Bioremediation of dyes using coconut parts via adsorption: a review

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Abstract

Coconut (*Cocos nucifera*) is a palm tree belonging to the Arecaceae family that possesses a thousand and one uses. Each part of the tree has its uses and can be made into products. Also, various parts of the coconut tree have been utilized to remove various types of dyes from water and waste water via chemical, physical and biological methods. Adsorption is one of the widely used physical methods over their counterparts owing to cost efficiency and ease in handling. The key parameters for the adsorption process are the initial concentration of adsorbate, dosage of adsorbent, the pH and contact time. Additionally, the kinetic parameters, equilibrium isotherm and thermodynamics of the adsorption of dyes on the adsorbent were explored.

Keywords Coconut · Dyes · Adsorption · Kinetic parameters · Equilibrium isotherm · Thermodynamic

1 Introduction

In this modern era, water pollution in Malaysia has escalated owing to the growing numbers of polluted rivers from 2006 to 2010 [1]. The major point sources of polluted rivers in Malaysia arises from the sewage treatment plants (54.1%), manufacturing (38.7%), agro-based industries (2.8%), and animal farms (4.5%). Also, the rivers in Malaysia are heavily contaminated by the diffused (non-point) sources such as agricultural activities and surface runoffs [2, 3]. According to Afroz and Rahman (2017a), the manufacturing industries comprise of food and beverage industry (23.7%), electricity and electronics (11.4%), chemical industry (11.2%), paper industry (8.8%) finishing industry (7.4%), textile (5.3%), effluents from oil palm industry (5.3%), effluents from rubber industry (2.0%) and others (24.9%) which have contributed to the rivers pollution in Malaysia. Although textile industry does not lead the rivers pollution but the industry is mushrooming rapidly due

to the high demand from the consumers for its finished goods. The industry alone produces tons of contaminants such as dyes into the stream during textile fiber dyeing and finishing processes [1].

Dye molecules are organic compounds that interact with the functional groups on the surfaces of the fabrics to impart color as well as the ability to withstand the action of detergents [4]. Each dye molecule is divided into two parts, namely chromophores and auxochromes [5]. Chromophores in the dye molecule are constructed by the delocalized electron-withdrawing groups (i.e. alkenes, carbonyl, nitro, $-C=N-$, $-N=N-$ and $-N=O$) that are responsible for the color of the dye. These delocalized electrons absorb visible region in the electromagnetic radiation. The amount of energy absorbed depends on the amount of double bond in the dye compound. Subsequently, the absorbed energy is used to excite the electrons to a higher energy level. At high energy level, the electrons are unstable, hence the electron falls to lower

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energy level by emitting ray. The emission of rays signified the color of the dye observed [6]. On the other hand, the auxochromes that attributes to the intensity of the color is formed by the electron-donating groups (i.e. amines, carboxylic acids, sulphonic acid and alcohols) [7]. Aside from determining the intensity of the color, the auxochromes groups are accountable for the solubility in the water and the bonding with the fabric [8].

There are several ways to classify dyes, namely: (a) natural and synthetic [9, 10], (b) chromophores [11] and (c) applications [11, 12]. Generally, dyes are predominantly divided into three categories, namely [13]: (a) anionic, (b) cationic and (c) non-ionic. Anionic dyes are negatively charged organic molecules. The presence of negative charge on the dye molecule is due to the oxygen atom that has great electronegativity towards the electron rich area in the carbonyl group for the entire chromophore system [14]. The formation of negative charge on the Acid Blue 25 is shown in Figure A1, Supporting Information. Cationic dyes are developed in lieu to the formation of positive charge which forms great interaction with negatively charged fabric [15]. Non-ionic dyes are neutral in nature because the electron rich area in the chromophore is shared equally between two identical atoms [16]. The non-polar covalent bond formed between two nitrogen atoms in the chromophore system for Disperse Orange 37 is shown in Figure A2, Supporting Information. The examples of non-ionic dyes are disperse and vat that contains either azo or anthraquinone group attached to benzene ring in their chromophore system [17].

Different types of dyes possess different disadvantages that cause severe harm to the environment and human health. Therefore, various methods (i.e. chemical, physical and biological) have been proposed to overcome this problem [18]. Chemical treatment methods consisted of electrolysis and oxidation. Oxidation is a method to remove dye by utilizing oxidizing agents (i.e. ozone, ultra violet, titanium(IV) oxide, fenton, photo-phenton and hydrogen peroxide). These oxidants trap the dye molecules through the bonding with the radicals [19]. However, the technique produces harmful decomposition products such as formate and benzene sulfonate ions as by-products [20]. Electrolysis is a process to break down the dye molecules by using electricity [21]. The process is costly due to the electricity consumed and electrodes replacements [22]. In this process, the current is used to break-down the dye molecules into free ions. The ions produced then flow to the electrodes which eventually be oxidized and reduced to less harmful products. On the contrary, the use of microorganisms such as bacteria, fungi, yeast and algae in the adsorption of dyes molecules is environmental friendly and low cost [20]. For instance, it does not require larger space to construct robust equipment for the

decolorization of dyes as well as less toxic decomposition products. However, the time needed to obtain a pure culture is relatively long. The mechanism to treat the effluents from the waste water depends on the type of microorganisms used. An alive microorganism will be immobilized on a support containing media for continuous growth. The microorganism ingests the harmful dye molecules through enzymes secretions in the intracellular cell. Subsequently, the microorganism will then excrete the less harmful digested product to the environment [23]. On the other hand, a dead microorganism removes the dye molecules from the waste water through adsorption technique. The physical techniques used to treat the dye molecules from the waste water consists of adsorption, coagulation/flocculation, filtration, reverse osmosis and electro-flotation. These techniques share the same mechanism which is in the use of chelating or coagulant agents to precipitate out the harmful dye molecules from the waste water through the formation of flocs or sediments. Electro-flotation is an improvise technique combining coagulation/flocculation and electricity. It traps the dye molecule through coagulation which will later be broken down to less harmful products by electric current. It is cheap, energy efficiency, safe, and versatile [24].

Still, adsorption is in favor over their counterpart methods due to low cost, hassle free and availability [25]. Basically, adsorption is an entrapment of dye molecules by the adsorbent through both physical and chemical interactions. This method relies strongly on the adsorbate (types of auxochromes) and criteria of adsorbents used (i.e. particle size, surface area, temperature, pH and contact time) [26]. Various adsorbents such as activated carbons, clays, metal oxides and metal hydroxides have been explored to remove dye molecules from waste water [27]. Activated carbon has been widely used because of its larger surface area and easy availability but it's production cost is high. Similarly, Elmoubarki et al. [18] mentioned that the lamellar structure of the clay creates larger surface area than the activated carbon in the removal of dyes from the contaminated water [18]. Meanwhile, metal oxides and hydroxides gained their popularity due the mesosphere structure created (i.e. flower, rod and etc.) which enable them to enhance the adsorption capacity [28].

The main goal of this review is to provide a summary of recent information concerning the use of coconut parts as adsorbents for dyes in wastewaters. Malaysia remains one of the world's top ten coconut-producing countries, and coconut is the country's fourth most important crop after oil palm, rubber and rice. Malaysia produces at least 168 million tons of biomass, including timber and oil palm waste, rice husks, coconut trunk fibers, municipal waste and sugarcane waste annually. Various coconut parts were modified to treat heavy metals in the waste water [29–31],

organic compounds in the water stream (i.e. butylparaben, benzene, toluene, carbofuran) [32–34], carbon dioxide gaseous from the flue gas [35] and inorganic pollutants from the drinking water [36–38].

2 Coconut shell

Coconut shell was the predominantly used part for the removal of dyes from the waste water. There are three ways to modify the coconut shell prior to the removal of dyes, namely activated carbon [39–43], acid or base treatment [44, 45], and as immobilizer for the bacteria [46]. Table 1 summarizes the physical parameters, adsorption kinetic and equilibrium isotherm of the modified coconut shell.

2.1 Physical parameters

2.1.1 Contact time

Among the parameters mentioned, contact time is the time for the adsorbent to interact with the adsorbate. It is a niche parameter in order to develop a cost effective method. Figure 1 demonstrates the effect of contact time for the uptake of Methylene Blue by the activated carbon using coconut shell treated with NaOH via hydrothermal treatment [42]. Based on Fig. 1, the time needed to adsorb 25 and 50 mg/L of Methylene Blue is less than 30 min. The contact time increased by four times to 2 h for the adsorption of 75 and 100 mg/L. As the concentration of Methylene Blue increased to 150, 200 and 250 mg/L, the adsorbent requires 6 h to achieve a steady maximum adsorption capacity. The dyes were adsorbed rapidly at initial stage owing to huge amount of available sites and the number of active sites increases with the concentration [47]. However, the available sites in adsorbent will eventually be saturated thereafter achieving a steady state [48].

2.1.2 pH

The pH of the adsorbate is another important parameter that affects the adsorption process. The interaction between dye molecule and adsorbent at different pH is shown in Figure A3, Supporting Information. At low pH, the concentration of H^+ ions are high. Hence, anionic (negatively charged) dye interacts well in acidic condition owing to ion–dipole interaction. In fact, the adsorption of anionic dyes will be elevated by the impregnation of phosphoric acid on the dried coconut shell prepared by Ndifor-Angwafor et al. [17] because the H^+ ions on the activated carbon provides sites to adsorb anionic dye molecules [45]. The result is in well agreement with the research conducted by Jóźwiak

et al. (2018) [44]. On the contrary, Islam et al. [42] modified the activated carbon based coconut shell via hydrothermal and sodium hydroxide (COSHTC3) treatments which facilitates more negatively charged sites on its surface for the adsorption of cationic dyes. In basic condition, the concentration of OH^- ions is high and hence it enables the entrapment of cationic dyes. The interaction was strengthened by the base modification on the activated carbon by coconut shell because it facilitates more available sites for cationic dyes [42].

Figure 2 depicts the effect of pH for the adsorption of Methylene Blue by COSHTC3. It indicates that the best pH for the adsorption of Methylene Blue by COSHTC3 is 9 because it achieves the maximum adsorption capacity of 107 mg/g. The adsorption capacity of Methylene Blue by COSHTC3 is low at both pH lesser and greater than 9. This is because at pH greater than 9, there are excessive hydroxide ions causes repulsion that hinders the smooth adsorption of cationic dye on the COSHTC3 [49]. Meanwhile, the low adsorption of Methylene Blue by COSHTC3 is low at pH lesser than 9 and this is because the sites provided by the adsorbent are taken up by the H^+ ions that is smaller than cationic dye molecules [44, 50].

2.2 Equilibrium isotherm models

2.2.1 Langmuir

Langmuir isotherm model states that a monolayer of the entire surface of the adsorbent has identical sorption capacity (homogeneous) with limited active sites for the non-interacting adsorbate. The Langmuir isotherm model can be written as follows [51]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

where q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g), K_L is the adsorption capacity constant (L/g), C_e is the concentration of adsorbate at equilibrium (mg/L) and q_m is the maximum adsorption capacity (mg/g).

The Langmuir isotherm model is rearranged for plotting the graph and it can be written as follows:

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

When a graph of $\frac{C_e}{q_e}$ is plotted against C_e , a linear graph is acquired with regression linear coefficient, R^2 , close to unity. The q_m and K_L are obtained from the gradient and intercept of the graph. Both the gradient and intercept of the graph represent the values for $\frac{1}{q_m}$ and $\frac{1}{q_m K_L}$, respectively.

Table 1 Physical parameters, adsorption kinetic and equilibrium isotherm of the modified coconut shell

Adsorbent	Adsorbate	Chemical structure	Characteristics		Maximum adsorption capacity (mg/g)	Equilibrium isotherm	Adsorption kinetic
			pH	Contact time			
Activated carbon/NaOH/hydrothermal [42]	Methylene Blue		9	24 h	200.01 mg/g at 303 K	Langmuir at 303 K qm: 200.01 mg/g KL: 0.2036 L/mg R2: 0.9689	Pseudo second order at 50 mg/L qactual: 48.01 mg/L qtheoretical: 46.01 mg/L k2: 1.481 g/mgmin R2: 0.9995
Charcoal purchased from BK Black Company (Bangkok) [43]	Basic yellow 13		11	120 min	19.76 mg/g at 298 K	Langmuir at 298 K qm: 19.76 mg/g KL: 0.0199 L/mg R2: 0.9830	NIL
	Basic red 14		11		22.93 mg/g at 298 K	Langmuir at 298 K qm: 22.93 mg/g KL: 0.0186 L/mg R2: 0.9980	NIL
Activated carbon/KOH [41]	Methyl orange		NIL	12 min		NIL	Pseudo second order at 30 mg/L qactual: 3.00 mg/g qtheoretical: 3.14 mg/g k2: 0.2266 g/mgmin R2: 0.9959
Dried coconut shell/H3PO4 [45]	Amaranth red (E123)/ Acid red 27 (anionic)		2	60 min	22.727 mg/g at 298 K	Langmuir qm: 22.727 mg/g KL: 0.3360 L/mg R2: 0.9810	Pseudo second order at 50 mg/L qactual: 15.385 mg/g qtheoretical: NIL K: 0.04 g/mgmin R2: 0.9970
Activated carbon/H2SO4/500°C [39]	Maxilon blue (GRL)		3	NIL	58.2523 at 303 K	Fritz-Schlunder at 303 K qm: 46.5624 mg/g KFS: 0.1281 L/mg n: 1.0892 R2: 0.9965	Elovich (Chemisorption) at 10 mg/L α : 7.7464 g/mgmin β : 0.3616 g/min R2: 0.9896
	Direct yellow (DY 12)		3		10.0211 at 303 K	Fritz-Schlunder at 303 K qm: 8.0254 mg/g KFS: 0.0756 L/mg n: 1.1470 R2: 0.9989	Elovich (Chemisorption) at 10 mg/L α : 0.4895 g/mgmin β : 1.3452 g/min R2: 0.9906
Coconut shells/H2SO4/NaOH [44]	Reactive Black 5		2	60 min	0.82 at 298 K	Langmuir qm: 0.8190 mg/g KL: 0.0350 L/mg R2: 0.9920 Langmuir 2 qm: 0.8190 mg/g KL1: 0.0350 L/mg b1: 0.4130 mg/g KL2: 0.0350 L/mg b2: 0.4060 mg/g R2: 0.9920	NIL

The highest adsorption capacity is observed by the adsorption of 200.01 mg of Methylene Blue by 1 g of activated carbon prepared by using coconut shell modified by

NaOH and hydrothermal treatments [42]. Subsequently, the research conducted by Srisorrachtr et al. [43] successfully adsorbed 22.93 mg and 19.76 mg of Basic Red and

Table 1 (continued)

Reactive Yellow 84		2		0.96 at 298 K	Langmuir qm: 0.962 mg/g KL: 0.038 L/mg R2: 0.975 Langmuir 2 qm: 0.962 mg/g KL1: 0.038 L/mg b1: 0.481 mg/g KL2: 0.038 L/mg b2: 0.481 mg/g R2: 0.9750	NIL
Acid Yellow 23		2–3	45 min	0.53 at 298 K	Langmuir qm: 0.526 mg/g KL: 0.043 L/mg R2: 0.9380 Langmuir 2 qm: 0.526 mg/g KL1: 0.043 L/mg b1: 0.263 mg/g KL2: 0.043 L/mg b2: 0.263 mg/g R2: 0.9380	NIL
Acid Red 18		2–3		0.66 at 298 K	Langmuir qm: 0.661 mg/g KL: 0.030 L/mg R2: 0.9810 Langmuir 2 qm: 0.661 mg/g KL1: 0.030 L/mg b1: 0.330 mg/g KL2: 0.030 L/mg b2: 0.331 mg/g R2: 0.9810	NIL

Basic Violet 10		3	180 min	28.54 at 298 K	Langmuir 2 qm: 28.544 mg/g KL1: 0.086 L/mg b1: 1.994 mg/g KL2: 0.005 L/mg b2: 26.550 mg/g R2: 0.996	NIL
Basic Red 46		6	90 min	68.52 at 298 K	Langmuir 2 qm: 68.515 mg/g KL1: 0.015 L/mg b1: 54.031 mg/g KL2: 0.378 L/mg b2: 14.484 mg/g R2: 0.993	NIL

Basic Yellow dyes, respectively for every gram of charcoal prepared by coconut shell procured from BK Black company [43]. Nonetheless, the only anionic type of dye that fits Langmuir isotherm model along with highest

adsorption capacity can be observed by the adsorption of 22.727 mg of Amaranth Red by 1 g of dried coconut shell impregnated with H_3PO_4 [45].

Fig. 1 The effect of contact time for the uptake of Methylene Blue by the activated carbon using coconut shell treated with NaOH via hydrothermal [42]

Fig. 2 The effect of pH for the adsorption of Methylene Blue by COSHTC3 [42]

2.2.2 Fritz–Schlunder

The Fritz–Schlunder isotherm model is an empirical three-parameter isotherm combining the Langmuir and Freundlich isotherms. The Fritz–Schlunder isotherm model can be written as follows [52]:

$$q_e = \frac{K_{FS} q_m C_e}{1 + q_m C_e^n}$$

where q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g), C_e is the concentration of the adsorbate at the equilibrium (mg/L), q_m is the maximum adsorption capacity (mg/g), K_{FS} is the Fritz–Schlunder model constant and n is the Fritz–Schlunder(III) model exponent. When a graph of q_e is plotted against C_e , a linear graph is acquired with regression linear coefficient, R^2 , close to unity. The research conducted by Aljeboree et al.

[39] fits Fritz–Schlunder and it was found that every 1 g of activated carbon prepared using coconut shell impregnated with H_2SO_4 at 500 °C adsorbed 46.5624 mg and 8.0254 mg of Maxilon Blue GRL and Direct Yellow DY12 dyes, respectively [39]. The Maxilon Blue GRL dye interacts greatly with the activated carbon impregnated with H_2SO_4 because the dye offers a lone pair of electron to the H^+ ions on the surface of the adsorbent. Likewise, the presence of $CH_3OSO_3^-$ ions creates ion–dipole interaction with protons, H^+ , on the surface of the adsorbent. In contrast, the stable delocalized electron and steric hindrance on the direct yellow dye hampered the interaction with the adsorbent. The result is reinforced by the greater K_{FS} value owned by the adsorption of Maxilon Blue GRL (0.1281 L/mg) compared to K_{FS} of the adsorption of Direct Yellow DY12 (0.0756 L/mg) by the activated carbon impregnated with H_2SO_4 .

2.2.3 Langmuir double (Langmuir 2)

The Langmuir double (Langmuir 2) isotherm model states that the adsorbent provides either one or two types of active sites for the adsorbate. The Langmuir double can be written as follows [53]:

$$q_e = \frac{q_{max1} K_{L1} C_e}{1 + K_{L1} C_e} + \frac{q_{max2} K_{L2} C_e}{1 + K_{L2} C_e}$$

where q_e is the maximum adsorption capacity at equilibrium (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), q_{max1} is the maximum adsorption capacity for Langmuir type 1 (mg/g), q_{max2} is the maximum adsorption capacity for Langmuir type 2 (mg/g), K_{L1} is the constant for Langmuir type 1 (L/mg) and K_{L2} is the constant for Langmuir type 2 (L/mg). The adsorbent provides one type of active sites for the adsorbate if the $q_{max1} = q_{max2}$ as well as $K_{L1} = K_{L2}$. It can be seen by the adsorption of anionic dyes (Reactive Black 5, Reactive Yellow 84, Acid Yellow 23 and Acid Red 18) by the coconut shell modified with H_2SO_4 and NaOH [44]. On the other hand, the adsorbent provides two types of active sites if $q_{max1} \neq q_{max2}$ as well as $K_{L1} \neq K_{L2}$. The scenario is manifested by the adsorption of cationic dyes (Basic Violet 10 and Basic Red 46) on the coconut shell modified with H_2SO_4 and NaOH (Jóźwiak et al., 2018). The q_{max1} , q_{max2} , K_{L1} and K_{L2} for adsorption of Basic Violet 10 are 1.994 mg/g, 26.550 mg/g, 0.086 L/mg and 0.005 L/mg, respectively. Meanwhile the q_{max1} , q_{max2} , K_{L1} and K_{L2} for adsorption of Basic Red 46 are 54.031 mg/g, 14.484 mg/g, 0.015 L/mg and 0.378 L/mg, respectively. Based on the result, the adsorbent with two active sites produces higher maximum adsorption capacity than the adsorbent with one active site. This is because each cationic dye molecule accommodates two sites (a group of

Lewis base by tertiary amine and a group of Lewis acid by the quaternary amine) to create synergistic effect with the surface of the adsorbent. However, the modified coconut shell adsorbs Basic Red 46 better than Basic Violet 10 because Basic Red 46 portrays lesser steric hindrance due to its small molar mass (401 g/mol).

2.3 Adsorption kinetic models

2.3.1 Lagergren's pseudo second order

Lagergren model is used to evaluate the equilibrium time needed for the transfer of adsorbate on the adsorbent. The factors affecting the overall mass transfer are [54]:

- Bulk diffusion* Diffusion of the solute from the bulk solution to the film (surrounding the particle)
- External surface diffusion* Diffusion across the film to the particle surface.
- Pore diffusion* Diffusion from the surface to the internal sites.

According to Table 2, most of the adsorption processes by the modified coconut shell fit Lagergren's pseudo

second order which is based on the rate limiting step for chemical sorption mechanism. The linear expression of Lagergren's pseudo second order is as follows [54]:

$$\frac{t}{q_t} = \left(\frac{1}{q_e} \right) t + \frac{1}{k_2 q_e^2}$$

where q_t is the amount of adsorbate at any time (mg/g), q_e is the amount of adsorbate at equilibrium (mg/g), k_2 is the rate constant for the pseudo second order (g/mg min) and t is the time taken for the adsorption process until it reaches equilibrium (min). When a graph of $\frac{t}{q_t}$ is plotted against t , a linear graph is acquired with regression linear coefficient, R^2 , close to unity. Additionally, the consistency of both the theoretical and experimental values for q_e confirms the adsorption kinetic process obeyed pseudo second order [55]. It was proven from the research conducted by Islam et al. [41, 42]. The q_{actual} for the adsorption of Methylene Blue by the activated carbon prepared using coconut shell impregnated with NaOH via hydrothermal method is 48.01 mg/L. The value differs by 4.35% from the $q_{theoretical}$ value that is 46.01 mg/L. Similarly, the adsorption of Methyl Orange by the activated carbon prepared through coconut shell and KOH treatment obtained

Table 2 Results for the adsorption of Methylene Blue by fallen coconut leaves (untreated and treated)

Characteristics	Adsorbents			
	Untreated	Treated		
	UCL [64]	PCL [65]	HACL [66]	FACL [67]
Adsorbate	Methylene Blue			
Initial pH	8.65	5–6	5.60	5.60
Average pore size (Å)	NIL	36.50	73.94	NIL
Maximum adsorption capacity (mg/g)	112.35 at 302 K	250.00 at 303 K	357.14 at 300 K	66.00 at 303 K
Adsorption equilibrium isotherms	Langmuir			
q_m (mg/g)	112.35	250.00	357.14	66.00
K_L (L/mg)	0.0792	0.2200	0.2750	0.0400
R^2	0.9963	0.9822	0.9950	0.9900
Adsorption kinetic	Pseudo-second order (50 mg/L)			
k_2 (g/mg min)	0.0292	0.0470	0.0002	0.0002
q_e theoretical (mg/g)	26.53	21.30	285.71	33.11
q_e actual (mg/g)	26.19	21.00	269.74	33.05
R^2	0.9999	1.0000	0.9980	0.9990
		Weber–Morris intraparticle diffusion model (50 mg/L)		
K_{id} (mg/gmin ^{1/2})		2.3		
C (mg/g)		10.56		
R^2		0.9420		
<i>Thermodynamics study</i>				
ΔG at 300 K (kJ/mol)	NIL	– 5.95	– 55.11	NIL
ΔH° (kJ/mol)	NIL	– 107.7 (exothermic)	21.91 (endothermic)	NIL
ΔS° (kJ/mol K)	NIL	0.3750	0.1096	NIL

3.00 mg/g via experimental testing and 3.14 mg/g via theoretical calculation. The q_e and k_2 are obtained from the gradient and intercept of the graph. Both the gradient and intercept of the graph represent the values for $\frac{1}{q_e}$ and $\frac{1}{k_2 q_e^2}$, respectively.

2.3.2 Elovich (chemisorption)

The kinetic adsorption of Maxilon Blue GRL and Direct Yellow DY12 by the activated carbon modified from coconut shells impregnated with H_2SO_4 portrays the Elovich equation. It has been used for slow and heterogeneous chemical adsorption process and the equation is as follows [56]:

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t)$$

where q_t is the maximum adsorption capacity at time t (mg/g), t is contact time (min), α is the initial adsorption rate (mg/gmin) and β is the desorption constant (g/min). When a graph of q_t is plotted against $\ln(t)$, a linear graph is acquired with regression linear coefficient, R^2 , close to unity. The α and β are obtained from the gradient and intercept of the graph. Both the gradient and intercept of the graph represent the values for $\left(\frac{1}{\beta}\right)$ and $\left(\frac{1}{\beta}\right) \ln(\alpha\beta)$, respectively. The research conducted by Aljeboree et al. [39] obeyed the Elovich equation (chemisorption process) because the R^2 value obtained was close to unity [40]. The adsorption of Maxilon Blue GRL by the modified coconut shell attained higher initial adsorption rate ($\alpha = 7.7464$ g/mg min) than Direct Yellow DY12 ($\alpha = 0.4895$ g/mg min). Therefore, the adsorption of Maxilon Blue GRL achieves greater adsorption capacity than Direct Yellow DY12. Subsequently, the desorption rate of Direct Yellow DY12 is faster ($\beta = 1.3452$ g/min) than Maxilon Blue GRL ($\beta = 0.3616$ g/min).

3 Coconut frond

Coconut fronds are the stiff mid-ribs of coconut leaves. A frond is divided into a few components, which are the frond base, cushion, keel, petiole, pinnae and rachis. The cushion part of a coconut frond is the component used as adsorbent by Mohammad et al. [57]. The cushion was rinsed with distilled water prior to dry under sunlight for 2 days. Later on, the cushion was cut into small pieces and was dried under the sunlight for 2 days. Finally, the dried cushion was grinded and sieved into different particle sizes (0.125, 0.300, and 0.710 mm) before being used as adsorbent for Malachite Green (N-methylated diaminotriphenylmethane), a cationic dye adsorption. The parts of

the coconut fronds and the chemical structure of Malachite Green are depicted in Figure A4(a) and (b), Supporting Information, respectively.

3.1 Physical parameter (particle size of adsorbent)

Figure 3 depicts the characteristics of coconut frond in the adsorption of Malachite Green. The highest removal percentage of dye was observed by the smallest particle size (0.125 mm) of coconut frond because it provides larger surface area for adsorption as shown in Fig. 3a. Moreover, Rani et al. (2017) mentioned if the adsorbent has a particle size smaller than 0.125 mm, the particles entangle and it decreases the availability of the active sites on the surface for adsorption [58]. Based on Fig. 3b, the most optimum contact time for the removal percentage to reach equilibrium is 16 h. If the contact time is longer than 16 h, the active sites on the adsorbent will be saturated and thus the removal percentage of dyes will decrease. On the other hand, the adsorption process is incomplete if the contact time is insufficient (less than 16 h). Generally, the adsorption of cationic dye by adsorbent is the best in acidic condition but at very low pH, the dye molecules compete with the H^+ ions over the active sites on the adsorbent as mentioned by Mohammad et al. [57]. However, the scenario is not noticeable by the study conducted by Mohammad et al. 2017 as shown in Fig. 3c [57]. This is because the small particle size of the coconut fronds remediated the competition and hence, the optimum pH for the adsorption is 1 [59]. Figure 3d infers that the adsorption isotherm for Malachite Green dye occurs at specific homogeneous sites on the coconut fronds because the R^2 value obtained equals to 1. The maximum adsorption capacity of Malachite Green is 18.98 mg/g.

4 Coconut fiber

Coconut fiber also known as coconut grate residue is the by-product of coconut gratings. The milked coconut gratings are obtained from the fresh coconut endosperm via wet processing for the production of virgin coconut oil [58]. Rani et al. (2017) treated the dry coconut fiber with acid followed by hexane at high pressure (CAH) for the adsorption of Congo Red [58]. The purpose of the acid treatment is to enhance the positive charge on the surface of coconut fiber for better entrapment of anionic dye. Likewise, addition of hexane dissolves the excess oil on the surface of the coconut fiber which could retard the interaction with the adsorbate. Congo Red as shown in Figure A5, Supporting Information attained the highest adsorption on the CAH at low pH (pH = 3). At low pH, the concentration of H^+ ions are

Fig. 3 Characteristics of coconut frond in adsorption of Malachite Green **(a)** adsorbent size **(b)** contact time **(c)** initial pH and **(d)** adsorption equilibrium isotherm [57]

high, hence it caters sites for Congo Red, an anionic dye, for electrostatic attraction [60].

4.1 Adsorption kinetics

4.1.1 Freundlich

The adsorption process fitted Freundlich isotherm and pseudo-second order kinetic models. Freundlich isotherm model states that there is exponential distribution of active sites on adsorbent for the heterogeneous sorption of adsorbate. The Freundlich isotherm model can be written as follows [61]:

$$q_e = K_F C_e^{\frac{1}{n}}$$

where q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g), K_F is the adsorption capacity constant (L/g), C_e is the concentration of the adsorbate at equilibrium (mg/L), n is the heterogeneity factor and $\frac{1}{n}$ is the adsorption intensity. The Freundlich isotherm model is rearranged for plotting the graph and it can be written as follows:

$$\log_{10} q_e = \frac{1}{n} \log_{10} C_e + \log_{10} K_F$$

When a graph of $\log_{10} q_e$ is plotted against $\log_{10} C_e$, a linear graph is acquired with regression linear coefficient, R^2 , close to unity. The n and K_F are obtained from the gradient and intercept of the graph. Both the gradient and intercept of the graph represent the values for $\frac{1}{n}$ and $\log_{10} K_F$, respectively. If the value of $\frac{1}{n}$ falls in between 0 and 1, it signifies

the easiness of the adsorption process [62]. The maximum adsorption capacity, K_F , $\frac{1}{n}$ and R^2 values for the adsorption of Congo Red by CAH are 128.94 mg/g, 1.23 L/mg, 0.6289 and 0.99, respectively. The outstanding performance of CAH is fully supported by the k_2 , actual q_e and R^2 values of 0.20 g/mg min, 4.93 mg/g and 0.99, respectively obtained from the pseudo-second order adsorption kinetic.

4.1.2 Brauner–Emmet–Teller (BET)

It is worth mentioning that the adsorption of Congo Red by CAH obeyed Brauner–Emmet–Teller (BET) isotherm. The BET isotherm model states that the gaseous adsorbate molecules move randomly on the adsorbent sites (i.e. empty, covered with monolayer or multiple layers adsorbate molecules) instead of the surface of the adsorbent. The BET isotherm model can be written as follows [63]:

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{K_B q_s} + \frac{(K_B - 1)}{K_B q_s} \times \frac{C_e}{C_s}$$

where q_s is the amount of adsorbate per unit mass of adsorbent when all layers are saturated (mg/g), K_B is the BET adsorption constant (a function of the energy of adsorption and temperature) and C_s is the concentration of adsorbate when all layers are saturated (mg/L). When a graph of $\frac{C_e}{(C_s - C_e)q_e}$ is plotted against $\frac{C_e}{C_s}$, a linear graph is acquired with regression linear coefficient, R^2 , close to unity. The K_B and q_s are obtained from the gradient and intercept of the graph. Both the gradient and intercept of the graph represent the values for $\frac{(K_B - 1)}{K_B q_s}$ and $\frac{1}{K_B q_s}$, respectively. The K_B , q_s and R^2 values obtained by the adsorption of Congo Red by CAH are 12.00, 92.59 mg/g and 0.97, respectively.

4.2 Thermodynamics study

Thermodynamic analysis is conducted to evaluate the spontaneity, type and the effect of temperature on the biosorption process. The criteria of the adsorption can be determined by the equations as follow:

$$\Delta G = -RT \ln K$$

$$K = \frac{q_e}{C_e}$$

$$\Delta G = \Delta H^\circ - T \Delta S^\circ$$

where ΔG is the Gibbs free energy at non-standard condition (J/mol), R is the molar universal gas constant (8.3145 J/mol K), T is the absolute temperature, K is the equilibrium constant, q_e is the maximum adsorption capacity at equilibrium (mg/g), C_e is the concentration of adsorbate remaining in the solution at equilibrium (mg/L), ΔH° is the

standard enthalpy change (J/mol) and ΔS° is the standard entropy change (J/mol K).

The adsorption process of Congo Red by CAH is non-spontaneous because the ΔG at 300 K is a positive value (16.51 kJ/mol). The result is in well agreement with the negative value of entropy change ($\Delta S^\circ = -0.12$ kJ/mol K) owing to the decreased disorder at the solid/liquid interface. The adsorption is a physical adsorption because the ΔH° values obtained CAH is -19.39 kJ/mol (negative, exothermic).

5 Fallen coconut leaves

Fallen coconut leaves are agricultural wastes largely available in Malaysia. The performance in adsorption of Methylene Blue by untreated fallen coconut leaves (UCL) was compared with fallen coconut leaves impregnated with H_3PO_4 followed by microwave pyrolysis (PCL). Table 2 summarizes the results for the adsorption of Methylene Blue by fallen coconut leaves (untreated and treated). The performance of PCL improved by 122.52% because the maximum adsorption capacity increased to 250 mg/g from 112.35 mg/g. However, the performance of coconut leaves impregnated with H_3PO_4 followed by carbonization at 700 °C (HACL) increased by 217.88% to 357.14 mg/g compared to UCL. Both PCL and HACL obtained high maximum adsorption capacity of 250 mg/g and 357.14 mg/g, respectively. The results are congruent to the negative values of ΔG at 300 K that are -5.95 kJ/mol and -55.11 kJ/mol by PCL and HACL, respectively which indicates spontaneity of the adsorption process. Moreover, the positive values of standard entropy change obtained by PCL and HACL are 0.3750 kJ/mol and 0.1096 kJ/mol, respectively indicating that the arrangement of atoms in the adsorption process are highly disorder. The adsorption of Methylene Blue by PCL is exothermic ($\Delta H^\circ = -107.70$ kJ/mol) whereas the adsorption of Methylene Blue by HACL is endothermic ($\Delta H^\circ = +21.91$ kJ/mol). Therefore, the adsorption of Methylene Blue by HACL requires heating to amplify the movement of atoms. Nonetheless, an attempt to impregnate coconut leaves with $FeCl_3$ followed by carbonization at 700 °C (FACL) requires additional improvement because it's adsorption capacity dropped by 41.26% to 66 mg/g compared to UCL.

The optimum pH for the adsorption of Methylene Blue by UCL is 8.65. At this pH, the concentration of hydroxide ions, OH^- is slightly higher than hydroxonium ions, H_3O^+ . It provides more active sites for the adsorption of cationic dyes through electrostatic force. The optimum pH for the adsorption of Methylene Blue depressed to the pH range from 5 to 6 for PCL, HACL and FACL. It was revealed that

the entrapment of dye molecules into the pore of the PCL and HACL strengthened the adsorption process at pH 5.60 apart from electrostatic force [68]. This is because the small ionic size of H^+ ions impregnated on the surface of fallen coconut leaves created a network for better entrapment of dye molecules. However, FACL adsorbent encountered a drop in adsorption capacity at pH = 5.60 because the impregnation of large ionic size of Fe^{3+} ions on the surface of fallen coconut leaves creating small pore network. The presence of steric hindrance in the network hinders the entrapment of dye molecules [69].

All the adsorption process obeyed Langmuir equilibrium isotherm. The linear regression values are close to unity and subsequently the Langmuir constant values, K_L , increase with the maximum adsorption capacity values.

Also, the adsorption kinetics fitted pseudo-second order. It is worth noting that the adsorption of Methylene Blue by PCL portrayed Weber–Morris intraparticle diffusion model. The model was developed in 1962 for the analysis of the adsorption kinetics. The model can be written as follows [70]:

$$q_t = K_{id}t^{1/2} + C$$

where q_t is the adsorption capacity at any time (mg/g), K_{id} is the intraparticle diffusion rate constant (mg/gmin^{1/2}), t is the time taken for the adsorption process (min) and C is a constant for the any experiment (mg/g). When a graph of q_t is plotted against $t^{1/2}$, a linear graph is obtained with regression linear coefficient, R^2 , close to unity. The gradient

Fig. 4 The Weber–Morris intra-particle diffusion model for the adsorption of Methylene Blue by PCL [65]

of the graph reveals the intraparticle diffusion rate constant, K_{id} . Figure 4 represents the Weber-Morris intraparticle diffusion model for the adsorption of Methylene Blue by PCL [65].

The adsorption of Methylene Blue by PCL is divided into three stages because when a graph of q_t is plotted against $t^{1/2}$, multiple linearity is obtained. The first linearity (first stage) represents the adsorption of Methylene Blue at the boundary layer. The second linearity (second stage) describes the diffusion of Methylene Blue into the pore of the adsorbent. The linear graph plotted at this stage is used to calculate the intraparticle diffusion rate constant, K_{id} (2.3 mg/gmin^{1/2} at 50 mg/L). The intraparticle diffusion will be extended until the adsorbent attained equilibrium (adsorbent is saturated with adsorbate) which is also known as third stage.

6 Babassu coconut

The activated carbon prepared by using babassu coconut (ACBC) obtained from Tobasa Bioindustrial Babaçu S.A company was used as received. It has been used to adsorb tartrazine yellow dye (anionic) which is also known as trisodium (4E)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl)hydrazono]-3-pyrazolecarboxylate as shown in Figure A6, Supporting Information. The adsorption process in an endothermic reaction because the ΔH° value is 39.06 kJ/mol. The suitable pH for the adsorption of tartrazine is 3, which is in well agreement with the theory. Generally, an anionic (negatively charged) dye constructs electrostatic attraction with H_3O^+ ions at acidic condition. It requires 12 h contact time to achieve equilibrium. ACBC is capable in adsorbing 31.10 mg/g of tartrazine at 298 K owing to its spontaneity ($\Delta G^\circ = -3.5878$ kJ/mol) and highly disorder arrangement of atoms ($\Delta S^\circ = 146.27$ J/mol K). The adsorption of tartrazine by ACBC met Freundlich isotherm and it is highly favorable because the R^2 and n values are 0.9796 and 1.3473, respectively as well as K_F equals to 2.84 L/mg. Likewise, the adsorption of tartrazine by ACBC comply with the pseudo-second order because the q_e theoretical (3.80 mg/g) is approximate to the q_e actual (3.66 mg/g). Also, the R^2 are close to unity (0.9646) along with k_2 equals to 0.0039 g/mg min, respectively.

7 Green coconut mesocarp

Green coconut mesocarp is a young coconut shell which is not treated and was used to adsorb Remazol Golden Yellow RNL-150% (RGY), anionic dye by Nascimento et al. (2016) [71]. The chemical structure of Remazol Golden Yellow RNL-150% (RGY) is shown in Figure A7, Supporting

Information. The dye unites harmoniously with protons on the adsorbent via electrostatic synergistic in acidic condition. As such, the optimum pH for the adsorption process is 2 and the green coconut mesocarp successfully adsorbed 9.6 mg/g at 298 K. The data for adsorption process fits Freundlich isotherm with R^2 value of 0.995. The adsorption process is favored because the n and K_F are equals to 2.3 and 1.8 L/mg. The analyzed data revealed that the rate-determining step satisfied pseudo-second order with R^2 value equals to 0.976. In fact, both the theoretical and actual q_e are identical (7.7 mg/g) along with k_2 equals to 0.031 g/mg min.

8 Coconut coir dust

Coconut coir dust (brown, spongy particle) is produced after the extraction of fibre from the coconut husk. It composed mainly lignins and tannins apart from cellulose, pentosane and furfural. It has been explored for the media for containerized crop production instead of waste materials. In the studies carried out, (Etim et al., 2016) did not modify the coconut coir dust whereas (Ikhuangbe et al., 2017) carbonized and activated the coconut fiber at 400 °C and 800 °C, respectively [72, 73]. The performances of the unmodified and modified coconut coir dust towards Methylene Blue and Erythrosine, respectively are shown in Table 3.

The optimum pH for the adsorption of Methylene Blue is 6. The adsorption of Methylene Blue by coconut coir dust is not suitable for too low pH owing to the competition between the H^+ ions and NH_4^+ ions for the active sites. The result obtained is in well agreement with the adsorption of Methylene Blue by activated carbon by coconut leaves impregnated with H_3PO_4 via microwave pyrolysis and carbonization at 700 °C [65, 66]. Generally, the amount of adsorbate increases with the increasing dosage of adsorbent at constant initial concentration [74]. As the amount of adsorbent increases, the surface area increases that led to the elevation of adsorption sites until it reaches equilibrium. At higher dosage of adsorbent, the percentage removal of dyes becomes constant owing to overlapping of active sites [75].

Figure 5 illustrates the relationship between the dosage of adsorbent and the adsorption capacity at 35 °C for 40 min [76]. Based on Fig. 5, at 20, 30, 40 and 60 mg/L Congo red, it requires 500, 600, 600 and 900 mg of coir pith carbon, respectively to attain equilibrium. Based on the result, every 1 g of coconut coir dust is able to adsorb 29.50 mg of Methylene Blue and the adsorption process suits Temkin Model. Figure 6 depicts the Temkin isotherm model for the adsorption of Methylene Blue by coconut coir dust [72]. Temkin model states that the strength of

Table 3 Performances of unmodified and modified coconut coir dust towards Methylene Blue and Erythrosine, respectively

Characteristics	Adsorbents	
	Coconut coir dust [72]	Coconut fiber [73]
Adsorbate	Methylene Blue	Erythrosine or Acid Red
pH	6	NIL
Adsorption equilibrium isotherm at 303 K	Temkin model isotherm	Freundlich isotherm
K_T	14.75	KF (L/mg) 0.8872
B_1	4.43	n 3.50
R^2	0.99	R2 0.8800
Adsorption kinetics at 50 mg/L	Pseudo-second order	
k_2 (g/mg min)	0.76	0.0465
q_e theoretical (mg/g)	11.90	1.7036
q_e actual (mg/g)	11.84	NIL
R^2	1.00	0.9970
<i>Thermodynamics study</i>		
ΔH°	17.87 kJ/mol (Endothermic)	28.73 kJ/mol (Endothermic)
ΔS°	51.10 kJ/mol K	0.09445 kJ/mol K
ΔG at 303 K	− 9.69 kJ/mol (Spontaneous)	− 0.10 kJ/mol (Spontaneous)

Fig. 5 The relationship between the dosage of adsorbent and the adsorption capacity at 35 °C for 40 min [76]

the interaction between adsorbent and adsorbate (gaseous physical state) is inversely proportionate to the heat of adsorption. The model can be written as follows [40]:

$$q_e = \frac{RT}{b} \ln(A_T C_e)$$

where q_e is the amount of adsorbate per unit mass of adsorbent (mg/g), R is the universal gas constant (J/mol K), T is the absolute temperature (K), A_T is the Temkin

equilibrium binding constant (L/mg), b is the Temkin isotherm constant and C_e is the equilibrium concentration of adsorbate (mg/L). The Temkin isotherm model is rearranged for plotting the graph and it can be written as follows:

$$q_e = \frac{RT}{b} \ln C_e + \frac{RT}{b} \ln A_T$$

Fig. 6 Temkin isotherm model for the adsorption of Methylene Blue by coconut coir dust [72]

When a graph of $\ln C_e$ is plotted against q_e , a linear graph is acquired with regression linear coefficient, R^2 , close to unity. The b and A_T are obtained from the gradient and intercept of the graph. Both the gradient and intercept of the graph represent the values for $\frac{R_T}{b}$ (related to the heat of adsorption) and $\frac{R_T}{b} \ln A_T$, respectively. The heat of adsorption ($\frac{R_T}{b}$) values increase with absolute temperature and thus the adsorption process is endothermic as supported by the ΔH° value of 17.87 kJ/mol. The A_T values increase with temperature until it reaches saturation. The A_T values increase to 17.42 L/mg at 313 K from 14.72 L/mg at 303 K. Following this, the amount of Methylene Blue adsorbed per mg of coconut coir dust reduced to 15.70 L and 14.42 L at 323 K and 333 K, respectively. The adsorption process is spontaneous and favored because the ΔG at 303 K equals to -9.69 kJ/mol and the standard entropy change is 51.10 kJ/mol K. Likewise, the adsorption of Erythrosine by modified coconut fiber is endothermic ($\Delta H^\circ = 28.73$ kJ/mol) and spontaneous ($\Delta G = -0.10$ kJ/mol) along with $\Delta S^\circ = 0.09445$ kJ/mol K. Both adsorption processes match to pseudo-second order which is in line with the R^2 value of 1.00. The adsorption of Methylene Blue by unmodified coconut coir dust shown more prominent results than the adsorption of Erythrosine by modified coconut fiber. This is because the q_e theoretical (11.90 mg/g) and k_2 (0.76 g/mg min) values of unmodified coconut coir dust are higher than q_e theoretical (1.7036 mg/g) and k_2 (0.0465 g/mg min) values of modified coconut fiber. In fact, the q_e experimental value (11.84 mg/g) differ from the q_e theoretical value (11.90 mg/g) by 0.504% for the unmodified coconut coir dust.

On the contrary, Freundlich isotherm model was obeyed by the adsorption of Erythrosine by modified coconut fiber owing to its close to unity R^2 value of 0.8800. The n and K_F values obtained are 3.50 and 0.8872 L/mg, respectively.

9 Conclusions

There are four important parameters (pH, contact time, amount of adsorbent and initial concentration of adsorbate) for the removal of dyes via adsorption technique. Generally, the adsorption of anionic dye is highly favored at low pH and in contrast, the adsorption of cationic dye is favored at high pH. The rate of adsorption of dye molecules on the coconut based adsorbents obeyed pseudo-second order, Elovich chemisorption and Weber–Morris intraparticle diffusion model. These coconut-based adsorbents fitted the Langmuir, Fritz–Schlunder, Langmuir type-2, Freundlich, Brauner–Emmet–Teller (BET) and Temkin isotherm models. In the thermodynamic studies, both the ΔG and ΔH values determine the spontaneity and the type of a reaction. The positive value of ΔG signifies the non-spontaneous of the reaction and vice-versa. On the other hand, positive value of ΔH indicates the reaction is endothermic and vice-versa.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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