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Reactive dyes adsorption via *Citrus hystrix* peel powder and *Zea mays* cob powder:

characterization, isotherm and kinetic studies

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ABSTRACT

Adsorption is one of the generally used treatment methods due to the low-cost, high removal effect and simple design The aim of the study was to investigate the adsorption efficiency of lignocellulosic waste such as lime peel (*Citrus hystrix*) and CC (*Zea mays*) for removal of Reactive Violet 5 (RV5) and Reactive Red 2 (RR2) dyes. The physical and chemical characteristics of the adsorbents were analyses by using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). Additionally, the solution acidity, adsorbent mass, duration of adsorption, and dye concentration were evaluated with isotherm and kinetic study to determine the mechanism of adsorption. The removal of RV5 for lime peel and CC achieved to 50 % and 48 % while the removal of RR2 for lime peel and CC reached 53 % and 46 %. The highest adsorption capacity for both adsorbents was 4.29 mg/g and 6.14 mg/g. In terms of physical characteristics, the adsorbent had large surface area that adsorbs more dyes in same amount of dye concentration. The results showed that Freundlich isotherm and Pseudo-first-order kinetic models were best fitted to the adsorption process with R² value of 0.9974 and R² value of 0.9919.

Keywords: Adsorption; Citrus hystrix; Zea mays; Reactive Violet 5 (RV5); Reactive Red 2 (RR2); isotherm; kinetic.

1. INTRODUCTION

Water is a resource required by all organisms for their survival. Although there is a large volume of water in nature, the water scarcity in the world is commonly increasing [1]. The statistic showed that the land covered 29% of the earth surface while the remaining is covered by the water. The 71% of the total global water contain oceans water 96.5%, freshwater 2.5%, saline groundwater 0.93% and saline lakes 0.07%. Among these total global water resources, there are only 2.5% of freshwater can be directly used by the human. The 2.5% of freshwater contain glaciers and ice caps 68.6%, groundwater 30.1% and surface water 1.3%. The use of freshwater can be distributed into three major which is industrial use, agricultural use and domestic use. Therefore, there is large volume of waste water produced from human daily use. In recent year, there are many products from the industries such as dyestuffs, paper, plastics, textile, leather, rubber and printing use dyes for color and chemicals for manufacturing. The dyes will be discharged into the surrounding environment with the wastewater from these textile industries. Due to the visibility and toxic impact, it can affect the photosynthetic activities in surrounding aquatic environments [1-3]. Therefore, the sunlight penetration will be reduced by the dyes and the dissolved oxygen in the aquatic environments will be depleted very fast. In addition, human health impacts such as cancer, skin irritation, allergies, tumors and jaundice can be affected by the dyes toxic effect. There are differences group of dye which imitate macroscopic behavior and prevailing functionalities such as metallic, solvent, Sulphur, direct, basic, acid, vat dyes, disperse, and mordant [4-5]. Therefore, an effective process that can remove these natural and synthetic dye effectively is required since the

removal from the waste water is considered an environmental challenge.

There are various treatment methods have been suggested such as adsorption, electrochemical oxidation, precipitation, filtration, chemical oxidation and coagulation to remove the dye from the waste water effluents [7]. The treatment of removal dyes can be alienated into two classes which is degradative (e.g., chemical treatment and biological treatment) methods and separative (physical treatment and physicochemical treatment) methods. Therefore, there are many restrictions (e.g., expensive, required more space and require using more chemical) to remove the dye from the waste water effluents [6-10]. Adsorption is one of the generally used treatment methods due to the low-cost, high removal effect and simple design. Activated carbon is commonly used as adsorbent to remove the dye in the waste water effluents for the adsorption process. Meanwhile, there are other adsorbents widely used to replace the activated carbon. Due to the toxic effect of the adsorbent that might cause the secondary pollution, it is highly recommended to find suitable adsorbent that produces less environmental impacts [11]. Therefore, many agricultural wastes have been tested to replace the adsorbent to remove the dye from the waste water effluents. In addition, different agricultural wastes have different properties and ability to remove the dye from the waste water effluents efficiently.

For this study, lime peel (*Citrus hystrix*) and CC (*Zea mays*) were used as adsorbent and treated with acid sulphuric for chemical modification. The agricultural waste came from different kind of shape, color and sources thus, its need pre-treatment before use as adsorbent. All pollutants and any soluble organic compounds of

adsorbent ought to remove with diverse types of modifying agents, such as oxidizing agents, organic compounds, acid and base solutions, dyes, and mineral [12]. The aim of this study was to apply agricultural waste material as a potential adsorbent to adsorb

2. MATERIALS AND METHODS

2.1. Characterization of the adsorbent.

The lime peel (LP) and CC(CC) used in this study were obtained from domestic market waste in Miri, Malaysia. The samples were cut into pieces and washed 3 times with distilled water to remove the impurities on the surface of the samples. Samples were dried at 100°C for at least 12 hours. The samples were ground into powder and sieved to get a similar size of the adsorbents between 300-500 mm. The adsorbent powders were kept in containers for the experiment.

2.2. Preparation of the dyes solution.

The reactive dyes and other solvents such as ethanol, methanol, sodium hydroxide, sulfuric acid were obtained from Qrec (Johor Bahru, Malaysia). RV5 and RR2 were chosen because they are frequently utilized in the stain and textile industries. The stock solution of RV5 and RR2 were prepared by dissolving 1000 mg/l dyes in distilled water. The properties and molecular structure of the dyes are shown in Table 1. The acidity of the solution was adjusted by using 0.1M of H₂SO₄ and NaOH.

reactive dyes. Various parameters condition on the adsorption, isotherm, kinetic studies and physical and chemical characteristic were also being examined.

2.3. Adsorption experiment.

The adsorption experiment was performed on LP and CC in 100-mL Erlenmeyer flasks containing 100 mg/l of RV5 and RR2 dye solutions. All batch studies were agitated at 120rpm and conducted in triplicate. The removal of dyes was measured by using a UV-Visible Spectrophotometer (NANOCOLOR VIS, Macherey-Nagel, Germany) at λ_{max} 558nm (RV5) and λ_{max} 513nm (RR2). The experiments were categorized into three section: (a) Various experimental parameters were summarized in Table 2, (b) isotherm equilibrium, and (c) kinetic studies.

The color removal and adsorption capacity were calculated using the equation as follows:

Removal (%) =
$$\frac{C_0 - C_x}{C_0} \times 100$$

Adsorption Capacity (mg/g) =
$$A = \frac{(C_0 - C_x)!}{M}$$

Where $C_0 (mg/L)$ and $C_x (mg/L)$ is initial and equilibrium of dyes concentrations in the solution, A (mg/g) is the adsorption capacity, V (l) is the solution volume, and M (g) is the mass of adsorbent.

Table 1. The chemical and physical properties of RV5 and RR2.							
Properties	RV5						
Chemical Structure	Na ⁺ O ⁺ O ⁺ O ⁺ O ⁺ O ⁺ O ⁺ O ⁺ O						
Molecular formula	$C_{20}H_{16}N_3Na_3O_{15}S_4$	$C_{19}H_{10}Cl_2N_6Na_2O_7S_2$					
Appearance	Powder	Powder / Crystalline powder					
Appearance (color)	Dark violet	Dark red, Red brown					
Physical state	Solid	Solid					
Molecular weight	735.58 g/mol	615.34 g/mol					
Solubility	Soluble in methanol and water (partially)	Soluble in water (1 mg/ml)					
Melting point	>360°C	Above 305°C					
Storage	Cool and well-ventilated place	Room temperature					

Table 7 Batch Analysis for the experiment

Parameter	Initial pH	Dosage of adsorbents (g)	Contact time (min)	Concentration (mg/l)
Effect of initial pH	3 -11	0.5	60	100
Effect of dosage	7	0.5 - 1.5	60	100
Effect of contact time	7	0.5	20 - 100	100
Effect of concentration	7	0.5	60	20 - 100

2.4. Physical and chemical Characterization.

The structural and the chemical properties of LP and CC were picturized and analysed before and after the adsorption process. Surface texture was picturized by using FESEM (FESEM, JEOL 6335f-SEM, Japan) and the functional group of the adsorbents was analysed by using FTIR (Spectrum one, Perkin Elmer, USA) at the spectral range of 400-4000 cm⁻¹.

2.5. Isotherm and Kinetic Studies.

Adsorption isotherm and kinetic models are mathematical equations that describe the efficiency of adsorbents interacting with the dye solutions or pollutants by optimizing the surface characteristics, adsorption capacity and the effectiveness of the design towards adsorption systems. The adsorption isotherm study of the samples was conducted by manipulating the concentration of dyes in experiments. Other parameters were controlled as optimized studied and were run for 24 h. To describe the best adsorption isotherms of dyes onto the adsorbents, the following isotherm models were used [13]:

a. Langmuir isotherm is to measure and contrast the adsorbent capacity. It can assume the monolayer coverage; equilibrium model and all adsorption sites are equally probable.

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

Where C_e is concentration of adsorbate at equilibrium (mg g⁻¹), q_e = amount of the adsorbate at equilibrium (mg g^{-1}), K_L is Langmuir rate constant (mg g⁻¹), q_m is amount of the adsorbate at equilibrium $(mg g^{-1}).$

b. Freundlich isotherm is to measure the surface heterogeneity and exponential distribution of active site. It can determine the relationship between the concentration of the dye in the liquid and the concentration of dye on the surface of an adsorbent.

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

Where q_e is the amount of the adsorbate at equilibrium (mg g⁻¹), K_F is adsorption capacity (L mg⁻¹), C_e is concentration of adsorbate at equilibrium (mg g^{-1}), and 1/n is adsorption intensity.

c. Harkin-Jura isotherm is to determine the adsorption of adsorbents containing heterogeneous pore distribution.

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right)\log C_e$$

Where q_e is the amount of the adsorbate at equilibrium (mg g⁻¹), A is Harkin-Jura constants obtain from plotting $1/q_e^2$ versus log C_e,

3. RESULTS

3.1. FESEM &FTIR.

The SEM micrographs were conducted to observe the effects of the adsorption processes of RV5 and RR2 on microstructures of LP and CC (Fig. 1). The dye particles were attached between the polymer component of the surface structure of LP. Raw LP can be further continuing for the adsorption process as there still some adsorption space to trap the dye particle and mostly attached to the surface of adsorbent. The image from Figure 1D shows that the surface is full of pores and irregular shape.



Figure 1. Field Emission Scanning Electron Microscope (FESEM) image of raw LP (A), LP after adsorbing RR2 (B) and LP after adsorbing RV5 (C), raw CC (D), CC after adsorbing PR (E) and CC after adsorbing RV5 (F).

This hilly structure shows the presence of heterogenous surface that have higher chance to trap the dye particles [14]. After B is Harkin-Jura constants obtain from plotting $1/q_e^2$ versus log C_e , C_e is concentration of adsorbate at equilibrium (mg g⁻¹).

d. Jovanovic isotherm is to determine possibly of mechanical contact between adsorbate and adsorbent based on Langmuir isotherm.

$$\ln q_e = \ln q_{max} - K_J C_e$$

Where q_e is the amount of the adsorbate at equilibrium (mg g⁻¹), q_{max} is maximum uptake of adsorbate from plot ln q_e versus C_e, K_J is Jovanovic constant, and Ce is concentration of adsorbate at equilibrium (mg g^{-1}).

For kinetic models, the adsorption process was analysed with the pseudo-first-order and pseudo-second-order and intraparticle diffusion. The kinetic study was calculated by using equation as follow [13]:

a. Pseudo-first-order model: $\ln(q_e - q_t) = \ln q_e - K_1 t$

b. Pseudo-second-order model: $\frac{t}{q_t} = \frac{1}{k^2 q_e^2} + \frac{t}{q_e}$ Where

Where q_e and q_t (mg/g) respectively indicate the amount 1 of the dyes adsorbed at equilibrium and at time t (min); K1 is the pseudofirst-order rate constant and K2 is

the adsorption process, dye particle was attached on the CC adsorbent. The adsorption capacity of CC is lower than the LP due to the remaining porosity surface and rough surface under same conditions. Thus, this study showed that the sulphuric acid treatment increases the growth of pore of the banana bunches, which increased the number of active sites and its ion-adsorption capacity [15-16].

FTIR analysis of LP and CC is shown in Fig. 2. For raw LP, the peak at the 3233.82 cm⁻¹ represents O-H stretch that indicating the presence of carboxylic acids groups. Peak at 2914.71 cm⁻¹ and 1738.24 cm⁻¹ shows the functional group of alkanes which have C-H stretch and the existence of carbonyls, ester, saturated aliphatic and aldehydes with C=O stretch, while 1426.47 cm⁻¹ shows the aromatics group with C-C stretch. The present of aliphatic amines (C-N stretch) and alkyl halides with C-Br stretch was shown at the peak of 1238.24 cm⁻¹ and 598.53 cm⁻¹. The functional group of alcohol, phenols, amines and alkanes represented at peaks 3383.82 cm⁻¹ and 2915.22 cm⁻¹ while peaks at 1630.34 cm⁻¹, 1401.25 cm⁻¹, 1238.46 cm⁻¹ and 1047.06 cm⁻¹ show the functional group of amines (N-H bend), aromatics (C-C stretch), alcohols, esters, carboxylic acids, and ethers. The peaks at 804.42 cm⁻¹ and 554.41 cm⁻¹ represent the functional group of aromatics with C-H and alkyl halides with C-Br stretch. From the Fig. 3B, the first peak of raw LP was 3233.82 cm⁻¹ shows the functional group of alcohols, phenols and carboxylic acids which have O-H stretch and H-Bonded. The functional group of carboxylic acids which have O-H stretch was shifted to peaks 3383.82 cm⁻¹ represented a broad and medium band of functional group of alcohols, phenols after RV5 adsorption process and 3392.09 cm⁻¹ represented a sharp and strong band of functional group of alcohols and phenols with O-H stretch and H-Bonded after RR2 adsorption process. The third peak of raw LP was 1738.24 cm⁻¹ shows the functional group of carbonyls, ester, saturated aliphatic and aldehydes with C=O stretch while it did not exist in LP after RR2 and RV5 adsorption process. The last peak

of raw LP was 598.53 cm⁻¹ represented the functional group of alkyl halides with C-Br stretch. The last peak of raw LP transformed into two peaks which were 789.78 cm⁻¹ and 789.78 cm⁻¹ and 539.71 cm⁻¹ show the existence of aromatics with C-H and alkyl halides with C-Br stretch for RV5 adsorption. Meanwhile, the last peak of raw LP transformed into two peaks which were 804.42 cm⁻¹ and 554.41 cm⁻¹ represented the functional group of aromatics with C-H and alkyl halides with C-Br stretch. For raw CC sample, the functional group of 10 amines with N-H stretch represented in Figure 4 at peak 3400.73 cm⁻¹ and the functional group of alkanes with C-H stretch at peak 2922.73 cm⁻¹ respectively. While peaks at 1725.76 cm⁻¹, 1634.85 cm⁻¹, 1377.28 cm⁻¹ and 1263.64 cm⁻¹ show that there was functional group such as aldehydes, saturated aliphatic with C=O stretch; 10 amines with N-H bend; nitro compounds with N-O symmetric stretch; and alkyl halides with C-H wag (-CH₂X). At the peak of 1051.62 cm⁻¹ shows the functional group of aliphatic amines with C-N stretch. Lastly, the peak of 612.12 cm⁻¹ shows the existence of alkyl halides with C-Cl stretch. The display of the peak at the 3377.27 cm⁻¹ was caused by the functional group of alcohol and phenols which have O-H stretch and H-bonded. At peak 2930.64 cm⁻¹ shows the functional group of alkanes which have C-H stretch. At peak 1632.18 cm⁻¹ showed the existence of the functional group of amines with N-H bend while peak of 1392.42 cm⁻¹ shows the functional group of nitro compounds with N-O symmetric stretch. The functional group of alkyl halides with C-H wag (-CH₂X) presented at the peak 1262.11 cm⁻¹ and 1013.77 cm⁻¹ for the functional group of alcohols, carboxylic acids, esters and ethers with C-O stretch. Lastly, the peak of 586.31 cm⁻¹ was represented the functional group of alkyl halides with C-Cl stretch. The functional group at first peak 3604.54 cm⁻¹ was alcohols and phenols with O-H stretch and free hydroxyl. The existence of alcohol and phenols which have O-H stretch and H-bonded at peak 3346.97 cm⁻¹. The functional group of alkanes with C-H bend, carboxylic acids with O-H stretch; carbon dioxide with O=C=O stretch; and 10 amines with N-H bend were shown at peaks 2931.82 cm⁻¹, 2574.24 cm⁻¹, 2349.00 cm⁻¹ and 1633.44 cm⁻¹. The functional group of nitro compounds with N-O symmetric presented at the peak 1390.11 cm⁻¹ and 1261.87 cm⁻¹ for the functional group of alkyl halides with C-H wag (-CH₂X). Lastly, the peaks at 968.11 cm⁻¹ and 566.67 cm⁻¹ represent the functional group of alkenes with =C-H bend and alkyl halides with C-Cl stretch. The peak of raw CC at 3400.73 cm⁻¹ shows the functional group of amines with N-H stretch. The functional group of amines with N-H stretch was shifted to peak 3377.27 cm⁻¹ represents a strong and board band of functional group of alcohol and phenols which have O-H stretch and H-bonded after RV5 adsorption and 3346.97 cm⁻¹ represents a sharp and strong band of functional group of alcohols and phenols with O-H stretch and H-Bonded after RR2 adsorption. Besides, the presence peak of 3604.54 cm⁻¹ was caused by the functional group of alcohols and phenols with O-H stretch and free hydroxyl after RR2 adsorption process. The peak at 1725.76 cm⁻¹ shows the functional group of aldehydes, saturated aliphatic with C=O stretch did not exist in CC after the RR2 and RV5 adsorption process. Two new strong, sharp band peaks 2574.24 cm⁻¹ and 2349 cm⁻¹ presence at the CC which functional group was carboxylic acids with O-H stretch and

carbon dioxide with O=C=O stretch after the RR2 adsorption process. The last peak of raw CC (612.12 cm⁻¹) shows the functional group of alkyl halides with C-Cl stretch shifted to a strong and sharp band. The most dominance element in the adsorbents was carbon, then, followed by oxygen that derived from carboxylic acid of functional groups. While the presence of Sulphur element in the adsorbents was derived from sulfuric acid that used as a modified agent for pre-treatment process [17].



3.2. Batch studies.

This experiment has been conducted to know the effect of acidity of dye solution. The initial pH of the solution was set from 3 to 11. Figure 3A and 3B show that the removal rate and adsorption capacity result of LP for both RR2 and RV5. It clearly shows that the removal rate for both dyes decrease while more alkaline added into the solution. Besides, the adsorption capacity also decreased while the solution becomes more alkaline. The percentage removal of RR2 dye solution and RV5 dye solution by the LP increased from 15.38% to 37.64% and 10.07% to 38.16% due to the decrease of pH from 11 to 3. For CC, the percentage removal of RR2 dye solution and RV5 dye solution increased from 5.50% to 53.95% and 5.90% to 54.90% while the pH decreased from pH 11 to 3. Under acidic condition, the anionic dye species can be attracted to the surface of the protonated adsorbent. The protonated adsorbent surface areas decreased as the pH increases and caused the decrease the attraction of anionic dye species to the protonated adsorbent surface. Meanwhile, the effect of pH directly caused the adsorption capacity of adsorbent. At higher pH condition, less protonated surface of adsorbent generated and caused the decrease of anionic dye species adsorb by the adsorbent. The previous study showed that the removal of Procion Orange dye by orange peel has the highest percentage removal at pH 3 and remain the same over the range of pH 5 to pH 9 and lowest percentage removal at pH 11. Besides that, the overall percentage removal of rhodamine-B dye also shows the same trend [11, 18-20]. Another study on CC shows that the

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adsorption capacity of Methylene Blue dye by raw corn have the lowest adsorption capacity at pH 3 and adsorption capacity increased while pH increased. The highest adsorption capacity reached to pH 12. The reason for the adsorption capacity increased due to the properties of the dye molecules and properties of the functional groups of the raw corn [21-22]. These indicated that the pH will affect the percentage of dye removal and pH also will affect the adsorbent characteristics.

Effect of adsorbent dosage on adsorption of dyes by CL and CC is shown in Figure 3C and Figure 3D. The adsorbent dosage was set from 0.5 gram to 1.5 gram. It clearly shows that the removal rate for both dyes increased while more adsorbents added into the solution. In addition, the adsorption capacity also decreased while more adsorbent added into the solution. The effect of adsorbent dosage was evaluated by applying different amount of LP and CC from 0.5 g to 1.5 g. The percentage removal of RR2 for LP increased from 24.91% to 52.77% while percentage removal for CC increased from 30.47% to 45.65%. For RV5, the percentage removal for LP increased from 24.38% to 50.37% and 32.50% to 47.91% for CC. A certain amount of adsorbent can remove a certain volume of dye solution; hence more dye will be adsorbed when more amount of adsorbent used. The extended surface areas of the adsorbent were the reason that the percentage of removal increased. There were more adsorption sites to adsorb the dye solution due to the extended of the surface areas of adsorbent [23].



Figure 3. Effect of pH on adsorption of RV5 and RR2 by CL (A) and CC (B); Effect of adsorbent dosage on adsorption of RV5 and RR2 by CL (C) and CC (D).

Effect of dyes concentration on adsorption of dyes by CL and CC is shown in Figure 4A and 4B. The dye concentration for the solution was set from 20 mg/L to 100 mg/L. The percentage removal rate for both dyes decreases when high concentration of dye dissolved in the solution. The overall trend showed that increased in initial dye concentration caused the percentage removal decreased due to the adsorbent reached to the maximum adsorption capacity in the dye solution. Although the higher concentration decreased the percentage removal of dye solution, the adsorption capacity of adsorbent increased in opposite trends. At high concentration dye solution, the ratio between dye particles and adsorbent surface are low in the solution, thus a lower chance for dye particles attached to the adsorbent [19, 24-25].

Figure 4C and 4D shows that the removal rate and adsorption capacity result of LP for both RR2 and RV5. The

percentage removal of RR2 dye solution and RV5 dye solution by the LP increased from 23.58% to 28.51% and 22.16% to 28.23% due to the increase in contact time. For CC, the percentage removal of RR2 dye solution and RV5 dye solution increased from 23.17% to 25.96% and 24.81% to 29.21% while the contact time increased from 20 min to 100 min. The batch analysis of contact time not sufficient to determine the adsorption capacity reached the equilibrium. Theoretical, the contact time should plot followed the equilibrium curve [26]. This means when reached to a certain time, the adsorption capacity reached equilibrium and no further adsorption process ongoing.

3.3. Adsorption Isotherm and Kinetics.

The isotherm studies were calculated by some models: Langmuir (Fig. 5), Freundlich (Fig. 6), Harkin-Jura (Fig. 7), and Jovanovic (Fig. 8). When the relationship between both the adsorbent and dye concentration reached the equilibrium, adsorption isotherms were carried out to measure the mechanism of adsorption reaction [13]. The Langmuir isotherm was carried out to measure and contrast the adsorbent capacity. Freundlich isotherm was carried out to measure the heterogeneous and distribution of the active site on the adsorbent surface. Harkin-Jura isotherm was carried out to measure the heterogeneous pore distribution of the adsorbents. Jovanovic isotherm was carried out to measure the mechanical contact of adsorbent and adsorbate. By comparing all obtained results, Freundlich isotherm equation providing the maximum R² value of 0.9948 for RR2 with orange peel, 0.9898 for RV5 with LP, 0.9974 for RR2 with CC and 0.9777 for RV5 with CC based on Figure 5. LP and CC surface were more heterogeneous and fitted with Freundlich isotherm model. This model also assumes that the surface of adsorbent was heterogenous indicated the heterogenous distribution of active sites onto the surface of the adsorbents [27]. The value of R^2 obtained indicated the type of Freundlich isotherm were favorable at the concentration studied since the R² value of more than 0 and less than 1 ($0 < R^2 < 1$). The correlation coefficient (R^2) of the experimental data fits quite well with the Freundlich isotherm since the value was more than 0.97 (>0.97), whereas, the correlation coefficients for Langmuir and Temkin model were less than 0.97 (<0.97) indicated that the experimental data have not fit with the models.



Figure 4. Effect of dyes concentration on adsorption of RV5 and RR2 by CL (A) and CC (B); Effect of contact time on adsorption of RV5 and RR2 by CL (C) and CC (D).



Figure 5. Langmuir model for RR2 adsorption onto LP (A) and CC (B); and RV5 adsorption onto LP (C) and CC (D).



Figure 6. Freundlich model for RR2 adsorption onto LP (A) and CC (B); and RV5 adsorption onto LP (C) and CC (D).

The outcomes indicated that RR2 and RV5 removal and adsorption capacity increase gradually over time. The most effective for RR2 and RV5 adsorption was at the first 20 min of experiment due to availability of readily accessible sites and the morphology effect of the adsorbents. The adsorption capacity was highly increased at the initial stage due to a lot of quantity of vacant pores. Thus, this impacted the increasing of binding between dye in the adsorbent and the decreasing the quantity of dye in solution [28]. After 24 h, the equilibrium for all adsorbents was occurred, which showed the highest removal rate, adsorption capacity, and indicating saturated adsorbent [29]. The observation after 24 h, showed that the adsorption rate tends to decrease. The adsorption data obtained were calculated with the pseudo-firstorder and pseudo-second-order models and were tabulated in Table 3. The adsorption of RV5 at equilibrium (q_e) for LP and CC was 3.07 mg/g and 3.19 mg/g, which is almost the same as the

4. CONCLUSIONS

LP and CC showed the ability to adsorb the reactive dyes with removal >50% and adsorption capacity > 5mg/g. The FTIR and FESEM have shown the functional group that presence in the adsorbents and the surface characteristic. Both adsorbents have a surface structure with a large area of pores have a good ability to adsorb. The functional groups presence in the adsorbent has shown the different adsorption efficiency. The removal of RV5 for lime peel and CC achieved to 50 % and 48 % while the removal of calculated value for pseudo-first-order model. While the R^2 in pseudo-first-order model gives a similar value of 0.99 that indicated a better fit, which is a little bit higher than the pseudo-first-order with R^2 value, was 0.965 and 0.97. However, the adsorption of RR2 at equilibrium (q_e) for LP and CC was 3.4 mg/g and 3.02 mg/g, which is almost the same as the calculated value for both pseudo-first-order and pseudo-second-order model. Thus, the adsorption mechanism was chemisorption.







Figure 8. Jovanovic model for RR2 adsorption onto LP (A) and CC (B); and RV5 adsorption onto LP (C) and CC (D).

Table 3. Kinetic parameters for RV5 and RR2 onto PP and CC

Tuble 5. Remetic parameters for Rev 5 and Rev2 onto 11 and CO.							
Adsorption	Adsorption	RV5		RR2			
kinetics	constant	LP	CC	LP	CC		
Pseudo-	qe calculated	3.07	3.19	1.42	3.02		
first-order	\mathbf{k}_1	0.0164	0.0189	0.0235	0.0098		
	R^2	0.9888	0.9919	0.8004	0.9729		
Pseudo-	qe calculated	4.1667	4.5620	3.4650	3.5336		
second-	k ₂	0.02	0.01	0.12	0.01		
order	R^2	0.9659	0.9719	0.9918	0.9094		

RR2 for lime peel and CC reached 53 % and 46 %. The highest adsorption capacity for both adsorbents was 4.29 and 6.14 mg/g. The value of R^2 obtained indicated the type of Freundlich isotherm were favorable at the concentration studied since the R^2 value of more than 0 and less than 1 (0< R^2 <1). The correlation coefficient (R^2) of the experimental data fits quite well with the Freundlich isotherm since the value was more than 0.97 (>0.97). The adsorption of RV5 at equilibrium (q_e) for LP and CC was 3.07

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mg/g and 3.19 mg/g, which is almost the same as the calculated value for pseudo-first-order model. However, the adsorption of RR2 at equilibrium (q_e) for LP and CC was 3.4 and 3.02 mg/g,

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