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Applicability of Iron (III) Trimesic (Fe-BTC) to Enhance Lignin Separation from Pulp and Paper Wastewater

(Kebolehgunaan Besi (III) Trimesik (Fe-BTC) untuk Peningkatan Pemisahan Lignin daripada Air Sisa Pulpa dan Kertas)

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ABSTRACT

This study assesses the application of iron (III) trimesic (Fe-BTC) as a coagulant-flocculant to remove lignin from pulp and paper (P&P) wastewater. In this research, Fe-BTC was characterized by X-ray diffraction (XRD), while the functional groups of Fe-BTC and lignin were analyzed by Fourier transform infrared (FT-IR) spectroscopy. Scanning electron microscopy (SEM) determined the surface morphology of the material. The influential parameters affecting lignin removal included the initial lignin concentration, the quantity of Fe-BTC, and the pH which were investigated using a single batch mixing system. The experimental and optimum operational conditions were determined using Box-Behnken design (BBD). Fe-BTC dosage plays a major role in efficiently removing lignin, while the pH and initial lignin concentration had no significant effect. Greater than 80% removal efficiency could be achieved with a Fe-BTC dosage as low as 2 g/L. The proposed mechanism of lignin aggregation was that Fe molecules were released from unsaturated sites of Fe-BTC and then formed new bonds with O in the methoxy lignin group. The interaction between Fe-BTC and lignin was π-π stacking (benzene ring), which explains the formation of F-O bonds in the lignin sludge.

Keywords: Box-Behnken design; Fe-BTC; lignin; metal-organic frameworks; MOFs; pulp and paper

ABSTRAK

Kajian ini menilai penggunaan besi (III) trimesik (Fe-BTC) sebagai bahan penggumpal untuk menyingkirkan lignin daripada air sisa pulpa dan kertas (P&P). Dalam kajian ini, Fe-BTC dicirikan oleh pembelauan sinar-x (XRD) manakala kumpulan fungsian Fe-BTC dan lignin dianalisis melalui spektroskopi transformasi Fourier inframerah (FT-IR). Mikroskop Elektron Imbasan (SEM) menentukan morfologi permukaan untuk bahan. Parameter penting yang menyebabkan penyingkiran lignin adalah termasuk kepekatan pemula lignin, kuantiti Fe-BTC dan pH yang dikaji menggunakan sistem campuran kelompok tunggal. Syarat uji kaji dan pengoperasian optimum telah ditentukan dengan menggunakan reka bentuk Box-Behnken (BBD). Dos Fe-BTC memainkan peranan penting dalam menyingkirkan lignin dengan cekap, manakala pH dan kepekatan pemula lignin tidak menunjukkan kesan yang ketara. Lebih daripada 80% kecekapan penyingkiran boleh dicapai dengan dos Fe-BTC serendah 2 g/L. Mekanisme cadangan daripada pengagregatan lignin adalah bahawa Fe molekul dibebaskan dari unsatured tapak Fe-BTC dan kemudian membentuk ikatan baharu dengan O dalam kumpulan lignin metoksi. Interaksi antara Fe-BTC dan lignin ialah susunan π-π (gelang benzena) yang menjelaskan pembentukan ikatan F-O dalam enap-cemar lignin.

Kata kunci: Fe-BTC; lignin; MOFs; pulpa dan kertas; rangka kerja logam-organik; reka bentuk Box-Behnken

INTRODUCTION

The Thai pulp and paper (P&P) industry is a major water consumer as the production process is water intensive, and therefore also generates a large quantity of wastewater. P&P wastewater treatment generally includes primary treatment and secondary using biological treatment systems. In some cases, activated carbon adsorption and chemical coagulation or sedimentation are also employed (Elwakeel & Guibal 2015; Fang et al. 2017; Moetaz et al. 2015). However, significant amounts of dissolved inorganic and organic compounds, heavy metals, and lignin remain in the treated effluent of such systems and discolor the water.

Lignin is typically present in the eucalyptus fibers, raw materials of P&P industry. Biological treatment is not effective in lignin removal, as lignin and its derivatives are difficult to degrade. Natural lignin is colorless or pale yellow, whereas the lignin in the black liquor from P&P industry is a colored substance (brown or dark brown). However small, residual lignin in treated effluent may cause color pollution in the aquatic environment. Color in surface water can prevent sunlight from penetrating down into the water column, and therefore affects the photosynthesis of aquatic plants and can lead to the depletion of dissolved oxygen. Lignin effluence has been through cooking and bleaching processes using chlorine, which may cause transformation into toxic substances (Ali & Sreekrishnan 2001; Kaur et al. 2018; Norgren & Edlund 2014; Nyman et al. 1986). Lignin can be recycled and some lignin-derived materials have good mechanical and physicochemical properties that can be used in the manufacture of plastics, resins, and fuel production (Naseem et al. 2016; Norgren & Edlund 2014), biosorbent materials (Klapiszewski et al. 2017a), adsorbents (Wang et al. 2018), super adsorbent polymer composites (Hao et al. 2016; Wang et al. 2014), polymeric hydrogel (Wang et al. 2017), surfactants (Wang et al. 2018), and material-assisted synthesis of catalysts (Wang et al. 2016). Few studies have attempted to separate and recycle lignin from treated effluent.

The coagulation-flocculation process is the conventional means of removing color and turbidity, and has been shown to outperform other wastewater treatment processes, despite using a simple and economic operation to achieve a high removal efficiency. The process involves the separation of solids and liquids using metal salts (coagulants) to destabilize the dissolved particles and polymeric materials (flocculants) to aggregate particles (Ashrafi et al. 2015; Ciputra et al. 2010; Hameed et al. 2018; Lee et al. 2014; Teh et al. 2016). Given the demonstrated ability of coagulation-flocculation to remove color and turbidity from water, it is reasonable to expect that this process can be potentially used for lignin removal.

Recent studies have focused on the development of new hybrid materials to replace conventional organic-based flocculant and aluminum-based and iron-based coagulants (Lee et al. 2012). Alum, polyaluminum chloride (PAC), aluminum chloride, and starch-g-PDMC have been studied in the treatment of P&P industrial wastewater (Teh et al. 2016). Although these chemicals were highly effective, they can result in greater metal content in the sludge and higher BOD in the treated effluent due to the addition of polymers. To address these drawbacks, the development of a new alternative material is needed. Desirable properties for alternative hybrid materials include greater separation performance, lower dosage, reduced sludge production, and non-aggregation with sludge to enhance recyclability (Cassey & Shazwan 2014; Lee et al. 2012; Roopan 2017). More specifically, a material that can simultaneously act as a coagulant-flocculant is desired to simplify the operation and decrease the size of the treatment facility.

Metal-organic frameworks (MOFs) are one of the hybrid materials that have been developed in this research field over the last decade to enhance their structural and functional properties. A significant advantage MOFs is that their properties can be engineered as required, for example to change their hydrophobicity, reactivity, porosity, surface area, solubility, and redox potential (Hasan & Jhung 2015; Khan et al. 2013). Given their unique characteristics, such as high chemical and thermal stabilities, and their physicochemical properties, MOFs have been highly promising materials for separation and treatment technologies. MOF applications include gas storage, adsorption, drug delivery, separation, sensors, and catalysis (Hasan & Jhung 2015; Sorachoti et al. 2017) clean water resources are decreasing everyday, because of contamination with various pollutants including organic chemicals. Pharmaceutical and personal care products, herbicides/pesticides, dyes, phenolics, and aromatics (from sources such as spilled oil. MOFs could also be potentially used as a coagulant to extract and recover lignin.

This study assesses the application of iron (III) trimesic (Fe-BTC) as a coagulant for lignin removal from wastewater. Fe-BTC consists of iron ion/clusters and benzene-1,3,5-tricarboxylate (BTC) synthesized using the hydrothermal technique. Lignin removal efficiency was examined under different conditions. The influential parameters affecting lignin removal included the initial lignin concentration, the quantity of Fe-BTC, agitation, and the acidity-alkalinity (pH), which were investigated using a single batch mixing system. The experimental and optimum operational conditions were determined using Box-Behnken design (BBD) (Archariyapanyakul et al. 2017; Kiattisaksiri et al. 2015; Sriprom et al. 2015; Tolod et al. 2016; Zhan et al. 2010).

Materials and Methods

MATERIAL SYNTHESIS

Fe-BTC was synthesized by a hydrothermal technique adapted from previous reports (Zhu et al. 2012). 1 mmol of ferric chloride hexahydrate (QRëC, New Zealand) was dissolved in 25 mL of deionized (DI) water, then 1 mmol of benzene-1,3,5-tricarboxylic acid (H_3BTC) (Sigma-Aldrich, Singapore) in 25 mL of ethanol was added to the solution. The mixed solution was stirred for 30 min. The solution was then kept in a Teflon-lined stainless-steel autoclave reactor and heated for 2 days in an oven at 100°C. After that, the solution was cooled to an ambient temperature and the product was then dried in a furnace oven at 100°C overnight. The orange-red powder of Fe-BTC was stored in a desiccator.

LIGNIN WASTEWATER

Synthetic lignin wastewater was prepared by dissolving lignin (alkaline) solid (TCI America) in reverse osmosis (RO) with analytical grade water. The synthetic wastewater was used in the coagulation-flocculation experiments to determine the influential factors that affect lignin removal, and in the statistical experiments to find an optimal condition to maximize removal efficiency. The treated effluent wastewater was obtained during the rainy season in August 2017 from a canal 1 km from the discharge point of a P&P factory. The factory is located in the northeastern region of Thailand where odor and color pollution has previously been reported. The samples were stored in a 6 L container at 4°C until being analyzed. The effluent samples were used in the experiments to evaluate the lignin removal efficiency of Fe-BTC under optimum conditions.

COAGULATION-FLOCCULATION TEST

The coagulation-flocculation experiments were performed using a jar test apparatus equipped with six paddle stirrers (Velp Scientifica JLT 6, Italy) at room temperature (27°C ± 1). The wastewater sample pH was adjusted by adding either nitric acid (HNO_3) or sodium hydroxide (NaOH) (RCI Labscan). The coagulation protocol entailed rapid mixing at 150 rpm for 5 minutes in a 500 mL beaker and settling for 30 min. The effect of environmental factors, including the Fe-BTC dosage, initial lignin concentration, agitation, and pH were investigated. The preliminary experiments indicated that only the Fe-BTC dosage, initial lignin concentration and pH affected the lignin removal efficiency. Thus, these three variables were investigated further using statistical design to find an optimum condition.

After settling, the supernatant was withdrawn from the beaker. Lignin residue was quantified by the UV absorbance of the sample at λ = 280 nm (Andersson et al. 2012), as measured with a UV-vis spectrophotometer (HACH DR 6000). The color appearance was measured using an ADMI method (method 10048). The efficiencies of lignin and color removal were defined as follows:

$$\text{Removal Efficiency (\%)} = \frac{C_i - C_e}{C_i} x\, 100 \quad (1)$$

where C_i is the initial absorbance/ADMI; and C_e is the final absorbance/ADMI, respectively.

STATISTICAL EXPERIMENTS

BBD was employed to optimize the lignin removal efficiency by varying the Fe-BTC dosage, the initial lignin concentration and the pH. The experimental conditions were designed and the data analyzed by the response surface regression procedure to fit the following second order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{j=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where Y is the response (removal efficiency, %); β_0, β_i(i = 1, 2, 3, 4) and β_{ij}(i = 1, 2, 3, 4; j = 1, 2, 3, 4) are the model coefficients; and X_i and X_j are the coded independent variables.

RESULTS AND DISCUSSION

MATERIALS CHARACTERIZATION

X-ray diffraction pattern The Fe-BTC crystallinity was identified by X-ray diffraction (XRD) at room temperature on a Bruker D8 Advance using CuKα radiation (λ = 1.54 Å). The 2theta from 5° to 50° was scanned for 40 min. Figure 1 shows the crystalline structure of Fe-BTC, which confirmed a successful synthesis by comparing it with the XRD pattern found in previous literature (2θ at 11.5°, 23.0°, and 27.3°) (Majano et al. 2013; Sciortino et al. 2015; Zhu et al. 2012).

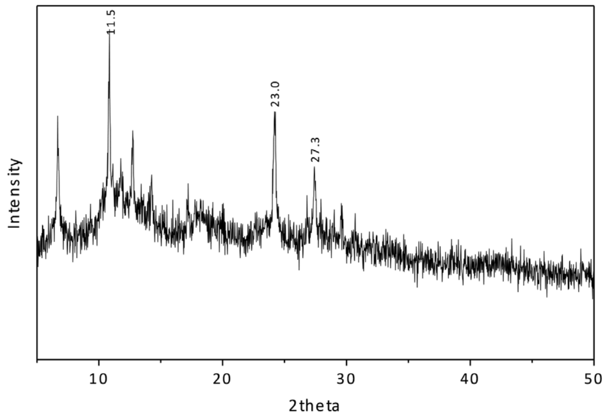

FIGURE 1. X-ray diffraction pattern of the synthesized Fe-BTC

Fourier transform infrared spectra The Fourier transform infrared (FT-IR) spectra of samples were obtained using a Shimazu FTIR 8601 PC spectrometer. The samples were recorded with KBr pallets and then analyzed over a wavenumber range of 4000 to 450 cm^{-1}. Figure 2 shows the spectra of lignin and Fe-BTC that were synthesized. The spectra absorption bands of Fe-BTC are similar to those found in previous studies (Autie-Castro et al. 2015; García et al. 2014; Mahmoodi et al. 2018). Infrared absorption bands from 1300 to 1700 cm^{-1} indicate the presence of the carboxylate functional group, while the bands below 1300 cm^{-1} suggest an aromatic benzene ring, which are consistent with the nature of the involved organic ligands. The ligand of OH was observed at the bands from 3300 to 3650 cm^{-1}, which showed the presence of water molecules.

The vibrations of Fe-BTC were observed at different wavenumbers, suggesting different bonds; O–H bond at 2950 cm−1; C=O bond at 1625 cm^{-1}; C–O bond at 1380, 1220 and 1050 cm^{-1}; and C–H bond at 759 and 711 cm^{-1}. Likewise, the lignin vibration peaks show that O–H bond at 3448 cm^{-1}, C–H bond at 2944 cm^{-1}, C–C bond at 1599 cm^{-1} and 1423 cm^{-1}, C–O–CH_3 at 1128 cm^{-1}, and the bands at 1215 cm^{-1}, 1044 cm^{-1} and 617 cm^{-1} display the sulfonic group (Klapiszewski et al. 2017; Wang et al. 2018).

Scanning electron microscope (SEM) The scanning electron microscope (SEM) was used to investigate the surface morphology of Fe-BTC using Zeiss (LEO) 1450 VP. The results in Figure 3 showed that the Fe-BTC surface is rough and porous. The flake-like shape on the surface might be $Fe(OH)_3$ - a molecule resulting from the Fe(III) in the material interacting with the OH of the water or the methoxy group of lignin (Figure 3(a) and 3(b)).

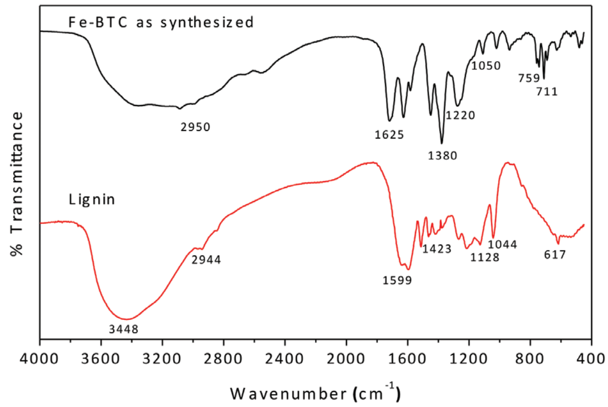

FIGURE 2. FT-IR spectra of lignin and the synthesized Fe-BTC

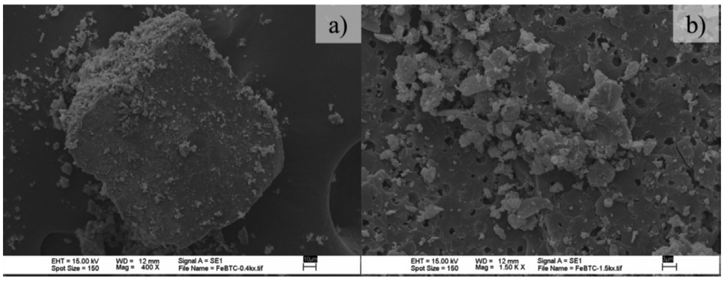

FIGURE 3. SEM photograph of the Fe-BTC surface: (a) 400X and (b) 15,000X

COAGULATION-FLOCCULATION ANALYSIS

The effect of agitation duration and speed on lignin removal were investigated using 200 ppm of synthetic lignin solution in a 1,000 mL beaker with 2.0 g of Fe-BTC additions. Rapid mixing was performed at 100, 150, and 200 rpm under contact times of 5, 10, 20, and 30 min before being left to settle for 30 min. The results show that the agitation duration and speed had no significant effect on lignin and color removal (Figure 4). Moreover, using Fe-BTC in the coagulation-flocculation tests resulted in the separation of wastewater into three layers; Fe-BTC powder at the bottom, lignin sludge in the middle and clear supernatant at the top (Figure 5).

STATISTICAL ANALYSIS

1,000 mL of synthetic lignin wastewater was tested for lignin removal under different conditions; the Fe-BTC dosage ranged from 1-3 g/L; the initial pH ranged from 4-9; and the initial lignin concentration ranged from 100-300 ppm. The uncoded and coded independent variables and the experimental design matrix obtained from the BBD are shown in Tables 1 and 2, respectively.

The samples were mixed for 5 min at 150 rpm and then settled for 30 min. The supernatants were filtered to remove suspended solids using Whatman (Piscataway, NJ) GF/C glass microfiber filters (pore size 1.2 µm, diameter 4.7 cm). The predicted lignin removal rates were obtained by quadratic model fitting techniques using MIMITAB16 software. The response was plotted as a function of

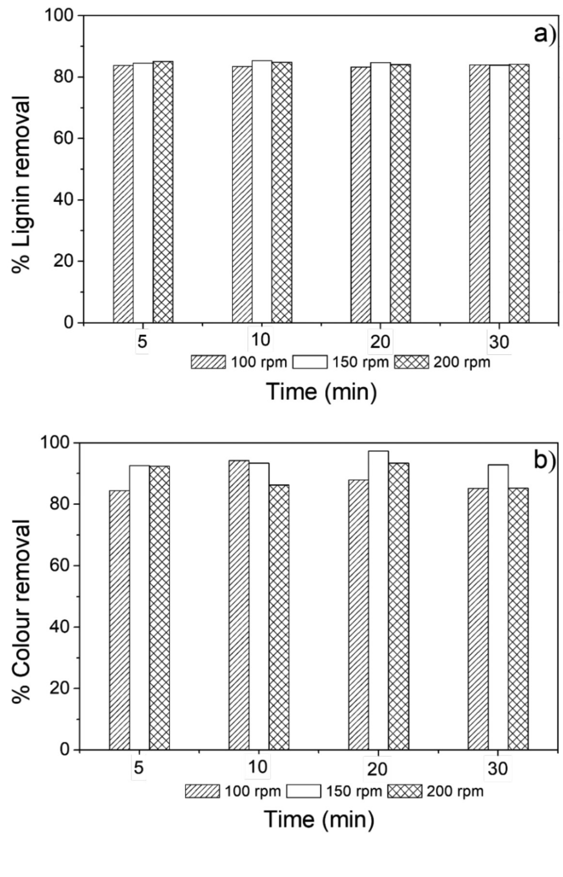

FIGURE 4. The effect of agitation and speed on (a) lignin removal and (b) color removal

FIGURE 5. Separation of wastewater into layers: Fe-BTC powder at the bottom, lignin sludge in the middle and clear supernatant at the top

TABLE 1. Range and levels of independent variables used for the experimental design

Variables	Representative	Range and levels		
		-1	0	+1
Fe-BTC (g.)	X_1	1	2	3
pH	X_2	4	6.5	9
Initial lignin concentration (ppm)	X_3	100	200	300

TABLE 2. Experimental design matrix and lignin removal from the experimental data compared to the predicted values obtained from BBD

Run No.	Independent variables			Removal efficiencies (%)	
	Fe-BTC X_1 (g)	pH X_2	[Lignin] X_3 (ppm)	Experimental data	Predicted value
1	2	6.5	200	84.25	85.05
2	3	9.0	200	81.71	71.40
3	1	4.0	200	0.00	9.96
4	1	9.0	200	0.00	11.76
5	3	6.5	100	69.53	71.04
6	2	4.0	100	76.82	87.60
7	2	9.0	300	86.94	75.76
8	1	6.5	300	0.00	0.00
9	3	4.0	200	82.22	70.10
10	1	6.5	100	82.76	61.15
11	2	6.5	200	86.28	85.05
12	2	4.0	300	81.05	71.36
13	2	9.0	100	77.00	86.30
14	3	6.5	300	86.12	107.65
15	2	6.5	200	85.19	85.05

independent variables to determined coefficients as presented by:

$$Y = -38.3145 + 110.4690X_1 + 23.5815X_2 - 0.8756X_3 - 1.8728X_1^2 - 32.5546X_2^2 + 0.0007X_3^2 - 0.0501X_1X_2 + 0.0057X_1X_3 + 0.2484X_2X_3 \quad (3)$$

where Y is the percentage of lignin removal; X_1 is the pH, X_2 is the quantity of Fe-BTC added (g); and X_3 is the Initial concentration of lignin (ppm). The coefficients prior to X_1, X_2, and X_3 represent the linear effects of the main factors. The coefficients prior to X_1X_2, X_1X_3, X_2X_3, and X_1^2, X_2^2, X_3^2 represent the interaction between two factors and the quadratic effects, respectively. The positive sign in front of each term indicates a synergistic effect while the negative sign indicates an antagonistic effect.

Table 3 shows that the predictability of the model achieved a greater than 95% confidence level based on Fe-BTC concentration ($p = 0.007$). The results showed that

TABLE 3. Estimated regression coefficients to predict lignin removal efficiency

Term	Parameters	Coefficients	P value
Constant	-	85.2420	0.001
Fe-BTC (g)	X_1	29.6016	0.007
pH	X_2	0.6960	0.922
[Lignin] (ppm)	X_3	-6.5013	0.383
pH *pH	$X_1 * X_1$	-11.7049	0.295
Fe-BTC (g) * Fe-BTC (g)	$X_2 * X_2$	-32.5546	0.023
[Lignin] (ppm) * [Lignin] (ppm)	$X_3 * X_3$	6.9159	0.520
pH * Fe-BTC (g)	$X_1 * X_2$	-0.1253	0.990
pH * [Lignin] (ppm)	$X_1 * X_3$	1.4291	0.888
Fe-BTC (g) * [Lignin] (ppm)	$X_2 * X_3$	24.8385	0.049

the predicted values obtained from (3) and the experimental data were strongly correlated (R^2 = 88.64%, Figure 6).

The most influential factor affecting lignin removal was the quantity of Fe-BTC (X_2), as indicated by *p*-value of 0.007 (Table 3). On the contrary, the initial lignin concentration (X_3) and pH of wastewater (X_1) had no significant effects (p = 0.383 for the resulting lignin concentration and p = 0.922 for pH).

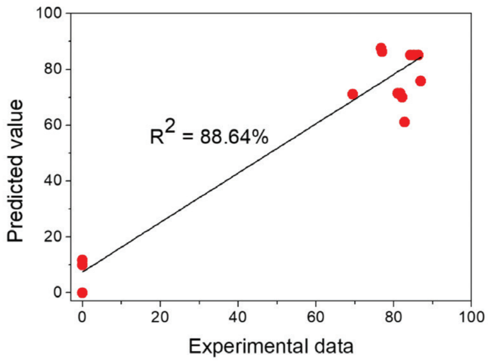

FIGURE 6. Predicted value and experimental data plots for lignin removal efficiency using Fe-BTC as a coagulant

The quantity of Fe-BTC was therefore selected for further investigation. The contour plot and surface plot of the lignin removal efficiency are depicted in Figure 7(a) and 7(b). The maximum lignin removal was greater than 80% with the optimum conditions of 2.0 – 3.0 g/L Fe-BTC dosages, initial lignin concentrations of 125 – 300 ppm, and pH of 5.5 – 7.5. When Fe-BTC dosages were lower than 2.0 g/L, the rate of lignin removal decreased at all pH ranges.

The main effects of the pH, Fe-BTC and the initial lignin concentration on lignin removal are shown in Figure 7(c). Lignin removal increased appreciably with Fe-BTC doses up to 2 g/L, while beyond that the rate of removal began to plateau. The lignin removal rate changed marginally under pH ranges of 4-9 and initial lignin concentration ranges of 100-300 ppm. 87% of the lignin removal was achieved with a pH (X_1) of 9.0, an Fe-BTC dosage (X_2) of 2 g/L, and an initial lignin concentration (X_3) of 300 ppm (Run 7, Table 2). Additionally, we found that the separation of wastewater into layers and the formation of lignin sludge occurred at all ranges of Fe-BTC dosage, pH levels and initial lignin concentrations.

LIGNIN REMOVAL FROM P&P WASTEWATER TREATMENT

Experiments with real P&P wastewater were conducted to confirm the efficiency of lignin removal by Fe-BTC. Treated effluent wastewater was collected from a P&P discharge canal and the wastewater quality parameters are presented in Table 4. Lignin and UV absorbance at 280 nm (UV_{280}) were reduced by Fe-BTC by 62.5% and 93.48%, respectively (Table 4). Fe-BTC successfully removed lignin from both the synthetic and the P&P wastewater. Lignin and color removals were in the range of 60-90% (Tables 2 and 4). This research achieved higher lignin removal using Fe-BTC than other studies (Table 5). These results illustrate the better performance of Fe-BTC over other coagulants and flocculants to remove lignin from wastewater without the addition of flocculent aid. Moreover, it is important to note the effect that Fe-BTC had on pH, as the formation of bonds between Fe-BTC and lignin resulted in the release of hydrogen ions (H^+). In all the performed experiments, the pH of the treated samples was below 3 (Table 4).

PROPOSED MECHANISM OF LIGNIN REMOVAL BY FE-BTC IN THE COAGULATION-FLOCCULATION PROCESS

The Fe-BTC and lignin sludge collected from the coagulation-flocculation process was analyzed by FT-IR. Compared to fresh Fe-BTC, the Fe–O bond at 569 cm^{-1} band in the used Fe-BTC had disappeared (Figure 8(a)) (Klapiszewski et al. 2017b). This Fe–O bond was observed in the lignin sludge derived from the synthetic and P&P wastewater after the coagulation-flocculation process (Figure 8(b)), suggesting that Fe molecules were released from unsaturated sites of Fe-BTC and then formed new bonds with O in the methoxy group of lignin.

Therefore, the interaction between Fe-BTC and lignin in wastewater could be π–π stacking (benzene ring), which is consistent with the results reported by Deng et al. (2011) and Hasan and Jhung (2015). This explanation agrees well with the formation of F–O bond in lignin sludge. In addition, the coagulation mechanism could be used for adsorption-charge neutralization because the final pH was

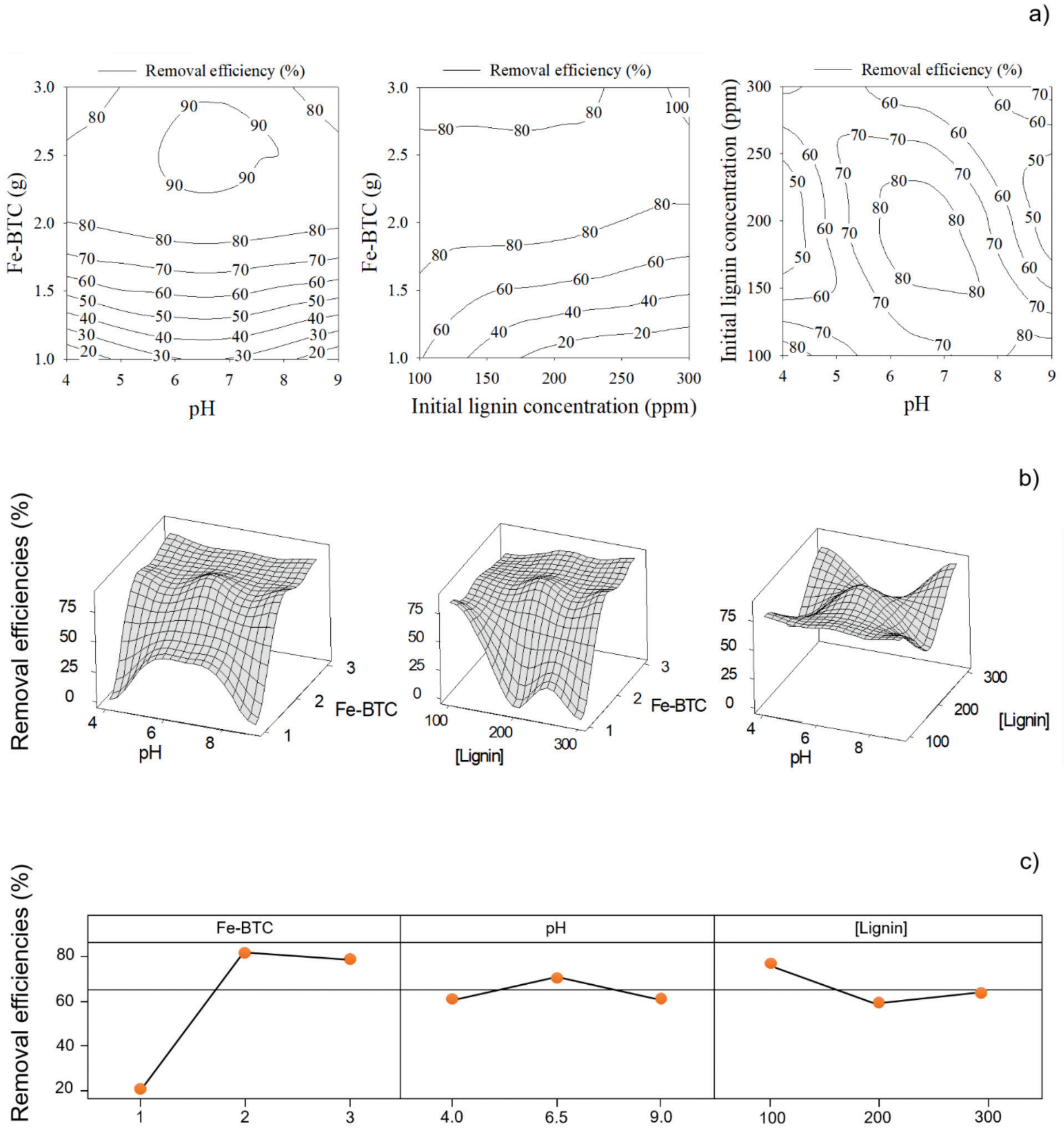

FIGURE 7. The effect of pH (X_1), Fe-BTC (g) (X_2) and the initial lignin concentration (ppm) ([lignin], X_3) on removal efficiencies: (a) contour plots, (b) surface plots and (c) main effect plots

TABLE 4. P&P wastewater characteristics before and after Fe-BTC treatment

Parameters	Before	After	% Removal
pH	7.84	2.78	-
Lignin (UV_{280})	0.80	0.30	62.50
Color	368	24	93.48

acidic (Wei et al. 2015). Figure 9 illustrates the mechanism of lignin coagulation-flocculation in aqueous solutions using Fe-BTC, based on the results found in this study and other peer-reviewed literature.

CONCLUSION

The removal of lignin from wastewater using Fe-BTC as a coagulant was investigated in batch experiments. BBD was used in the experiment design to obtain the optimal condition for the highest lignin removal efficiency. Influential factors in this study included pH, the amount of Fe-BTC and the initial lignin concentration. The quantity of Fe-BTC was found to be the most significant factor to achieve a higher efficiency of lignin removal. Lignin removal in real P&P wastewater was consistent with the results obtained from the synthetic lignin solution. The high lignin and color removal efficiencies of Fe-BTC

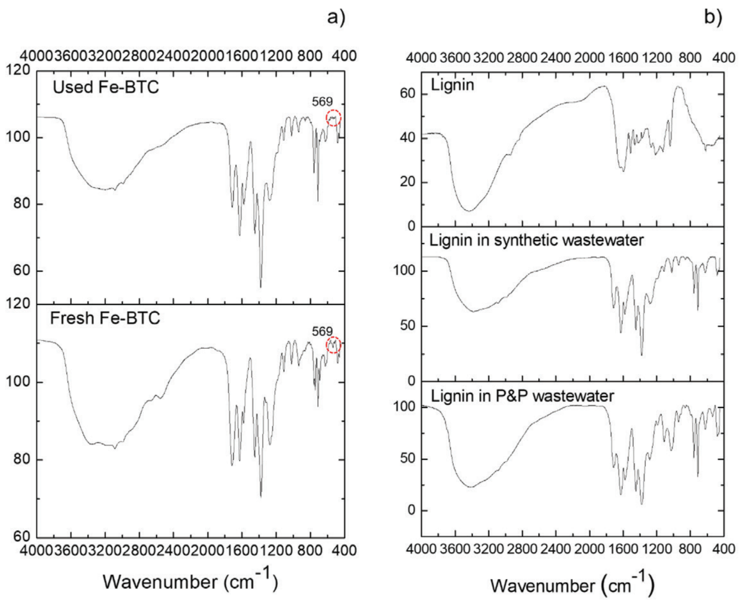

FIGURE 8. FT-IR spectra of (a) Fe-BTC and (b) lignin

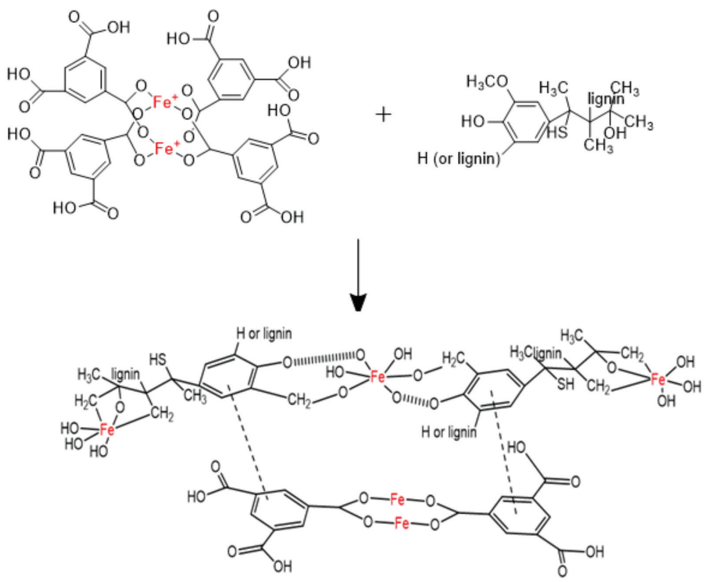

FIGURE 9. The proposed mechanism of lignin coagulation-flocculation using Fe-BTC

TABLE 5. Comparison of lignin removal efficiency using different coagulants and flocculants

Coagulants	Flocculants	Lignin removal efficiency (%)	Reference
Fe-BTC	-	87	This study
Aluminium chloride poly-diallyldimethy ammonium chloride (polyDADMAC)	starch-g-PDMC	83.4	Andersson et al. 2012
	calcium lactate	50-68	Zahrim et al. 2015
	Acrylamide + Starch + 2-Methyarcyloyloxyethyl trimethyl ammonium chloride (DMC)	83.4	Wang et al. 2011
Aluminum sulphate	Modified natural polymer, starchg-PAM-g-PDMC [polyacrylamide and poly (2-methacryloyloxyethyl) trimethyl ammonium chloride]	72.7	Wang et al. 2011
	Poly-ethylene	15	Shi et al. 2011

suggest its potential use as a coagulant for P&P wastewater treatment. The polynomial model developed based on these influential factors could explain more than 80% of the lignin removal variability. The high predictive power of the model (R^2 = 88.64%) indicates a high model accuracy and the experimental results are predictable.

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