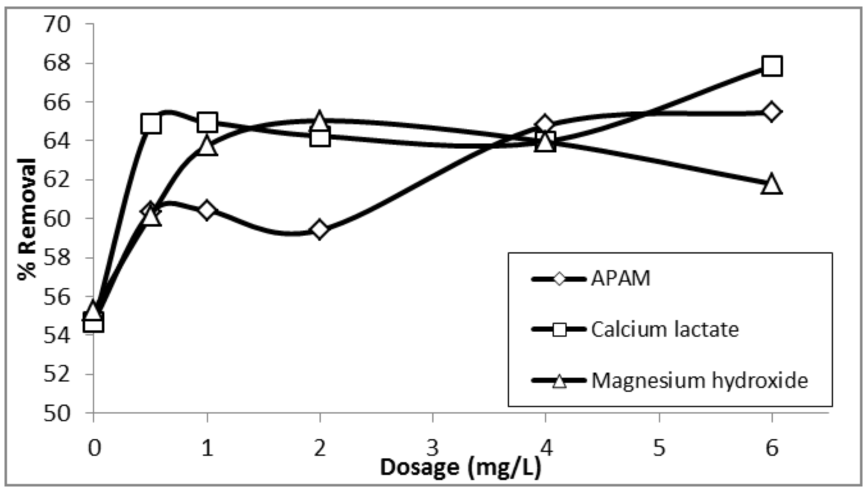

Figure 4: Effect of flocculants dosage on the % removal during coagulation/flocculation 2000 mg/L of lignin with 8 mg/L polyDADMAC.

The flocculation using APAM can be described via a bridging mechanism. The APAM serves as a bridge by forming larger flocs through particle-polymer-particle attachment (Teh et al., 2014). As expected, there is low lignin removal occurs at dosages less than 2 mg/L due to insufficient bridging contacts (Bolto and Gregory, 2007).

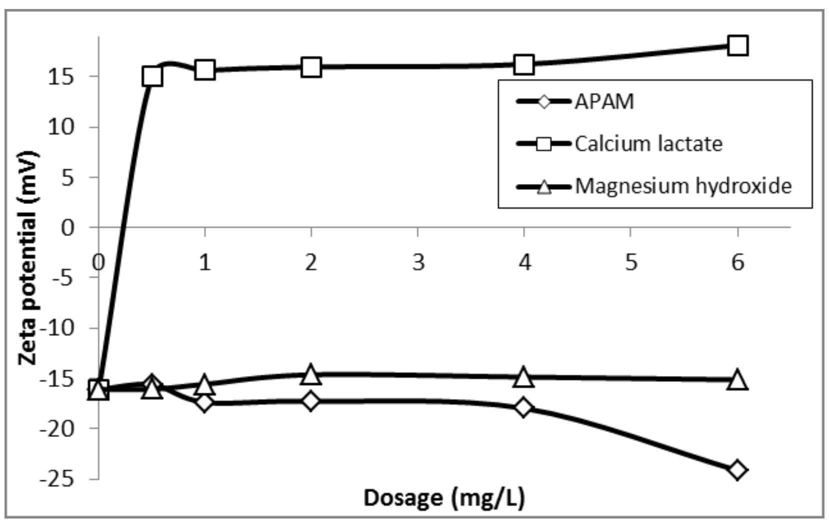

Figure 5: Effect of flocculants dosage on zeta potential during coagulation/flocculation 2000 mg/L of lignin with 8 mg/L polyDADMAC.

From Figure 5, the zeta potential shows a positive value after the addition of various dosages of calcium lactate indicating that the solution was dominated by residual Ca^{2+} ions. Although the solution was dominated by positive ions, the lignin removal was not decreased as normally shown by a charge neutralisation mechanism (Zahrim et al., 2010a). Therefore, lignin removal using polyDADMAC-calcium lactate system is dominated by adsorption-precipitation mechanism (Peng and Di, 1994).

At dosages of less than 1 mg/L, the lignin removal for magnesium hydroxide is lesser than calcium lactate probably due to minimal ionization by magnesium hydroxide when dissolved in water at pH around 7.0 (Shak and Wu, 2014). Weak ionisation of magnesium hydroxide might be the caused for unchanged zeta potential value after the addition of polyDADMAC-magnesium hydroxide. It is anticipated that the lignin removal will be increased if the solution is raised to higher pH. Higher pH could enhance the magnesium ionization energy (Judkins and Hornsby, 1978).

The slight decrease in zeta potential into a more negative value (Figure 5) was due to the negatively charged polymer chain of APAM. As the polyDADMAC-lignin surface particles are adsorbed to the APAM chain, a series of loops and trains are formed. Then the aggregation of polyDADMAC-lignin-APAM form as a second lignin particle with vacant adsorption site comes in contact with the extended loops and trains (Teh et al., 2014).

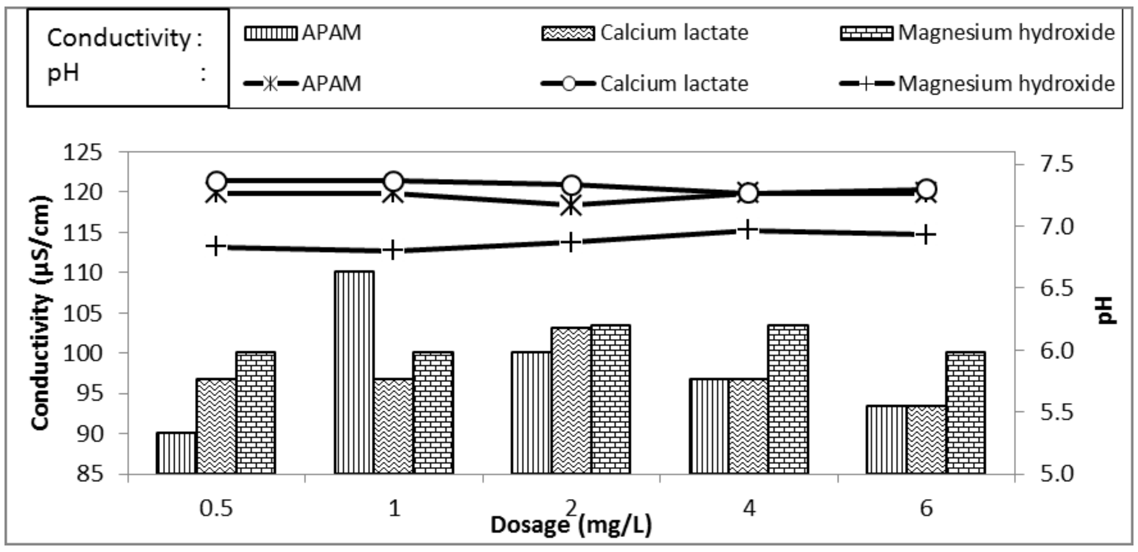

Figure 6: Effect of flocculant dosage on the pH and conductivity after coagulation/flocculation (Initial lignin concentration = 2000 mg/L, Initial solution pH = 7.2, Initial solution conductivity = 133 µS/cm, polyDADMAC concentration = 8 mg/L)

Interestingly, for all flocculant types and dosages, the treated solutions' conductivity is very much less than the treated solution conductivity for polyDADMAC alone (~130 µS/cm). This fact indicates that the addition of flocculants obviously enhanced the lignin removal and hence it is useful in single mixing tank coagulation system (Figure 4). The treated solution pHs for APAM and calcium lactate are slightly higher than magnesium hydroxide. It might be due to the magnesium hydroxide having a greater tendency to donate protons to water than the other two flocculants i.e. calcium lactate and APAM (Figure 6). The treated solution conductivities and pHs (Figure 6) at all dosage of flocculants remain similar/stable to each another due to very high lignin concentration that might act as a buffer solution.

3.3 Response surface methodological approach for optimization of process variables

After designing the experiment based on the CCD method, as shown in Table 3, the RSM was applied to develop the polynomial regression equations. As noted, the output response for this study is the maximum absorbance. A second-order polynomial model, where interaction terms between the output response and the input factors have been fitted to the experimental data, is stated in the form of the following equation:

$$\hat{Y} = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i<j}^{n} b_{ij} x_i x_j + \xi \quad \text{(Eq.1)}$$

Where $\hat{Y}$ is the predicted response, x_i refers to the coded variables, b_0, b_i, b_{ii}, b_{ij} are the regression coefficients and ξ is the statistical error.

A set of batch experiments were conducted by using RSM approach with CCD model to visualize the effects of independent factors on the response along with the experimental conditions as shown in the Table 2. The obtained regression equation in terms of the coded variables is:

$$\hat{Y} = +0.045 + 0.011x_1 + 0.026x_2 + 0.066x_3 + 0.097x_4 - 0.013x_1x_2 + 0.016x_1x_3 + 0.023x_1x_4 + 0.029x_2x_3 + 0.006438x_2x_4 - 0.044x_3x_4 + 0.027x_1^2 + 0.027x_2^2 + 0.039x_3^2 + 0.15x_4^2 \quad \text{(Eq. 2)}$$

Where x_1, x_2, x_3 and x_4 are the coded values of the independent variables. The final empirical model obtained in terms of actual parameters is interpreted and written in general form as follows:

$$\text{Absorbance} = +0.89785 - 0.036428C_p - 0.049374C_C - 0.21027pH - 0.00338587MS - 0.000856612C_pC_C + 0.00252451C_ppH + 0.000107647C_pMS + 0.00548183C_CpH + 0.000036944C_CMS - 0.00059125pHMS + 0.00151217C_p^2 + 0.00221804C_C^2 + 0.017250pH^2 + 0.0000617254MS^2 \quad \text{(Eq. 3)}$$

Where 0.5 mg/L $\leq C_p \leq$ 9.0 mg/L (polyDADMAC dosage); 0.03 mg/L $\leq C_C \leq$ 7.0 mg/L (calcium lactate dosage); 6.25 $\leq$ pH $\leq$ 9.25 (initial pH); 25 rpm $\leq$ MS $\leq$ 125 rpm (mixing speed).

The experimental data (Table 3) were used to calculate the coefficient of quadratic equation. In addition, Table 4 summarizes the ANOVA results for the coefficient significance. The test of statistical significance was performed on the total error criteria, with a confidence value of 21%. In any of the model terms, a large regression coefficient, a small *p*-value and smaller *F*-value that the tabulated F-value would indicate a more significant effect on the respective response variables (Khayet et al., 2011, Krishnaiah et al., 2015). ANOVA results show that the R^2-value is 0.9652, which is desirable. This implies that more than 96.52% of the data deviation can be explained by the developed empirical models. However, a large value of R^2 does not always imply the adequacy of the model. Therefore, the adjusted-R^2 need to be use in order to evaluate the model adequacy and the adjusted- R^2 value is appropriate with over 90% and higher (Krishnaiah et al., 2015).

Table 4: Analysis of variance (ANOVA) for the developed RSM model.

Source	DF	SS	MS	*F*-value	*p*-Value prob > *F*	R^2	R_{adj}^2	Pred R^2
Model	14	0.69	0.049	29.7	<0.0001	0.9652	0.9327	0.7642
Residual	15	0.025	0.001666					
Total	29	0.72						

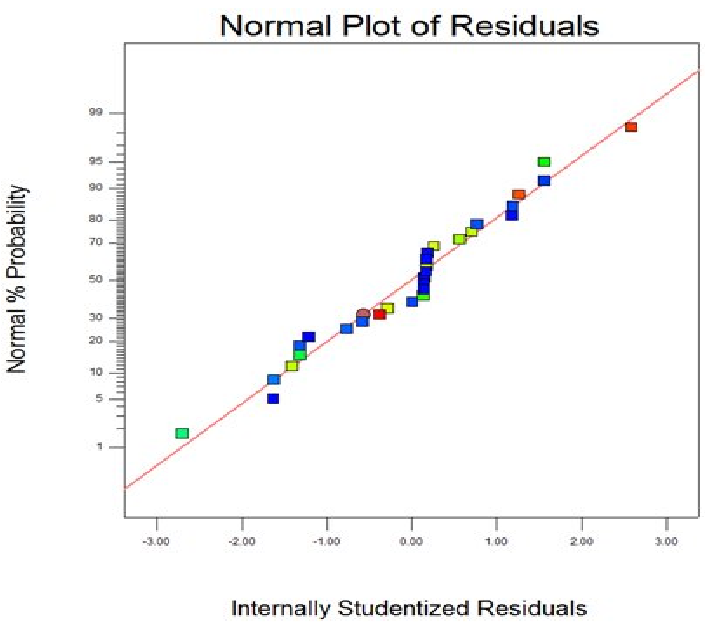

Figure 7: The internally studentized residual and normal % probability plot of lignin residual absorbance by coagulation/flocculation.

The normal plot of residuals show how well the model satisfies the asumptions of the analysis of variance. The internally normal probability and studentized residuals are shown in Figure 7 for lignin removal (measured as absorbance). It should be noted that lower residual absorbance indicates higher lignin removal. The internally studentized residuals measured the number of standard deviations separating the actual and predicted values. As the normal probability plot of residuals distributed along the straight line (Figure 7), these indicate no abnormalities of the model since the errors are distributed normally for all the responses.

The graphical representations of the response surfaces were plotted based on this model, i.e. Eq. (3). Some relevant response surface plots and the corresponding contour plots are reported in Figs. 8-12.

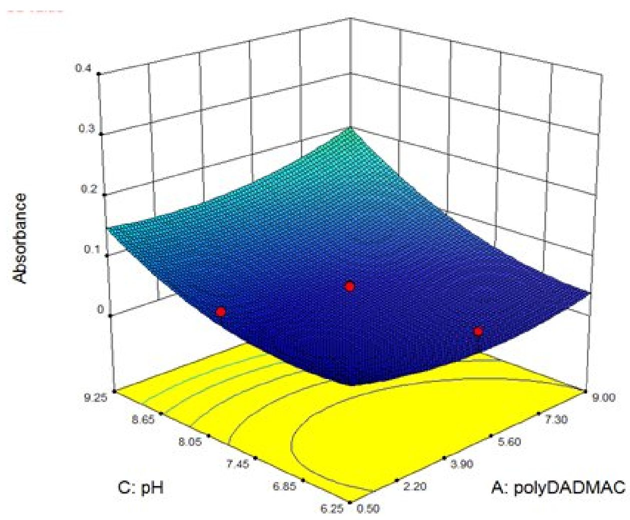

Figure 8: Response surface plot of predicted lignin residual absorbance as function of the initial pH and concentration of polyDADMAC at 3.52 mg/L of calcium lactate and 75 rpm.

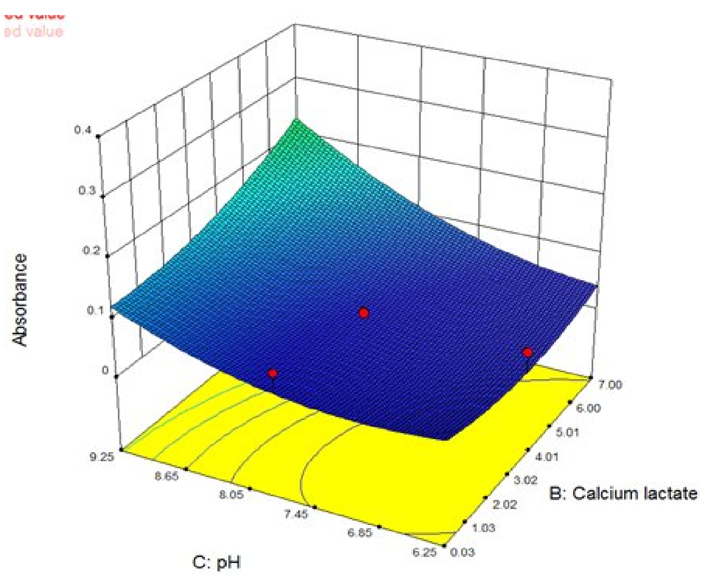

Figure 9: Response surface plot of predicted lignin residual absorbance as function of the initial pH and concentration of calcium lactate at 4.75 mg/L of polyDADMAC and 75 rpm.

The plots shown in Figs. 8-9 indicate the influence of the initial pH on the absorbance. The initial pH range (6.25-9.25) was chosen since the anaerobicallly digested palm oil mill efffluent pH is within this range (Zahrim, 2014, Zahrim et al., 2014a). The results show that the decreasing of initial pH leads to an increasing of the lignin removal up to a maximum as the absorbance shows a decreasing trend. As initial pH increases from 6.25 to 9.25, more anionic charges were available at the lignin surface due to ionization of phenolic groups and consequently, enhancement of the surface excess of anionic charges (Chen et al., 2014). The adsorbed amount of polyDADMAC under alkali conditions is low compared to that under acidic conditions (Figure 8) due to the competitive adsorption of counterions to the lignin surface (Notley and Norgren, 2008). At high dosages of calcium lactate, the absorbance was also found to be high (indicating lower removal of lignin) (Figure 9) due to lignin particles restabilisation(Zahrim et al., 2014b).

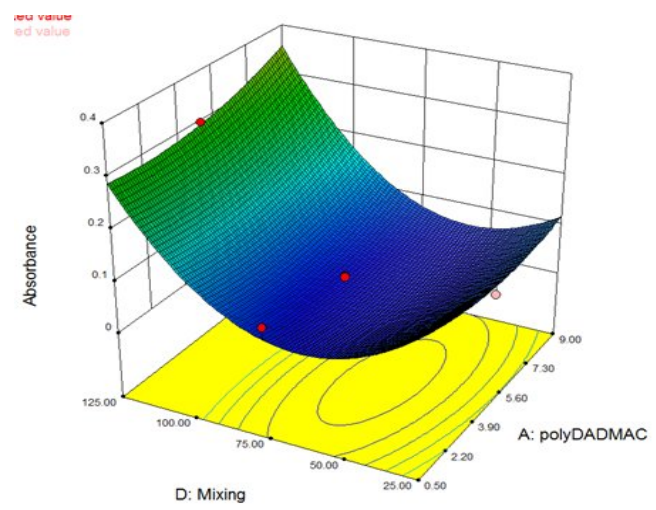

Figure 10: Response surface plot of predicted lignin residual absorbance as function of the mixing rate and concentration of polyDADMAC at initial pH 7.75 and 3.52mg/L of calcium lactate.

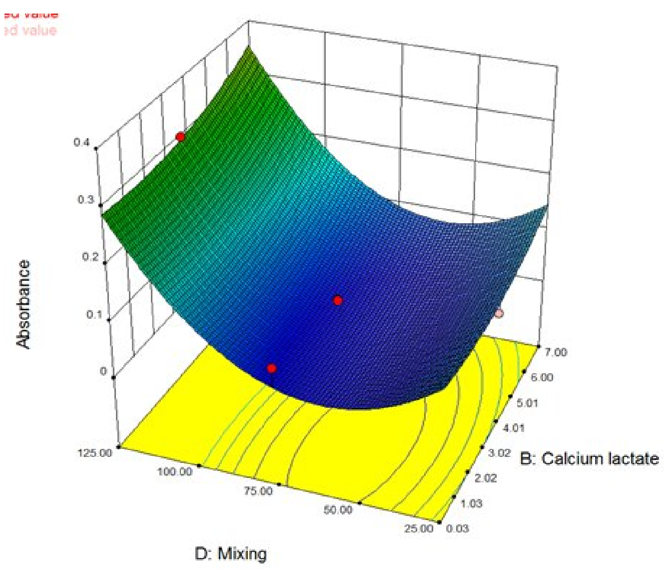

Figure 11: Response surface plot of predicted lignin residual absorbance as function of the mixing rate and concentration of calcium lactate at initial pH 7.75 and 4.75mg/L of polyDADMAC.

The plots shown in Figure 10-11 indicate the influence of mixing speed on the absorbance. As the mixing speed increased from 75-125 rpm, the absorbance also increased. A high shear rate tends to break flocs generated during the coagulation/flocculation process (Zhao et al., 2014).

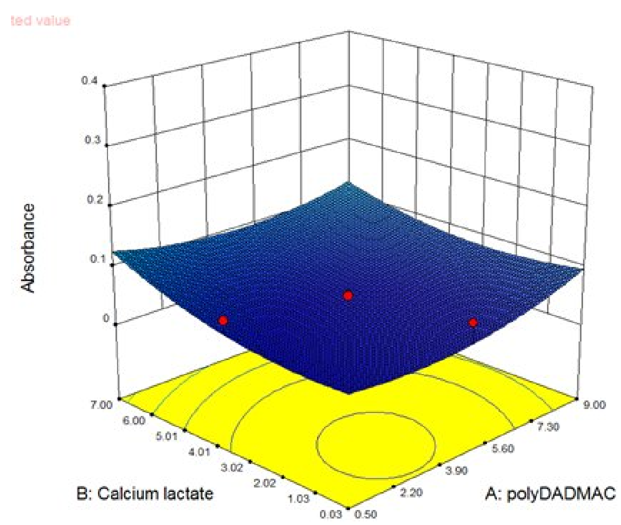

Figure 12: Response surface plot of predicted lignin residual absorbance as function of the concentration of calcium lactate and pDADMAC at initial pH of 7.75 and 75 rpm.

The removal of lignin occurs at every combination of polyDADMAC and calcium lactate dosage (Figure 12). The minimum absorbance, i.e. maximum lignin removal, occured at 9 mg/L of polyDADMAC and medium calcium lactate dosage in the range 2.02-4.01 mg/L. On the other hand, at maximum dosage of calcium lactate i.e. 7 mg/L, the minimum absorbance also occurs at medium polyDADMAC dosage in range (3.9-5.6 mg/L). These findings are important to decide suitable coagulant/flocculant that can produce maximum lignin removal based on the lowest cost.

Equation 4 shows the possible reaction for coagulation/flocculation of lignin at alkaline condition. Since the surfaces of lignin particles contain hydroxyl groups (Huijgen et al., 2014), polyDADMAC will neutralize the negatively charged sites of the hydroxyl group by electrostatic attraction forces (Equation 4) (Bolto and Gregory, 2007).

$$poly - CH_2CH_2(CH_2)(CH_2)N(CH_2)(CH_2)CH_2CH_2.Cl \ + \ XOH \ \rightarrow \ poly - XCl \ + \ CH_2CH_2(CH_2)(CH_2)N(CH_2)(CH_2)CH_2CH_2.OH$$

(Eq. 4)

Where: poly- $CH_2CH_2(CH_2)(CH_2)N(CH_2)(CH_2)CH_2CH_2.Cl$ (polyDADMAC); XOH (alkaline lignin).

Thus, the calcium ions may also react with previously unreacted lignin particles as shown below (Equation 5). In addition, lactate ion may be attached to polyDADMAC during the reaction since zeta potential for calcium lactate shows positive value (Figure 5); which is indicative of the releasing of calcium ions to the bulk solution.

$$CH_3CH(OH)COO.Ca.5H_2O \ + \ 2XOH \ \rightarrow \ CH_3CH(OX)COOX \ + \ CaOH^+ \ + \ 6OH^- \ + \ 6H^+$$

(Eq. 5)

Where: $CH_3CH(OH)COO.Ca.5H_2O$ (calcium lactate).

3.4 Optimization and verification

Optimisation of coagulation parameters, i.e. polyDADMAC dosage, calcium lactate dosage, initial pH and mixing speed, was carried out by RSM. The best parameter for polyDADMAC dosage, calcium lactate dosage, initial pH and mixing speed is 5.27 mg/L, 2.78 mg/L, 6.66 and 56.72 rpm, respectively (Table 5). Although the optimisation result shows several acceptable values as shown in the Table 5, the Option 1 was selected due to lowest polyDADMAC dosage and mixing speed.

Table 5: Optimal point in terms of the actual operating variables and the output response, lignin removal (%).

Option	PolyDADMAC dosage (mg/L)	Calcium lactate dosage (mg/L)	Initial pH	Mixing speed (rpm)	Absorbance	
					Predicted	Experimental
1	5.27	2.78	6.66	56.72	-0.0088	0.047
2	6.61	2.62	6.54	65.61	0.00276	0.047

From Table 4, it can be observed that the optimum predicted absorbance factor occured to be a negative value, which is not logical from the experimental point of view. This is because in the optimization step, a restriction condition for the response must be greater than zero value, was not considered (Khayet et al., 2011). The reconformation run was carried out in order to check experimentally the optimal point. The experimental value of the output response shows both Option 1 and 2 resulted in similar absorbance. This finding indicates that confirmed that the lowest absorbance can be achieved is 0.047.

3.5 Effect of initial lignin concentration

To investigate the effect of initial lignin concentration on its removal using optimum condition, initial lignin concentration was varied (50-3000 mg/L). The initial lignin concentration range i.e. 50-3000 mg/L was chosen to simulate lignin concentration for palm oil mill effluent after anaerobic digestion (Zahrim et al., 2014a). Figure 13 shows the % lignin removal at various initial lignin concentration. The optimum conditions of the coagulation/flocculation process was obtained from the previous RSM study. At 50 mg/L initial lignin concentration, polyDADMAC-calcium lactate may adsorb to the small lignin particles and then floc is formed due to charge the neutralisation mechanism. Another possible mechanism might be due to complexes binding between the lignin particles by a bridging mechanism. This can occur more easily under that specific mixing condition (Hankins et al., 2006).

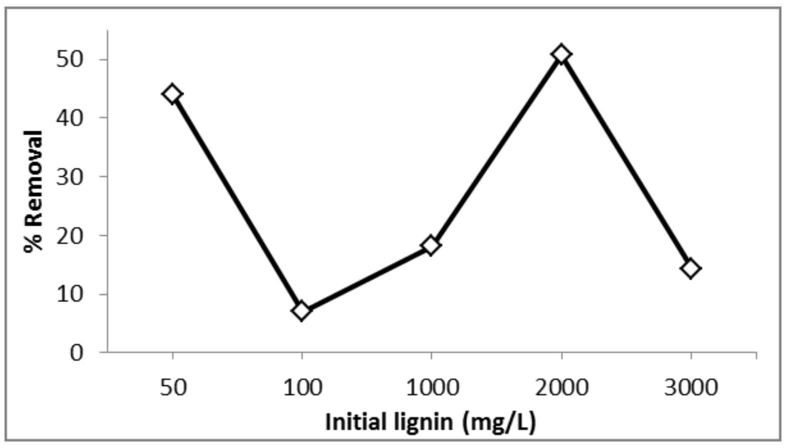

Figure 13: Effect of initial lignin concentration on the % removal during coagulation/flocculation of lignin with 5.27 mg/L polyDADMAC and 2.78 mg/L of calcium lactate (initial pH=6.66,mixing speed=56.72 rpm).

As the lignin concentration increased to 100 mg/L, the removal decreased due to an underdosing effect of coagulant (polyDADMAC-calcium lactate). After the lignin particle concentration passed 1000 mg/L, it is believed that the effect of self-aggregation of lignin to produce bigger microfloc become significant. At this condition, charge neutralization (due to "electrostatic path" mechanism) may occur and produces macroflocs (Bolto and Gregory, 2007, Norgren et al., 2001). Consequently, the macroflocs will be bridged together by the polymer (Tian et al., 2006) and this mechanism contributes to the highest lignin removal at lignin concentrations of 2000 mg/L. After lignin concentration of 2000 mg/L, again the underdosing effect of polyDADMAC-calcium lactate occurs and consequently weakens the bridging mechanism.

4.0 Conclusions

In this study, lignin particle removal from aqueous solution was investigated using a single mixing tank system utilising poly-diallyldimethyl ammonium chloride (polyDADMAC) as destabilizer. At 8 mg/L polyDADMAC, the lignin removal is about 55% without increasing conductivity. As the polyDADMAC dosage increases, the treated solution pH decreases but the conductivity increases.

Addition of flocculant e.g. calcium lactate, APAM and magnesium hydroxide, increase the maximum lignin removal to 68, 65, and 65%, respectively. RSM findings are important to model the relationship between important parameters in a single mixing tank system that can produce maximum lignin removal based on the lowest cost. The design of experiment (DoE) and response surface methodology (RSM) study demonstrated that the optimization operational conditions for coagulation of 2000 mg/L lignin particles are as follows: 5.27 mg/L polyDADMAC dosage, 2.78 mg/L calcium lactate dosage, pH 6.66 and 56.72 rpm mixing speed. The removal behavior depends on the initial lignin concentration in the solution. Study on various concentration of lignin indicates that self-aggregation of lignin could contribute to the removal of lignin particles from bulk solution. The results showed that the lignin removal from aqueous solution is possible in a single stage mixing tank by utilizing polyDADMAC-calcium lactate as dual coagulant. The method mentioned here is useful for the treatment of lignin containing wastewater from several industrial processes such as palm oil mill, pulp and paper, olive mill etc.

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