

Utilisation of Cationic Surfactant Modified Grated Coconut Residue for the Removal of Reactive Orange 16 Dye from Aqueous Solutions: A Fixed-Bed Column Study

Nor Syahirah Saidin¹, Megat Ahmad Kamal Megat Hanafiah², Is Fatimah³,
Shahab Faisal Shaharuddin⁴ and Shariff Ibrahim^{1*}

¹School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

²Faculty of Applied Sciences, Universiti Teknologi MARA Pahang, 26400, Jengka, Pahang, Malaysia

³Chemistry Department, Universitas Islam Indonesia, Kampus Terpadu UII, Jl. Kaliurang Yogyakarta, Indonesia

⁴Sentiex Sdn Bhd, Kulim Hi-Tech Park 09000 Kulim, Kedah, Malaysia

*Corresponding author (e-mail: sha88@uitm.edu.my)

The use of shredded coconut residue as a new low-cost adsorbent for the removal of Reactive Orange 16 (RO16) dye was investigated. A continuous adsorption technique on a fixed-bed column was used to remove RO16 using an adsorbent produced from grated coconut residue that had been chemically treated with the cationic surfactant cetylpyridinium chloride (CPC). The raw grated coconut (RGC) and surfactant modified grated coconut (SMGC) were characterised by Fourier Transform Infrared (FTIR) spectrophotometry and Field Emission Scanning Electron Microscopy (FESEM). The FTIR spectra demonstrated CPC adherence to the SMGC, with two distinct peaks originating from CPC appearing at 2921 and 2853 cm^{-1} . The FESEM image indicated that SMGC had an irregular and uneven surface. The column breakthrough investigation revealed that column characteristics such as adsorbent bed height and inlet dye flow rate impacted the results. Although breakthrough time increased with bed height, it was discovered that a higher initial dye input concentration and a quicker flow rate resulted in a shorter breakthrough time. The adsorption data were fitted to the Yoon-Nelson mathematical model for predicting breakthrough curves and timings. The findings of the Yoon-Nelson model for the 50% breakthrough time varied from 5.25 to 35.45 min. The results of this model agreed with the experimental data as the correlation coefficients, R^2 , for all three parameters were > 0.99 . SMGC was thus found to be an efficient adsorbent for removing RO16 from aqueous solution.

Key words: Adsorption; cetylpyridinium chloride; grated coconut; fixed-bed column; Yoon-Nelson model

Received: December 2021; Accepted: February 2022

Due to their extensive usage, some 5,000–10,000 tonnes of dyes are dumped into rivers each year [1]. Azo reactive dyes are the most common among the many dyes [2]. An azo reactive dye can produce potentially carcinogenic aromatic amines via metabolic breakdown of the azo link [2]. Reactive Orange 16 (RO16) is an anionic azo dye because its molecule has a negative charge when dissociated in water. When this dye is dumped directly into surface waterways, it hinders sunlight from penetrating the water.

Due to its simplicity and low cost, adsorption is a well-developed method for dye removal from wastewater [3]. In recent years, the usage of a variety of biomass-based derived adsorbents has attracted much attention due to its perceived low process cost compared to commercial activated carbon [4]. However, raw biomass adsorbent has been assessed as

a poor performer [5]. These factors motivated researchers to consider modifying raw biomass adsorbent to improve its efficiency by chemically treating the adsorbent precursors, such as acids and bases [6, 7], and impregnating ionic polymer groups of surfactants [8]. Modified biomass has been proven effective at removing dyes and heavy metals from wastewater [9], making it an appealing alternative to activated carbon, which must be carbonised and activated before use. This study used modified grated coconut residue in packed bed column mode as an adsorbent. Grated coconut residue has many different functional groups on its surface, like carboxylic acids, alcohol, and hydroxyl groups [10], making it a good candidate for an adsorbent material and flexible enough to be changed [5]. Previously, coconut residue was employed as an adsorbent to remove metal ions such as cadmium [11], lead [12], nickel [13] and chromium [10], as well as dyes [14]. Although much

research has been done on coconut as an adsorbent, most have focused on other parts of the coconut, such as the frond, husk, coir pith, and shell [15]. The use of surfactant-modified grated coconut is rarely reported. As a result, this study lays a strong foundation for future research.

Investigations, however, have demonstrated that raw biomass adsorbent is not very effective at removing anionic dyes due to the negative charge on the biomass surface [16]. Thus, surfactant modification was proposed to convert the surface to a positive potential, which is favourable in removing anionic pollutants [17, 18]. Oei et al. [19] found that using cetylpyridinium chloride modified barley straw significantly improved the removal of the anionic dye Reactive Black 5. In the present study, grated coconut residue was reacted with cetylpyridinium chloride (CPC) to modify its surface qualities and facilitate the capture of an anionic dye (RO16) from solution using a continuous adsorption procedure on a fixed-bed column. Column operations are advantageous because of their low reagent handling requirements, versatility to various procedures, and low operating costs [20]. The column bed height, intake concentration, and fluid flow rate are critical design parameters [21].

This work aims to demonstrate the removal of RO16 from an aqueous solution using a surfactant-modified grated coconut residue as the adsorbent. Characterisation of the adsorbent involved determining the surface functional groups and surface morphology. A fixed-bed column experiment was utilised to determine the adsorbent's suitability for removing RO16. By fitting the data to the Yoon-Nelson model, the column's adequacy was determined.

MATERIALS AND METHODS

Adsorbent Preparation

Grated coconut (Fig.1) was collected from a local market in Shah Alam, Malaysia. It was cleaned with

distilled water to eliminate dust and then dried overnight in the oven at 60°C. The dried grated coconut was mixed with hexane (R & M Chemicals, UK) at a 1:10 (w/v) ratio and stirred for 16 h to remove fat [22]. The pretreatment sample was collected by filtration using a strainer (hole size: 1 mm) and oven-dried for 3 h at 60°C, hand crushed using a mortar and pestle and sieved to a particle size of 120-250 µm. This was labelled RGC (raw grated coconut).

The surfactant modified grated coconut residue was prepared by soaking the raw grated coconut residue (RGC) in 1 L of 2.5 mmol/L cetylpyridinium chloride (CPC, C₂₁H₃₈NCl) (98% purity), obtained from Aldrich (Singapore). The suspension was shaken with an orbital shaker at a speed of 170 rpm at room temperature (25°C) for 24 h. The modified grated coconut residue was then filtered using a syringe filter (0.45 µm), and then washed with distilled water several times to remove excess CPC. The residue was dried overnight in a Memmert UF450 oven (Mettler, Germany) at 60°C and then stored in an airtight glass container labelled SMGC.

Dye Solution

An anionic dye solution of Reactive Orange 16 (RO16, MW=617.54 g/mol), obtained from Aldrich (USA), was prepared by dissolving the dye in distilled water. The dye concentration was measured using a HACH DR2800 portable spectrophotometer (UK) at a maximum absorbance wavelength of 493 nm.

Adsorbent Characterisation

RGC and SMGC were characterised chemically and physically. A Field Emission Scanning Electron Microscope (FESEM-Zeiss Supra 40v) was used to examine the surface morphology. CPC, RGC, SMGC and dye-loaded SMGC functional groups were investigated using an Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectrometer (PerkinElmer Spectrum One, USA). The spectra were recorded at 4 cm⁻¹ between 650 and 4000 cm⁻¹.



Figure 1. Raw Grated Coconut (RGC)

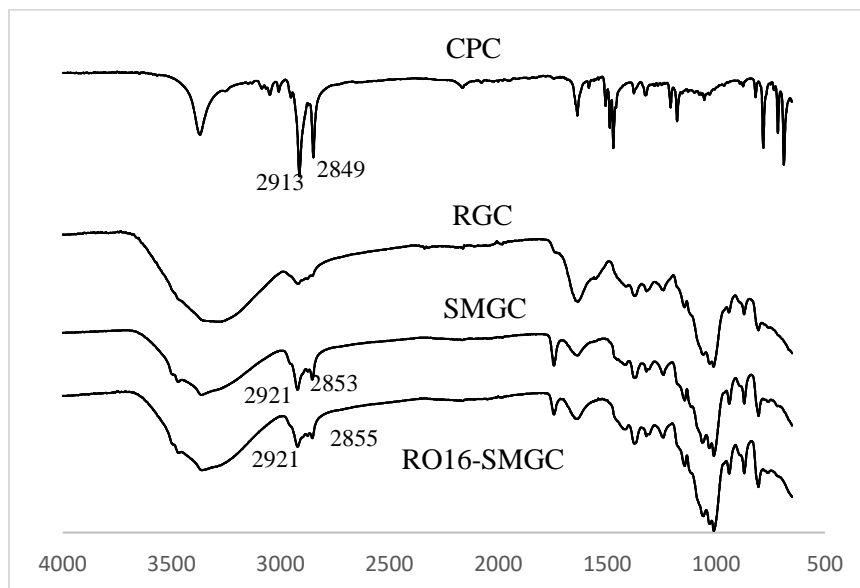


Figure 2. FTIR spectra of CPC, RGC, SMGC and RO16-loaded SMGC

Dynamic Adsorption Column Studies

The experiments were carried out in a clear cylindrical polypropylene column (2.7 cm in diameter and 10 cm in height) filled with a known amount of SMGC. At the bottom of the column was a plastic sieve. To achieve the appropriate bio-sorbent bed heights, a known quantity of SMGC was packed into the column (2, 4, and 6 cm). A peristaltic pump (Minipuls 2, Gilson, France) was used to pump a 50 to 150 mg/L RO16 dye solution upward to prevent column flooding at the required flow rates (1, 3, and 5 ml/min). The dye solution at the column's exit was collected at regular intervals. The concentration of dye effluent was then determined using a spectrophotometer. The time required for a breakthrough was set at 30% of the effluent RO16 to feed concentration, as suggested by Goel et al. [23]. Column exhaustion time was determined when the effluent concentration was 95.0% of its initial concentration. All experiments were carried out at room temperature.

Experimental column parameters like bed height and feed flow rate were varied to study the effects of these variables on RO16 removal. The flow rate was run at 1-5 ml/min, while the bed height was varied from 2 to 6 cm. The initial dye concentration was fixed at 100 mg/L. The Yoon-Nelson model was fitted to experimental data from the fixed-bed column breakthrough using the Polymath Education programme to forecast column breakthrough curve data. Unless stated, the column experiments were duplicated, with a relative standard deviation of < 4 %.

RESULTS AND DISCUSSION

1. FTIR Analysis

The FTIR spectra of CPC, RGC, SMGC and RO16-loaded SMGC were studied in the range of 650-4000 cm^{-1} (Fig.2). This range was crucial to identify changes in the functional groups present in those samples, before and after modification, and before and after dye adsorption. The region between 2000 and 3000 cm^{-1} contained two significant peaks at 2921 and 2853 cm^{-1} in CPC, RGC and SMGC. Majdan et al. [24] reported these peaks as the asymmetric and symmetric stretching vibrations of methylene C-H. CPC had peaks at 3370, 3047, 1637 and 1179 cm^{-1} , corresponding to the -OH stretching in water, =C-H stretching, C=C and C=N stretching, respectively. RGC indicated the presence of carboxylic acid, represented by the broad peak in the region of 2500 to 3700 cm^{-1} . The overlapping of -OH and -NH₂ groups were also present at 3000 to 3600 cm^{-1} , suggesting the presence of cellulose, lignin, pectin and protein in RGC. The shoulder at 1716 cm^{-1} can be ascribed to the ester group, while the peak at 1640 cm^{-1} is indicative of the C=O and C=C groups [25]. The broad and strong peak at 1013 cm^{-1} represents the C-OH stretching of cellulose, hemicellulose and lignin. The interaction between CPC and RGC led to more -CH₂, -CH₃ and =N⁺R₂ groups (originating from CPC), as demonstrated by the higher intensities of the peaks at 2921 and 2853 cm^{-1} . There was no apparent difference between the spectra of SMGC and RO16-loaded SMGC, possibly due to the weak interaction or physical

adsorption between RO16 and the SMGC surface, such as hydrogen bonding and $\pi - \pi$ attraction. The higher intensity of the peak at 1638 cm^{-1} suggests that more C=C groups originating from RO16 were adsorbed on SMGC.

2. Surface Morphology of Grated Coconut

The SEM images of RGC and SMGC are presented in Fig.3. At a glance, the surface morphology of the SMGC and RGC seem similar. It appears that chemical treatment did not change the surface of the grated coconut. Also, there was no physical

modification done, which may be why there were no noticeable physical changes. However, on careful scrutiny, the surface of the SMGC was a bit smoother than the RGC, probably due to the formation of a cationic surfactant layer on the modified grated coconut surface. The existence of the cationic surfactant on grated coconut has already been discussed in terms of their FTIR spectra (Fig 2). A similar suggestion was made by Xue et al. [26], who found that upon modification with sodium dodecyl sulfate, the walls of ashitaba-based activated carbons (ABAC) were smoother and flatter compared to those of the unmodified ABAC.

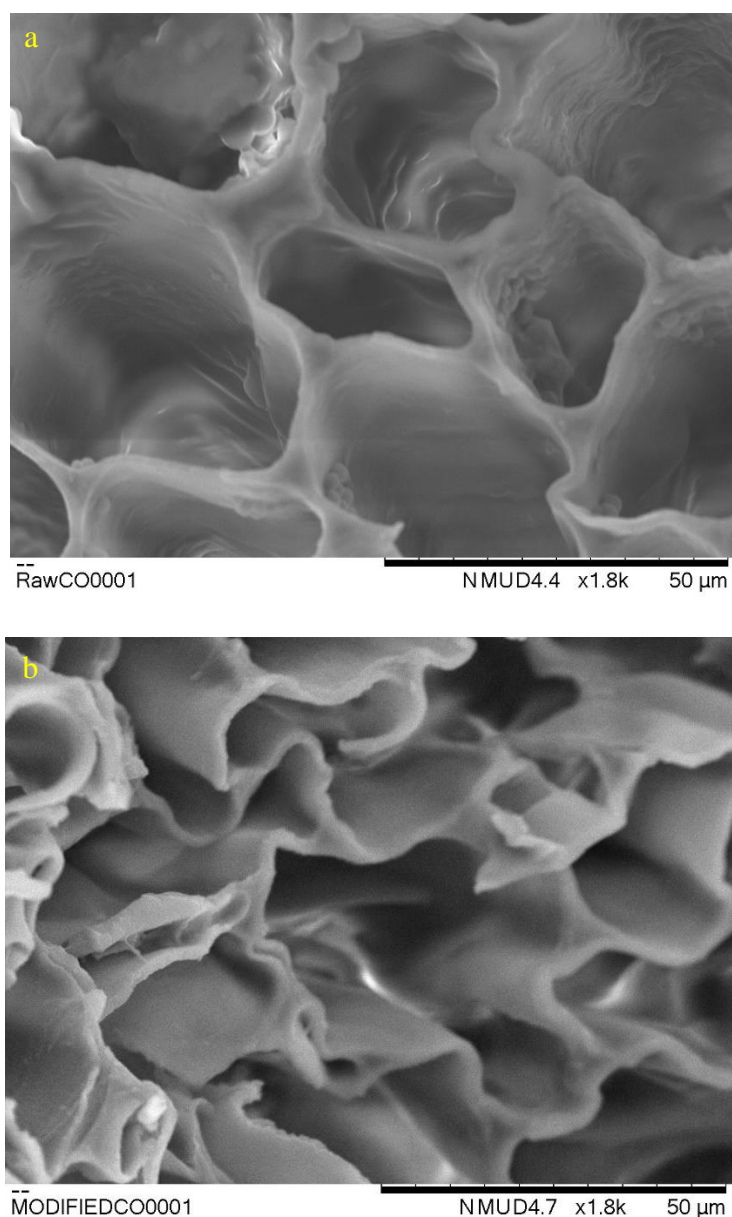


Figure 3. SEM micrographs of (a) RGC and (b) SMGC at 1800x magnification

Table 1. Column experiment breakthrough parameters by bed height

Parameter		t_b	t_{exh}
		(min)	(min)
Bed height (cm)	6.0	29.0	46.76
	4.0	19.7	31.73
	2.0	8.5	18.37

3. Adsorption Column Studies

3.1. Effect of Column Bed Height

The effect of bed height on SMGC adsorption performance was investigated by varying the bed height from 2 to 6 cm (Table 1). The flow rate was set to 3 ml/min, and the starting concentration of RO16 was set at 100 mg/L. It was discovered using breakthrough curves that raising the bed height increased the breakthrough time (t_b) and column exhaustion time (t_{exh}). The t_b and t_{exh} values, respectively, increased from 8.5 to 29 min and 18.37 to 46.76 min when the bed height was increased from 2 to 6 cm. Increased bed height increases the surface area of the adsorbent, hence providing more binding sites for adsorption [27] and more contact time [17].

3.2. Effect of Column Flowrate

The effect of flow rate on the adsorption of RO16 dye was studied over a range of 1 to 5 ml/min (Table 2). The bed height was set at 2 cm, and the initial concentration of RO16 was 100 mg/L. It was observed that a breakthrough occurred more rapidly at higher flow rates, and the bed became saturated more quickly. Additionally, the increased turbulence associated with a greater flow rate may result in poor contact and 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 [17]. Table 2 shows the breakthrough time decreased from 28 to 4.2 min, when the flow rate was increased from 1 to 5 ml/min.

RO16's contact time in the column was shorter at a higher flow rate, resulting in a shorter breakthrough time. The column exhaustion time followed a similar pattern, decreasing from 55 to 8 min as the flow rate increased.

4. Modelling of Column Data: Yoon-Nelson Model

Yoon and Nelson introduced the breakthrough curve model based on the rate of adsorption reduction for each adsorbate molecule being proportionate to the molecule's chance of breaking through [28]. The column data were fitted to the Yoon-Nelson model [29] to plot the Yoon-Nelson breakthrough curves (Fig 4). The k_{YN} (rate constant) and τ (the time required for 50% RO16 breakthrough) could be determined from the plots. As shown in Table 3, in general, the model's breakthrough time (τ) was highly consistent with experimental breakthrough data ($t_{50\%, exp}$). With breakthrough (τ) values increasing from 10.73 to 33.09 min, k_{YN} decreased from 0.44 to 0.24 min. This condition was also noticed in the intake flow rate, as the k_{YN} values rose from 0.14 to 1.05 mL.mg⁻¹.min⁻¹ while there was a decline in τ values from 35.45 to 5.25 min as the feed flow rate increased. For all fitted values in the model, the coefficient correlations, $R^2 > 0.99$. Yoon-Nelson's breakthrough value ($t_{50\% YN}$) and the experimental value ($t_{50\%, exp}$) were quite close to one other for both column bed height and flow rate. Both of these findings support the Yoon-Nelson model's applicability for explaining the overall kinetics of RO16 adsorption in the column.

Table 2. Column experiment breakthrough parameters by flow rate

Parameter		t_b	t_{exh}
		(min)	(min)
Flow rate (ml/min)	5.0	4.2	8.0
	3.0	9.0	18.37
	1.0	28	55.0

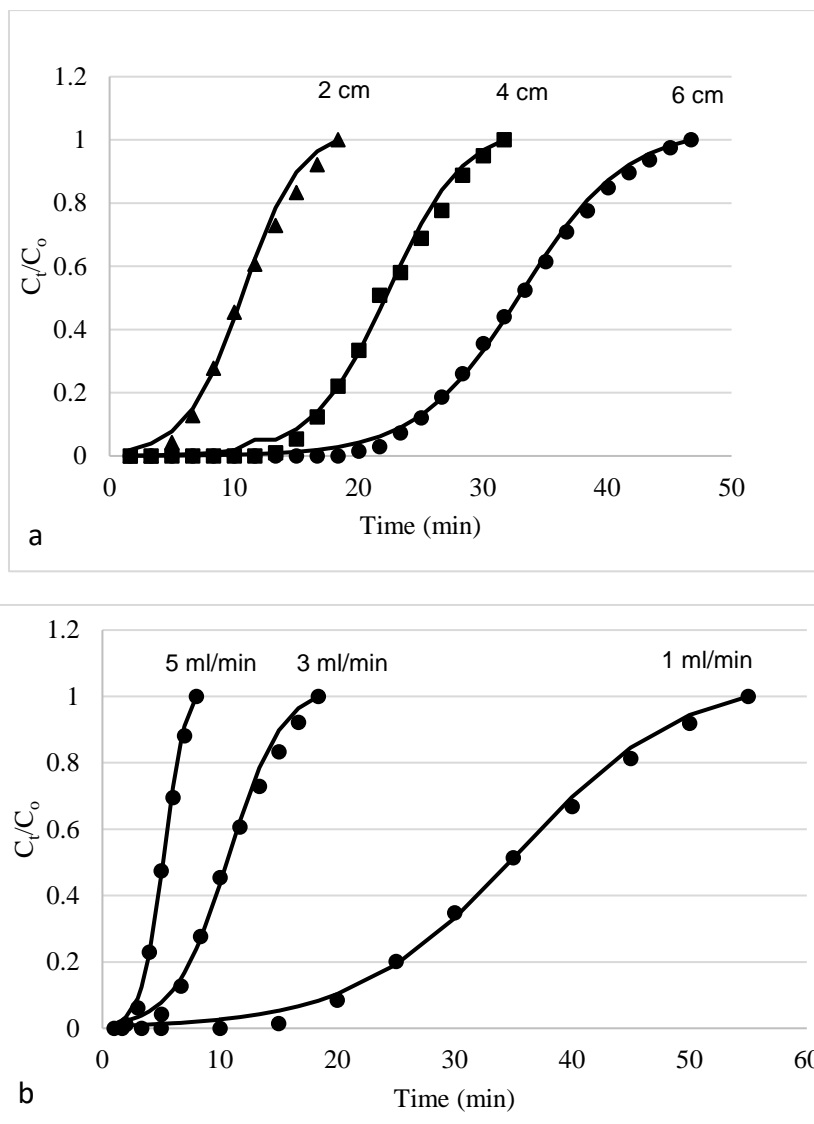


Figure 4. Experimental and calculated Yoon-Nelson Model breakthrough curves for different parameters: (a) bed height and (b) flow rate

Table 3. Yoon-Nelson model for different parameters using non-linear regression analysis

Parameter		k_{YN} mL.mg ⁻¹ min ⁻¹	Breakthrough Time		R^2
			($t_{50\% YN}$) min	($t_{50\%,exp}$) min	
Bed height (cm)	6.00	0.24	33.09	33.0	0.99
	4.00	0.33	22.39	21.7	0.99
	2.00	0.44	10.73	10.3	0.99
Flow rate (ml/min)	5.0	1.05	5.25	5.1	0.99
	3.0	0.44	10.73	10.5	0.99
	1.0	0.14	35.45	34.5	0.99

CONCLUSION

In this study, SMGC was prepared, characterised, and tested as an adsorbent the removal of RO16 dye from water. FTIR spectra showed that CPC was well-adhered to the surface of RGC. Two distinct peaks were observed at 2921 and 2853 cm^{-1} in the SMGC. Physical adsorption was most likely involved between RO16 and the SMGC via hydrogen bonding and $\pi - \pi$ attraction. The SEM images showed that the SMGC surface was slightly smoother than that of the RGC due to the cationic surfactant coating on the grated coconut surface. The column study revealed that adsorption was a function of bed height and flow rate. Higher breakthrough data was obtained at a lower flow rate. However, the opposite trend for breakthrough data was observed with increasing bed height. The Yoon-Nelson model fit well with the experimental data as the regression (R^2) values for all the column parameters were > 0.99 . The 50% breakthrough time from the experiment was close to the Yoon-Nelson model prediction. The highest k_{YN} value at breakthrough was 33.09 $\text{mL.mg}^{-1} \text{min}^{-1}$ for a bed height of 6.0 cm, and the lowest was 5.25 $\text{mL.mg}^{-1} \text{min}^{-1}$ for a 1 ml/min flow rate.

ACKNOWLEDGEMENT

The authors would like to acknowledge the support of the Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM) Shah Alam, Selangor.

REFERENCES

1. Pirkarami, A. and Olya, M. E. (2017) Removal of dye from industrial wastewater with an emphasis on improving economic efficiency and degradation mechanism. *Journal of Saudi Chemical Society*, **21**, S179–S186.
2. Mitrović, J., Radović, M., Bojić, D., Anđelković, T., Purenović, M. and Bojić, A. (2012) Decolorisation of textile azo dye reactive orange 16 with UV/H₂O₂ process. *Journal of the Serbian Chemical Society*, **77** (4), 465–481.
3. Kumar, P. S., Joshiba, G. J., Femina, C. C., Varshini, P., Priyadarshini, S., Karthick, M. A. and Jothirani, R. (2019) A critical review on recent developments in the low-cost adsorption of dyes from wastewater. *Desalination and Water Treat*, **172**, 395–416.
4. Yeow, P. K., Wong, S. W. and Hadibarata, T. (2021) Removal of azo and anthraquinone dye by plant biomass as adsorbent—a review. *Biointerface Research in Applied Chemistry*, **11**, 8218–8232.
5. Ngah, W. W. and Hanafiah, M. M. (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource Technology*, **99**(10), 3935–3948.
6. Kaya, N. (2021) Removal of Congo Red and Rhodamine B dyes from aqueous solution using unmodified and NH₃/HCl-modified wood charcoal: a kinetic and thermodynamic study. *Fullerenes Nanotubes and Carbon Nanostructures*, **29**(3), 183–195.
7. Priyanthaa, N., Romzib, A. A., Chanb, C. M. and Limb, L. B. (2021) Enhancing adsorption of crystal violet dye through simple base modification of leaf adsorbent: isotherm, kinetics, and regeneration. *Desalination and Water Treatment*, **215**, 194–208.
8. Abdelwahab, N., Shukry, N. and El-kalyoubi, S. (2021) Separation of emulsified oil from wastewater using polystyrene and surfactant modified sugarcane bagasse wastes blend. *Clean Technologies and Environmental Policy*, **23**(1), 235–249.
9. Afroze, S. and Sen, T. K. (2018) A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water, Air, & Soil Pollution*, **229**(7), 1–50.
10. Thennakoon, T., Samaraweera, A. and Priyantha, N. (2021) Adsorption of Cr (III) from aqueous solution on NaOH-treated scraped coconut waste. *Ceylon Journal of Science*, **50**(5), 391–401.
11. Ofomaja, A. E. and Ho, Y. -S. (2007) Effect of pH on cadmium biosorption by coconut copra meal. *Journal of Hazardous Materials*. **139**(2), 356–362.
12. Rahim, A. R. A., Rabat, N. E., Johari, K., Saman, N. and Mat, H. (2019) Removal of lead (II) ions from aqueous solution using desiccated coconut waste as low-cost adsorbent. *Chemical Engineering Transactions*, **72**, 169–174.
13. Saleem, M., Wongsrisujarit, N. and Boonyarattanakalin, S. (2016) Removal of nickel (II) ion by adsorption on coconut copra meal biosorbent. *Desalination and Water Treatment*, **57**(12), 5623–5635.
14. Khalid, K. and Hanafiah, M. A. K. M. (2014) Kinetic and isotherm adsorption studies of methylene blue on sulfuric acid treated spent grated coconut (*Cocos nucifera*). *Advanced Materials Research*, **970**, 192–197.
15. Chong, M. Y. and Tam, Y. J. (2020) Bioremediation of dyes using coconut parts via adsorption: a review. *SN Applied Sciences*, **2**(2), 1–16.

16. Ibrahim, S., Fatimah, I., Ang, H. -M. and Wang, S. (2010) Adsorption of anionic dyes in aqueous solution using chemically modified barley straw. *Water Science and Technology*, **62(5)**, 1177–1182.
17. Rouf, S. and Nagapadma, M. (2015) Modeling of fixed bed column studies for adsorption of azo dye on chitosan impregnated with a cationic surfactant. *International Journal of Scientific and Engineering Research*, **6(2)**, 124–132.
18. Sureshkumar, M. and Namasivayam, C. (2008) Adsorption behavior of Direct Red 12B and Rhodamine B from water onto surfactant-modified coconut coir pith. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **317(1-3)**, 277–283.
19. Oei, B. C., Ibrahim, S., Wang, S. and Ang, H. M. (2009) Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution. *Bioresource Technology*, **100(18)**, 4292–4295.
20. Uddin, M. T., Rukanuzzaman, M., Khan, M. M. R. and Islam, M. A. (2009) Adsorption of methylene blue from aqueous solution by jackfruit (*Artocarpus heterophyllus*) leaf powder: a fixed-bed column study. *Journal of Environmental Management*, **90(11)**, 3443–3450.
21. Rajeshkannan, R., Rajasimman, M. and Rajamohan, N. (2013) Packed bed column studies for the removal of dyes using novel sorbent. *Chemical Industry and Chemical Engineering Quarterly*, **19(4)**, 461–470.
22. Raghavendra, S., Swamy, S. R., Rastogi, N., Raghavarao, K., Kumar, S. and Tharanathan, R. (2006) Grinding characteristics and hydration properties of coconut residue: A source of dietary fiber. *Journal of Food Engineering*, **72(3)**, 281–286.
23. Goel, J., Kadirvelu, K., Rajagopal, C. and Garg, V. K. (2005) Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies. *Journal of Hazardous Materials*, **125(1-3)**, 211–220.
24. Majdan, M., Maryuk, O., Pikus, S., Olszewska, E., Kwiatkowski, R. and Skrzypek, H. (2005) Equilibrium, FTIR, scanning electron microscopy and small wide angle X-ray scattering studies of chromates adsorption on modified bentonite. *Journal of Molecular Structure*, **740(1)**, 203–211.
25. Khalid, K. and Kamal Megat Hanafiah, M. A. (2018) Kinetics, Isotherm, Thermodynamics, and Mechanisms of Pb (II) Adsorption on Chemically Modified Spent Grated Coconut (*Cocos nucifera*). *Recent Innovations in Chemical Engineering (Formerly Recent Patents on Chemical Engineering)*, **11(3)**, 201–224.
26. Xue, H., Wang, X., Xu, Q., Dhaouadi, F., Sellaoui, L., Seliem, M. K., Lamine, A. B., Belmabrouk, H., Bajahzar, A. and Bonilla-Petriciolet, A. (2022) Adsorption of methylene blue from aqueous solution on activated carbons and composite prepared from an agricultural waste biomass: A comparative study by experimental and advanced modeling analysis. *Chemical Engineering Journal*, **430**, 132801.
27. Zulfadhly, Z., Mashitah, M. and Bhatia, S. (2001) Heavy metals removal in fixed-bed column by the macro fungus *Pycnoporus sanguineus*. *Environmental Pollution*, **112(3)**, 463–470.
28. Mondal, S., Aikat, K. and Halder, G. (2016) Ranitidine hydrochloride sorption onto superheated steam activated biochar derived from mung bean husk in fixed bed column. *Journal of Environmental Chemical Engineering*, **4(1)**, 488–497.
29. Yoon, Y. H., Nelson, J. H., Lara, J., Kamel, C. and Fregeau, D. (1992) A theoretical model for respirator cartridge service life for binary systems: Application to acetone/styrene mixtures. *American Industrial Hygiene Association Journal*, **53(8)**, 493–502.