

Utilization of galactomannan from spent coffee grounds as coagulant aid to treat synthetic Congo red wastewater

Hans Kristianto (✉ hans.kristianto@unpar.ac.id)

Parahyangan Catholic University Faculty of Industrial Technology: Universitas Katolik Parahyangan
Fakultas Teknologi Industri <https://orcid.org/0000-0003-4747-4361>

Sekar Astari Saraswati

Parahyangan Catholic University Faculty of Industrial Technology: Universitas Katolik Parahyangan
Fakultas Teknologi Industri

Susiana Prasetyo

Parahyangan Catholic University Faculty of Industrial Technology: Universitas Katolik Parahyangan
Fakultas Teknologi Industri

Asaf K Sugih

Parahyangan Catholic University Faculty of Industrial Technology: Universitas Katolik Parahyangan
Fakultas Teknologi Industri

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Introduction

Coagulation and flocculation is a water-wastewater treatment process that is still widely used due to its high efficiency and effectiveness. Inorganic coagulant such as aluminium sulphate, ferrous sulphate, and ferric chloride are commonly used in various treatment conditions. However there are some drawbacks of the previously mentioned metallic salts, such as relatively high coagulant costs, neurotoxic, corrosive and also high sludge volume generation. Therefore many efforts to substitute and reduce utilization of inorganic coagulants have been extensively studied in recent years; one of them is utilization of natural coagulant and coagulant aid.

Generally, based on the active ingredients, natural coagulant could be classified as protein, polyphenol, and polysaccharide (Kristianto 2017). Protein from *Moringa oleifera* (Baptista et al. 2017), *Moringa stenopetala* (Dalvand et al. 2016), *Leucaena leucocephala* (Kristanda et al. 2020; Kristianto et al. 2020), *Cocos nucifera* (Fatombi et al. 2013), etc. as active coagulating agent has been extensively studied. The utilization of protein based natural coagulant – coagulant aid showed prospective results in treating water and wastewater. However the purification of protein extract poses some challenges to its application (Choy et al. 2014). The research polyphenol based coagulant is relatively limited. Among wide range of polyphenols, only tannin based coagulant is explored and commercialized (Kuppusamy et al. 2015). On the other hand, polysaccharide is a promising alternative coagulant – coagulant aid, due to its abundance. Polysaccharide as natural coagulant could be obtained from plant and non-plant. Non plant based polysaccharides such as chitosan and sodium alginate have been studied and used to treat water and wastewater (Saranya et al. 2014). Plant based polysaccharide comprises in various form, such as starch, pectin, gum, etc. Rice, wheat, corn, and sago starch have showed a

promising result as natural coagulant (Teh et al. 2014; Aziz and Sobri 2015; Choy et al. 2016); however its utilization could pose some problems due to food issues, thus non-food alternatives should be explored to handle this problem.

Coffee beans are rich in polysaccharides and could become a promising source. With world coffee consumption 10 million tons in 2019/2020 (ICO 2020), abundant waste is generated. It is known from coffee cherry, 49 to 53%w would become spent coffee grounds that are usually discarded without further use (Vandepoosele et al. 2020). On the other hand, it is known that 50% of the beans dry weight is polysaccharides, and half of it is galactomannan fraction (Moreira et al. 2015). Galactomannan is a polymer chain of β -(1 \rightarrow 4)-mannose as main backbone that interrupted with glucose and branched with α -(1 \rightarrow 6)-galactose or arabinose (Buckeridge et al. 2000; Moreira et al. 2015). Galactomannan from seeds such as *Ipomoea dasysperma* (Sanghi et al. 2006a), *Cassia javahikai* (Sanghi et al. 2006b), *Cassia obtusifolia* (Shak and Wu 2015), *sesbania* (Chua et al. 2020), and *Guazuma ulmifolia* (Tavares et al. 2020) have been utilized as coagulant aid. It was evident from the previously mentioned researches, galactomannan could assist coagulation process by increasing coagulation performance of inorganic coagulants (FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, etc.)

In this study, we focused on utilization of galactomannan extracted from spent coffee grounds as coagulant aid. Various coagulation parameters such as galactomannan dosage and Congo red concentration were explored. To the best of authors knowledge, similar study has never been done before, thus the results obtained in this study could open up the possibility for utilization of spent coffee grounds.

Methodology

Extraction of galactomannan

Spent coffee grounds were collected from coffee shops in Bandung, Indonesia. The coffee grounds were then washed using distilled water and then dried using tray dryer at 50°C until the water content below 10%w. The dried spent coffee grounds were then sieved using standard sieve to obtained grounds size 80-10 mesh. The extraction process was done by mixing spent coffee grounds with distilled water at feed to solvent ratio 1:20 (w/v). The extraction was done at 70°C and neutral pH for 2h. After extraction, the extract was then separated and then ethanol (90% v/v) was added to separate the galactomannan from the solvent at ethanol to extract ratio of 3:1 (v/v). The galactomannan would be obtained as whitish precipitate after 48h. The precipitate was then separated using muslin cloth and then dried using tray dryer at 50°C until the water content below 10%w. The dried precipitate was stored in a desiccator for further analysis and coagulation study. The obtained galactomannan was characterized using Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscopy (SEM-EDS; Hitachi SU3500), X-ray Diffraction (XRD; Bruker D8 Advance with Cu K- α radiation) and Fourier Transform Infrared (FTIR) Spectroscopy (Prestige 21 Shimadzu Instruments) by KBr pellet method.

Jar test study

The coagulation test was done using a standard jar test apparatus. Congo red solution was used as a model dye for the coagulation study. A stock solution of 1g/L was prepared and further diluted to obtain solution with desired concentration. The coagulation study was done at various galactomannan dosage and Congo red concentration, presented in Table 1, at fixed pH 6.0, which is known as the optimum pH for FeCl₃ (Boughou et al. 2018; Bakar and Halim 2013), and FeCl₃ dosage of 80 mg/L. The coagulation was done by mixing Congo red solution, FeCl₃ and galactomannan at rapid mixing of 200 rpm for 3 min, followed by slow mixing (60 rpm, 30 min) and settling (1 h). The initial (C_i) and final concentration (C_e) of Congo red was measured using

a visible spectrophotometer (Genesys 20) at its maximum wavelength of 500 nm. Congo red removal was calculated using Equation 1. The sludge volume formed after coagulation was measured after 1 h settling by using Imhoff cone, and calculated by following Equation 2. The obtained sludge with and without galactomannan was characterized using SEM-EDS to observe the morphology and atomic composition.

$$\% \text{ removal} = \frac{C_e - C_i}{C_i} \times 100\% \quad (1)$$

$$\text{sludge volume} = \frac{V_{\text{sludge}} \text{ (mL)}}{V_{\text{solution}} \text{ (L)}} \quad (2)$$

[Table 1]

Coagulation isotherm adsorption study

Investigation of the possible coagulation mechanism in this study was done by approach of isotherm adsorption models, namely the Langmuir, Freundlich and Brunauer – Emmett – Teller (BET) isotherm models. Coagulation adsorption capacity (q_e ; mg/mg) was calculated from the data of various Congo red concentration coagulation study by following Equation 3, where m is the coagulant dosage (mg/L) and V is the total solution volume (L).

$$q_e = \frac{(C_i - C_e)}{m} \times V \quad (3)$$

Results and Discussion

Characterization of galactomannan

The characteristics of galactomannan extract from spent coffee grounds are presented in Figure 1. Based upon the observation of galactomannan morphology using SEM (Fig 1.a), it

could be observed that the galactomannan extract possessed irregular shape with some cavities on the surface. Similar shape was reported by previous researchers (Niknam et al. 2020; Prashanth et al. 2006). Furthermore from the EDS analysis (Figure 1.b), the extract consisted of C and O atom, indicated the obtained extract was relatively pure. From the XRD spectra (Figure 1.c), it could be observed that the galactomannan was in amorphous phase. A sharp crystalline peak was observed at 2θ of 20° , similar with galactomannan from guar (Mudgil et al. 2012; Liyanage et al. 2015), fenugreek seeds (Niknam et al. 2020), and *Leucaena leucocephala* seeds (Mittal et al. 2016). The FTIR spectra is presented in Figure 1.c with several notable peaks discussed as followed. It could be observed that peak at 3388.9 cm^{-1} due to O-H stretching that comes from O-H functional groups in carbohydrates and moisture. The presence of moisture is confirmed by the existence of peak at 1643.35 cm^{-1} (Tarigan et al. 2020). The peaks around $2800\text{-}3000\text{ cm}^{-1}$ indicate C-H stretching, while peaks around $1000\text{-}1200\text{ cm}^{-1}$ indicate the presence of C-O-C and C-O functional groups (Mittal et al. 2016). The peak at 812.03 cm^{-1} associated with the presence of anomeric configuration and 873.75 cm^{-1} that indicate glycosidic bonds of $\alpha\text{-D-galactopyranose}$ and $\beta\text{-D-mannopyranose}$ units (Rashid et al. 2018; Nascimento et al. 2019). Based on previously discussed characterization, it could be confirmed that the extract obtained from spent coffee grounds was galactomannan in relatively pure condition. This galactomannan was then further used as the coagulant aid in this study.

[Figure 1]

Effect of galactomannan dosage

The effect of galactomannan addition in the coagulation system is presented in Figure 2. It could be observed that without any coagulant aid, the FeCl_3 could give 27.5% removal of

Congo red. Addition of galactomannan increased the %removal with the highest removal of 40% was obtained at galactomannan dosage of 80 mg/L. This increase was possible due to interparticle bridging mechanism of galactomannan that played an important role in aggregation and flocs formation that resulted in higher %removal (Sanghi et al. 2006b). Further addition of galactomannan did not give any increase to the coagulation performance, instead slight decrease of %removal was observed. This was possible due to overdosing of galactomannan resulted in saturation of polyelectrolyte bridge sites with adsorbed Congo red molecules that could cause electrostatic steric repulsion (Awang and Aziz 2012). The repulsion could cause colloid re-stabilization phenomenon, thus lowering the coagulation performance (Choy et al. 2016). Similar colloid re-stabilization due to overdosing of coagulant aid also reported by previous researchers (Awang and Aziz 2012; Wong et al. 2007; Al-Hamadani et al. 2011). The generation of sludge volume was gave similar trend with the %removal, where increase of galactomannan dosage gave higher sludge volume. At removal of 27.5%, no sludge volume could be observed due to low removal. With addition of galactomannan, the sludge volume also increased, confirming the role of galactomannan as particle bridges that helped formation of flocs. At overdosing condition, the sludge volume was slightly higher that possibly due to repulsion forces between flocs that making the sludge become more voluminous (Kristianto et al. 2019).

[Figure 2]

Effect of Congo red concentration

The study of effect of Congo red concentration was done at pH 6.0 and galactomannan dosage of 80 mg/L which gave the highest Congo red removal. The profile of % removal and sludge volume at various Congo red concentrations without and with galactomannan are

presented in Figure 3. It could be observed that high removal was obtained at low Congo red concentration (20 ppm) due to adequate presence of coagulant (FeCl_3) to neutralize the negatively charged Congo red molecules. Along with the increase of Congo red concentration, at the same coagulant dosage, the % removal was decreased due to insufficient active coagulating agent in the solution to neutralize Congo red molecules. Comparing the presence of galactomannan during coagulation, it could be observed that galactomannan increase the %removal, even at high Congo red concentration (60-70 ppm), where in FeCl_3 only no removal was observed. We speculate that galactomannan and Fe^{3+} ions could form complexes around coagulation pH that could increase the coagulation efficiency. It is known that galactomannan and Fe^{3+} could form metal-biopolymer complex at wide pH range (Mercê et al. 2001). Synergistic effect between natural active ingredient with metal ions has been reported before to increase coagulation performance (Okuda et al. 2001; Moral et al. 2016; Devrimci et al. 2012).

[Figure 3]

The sludge obtained from the coagulation process at Congo red concentration of 20 mg/L was furthermore observed using SEM-EDX, presented in Figure 4. It could be observed that the sludge from coagulation using FeCl_3 only (Figure 4.a) gave relatively compact structure, compared with flaky and smaller structure under the presence of galactomannan (Figure 4.b). This observation could justify the obtained sludge volume with galactomannan was higher compared to FeCl_3 only, as smaller sludge particles could result in more porous sludge, reflected in higher sludge volume (Kristianto et al. 2019). The atomic composition of both sludge samples gave similar elements, with different composition. The sludge obtained from coagulation using coagulant aid (Figure 4.d) gave higher carbon and oxygen content, possibly due to the presence of galactomannan in the sludge.

[Figure 4]

Isotherm adsorption

It is known that both charge neutralization and interparticle bridging coagulation mechanisms are preceded by adsorption which the rate determining step of the coagulation process. Based on this assumption, utilization of isotherm adsorption models is justified. The Langmuir isotherm model assumed on monolayer – homogenous adsorption process with finite number of adsorption sites (Foo and Hameed 2010). The Langmuir equation and its linearized form is presented in Equation 4 and 5, respectively, where K_L (L/mg) is Langmuir constant and q_m (mg/mg) the maximum adsorption capacity. Furthermore, a dimensionless constant called separation factor (R_L) could be calculated to define favorability of the adsorption process (Foo and Hameed 2010), presented in Equation 6.

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (4)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (5)$$

$$R_L = \frac{1}{1 + K_L C_i} \quad (6)$$

The Freundlich isotherm model is based on multilayer adsorption, non-uniform distribution on a heterogeneous surface (Al-Ghouti and Da'ana 2020). The Freundlich equation and its linearized form is presented in Equation 7 and 8, respectively. The K_F is Freundlich affinity constant (L/mg), $1/n$ is dimensionless constant to describe the adsorption favorability.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

$$\log qe = \frac{1}{n} \log Ce + \log K_F \quad (8)$$

The BET isotherm model is said to be modification from Langmuir model, where in BET model, the adsorbate was assumed to be multilayer - randomly distributed on the surface of adsorbate (Al-Ghouti and Da'ana 2020). The BET equation and its linearized form is presented in Equation 9 and 10, respectively, where A is the BET constant and X_m is the amount of adsorbate adsorbed in form of monolayer (mg/mg) (Hossain et al. 2019).

$$qe = \frac{ACeX_m}{(C_i - Ce) \left[1 + (A-1) \frac{Ce}{C_i} \right]} \quad (9)$$

$$\frac{Ce}{(C_i - Ce)qe} = \frac{(A-1) Ce}{AX_m C_i} + \frac{1}{AX_m} \quad (10)$$

The parameters of Langmuir and BET isotherm models are presented in Table 2. It could be seen based on the high R² values, the coagulation process could be described by Langmuir isotherm model. Furthermore for coagulation using FeCl₃ the R_L values were in range 0 < R_L < 1, indicating a favorable adsorption. However the Langmuir isotherm model could not be used to describe the adsorption-coagulation process with the presence of galactomannan, depicted with negative K_L and R_L value. The negative value of K_L could indicate the coagulation mechanism was multilayer in a non-uniform or random distribution (Hossain et al. 2019). The Freundlich constant (1/n) for FeCl₃ coagulation showed a negative value, confirming that the adsorption process was monolayer. As for the coagulation in the presence of galactomannan, the adsorption was favorable, as shown in the 1/n value between 0 and 1. Furthermore, it could be said that the adsorption was heterogeneous as the value was close to 0 (Foo and Hameed 2010). However the low R² value for both coagulation conditions might implicate that Freundlich isotherm model was not suitable to describe the adsorption-coagulation process in this study. The BET isotherm

model could be moderately fitted to the experimental data, as shown in R^2 value around 0.88. Negative value of A could indicate the surface of coagulant was already saturated with the dye and the adsorption was in multilayer (Hossain et al. 2019; Ngteni et al. 2020). Based on suitability of the isotherm models, it could be considered that the Congo red coagulation using FeCl_3 was monolayer – homogeneous adsorption. Similar observation was reported when using FeCl_3 as coagulant (Agbovi and Wilson 2017; Kastl et al. 2004). On the other hand, under the presence of galactomannan as coagulant aid, the adsorption was multilayer and heterogeneous, indicating an interparticle bridging mechanism of polymer (galactomannan) during colloid aggregation (Szilagyi et al. 2014).

[Table 2]

Conclusion

In this study we have successfully utilized galactomannan extract from spent coffee grounds as natural coagulant aid. It was obtained at various galactomannan dosages; the increase of galactomannan dosages increased the removal of Congo red until 80 mg/L, while further addition did not further influence the dye removal. At various Congo red concentrations, it could be observed that high removal was obtained at low Congo red concentration of 20 mg/L, while at Congo red concentration above 60 mg/L, low removal was observed when only FeCl_3 was used as coagulant. In other hand, under the presence of galactomannan, apparent removal was still obtained even at high Congo red concentration of 70 mg/L. Furthermore, from the fitting of experimental data to adsorption isotherm models, it was obtained that without galactomannan, the adsorption was monolayer and homogenous. While with the presence of galactomannan as

coagulant aid, the adsorption became multilayer and heterogeneous due to interparticle bridging mechanism of galactomannan.

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Table 2. Parameters of Langmuir, Freundlich, and BET isotherm models

Table 1. Variation of initial galactomannan dosage and Congo red concentration in this study

Study	pH	FeCl₃ (mg/L)	Galactomannan (mg/L)	Congo red concentration (mg/L)
Effect of galactomannan dosage	6	160	0 - 140	50
Effect of Congo red concentration	6	160	Best galactomannan dosage	20-70
	6	160	0	20-70

Table 2. Parameters of Langmuir, Freundlich, and BET isotherm models

Coagulant	Langmuir			Freundlich			BET		
	K_L	q_m	R²	K_F	1/n	R²	A	X_m	R²
FeCl ₃	37.443	0.099	0.978	4.539	-0.55	0.397	-621.3	1.27×10 ⁻⁵	0.879
FeCl ₃ + galactomannan	-0.948	0.080	0.997	0.0032	0.0105	0.015	-304.5	5.0×10 ⁻⁴	0.888

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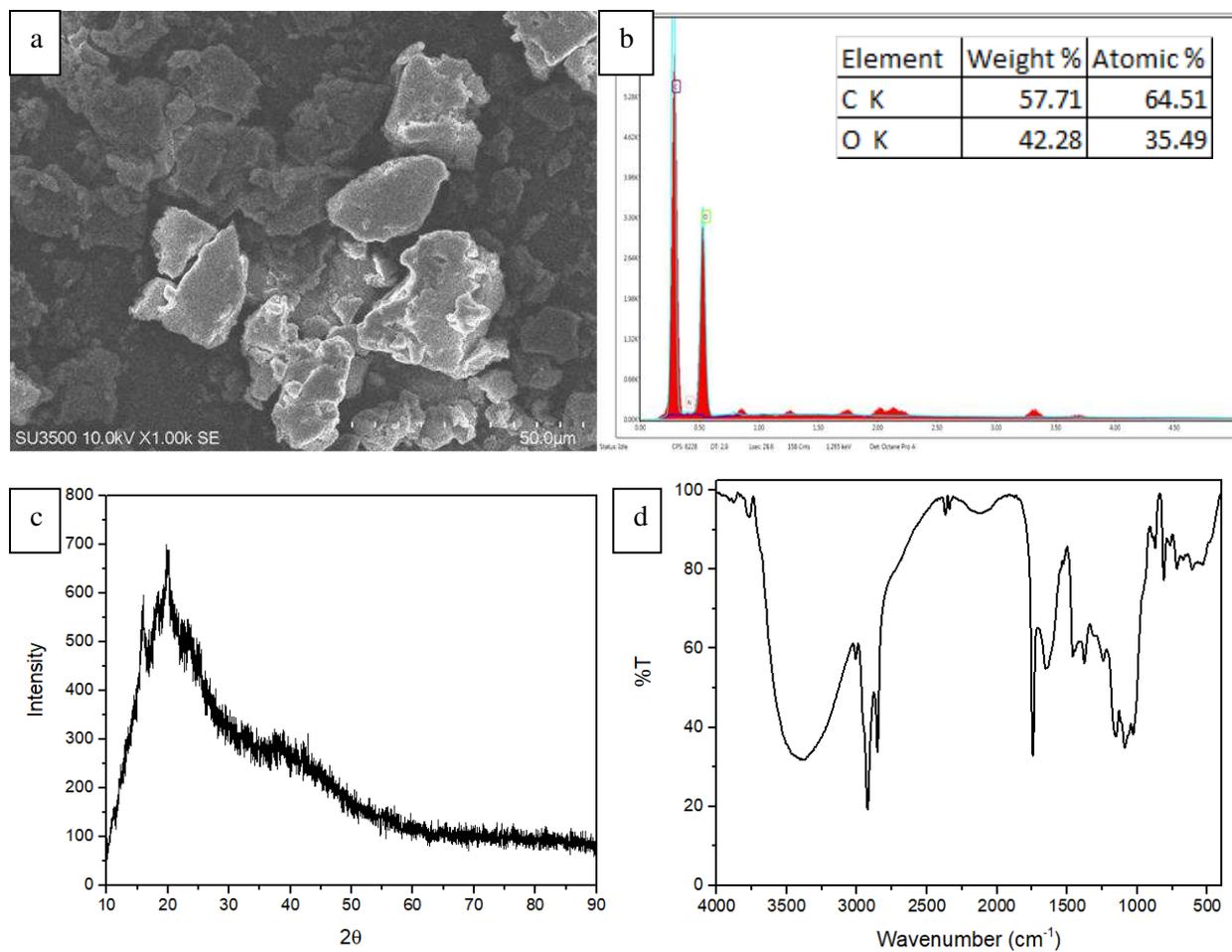


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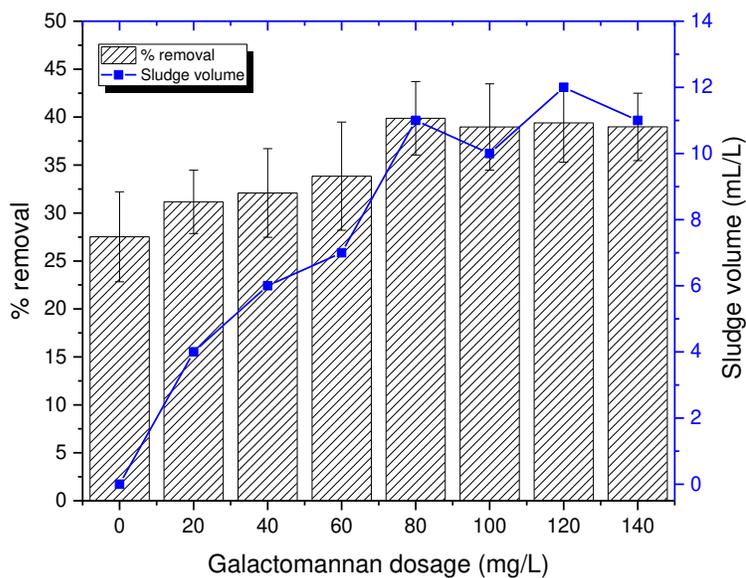


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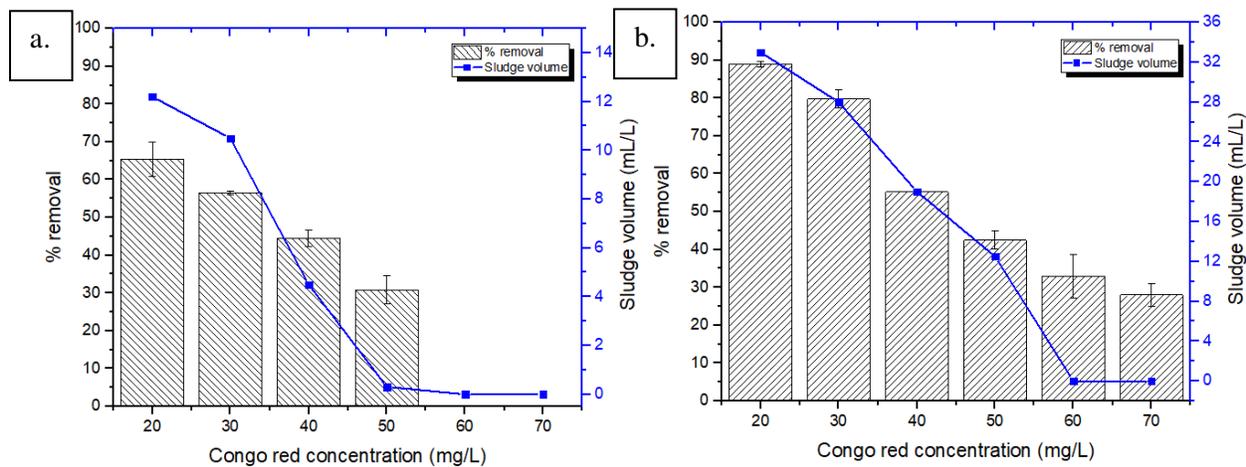


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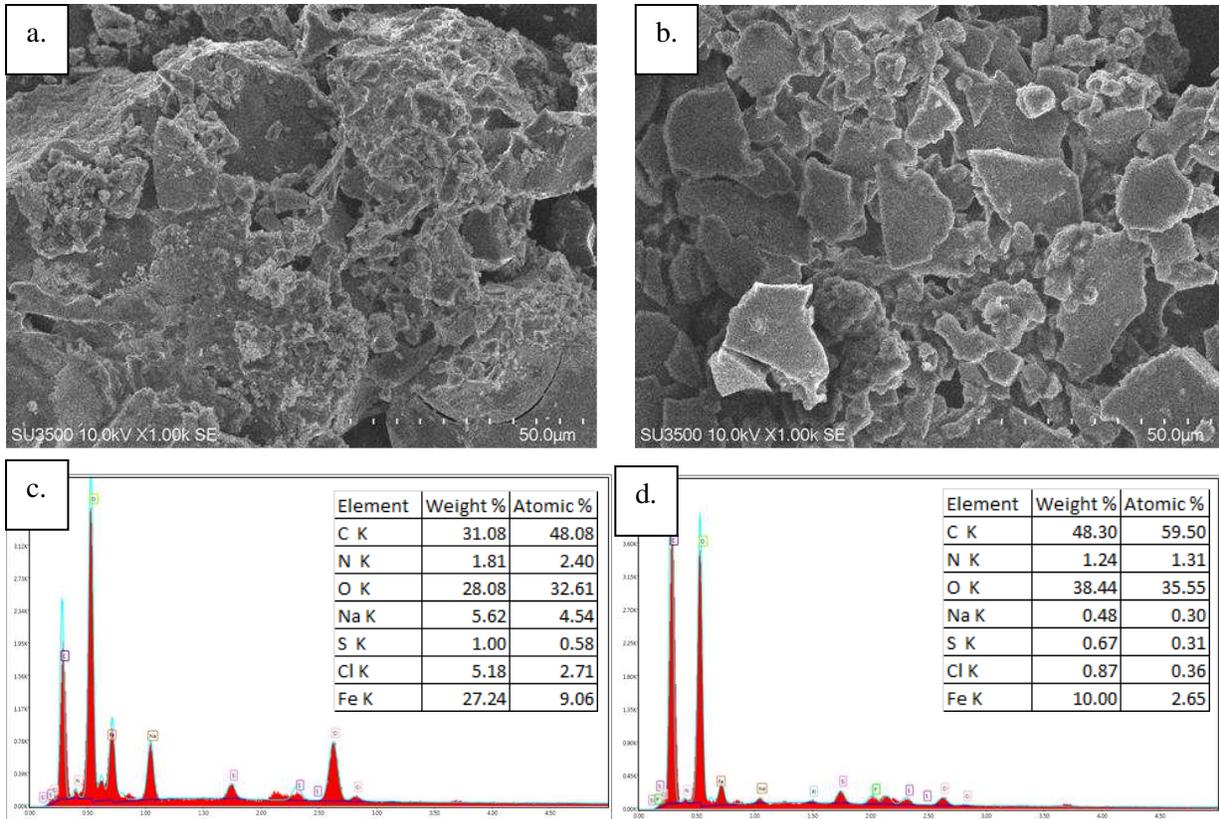


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