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Application of Cationic Surfactant Modified Mengkuang Leaves (*Pandanus atrocapus*) for the Removal of Reactive Orange 16 from Batik Wastewater: A Column Study

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ABSTRACT

The feasibility of Mengkuang leaves (*Pandanus atrocarpus*) as a non-conventional low-cost adsorbent for the removal of an anionic dye, Reactive Orange 16 (RO16), was investigated. Among the dyes that have been commonly used in the Batik industry was reactive dye. In this study, Mengkuang leaves were chemically modified with cetyltrimethylammonium bromide (CTAB), a cationic surfactant, to improve their adsorption performance toward anionic dyes. The adsorbent's morphological characteristics were analyzed using a scanning electron microscope (SEM). The surface of modified Mengkuang leaves seems to be irregular and uneven, with more porous structures than raw Mengkuang leaves. Adsorption of RO16 dye in fixed bed column using modified Mengkuang leaves adsorbent indicated the breakthrough time increased at higher bed height and lower flow rate. The breakthrough times for bed height of 0.5, 2, and 4 cm were at 16, 68, and 165 min, respectively. Meanwhile, breakthrough time for the flow rate of 2,5 and 7 $mL.min^{-1}$ were at 327, 104, and 43 min, respectively. However, the study utilizing raw Mengkuang leaves showed no significant removal of RO16. Thus, it can be concluded that the cationic surfactant modification of Mengkuang leaves is advantageous for anionic dye removal. This anionic dye removal is significantly influenced by column parameters such as bed height and flow rate as the plotted breakthrough curves obtained from experimental data were similar to the typical breakthrough curve. When applied to the Yoon-Nelson model, the adsorption data provided the best fit with the R^2 value above 0.95. The time taken for the breakthrough is very similar to model prediction values. Experiments with real batik dye wastewater showed the immense potential of modified Mengkuang leaves where total removal of real Batik wastewater was instantaneous.

INTRODUCTION

Batik industry is one of the oldest cottage textiles industries in Malaysia. More than 1500 batik factories are distributed mostly in Kelantan and Terengganu, Malaysia (Rashidi et al. 2013). The resulting waste is mostly discharged into water bodies with minimal or in most cases it was directly discharged without any prior treatment (Mahmudi et al. 2020). This is because most of these industries are typically practiced on a small scale with no appropriate waste disposal system (Sridewi et al. 2011). Only 5% of these dyes are fixed during the coloring process, where the rest are discarded as liquid waste (Wibowo et al. 2017). Among the many dyes, azo reactive dyes represent the large group as the production volume and number are concerned (Mitrović et al. 2012), where the reactive dyes are the most used in batik textiles industries (Rashidi et al. 2013). The azo reactive dye, which compounds contain one or more azo groups (–N=N–), could produce potentially carcinogenic in aromatic amines via metabolic cleavage of the azo linkage (Mitrović et al. 2012). Due to this, remediation of dye wastewater is often crucial. Moreover, the wastewater generated from this industry contains a non-biodegradable organic compound, which can cause ecological contamination, especially for the aquatic environment (Wibowo et al. 2017).

Many techniques are employed for dye-containing batik wastewater removals such as the application of hybrid wetland (Rahmadyanti et al. 2020) and membranes (Febriasari et al. 2021). However, due to their simple yet efficient effectiveness, adsorption methods are often preferred (Yagub et al. 2014). The use of plant-based sorbents has been shown to work well for the removal of dye where different biomass has been successfully investigated for the removal of dye (Yagub et al. 2014). Different functional groups such as carboxyl, hydroxyl, sulfate, phosphate, ether, and amino groups are available on the plant-based sorbent, which has been identified to function as adsorption sites (Ngah & Hanafiah 2008). In this study, Mengkuang leaves, a Pandanus family, have been selected for potential adsorbent of RO16, an azo reactive dye. Mengkuang is the Malaysian name for the *Pandanus atrocarpus*, a plant belonging to the Pandanaceae family (Sheltami et al. 2012). It can be found in wet, damp places such as mangroves and tropical jungles. Mengkuang leaves specifically have not been researched for any adsorbent purpose. But, the Pandanus family was found successful in removing aqueous-based pollutants, such as methylene blue dye (Ismail et al. 2013), copper (Ngadi et al. 2015), and lead (Abdullah & Loo 2006).

Despite the advantages of plant-based sorbent, many works found the less satisfactory raw biomass adsorbent to remove anionic dye due to negative surface charge on the biomass surface (Ibrahim et al. 2010a). This observation has been reported by many works (Oei et al. 2009). Due to this, surfactant modification was employed to render the surface to a positive potential, which is conducive to removing anionic contaminants. This kind of modification has been reported by many works (Akl et al. 2013, Bingol et al. 2004, Ibrahim et al. 2010b). Ibrahim et al. (2010b) found a vast improvement in anionic dye removal, Reactive Blue 4, upon using a modification of barley straw with cationic surfactant for anionic reactive dye adsorption. Hence in this work, the Mengkuang leaves were modified with a cationic surfactant, cetyltrimethylammonium bromide (CTAB). CTAB consists of a 19-carbon chain tail group, is a quaternary ammonium surfactant. CTAB has been used to chemically modify adsorbent surfaces, particularly for removing anionic contaminants in some works (Akl et al. 2013, Bingol et al. 2004). The surfactant was also applicable for attapulgite modification in the enhancement of anionic dye adsorption (Xu et al. 2015).

In this paper, a study on the physicochemical change of CTAB-modified Mengkuang leaves and its applicability for removing model anionic dye, RO16 as well as real wastewater from batik industries, was presented. Based on the literature search, limited studies on the utilization of modified surfactant adsorbent for removal of dye contaminants, especially real dye from batik wastewater were reported, thus making this study even more interesting.

A continuous column experiment was applied to explore the effects of parameters such as the bed height of the adsorbent and inlet dye flow rate on the column breakthrough volume. The data was fitted to the Yoon-Nelson model to determine the fitness of the column experimental data.

MATERIALS AND METHODS

The Mengkuang leaves were collected, cut into smaller pieces, washed, and dried under sunlight, and further dried in the oven overnight at 80°C. It was then ground to the powder form and labeled as Raw Mengkuang Leaves (RML). The cationic surfactant modification method was adopted from (Zhou et al. 2015) with some modifications. A mixture of RML powder and 200 mL, 1% (w/v) cetyltrimethylammonium bromide (CTAB, Aldrich, USA) solution, were shaken by an orbital shaker at 180 rpm at room temperature for 24 h. RML powder was separated from the mixture and washed with distilled water to remove superficially retained CTAB. Finally, the modified RML powder was dried in an oven at 60°C overnight and labeled as Modified Mengkuang Leaves (MML). The anionic dye solution, Reactive Orange 16 (RO16, MW = 617.54 g.mol^{-1}) obtained from Aldrich, USA, was prepared by dissolving the dye in distilled water. The dye concentrations were measured using the HACH DR2800 Portable spectrophotometer at a maximum absorbance wavelength of 492 nm. The chemical structure of RO16 is shown in Fig. 1.

The RML and MML were then characterized physically and chemically by Fourier Transform Infrared Spectroscopy (Thermo Scientific Nicolet 6700 FT-IR spectrophotometer, USA) at a scanning range of 650-4000 cm^{-1}. Meanwhile, the surface morphologies were observed directly using a Tabletop Scanning Electron Microscope (SEM, Hitachi TM3030 Plus, Japan) with an acceleration voltage of 5kV and magnification of 1000x.

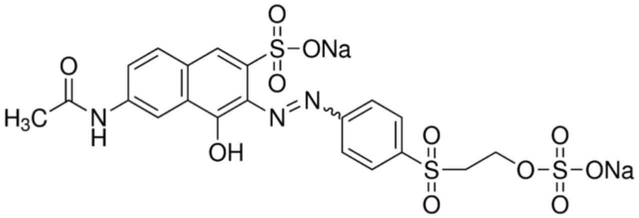

Fig. 1: Chemical structure of RO16.

General Adsorption Column Studies

Column studies were conducted in a transparent cylindrical polypropylene column (2.7 cm and 10 cm height), packed with a known quantity of MML. A layer of the plastic sieve was attached at the bottom of the column. A known amount of the MML was packed in the column to produce the desired bed heights of the adsorbent (0.5, 2, and 4 cm). A 100 mg.L^{-1} of RO16 dye solution was pumped upward through the column at the desired flow rates (2, 5, and 7 mL.min^{-1}) controlled by a peristaltic pump. The dye solutions at the outlet of the column were collected at regular time intervals. The concentration of the dye effluent was then determined using a spectrophotometer. Breakthrough time was set at 30% of the effluent RO16 to feed concentration, as suggested by Goel et al. (2005). Column operation was stopped when the effluent concentration exceeded 99.0% of its initial concentration. All experiments were carried out at room temperature. The effects of experimental column parameters such as bed height, feed flow rate on the dye removal were investigated by varying the one parameter above while at the same time keeping the other parameters constant. To study the effect of flow rate and bed height, the flow rate was run at 2-7 mL.min^{-1}, whereas the bed height was varied at 0.5 to 4 cm, respectively.

Column Experiment for Real Batik Dye Wastewater

To prove the applicability of MML in remediating batik dye wastewater, the MML was further tested with real batik dye wastewater. The wastewater was collected from Master Wan Batik Industry, located in Dengkil, Selangor, Malaysia at the discharged point. The collected wastewater was preserved with few drops of 1% concentrated nitric acid (HNO_3) and stored in the refrigerator for further use. The column was packed with MML (2 cm height), and real batik dye wastewater was pumped through the column at a flow rate of 5 mL.min^{-1}. The effluent was collected at the outlet of the column every 1 min. The color variations of the batik dyes were then measured using a stored program in a HACH 16 DR2800 Portable spectrophotometer at 465 nm wavelength, utilizing the color, true and apparent (Platinum-Cobalt (Pt-Co)) method. The results are expressed in mg/L Pt-Co.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FT-IR) was used to examine the surface groups of the adsorbents and to identify some characteristic functional groups. The FT-IR spectra of RML, MML, and dye-loaded MML were studied in the range of 650-4000 cm^{-1}. The indication of CTAB impregnated on Mengkuang leaves surface was observed at peaks of 2921.66 and 2852.25 cm^{-1}, where's these two peaks were not visible in RML spectra. The same conclusion has been made by Akl et al. (2013), where they assigned these peaks to the asymmetric and symmetric stretching vibrations of the CH_3 and CH_2 of the aliphatic chain of the CTAB. Meanwhile, Spectra for dye loaded- MML does not differ much, except that the peaks at 2921.66 and 2852.25 cm^{-1} in MML are shifted to 2922.32 and 2851.96 cm^{-1} in loaded MML with a significant increase in intensity This indicate the dye component combining with hydrophobic groups of surfactant (Ibrahim et al. 2010a). A preliminary study done by soaking the modified MML in DI water resulted in a negligible amount of CTAB being desorbed, indicating the existence of intermolecular attraction between CTAB and MML surface. A similar conclusion has been suggested by Ibrahim et al. (2010) in their study on the modification of barley straw using a cationic surfactant, hexadecylpyridinium chloride monohydrate (CPC).

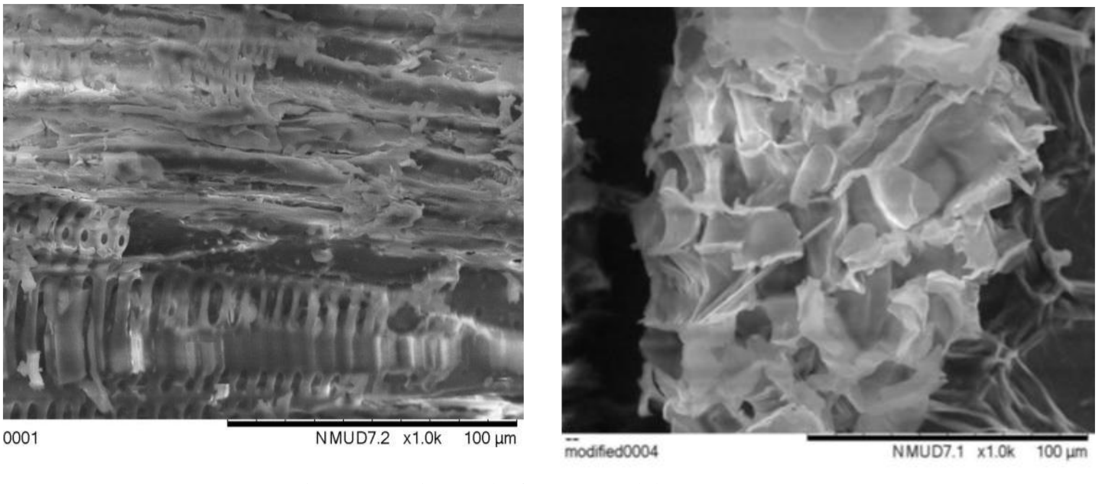

Fig. 2: SEM micrograph of (a) RML and (b) MML at 1000x.

Surface Morphological of Mengkuang Leaves

The adsorbent's surface features and morphological characteristics were studied using a scanning electron microscope (SEM, Hitachi TM3030 Plus, Japan). Fig. 2 shows the images of Mengkuang leaves before and post-modification with CTAB. The surface of MML seemed to be irregular and uneven, with more porousness compared to RML. According to Wang et al. (2020), this feature can be considered as an excellent character with a high possibility for dyes to be adsorbed on its surface. Meanwhile, Hameed and El-Khaiary (2008) suggested uneven and rough surface of an adsorbent offered more opportunity for dyes to be trapped or adsorbed.

Adsorption Column Studies

The effect of bed height on the adsorption performance of MML has been investigated by varying the bed height from 0.5 to 4 cm. The flow rate was fixed at 5 mL.min^{-1}, and the initial concentration of RO16 is at 100 mg.L^{-1}. From breakthrough curves, it was found that by increasing the bed height, the breakthrough time (t_b) increased accordingly. The dye solution had more contact time with the adsorbent, resulting in high dye removal. (Rouf & Nagapadma 2015). The t_b values increased from 16 to 165 min, as the bed height was increased from 0.5 to 4 cm. An increase in the adsorbent's surface area may provide more binding sites for adsorption (Zulfadhly et al. 2001), thus enhancing the breakthrough time. A similar trend was found for the column breakthrough volume (V_b) (Table 1). The effects of the flow rate on the adsorption of RO16 dyes have been studied over a range from 2 to 7 mL.min^{-1}. The bed height was 2 cm, and the initial concentration of RO16 was at 100 mg.L^{-1}. It can be seen that the breakthrough generally occurred faster at a higher flow rate, and it would take less time for the bed to get saturated. Moreover, the higher turbulence at a higher flow rate may cause a weaker interaction and interparticle mass transfer between the dye molecules and the biosorbent. However, at a lower flow rate, the dye solution has adequate time to get adsorbed on the adsorbent surface (Rouf & Nagapadma, 2015). Table 2 shows the breakthrough time decreased from 327.5 to 42.85 min, increasing the flow rate from 2 to 7 mL.min^{-1}. At a higher flow rate, the contact time of RO16 in the column was shorter, thus decreasing breakthrough time. A consistent trend was as well found for V_b. A similar observation has been made by Jain & Gogate (2017).

Modeling of Column Data: Yoon-Nelson Model

The Yoon-Nelson model basically predicts the possibility of adsorbate breakthrough being proportional to the rate of reduction and the adsorption of adsorbate (Bharathi & Ramesh 2013), but it does not describe the sorption mechanism. The column data were fitted to the Yoon-Nelson model (Yoon & Nelson 1984) to plot the Yoon-Nelson breakthrough curves (Fig. 3). From the plots, the k_{YN} (rate constant), and τ (the time required for 50% RO16 breakthrough) could be determined. As seen in Table 3, in general, the model breakthrough time (τ) showed good agreement with the experimental breakthrough data ($t_{50\%, exp}$). As for Yoon-Nelson's constant (k_{YN}), the value decreased from 0.0667 to 0.0313 min with increasing τ values from 23.7 to 192.5 min as the column bed height increased. This situation was also observed in the inlet flow rate as the k_{YN} values increased from 0.0087 to 0.0606 mL.mg^{-1}.min^{-1}, whereas the τ values decreased from 461.0 to 56.3 min with increasing feed flow rate. The coefficient correlations, R^2 was > 0.96 for all the fitted values in the model, indicating that this model is appropriate to explain the overall kinetics in the column for the RO16 adsorption.

For the actual batik wastewater experiment, color was removed almost instantly. The initial color was 134 mg/L Pt-Co. As batik dye wastewater consists mainly of reactive

Table 1: Effect of bed height on column breakthrough curve.

Bed height (cm)	HRT (min)	t_b (min)	V_b (ml)
0.5	0.27	16	80
2	1.08	68	340
4	2.16	165	825

Table 2: Effect of flow rate on column breakthrough curve.

Flow rate (mL.min^{-1})	HRT (min)	t_b (min)	V_b (ml)
2	2.7	327	660
5	1.08	104	490
7	0.77	43	370

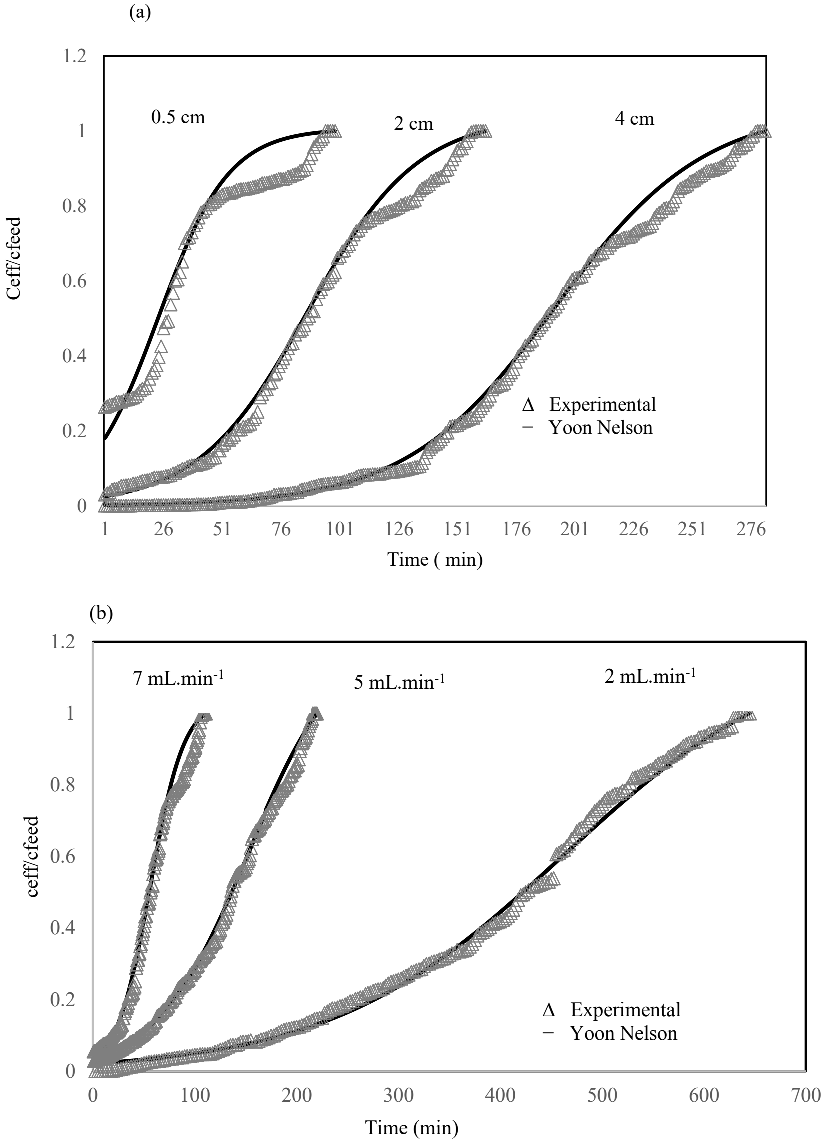

Fig. 3: Experimental and calculated Yoon-Nelson model breakthrough curves for different parameters (a) bed height and (b) flow rate.

dye, this demonstrates our previous finding of the superiority of MML in the removal of reactive dye wastewater.

CONCLUSION

In this study, modified Mengkuang leaves (MML) were prepared, characterized by several physicochemical methods, and tested as an effective adsorbent for RO16 dye removal from aqueous solutions. Some significant conclusions are summarized as follows:

The SEM images showed that the surface of MML seems to be irregular and uneven with more porous compared to RML, which is favorable for the adsorption process.

The column study revealed that adsorption was a function of bed height and flow rate. A higher bed height and a low flow rate were observed to increase the column breakthrough volume.

Yoon-Nelson model revealed that the model agreed well with experimental data as the regression (R^2) values for all the column parameters were > 0.96. The 50% breakthrough time from the experiment was closed to the Yoon-Nelson breakthrough prediction. The highest k_{YN} breakthrough times were at 192.2 and 461 mL.mg^{-1} min^{-1} for bed height of 4.0 cm and flow rate of 2 mL.min^{-1}, respectively.

The column experiment with real batik dye wastewater showed that total removal of color occurred instantly by MML.

Table 3: Yoon-Nelson model at different parameters using A non-linear regression analysis.

Parameter		k_{YN}	Breakthrough Time		R^2
		mL.mg^{-1} min^{-1}	($t_{50\%\ YN}$) min	($t_{50\%,exp}$) min	
Bed Height (cm)	4.00	0.0313	192.5	188	0.99
	2.00	0.0427	87.3	88	0.99
	0.50	0.0667	23.7	28	0.96
Flow Rate (mL.min^{-1})	7.0	0.0606	56.3	57	0.99
	5.0	0.0313	192.5	136	0.99
	2.0	0.0087	461.0	421	0.99

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