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Original Research Article

Biosorption, Isotherm and Kinetic Studies of Methylene Blue Dye Removal from Aqueous Solution using Citrus Peels as Adsorbent

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ABSTRACT

Waste water generated by many industries such as textiles and cosmetics industries contain organic dye stuff that is harmful to humans and aquatic organisms. As a result, this study was conducted on the biosorption of methylene blue using various bio-waste materials namely, sweet orange peels (OP), grape fruit peels (GP) and lime peels (LP) and their combinations (OP + GP and OP + LP) as biosorbents for the removal of methylene blue dye from solution. The peel samples were dried, pulverized and characterized for functional groups and surface morphology using Fourier transform infra-red (FTIR) spectroscopy and scanning electron microscopy (SEM) respectively. Batch experiments were performed to investigate the effect of factors such as contact time, initial dye concentration and adsorbent dosage on methylene blue adsorption. Experimental data were analyzed using Langmuir and Freundlich isotherm models. The data was found to be best described by Langmuir adsorption isotherm (R^2 = 0.998) with maximum adsorption capacity of 29.533mg/g for monolayer coverage. Optimum methylene blue removal efficiencies at 0.6g/20ml dosage was found to be 82, 85 and 84% respectively for OP, OP+GP and OP+LP, whereas at 0.8g/20ml dosage, 68 and 61% efficiencies were recorded for GP and LP respectively. Maximum removal efficiency of 85% for OP+GP was achieved at 150 minutes contact time. Several biosorption kinetic models were tested and the results showed that citrus peel biosorbent followed the pseudo-second-order kinetics.

1. INTRODUCTION

After use in the laboratory, methylene blue dye effluent is mostly emptied into water bodies or the environment without proper treatment (Mohammed, 2014). Consequently, this pollutant enters both surface

and groundwater causing significant threat to the environment (Gercel *et al.*, 2008). Removal of methylene blue from wastewater has received considerable attention over the past decades. Among the numerous dye removal techniques, adsorption is the preferred method and gives the best results as it can be used for the removal of several coloring materials (Crini, 2006). Activated carbon is the most widely employed adsorbent for color removal in textiles effluents due to its effectiveness and high adsorption capacity. However, its use is limited because of high operating costs (Huang *et al.*, 2009). To lower the cost of wastewater treatment, many researchers have focused on finding non-conventional alternative adsorbents from biological wastes generally referred to as non-hazardous waste produced from industries and agriculture (Malekbala *et al.*, 2012). Extensive list and reviews of these types of biosorbent for contaminant removal have been made (Babel and Kurniawan, 2000). In particular, the use of agricultural waste in bio-sorption system has drawn attention because of its availability. More so, most agricultural wastes do not require complex pretreatment step or activation process before application.

The biosorption process involve a solid phase (biosorbent-biological material) and a liquid phase (solvent-normally water) containing dissolved species to be sorbed (sorbate-metal ions). Due to higher affinity of the sorbent to the sorbate species, the latter is attracted and removed by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimized chemical and biological sludge, and regenerability (Malekbala *et al.*, 2012).

Many works reported the use of biological waste materials to treat different pollutants ranging from metals to organic dyes found in waste water. For example, Bello et al., (2013) studied the removal of basic dye from aqueous solution by adsorption on melon husk in binary and ternary system. Velmurugan et al. (2011) studied the removal of methylene blue from aqueous solution using low cost adsorbent. Hameed et al. (2009) carried a review on novel agricultural waste adsorbent for the removal of cationic dye from aqueous solution. All these wastes showed good adsorption capacities for methylene blue dye adsorption.

In this study, citrus peels were conditioned and tested for methylene blue uptake from aqueous solution. Characterization of biosorbent was done using FTIR and SEM. Isotherm and kinetic studies on the data generated were carried out. Sorption of methylene blue was made at various contact time, initial dye concentration and adsorbent dosage.

2. MATERIALS AND METHODS

2.1. Materials

Citrus peels (orange, lime and grape peels) were collected from Muda Lawal market, Bauchi, Nigeria. Microwave oven MC21438BPP was used to dry the sorbent.6705 UV/VISUV visible spectrophotometer (manufactured by JENWAY) was used to measure the residual concentration of the methylene blue aqueous solution after shaking. PH/COND-430pH meter was used to determine the pH of the mixtures. A HY-4A VIBRATOR shaker (manufactured by JENWAY) was used to carry out the sorption experiments. A BLG-401-18N blender was used in converting the sample peels to powder and sieves were used to classify it into different sizes (425 microns). Perkin Elmer Spectrum 100 FTIR spectrometer was used for the infra-red spectroscopic studies at wave numbers 4000-400 cm^{-1}. The Hitachi X-650 Scanning Electron Microscope (Tungsten filament, EHT 20.00kV) and LEO 1450Scanning Electron Microscope (Tungsten filament, EHT 20.00kV) were used for the SEM imaging.

2.2. Methods

2.2.1. Biosorbent preparation

Lime, orange and grape peels were collected and washed with distilled water to remove surface adhered particles and water-soluble materials. In order to reduce the moisture content and facilitate crushing, the peels were heated in a microwave oven at 45ºC for 3 hrs. After the drying process, the peels were grounded to fine powder and extraction carried out to remove the oil content of the peels using soxhlet extractor. The biosorbent was then washed, dried and sieved to 425 µm size.

2.2.2. Adsorbate preparation

Methylene blue (MB) was used as the basic dye for the purpose of this study without further purification. The stock dye solution was prepared by dissolving 1 g of methylene blue in 1000 ml distilled water. The experimental solutions were obtained by diluting the stock dye solution with distilled water to give the appropriate concentration of the experimental solutions. The pH of the experimental solution was adjusted by the addition of either dilute 0.1 M HCl or 0.1 M NaOH solutions.

2.2.3. Batch adsorption experiments

Adsorption measurement was determined by batch experiments of known amount of the adsorbent in 20 ml of aqueous methylene blue solutions of known concentration in 250 ml conical flasks. The mixture was shaken at 120 rpm for 30 minutes. At preset time, the conical flasks were withdrawn from the shaker, and the residual dye concentration in the reaction mixture was analyzed at 665nm using an ultra-visible spectrophotometer. Dye concentration in the reaction mixture was calculated. The pH value of suspension was adjusted with either dilute HCl or NaOH solution. Adsorption experiments were conducted by varying initial solution's pH, contact time, adsorbent dose and initial methylene blue dye concentration. The percentage color removal was expressed as:

$$\text{Colour Removal (\%)} = \left(\frac{C_o - C_t}{C_o}\right) \times 100 \quad (1)$$

Where C_t is the concentration at a particular time (seconds), C_o is initial concentration (mg/L).

2.2.4. Adsorption isotherms

The equilibrium data were analysed using adsorption isotherms. Equilibrium isotherm equations are used to describe experimental sorption data. Among several models that have been published in literature, Langmuir and Freundlich are the most frequently used models. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent.

2.2.4.1. Freundlich isotherm

In 1906, Freundlich presented the earliest known sorption isotherm equation. This empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption (El-Nafaty et al., 2014, Dawodu and Akpomie, 2014) and is expressed by Equations 2 and 3.

$$q_e = K_f \ C_e^{1/n} \quad (2)$$

Where, K_f is adsorption capacity, C_e equilibrium liquid phase concentration of the solvent, (mg/L), 1/n adsorption intensity values for n > 1 and qe amount of sample adsorbed (mg/g) at equilibrium.

The linearized Freundlich equation is shown in Equation 3.

$$\log q_e = \log a_f + b_f \log C_e \quad (3)$$

A plot of $\log q_e$ versus $\log C_e$ is a straight line with slope, b_f and intercept, $\log a_f$.

2.2.4.2. Langmuir isotherm

Langmuir developed a theoretical equilibrium isotherm relating the amount of gas sorbed on a surface to the pressure of the gas. The Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced good agreement with a wide variety of experimental data and may be represented as in Equation 4. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many monolayer adsorption processes. The linearized Langmuir can be used as expressed in Equation 5.

$$q_e = \frac{q_o b C_e}{1 + b C_e} \quad (4)$$

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{1}{q_o} C_e \quad (5)$$

Where, C_e is the equilibrium concentration of the sorbate (mg/L), q_e is the amount of sorbate per unit mass of biosorbent (mg/g), q_o is a constant representing the strength with which the solute is bound to the substrate (L/mg) and b is the adsorption capacity of the substrate (gram solute/gram adsorbent).

Plotting $\frac{C_e}{q_e}$ against C_e, a straight line with slope $\frac{1}{q_o}$ is obtained with intercept $\frac{1}{q_o b}$.

The value of R_L (separation factor) indicates the type of the isotherm to be either unfavorable (R_L>1), linear (R_L =1),

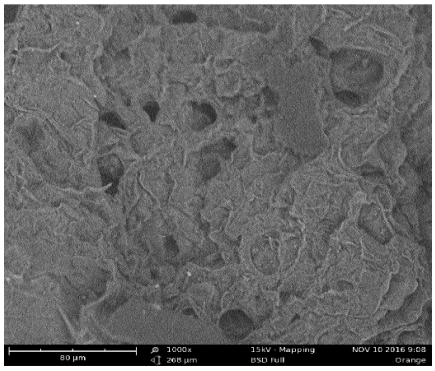
3. RESULTS AND DISCUSSION

3.1. Biosorbent Characterization

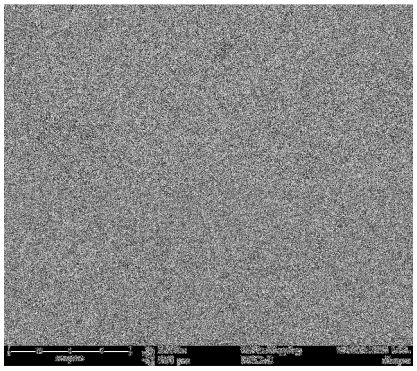
The raw citrus peel (RCP) biosorbent was characterized using FT-IR and SEM.

3.1.1. Scanning electron microscopy (SEM)

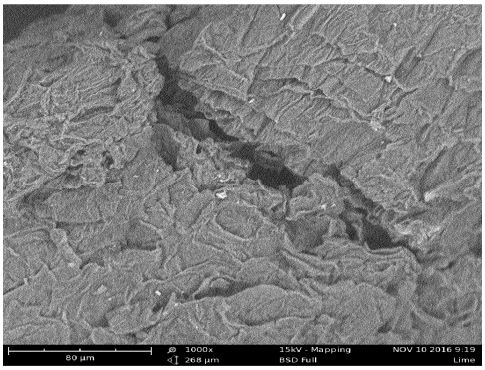
The surface of OP, GP and LP were analyzed by SEM with magnification of 1 000 at 15 kV and the sample morphology was characterized as shown in plates a, b and c micrograph (Figure 1). SEM micrograph pores within OP, GP and LP are good for adsorption due to irregular and porous surface with considerable number of pores and cavity that can provide suitable binding site for adsorption of dye (Mafra *et al*., 2013). High porous surface was noted to be more on the surface of orange peel compared to grape peel and lime. The plate also revealed that the pores on the surface of the orange peel, grape peel and lime peel were highly homogeneous.



a: SEM of orange peel



b: SEM of lime peel

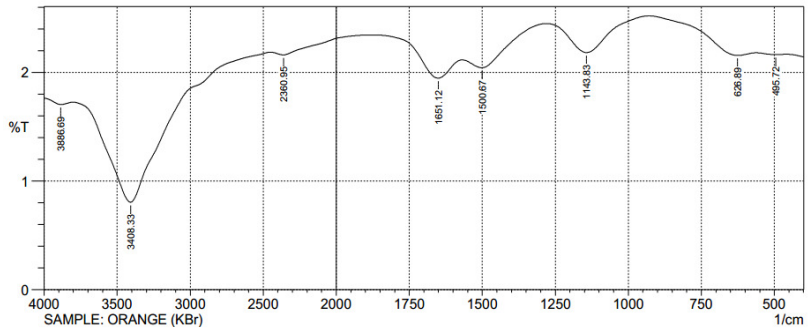


c: SEM of grape peel

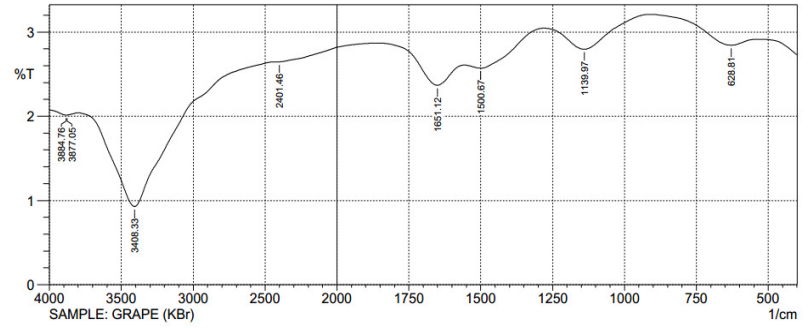
Figure 1: SEM of citrus peel samples

3.1.2. Fourier transforms infra-red (FTIR) spectroscopy

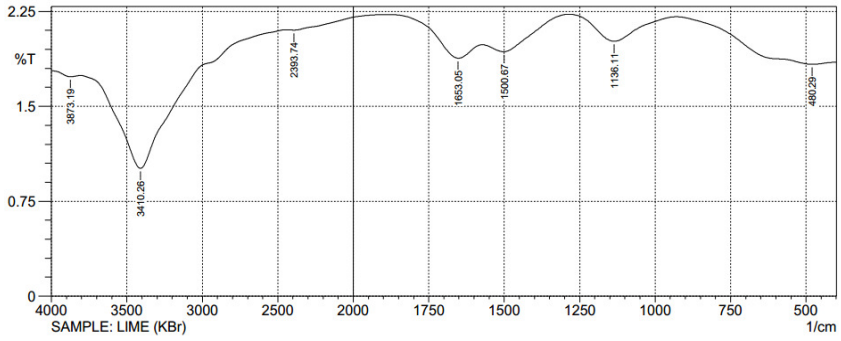
Figure 2 shows the FTIR spectra obtained for the prepared orange, grape and lime peel sorbents. From the figure, the spectra displayed a number of adsorption peaks indicating the nature of the materials examined. All assignments to peaks were made according to the interpretation of infrared by (Coates, 2000). The broad intense adsorption peaks 3 886.67 cm^{-1}, 3 884.76 cm^{-1} and 3 873.19 cm^{-1} for Orange peel, Grape peel, and Lime peel respectively are indication of adsorption of water molecules, resulting from O-H stretching mode of the hydroxyl group. The peaks at the region of 2 360.9 cm^{-1} for Orange peel, 2 401.46 cm^{-1} for Grape and 2 393.74 cm^{-1} for Lime peel were attributed to C-H interaction with the surface of the adsorbent indicating the carbon dioxide of normal air. Absorption at 1 143.83 cm^{-1}, 1 139.97 cm^{-1} and 1 136.11 cm^{-1} respectively for Orange peel, Grape peel and Lime peel were assigned a secondary amine CN stretch. 1 500.67 cm^{-1} obtained for Orange peel, Grape peel and Lime peel is due to the C=C stretching that could be attributed to the aromatic C-C bond. The peak 628.81 cm^{-1} for Grape peel indicates Alkyne C-H band while the 495.72 cm^{-1} for Orange peel and 480 for Lime peel indicates a poly-sulfides S-S stretch.



a: Orange peel



b: Grape peel



c: Lime peel

Figure 2: FTIR profile of orange, grape and lime peel

3.2. Effect of Contact Time, Biosorbent Dosage and pH on the Adsorption of Methylene Blue

Figures 3 to 5 present results of the effects of adsorbent dosage, contact time and initial dye concentration on the adsorption of methylene blue solution. In Figure 3, it could be seen that the effect of adsorbent dosage with time is in the range of 0.2 to 1 g/ 20 ml in 100 mg/L initial dye concentration and pH of 6.7. The removal percentage was observed to increase with increase in adsorbent dosage and reached equilibrium at 0.6 g for OP, OP+GP and OP+LP after 180 minutes. A similar trend was recorded for GP and LP, however, they attained equilibrium at 0.8 g adsorbent dosage after 180 minutes. This could be attributed to the increase in the number of adsorption sites with increasing adsorbent dosage thus allowing more dye molecules to adhere to it. However, as the sites become saturated after maximum adsorption capacity, the percentage removal reaches equilibrium (Ahmad *et al.*, 2009). Hence, optimum adsorbent dosage was achieved at 0.6 for OP, OP+GP, OP+LP and 0.8 for GP, LP g/20 ml in 180 minutes.

Figure 4 shows the effect of contact time on adsorption of MB. This was studied for 30-180 minute in 100 mg/L of initial concentration with an adsorbent dosage of 0.2-1g for OP, GP, LP, OP+GP and OP+LP in methylene blue at a pH of 6.7. Results obtained showed that, biosorption increases with increase in contact time until maximum percentage removal was achieved respectively at 120 minutes for OP, OP+LP and OP+GP and 150 minutes for GP and LP at a maximum dosage of 1 g where the removal reached an equilibrium. This is because the capacity of biosorbent gets exhausted and thus the uptake rate is controlled by the rate at which the methylene blue is transported from the exterior to the interior sites of the biosorbent (Belbahloul *et al*., 2017).

The effect of initial dye concentration was studied in the range of 25-150 mg/L MB at 0.8 g adsorbent dosage at various time intervals (Figure 5). Result obtained showed that with increase in initial dye concentration, the percentage removal decreases. This could be due to the fact that, the adsorbent has limiting number of adsorption sites, which becomes saturated at a particular concentration (Kassa and Akeza, 2014). The maximum percentage removals achieved in 30 minutes were 99% for OP and OP+GP, 96% for OP+LP, 94% for GP and 78% for LP.

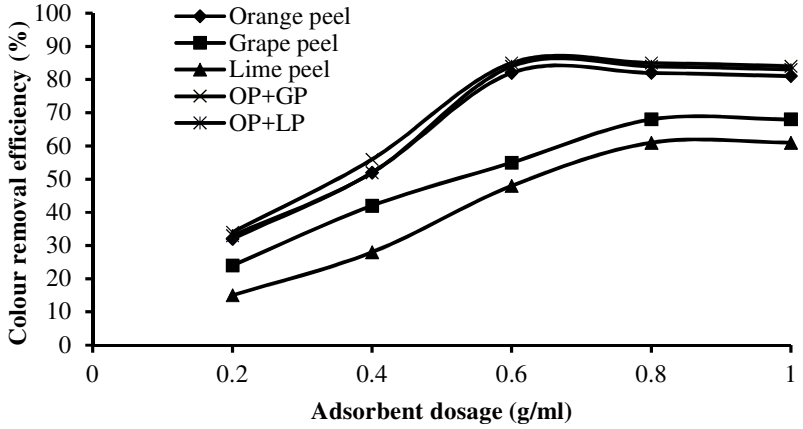


Figure 3: Effect of adsorbent dosage on adsorption of MB

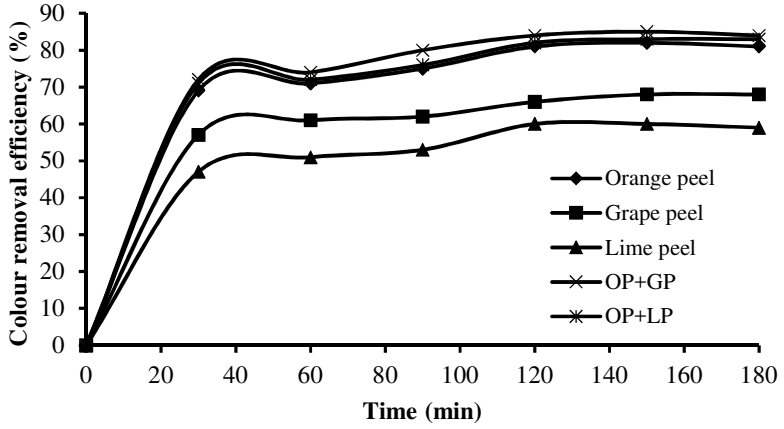


Figure 4: Effect of time on the adsorption of Methylene blue

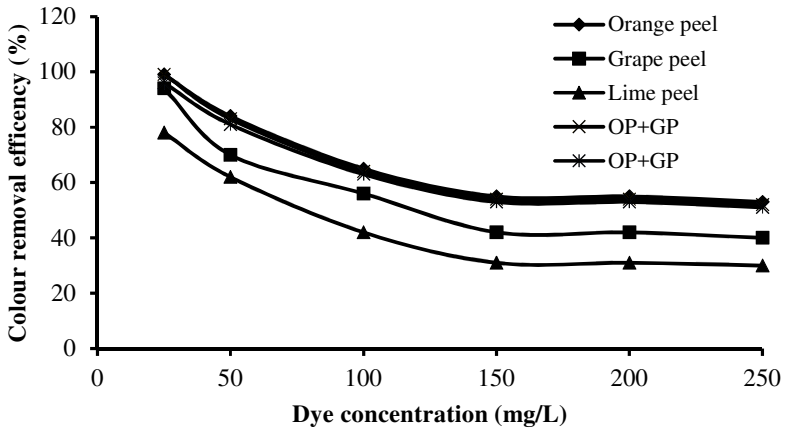


Figure 5: Effect of initial dye concentration on adsorption of MB

3.3. Adsorption Isotherm Models

The linearized form of Freundlich and Langmuir isotherms (Equations 3 and 5) were used to generate Tables 1 and 2 respectively. It can be seen from Tables 1 and 2 that the R^2 values for the charts were satisfactory as their coefficient of determination were close to 1. It is clear that the sorption process is better described by Langmuir isotherm as its R^2 (up to 0.998 for OP+LP) was found to be higher than those of Freundlich (up to 0.943 for OP+LP). This indicates that sorption by citrus peel is mono-layer as suggested by Langmuir. R_L was obtained as 0.4268 for OP. The value of the dimensionless equilibrium parameter R_L is satisfactorily good as its value falls within a favorable range of $0<R_L<1$.

Table 1: Freundlich isotherm constant for effect of concentration 25 mg/L

Freundlich	Orange peel	Grape peel	Lime peel	OP+GP	OP+LP
K_f (mg/g)	1.2912	0.9727	0.7047	1.3002	1.1588
N	16.3934	5.7803	2.3753	16.6667	9.2593
R^2	0.764	0.923	0.980	0.792	0.943

Table 2: Langmuir isotherm constant for effect of concentration 25 mg/L

Langmuir	OP	GP	LP	OP+GP	OP+LP
q_o (mg/g)	30.170	23.853	21.740	30.673	30.337
b(L/mg)	1.3280	1.0787	0.8039	1.3569	1.3038
R^2	0.995	0.988	0.992	0.997	0.998
R_L (mg/g)	0.4268	0.4783	0.5516	0.4216	0.4313
K_d	6.7897	3.2743	2.5562	7.5936	7.1067

3.4. Kinetic Studies

Table 3 shows the adsorption kinetic parameters of concentration 25 mg/L for both pseudo-first and second order kinetics. It can be seen that pseudo-second-order kinetic model gave the best fit, with high correlation coefficient of $R^2 > 0.9$ as compared to those of pseudo-first order with $R^2 < 0.2$. This suggests that the overall rate of adsorption process was control by chemisorption which involved valency forces through electrons sharing between adsorption and adsorbate.

Table 3: Adsorption kinetic parameter of OP, GP, LP, OP+GP, OP+LP concentration 25 mg/L

Kinetic	Parameter	OP	GP	LP	OP+GP	OP+LP
Pseudo-first order	q_e (mg/g) cal	2.864	1.730	2.2336	4.3652	6.3826
	q_e (mg/g) exp	1.669	1.6	1.324	1.669	1.618
	K_1 (min)	0.004606	0.002303	0.004606	0.004606	0.002303
	R^2	0.075	0.075	0.110	0.040	0.009
Pseudo-second order	q_e (mg/g) cal	1.3193	1.0438	0.9709	1.3495	1.3387
	q_e (mg/g) exp	1.669	1.6	1.324	1.669	1.618
	K_2 (min)	-0.0765	-0.0738	-0.0933	-0.0776	-0.0820
	R^2	0.989	0.997	0.995	0.989	0.989

4. CONCLUSION

Citrus peel was characterized using FTIR and SEM. The characterization using FTIR revealed the functional groups present on the citrus peel while SEM revealed the surface morphology of the sorbent. Biosorption studies with the peel showed that it can be used in the removal of methylene blue from aqueous solution providing up to 85% removal at an equivalent dosage representing 29.533mg/g for monolayer coverage. The data was found to be best described by Langmuir adsorption isotherm with maximum adsorption capacity of 29.533 mg/g for monolayer coverage. Removal efficiency for optimum dosage 0.6g/20 ml was found to be 82, 85and 84% for OP, OP+GP, OP+LP respectively. For 0.8 g/20 ml, 68 and 61% were recorded for GP and LP respectively. Maximum removal efficiency of 85% for OP+GP was achieved at 150 minutes contact time. Tested biosorption kinetic model result showed that citrus peels biosorbent followed pseudo-second-order kinetics.

5. ACKNOWLEDGMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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