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Coagulation/flocculation of lignin aqueous solution in single stage mixing tank system: Modeling 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 destabilizer 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 and 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.

Introduction

Lignin is the second most abundant biopolymer in nature [1] and the most abundant in terms of aromatic biopolymers [2]. In an agro-based industry, dissolved lignin, its degradation products, hemicellulose, resin acids and phenols contribute to the dark brown color of the wastewater [3]. Although most of the organic compounds are removed, the wastewater still remains colored even after biological treatment [4]. In addition, the lignin compounds may cause fouling on membrane filtration systems [5]. The treatment of lignin containing wastewater is challenging and has attracted the attention of several researchers for lignin removal/recovery from wastewater [1,3,6,7]. The recovered lignin can be used as a flocculating agent [8,9] and fuel [10].

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 [11]. 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 [12].

Inorganic coagulants, such as alum and ferric chloride, have been widely used due to their efficiency [8]. 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 [9].

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 [3]. In another study, Zahrim et al. found that the lignin removal from synthetic solution for calcium lactate alone,

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calcium lactate–polyDADMAC, calcium lactate–magnesium hydroxide and calcium lactate–APAM is 44, 60, 50, and 64%, respectively [13]. 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.

Methodology

Coagulation/flocculation of lignin aqueous solution

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, 39 wt%), were also prepared by dissolving in distilled water and were used within 24 h. 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.

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 [3,14].

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 [15]. 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).

Analytical methods

The lignin content was tested by using a Biospectrometer (Eppendorf), monitoring absorbance at λ_{max} = 286 nm [13]. 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).

Result and discussion

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).

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 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 (°C)	>100	NA
Water solubility	Completely soluble	Completely soluble
Melting point/range (°C)	−2.8 – 0	NA
Flash point (°C)	>100	>93
Freeze point (°C)	NA	1.7
Vapor pressure, mm @ 25 °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