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ADSORPTION OF DYES ONTO ACTIVATED WATERMELON (*Citrullus Lanatus*) RINDS (AWR)

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ABSTRACT

Liquid phase adsorption experiments were conducted to study the removal of Methyl Orange (MO), and Rhodomine B (RB) dyes from aqueous solution using activated Watermelon rinds (AWR). The effect of adsorption parameters (pH, initial adsorbate concentrations, contact time and temperature) were studied on the percentage of the dyes removal The surface characterization of the adsorbent was achieved through infrared analysis (FTIR), microscope analysis (SEM) and potential of zero charge (pH_{pzc}) measurements.. Three different kinetic theories were applied to the experimental data. The kinetic rates were modeled using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion. The pseudo-second-order model with correlation coefficient ($R^2 = 0.999$ for MO and 1 for RB) was found to explain the adsorption kinetics most effectively. Surface characterization of the adsorbent revealed that upon activation the cloudy and flaky nature of the raw rind tend to disappeared leading to higher surface area for adsorption and the highest removal was observed at pH 2 as ascertained by the Potential charge of zero point. The results indicated a significant potential of the Activated Watermelon Rinds (AWR), as a low cost adsorbent for MO and RB dyes removal from aqueous solution .

Keywords: Activated Watermelon Rinds ; Adsorption; Kinetics models; Dyes; Wastewater treatment.

INTRODUCTION

The periodic expansion in population alongside industrialization have significantly impacted humanity and at the same time enhanced environmental pollution (Hannachi *et al.*, 2012). Pollutants discharged from various industries are posing threat to the Earth's biodiversity.Environmental pollution occurred from a variety of sources such as sewage, effluents, agricultural wastes and waters used for mineral processing and industrial works (Bowen, 1979).

Water pollution is one of the most serious environmental problems being faced by modern society. Dyes forming this pollution are commonly used substances for dying cotton, wood and silk. They can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, They can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia. Therefore, the treatment of effluent containing such dyes is of interest due to their harmful impacts. Various techniques are in use for the removal of dyes from water discharge. Amongst the numerous techniques, adsorption utilizes the ability to accumulate dye from wastewater and gives the best results as it can be used to remove different types of coloring materials (Ali *et al*,.2017).

Adsorption is considered to be one of the most effective technology widely used in global environmental protection areas (Xunjun, 2015). The molecules at a surface of a material experience imbalanced forces of intermolecular interaction which contribute to the surface energy. It causes accumulation of molecules of a solute or gas in contact with the substance. This preferential accumulation of substrate molecules at the surface is called adsorption which is purely surface phenomenon. The surface active material is referred to as the adsorbent and the molecules which are accumulated on the adsorbent are called adsorbate molecules. Greeks and Romans used materials as clays, sand and wood charcoal to make the vessels for preservation of drinking water (Ibrahim and Sani, 2014).

MATERIAL AND METHODS

Materials

The materials used include routine laboratory glass wares; weighing balance(FA2004 Electronc Balance, NO:SHP02004413 2011-06), UV-Vis spectrometer (Cary 50, version 3.0), Fourier transform infrared spectroscopy (Cary 630; Agilent Technologies), Scanning Electron Microscope (SEM, Leica Stereoscan-440 interfaced with Phoenix EDX, Furnance (LF3 from V. Ltd) and pH Meter (JENWAY, 3510).

Analytical grade reagents were; $CuCl_2.2H_2O$, Congo Red(C.I:22120,Loba Chemie),Methyl Orange,((C.I:113025, BDH) Rhodomine B(C.I:45170, BDH),NaOH(JDH, 99%) HCl(Sigma Aldrich, 37, sp.gr.1.18gcm^3),H_2SO_4(Sigma Aldrich, 98% pure, sp.gr. 1.84 gcm^3)

Fig. 1: ***Citrullus Lanatus*** **Plant**

Methods

Preparation and Activation of Watermelon Rinds

The watermelon rind wastes were cut into small pieces and sun dried. The dried watermelon rind wastes were further activated according to the procedure reported by Yamuna and Kamaraj. (2016). The rinds wastes were completely mixed with concentrated sulphuric acid in the ratio 1:1 and Placed in a Muffle furnace(LF3 from V. Ltd.) at 300°C for 3 hours. The sample was then removed, cooled and washed with distilled water till the pH reaches 7. The sample was then sieved to ≤75 μm, ≤150 μm, ≤250 μm, ≤300 μm and >300 μm particle sizes and then each portion was further oven dried at 105°C to constant weight and stored.

Raw Rind **Rind+1:1H_2SO_4** **Activated Rind**

Fig. 2:Formation of Activated Rind

Preparation of the Dye stock and Working solutions

Stock solutions (1000mg/L) of each dye was prepared by dissolving 1.0g in a beaker containing small amount of distilled water until homogeneous solution was obtained. The resulting solution was quantitatively transferred to 1000cm^3 volumetric flask and diluted to the mark. Intermediate solutions of 100mg/L and 10mg/L were prepared from the stocks by serial dilution. Working concentrations were prepared from the intermediate stocks using the same dilution formula. In each case 2.0 mg/L was used for analysis of wavelength of maximum absorption and series of standards (0.2-1.0mg/L)/(2.0-10.0mg/L) were used to establish calibration curves for the dyes(Haddadian *et al.*, 2013).

Batch Adsorption Experiments:

Experiments on the adsorption of methyl orange and Rhodomine B by activated Watermelon rind (AWR) was carried out by batch method in accordance to the procedure reported by Sani and Ibrahim (2014). The influence of various parameters such as agitation time (5 – 120 min), adsorbent dosage (0.1 – 0.5g), particle size, initial dye concentration (10 – 310mg/L) and initial dye pH (2-12) were studied at constant agitation speed of 300 rpm at room temperature (25°C) in triplicates. The adsorption measurements were conducted by mixing various amounts of adsorbent in 100cm^3 Erlenmeyer flasks containing 10 cm^3 of dye solutions of known concentration.

The initial pH of the dye solutions was adjusted to the desired values by adding few drops of 0.1M HCl or 0.1M NaOH aqueous solutions (Suyamboo and Perumal, 2012). The solutions were agitated using an orbital shaker until equilibrium was attained; after which the samples were then be taken out and the supernatant solutions were filtered using Whatman No. 41 filter paper and centrifuged at 2000rpm for 15 minutes.The clear supernatant was used for analysis usin UV- Visible. In each case, the percentage adsorption and substrate's equilibrium adsorption capacity, (mg/g) were evaluated using Equation (1) and (2).

$$\% \, adsorption = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{w} \qquad (2)$$

Where C_o and C_e are the initial and final dye concentration(mg/L), W is the weight of the adsorbent (g) and q_e is the amount adsorbed (mg/g) and V is the volume of the flask in cm^3.

RESULTS AND DISCUSSION

Adsorption Parameters

Effect of Contact Time on Adsorption of MO and RB

The results of percentage adsorption removal with increasing contact time are presented in Figs. 3. and 4. The increase in contact time at 250 rpm stirring rate led to enhancement in the dye adsorption in which about 80% and 98% of the dye removal took place within first 60 min for both MO and RB. Which may be attributed to the high affinity and interaction between adsorbent and dye due to the sufficient equilibrium time between the activated rind for the dye solution. With agitation the external mass transfer coefficient increases resulting in quicker adsorption of the dye molecule. In the process of dye adsorption, the dye molecules have to first encounter the boundary layer effect, then adsorption from the surface and finally, they have to diffuse into the porous structure of the adsorbent. This phenomenon will take a relatively longer contact time as reported by Malik (2003).

Subsequently, the amounts of adsorption reached a limiting value beyond which no significant improvement in adsorption took place, this is because the active sites for further adsorption might not be available. As such final equilibrium adsorption occurred at about 60 min; this time was considered as the equilibrium time in kinetic adsorption experiment. This is in agreement with the result obtained by Subasri *et al.*, (2015) in the removal of Rhodomine B by activated *Corchorus Olitorous* Leaves.

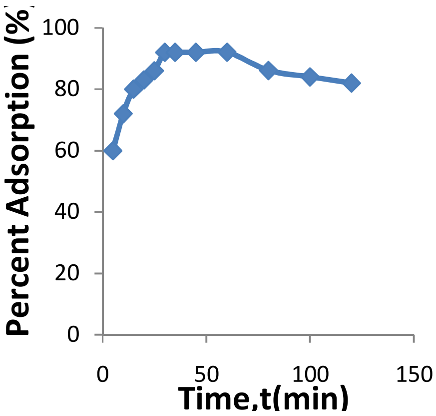


Fig.3.: Percentage adsorption of Methyl Orange red as a function of time.

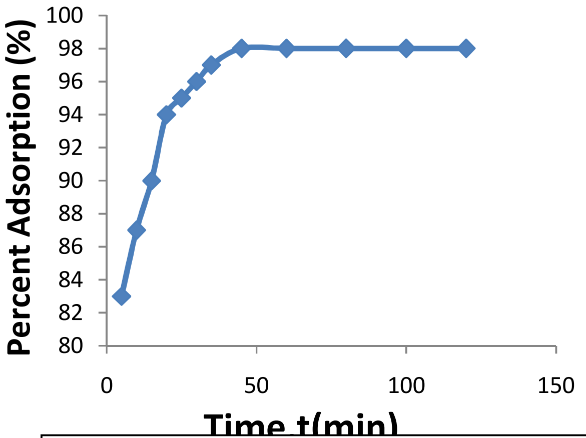


Fig.4: Percentage adsorption of Rhodomine B as a function of time.
Effect of Adsorbent Dosage

The effect of adsorbent dosage(0.1-0.5g) on percent removal of RB and MO was depicted in Figure 5. . The percent removal increased with an increase in adsorbent dose which might be due to an increase in the number of sorption site available for adsorption. The maximum sorption qe (mg/g) decreases with an increase in dye concentration which might be due to aggregation of solute for the sorption site, which led to a decrease in total surface area of the adsorbent and an increase in diffusional path length(shukla *et al.*, 2002).

The number of sorption site available for the sorbent solute interaction increases with an increase in sorbent dose weight. This agreed with the result reported by many researchers (Zaharraddeen *et al.*, 2015, Wong *et al.*, 2009, sadik, 2014).

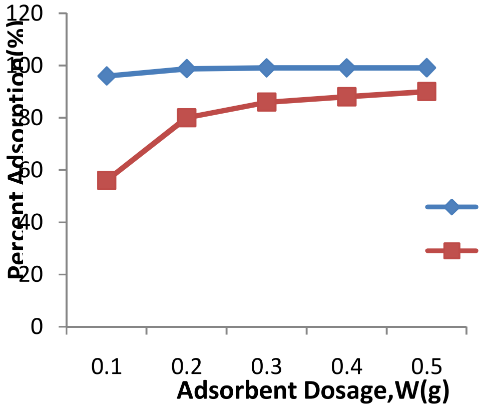


Fig 5 Percentage adsorption as a function of the adsorbent mass.

Effects of Initial Dye Concentration

The effect of initial concentration of MO and RB on their removal efficiency by activated rind adsorbent in the range of 10-310ppm was studied and respective results are shown in 6. As is shown, the removal percentage of all the dyes was found to decrease with the increase in the initial concentration. This phenomenon can be attributed to the lack of available active sites required for the high initial concentration of the dyes. These results agree with the results reported by Ghaedi *et al.* (2014).

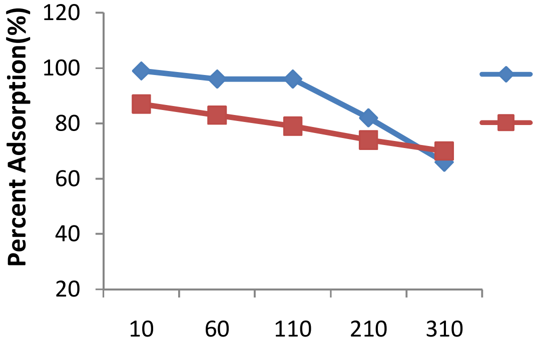


Fig .6: Percentage adsorption as a function of Dye initial Concentration .

Effect of pH

From figure 7 there was high percentage removal at lower pH, this may be attributed to the fact that at low pH values functional groups on the activated rinds are protonated and consequently becomes positively charged which can interact with the negatively charged MO dye, due to electrostatic attractions adsorption process is favoured which lead to high percentage removal. This result is in agreement with the result obtained by Farida *et al.* (2015).

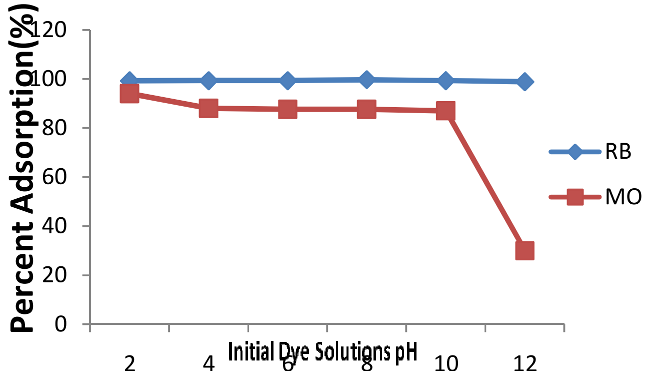


Fig 7 Percentage adsorption as a function of the pH.

However, it was found that the highest adsorption capacity for MO adsorption onto AWR was obtained at pH 12 respectively while the highest adsorption capacity for RB adsorption onto AWR was obtained at pH 2. Their different behaviours at different pH values may be attributed to the nature of the adsorbents, especially the pH at point of zero charge (pHpzc), and the nature of the dyes (CR is diazo dye and MO is monoazo dye) while the RB cationic dye.

Effect of Temperature

The result of effects of temperature on the percentage adsorption of MO and, RB in was depicted in fig. 8. The result shows that adsorption of dyes increases with increase in temperature and reached a maximum value at 318K. This may be explained on the basis that elevating the temperature leads to the dislodging of the solvent molecule (water) from interfacial region thereby providing and exposing more number of adsorption sites. This behavior enhances the possibility of interaction between the dyes and activated rinds. In addition, at elevated temperatures, due to increase in free volume (number of active sites) of adsorbent, the adsorption percentage improved.

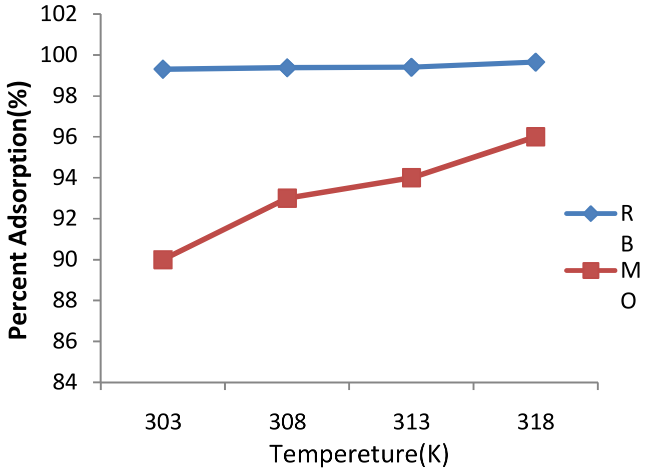


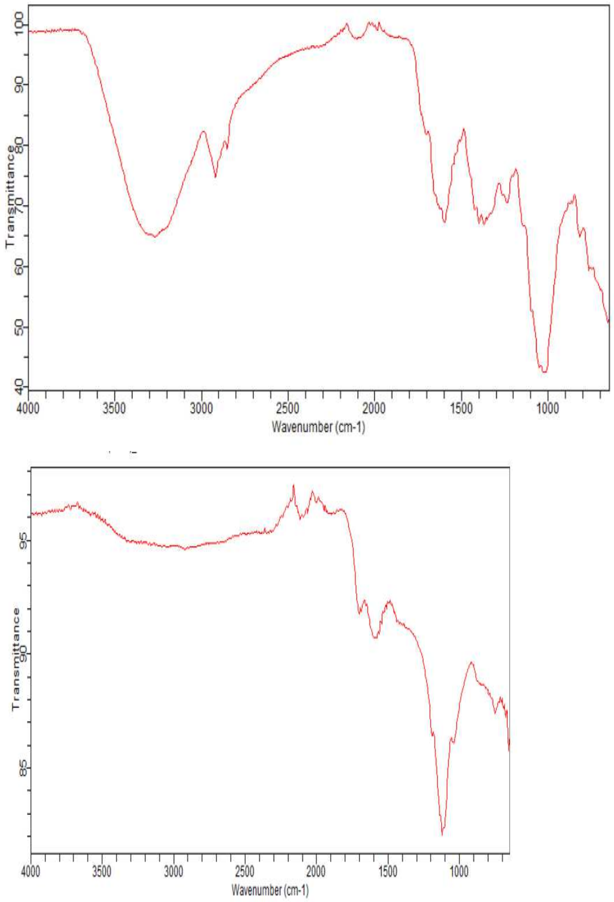
Fig.8 Percentage adsorption as a function of tempereture

Surface Characterization of the Adsorbent

The surface characterization of the adsorbent was achieved through infrared analysis (FTIR) and microscope analysis (SEM) and Potential of Zero Charge measurements.

Fourier Infrared Spectroscopic Analysis (FT-IR)

The FTIR spectra of the Adsorbents before and after adsorption of Methyl Orange and Rhodomine B were depicted in Fig 9(a and b), which revealed that, the carbon based watermelon rind contains C-H stretching of sp^3 and –OH stretching of carboxylic within the diagnostic region. Upon activation(Fig.9b), the existed surface functional groups within the diagnostic region tend to disappeared.The disappearance of the functional groups may be caused by factors such as chelating effect, intermolecular as well as intramoleculer. This assertion agrees with result reported by Sivakumar *et al* (2012).

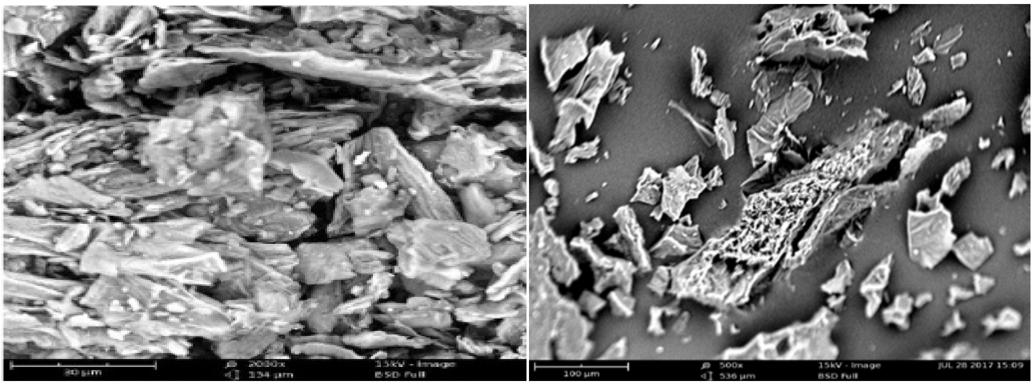


(a) **(b)**

Fig.9. FT-IR Spectrum of the raw(9a) and activated(9b) Watermelon Rind (AWR)

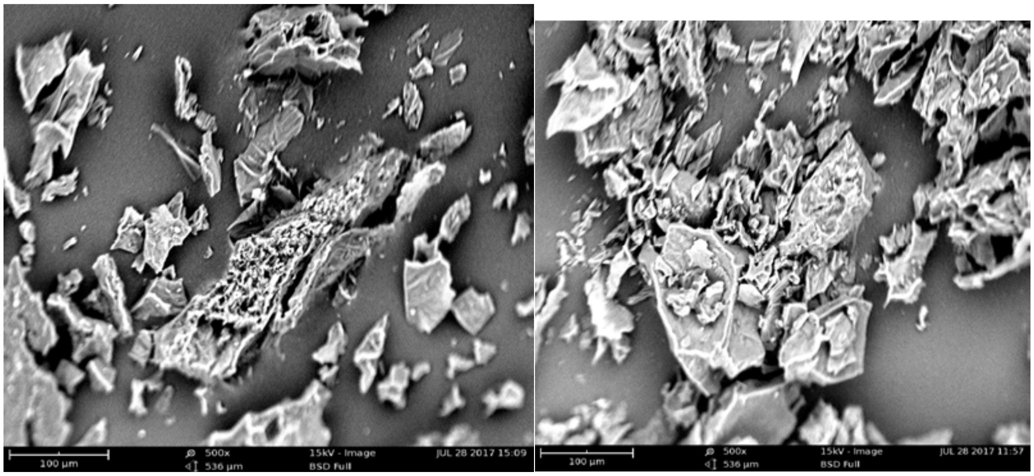
Scanning Electron Microscopy(SEM)

SEM images of the adsorbents before and after adsorption of the dyes were depicted in Fig.10 .Tthe RWR is characterized by irregular, flaky and heterogeneous surface (Ibrahim and Sadiq, 2014). The irregular and flaky surface turns to cloudy and accumulated at the center leading to high single point ratio **($p/p_{o>0.03mg/g}$)** which elucidated the activation of the raw adsorbent(Fig.10b). Following the adsorption of the dyes (MO and RB) as depicted in figure 11, some pores were absent and the surface of the AWR becomes cloudy, suggesting sorption of the dyes onto the AWR adsorbent.



(a) **(b)**

Fig10. SEM image for (a) raw and (b) activated watermelon rind



(a) **(b)**

Fig11. SEM Images of AWR (b) after adsorption of MO, (b) after adsorption Rhodomine B

Potential of zero charge (pH_{pzc})

The point of zero charge (pHpzc) is an important factor that determines the linear range of pH sensitivity and then indicates the type of surface active centers and the adsorption ability of the surface.Many researchers studied the point zero charge of adsorbents prepared from agricultural solid wastes in order to better understand the adsorption mechanism. Cationic dye adsorption is favored at pH>pHpzc, due to presence of functional groups, such as OH−, COO− groups. Anionic dye adsorption is favored at pH<pHpzc, where the surface becomes positively charged(Ebrahimian,2013).

Fig.12 reveals that , the point of zero charge of the activated watermelon rinds(AWR) was found to be 2.At a point above this zero charge, the surface of the adsorbent becomes negatively charged, which enhances the adsorption of positively charged dye (RB) and decreases the adsorption efficiency of the other two anionic dyes MO. This is in agreement with the result obtained by (Tamilarasan *et al*,.2014) using drift method.

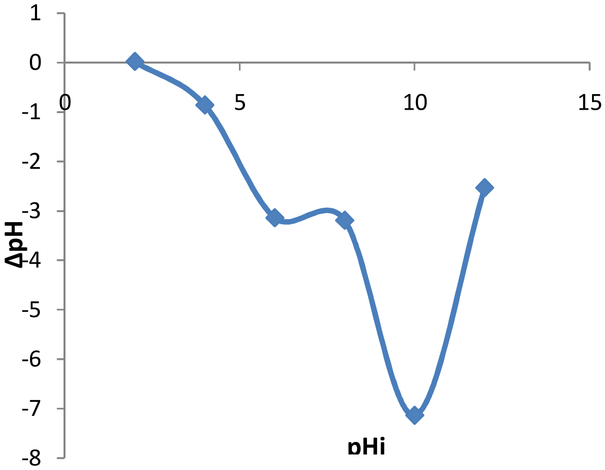


Fig.12: Zero Point Charge (pHzpc) of the used substrate during the Adsorption procest

Adsorption Kinetics

The adsorptions data were tested using pseudo-first order, pseudo-second order kinetics and intra-particle diffusion model. Values of correlation coefficient (R^2) of the plots were used to determine the prevailing mechanism(s) involved in the adsorption processes. The linearised forms of the kinetic models investigated were:

I. Pseudo-First Order Kinetics

$$\mathrm{In}(C_o - C_t) = \mathrm{In}C_o - Kt \quad 3$$

Where C_o stands for Initial concentration (mg/L), C_t stands for final concentration after time t and K stands for pseudo-first order rate constant respectively.

Plot of $\mathrm{In}(C_o - C_t)$ against time t will give straight line if the data obey the equation.

Pseudo-Second Order Kinetics

$$t/C_t = 1/KC_o^2 + (1/C_o)t \quad 4$$

A plot of t/C_t against time (t) will give a linear.

II. Intra-Particle Diffusion Model

$$q_t = K_i t^{1/2} + I \quad 5$$

A plot of q_t against square root of time ($t^{1/2}$) will give a linear plot.

Table 1 lists the kinetics order, rate constants accompanied by corresponding correlation coefficients. The highest vaalue of correlation coefficients ($R^2>0.99$) were noticed on pseudo-second order plots which proved its better applicability in the description of the mechanisms of the basic dyes adsorptions onto the Activated Watermelon Rinds.

More so, the kinetic data were also modeled using intra-particle diffusion model which indicates that two or steps occur in the adsorption processes. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage where the intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage, where the intraparticle diffusion starts to slow down due to the extremely low solute concentration in solution (Sun and Yang, 2003).

Table 1 Adsorption Kinetic Parameters of CR,MO and RB Using 10ppm

Dyes		Methyl Orange (MO)	Rhodomine B (RB)
Pseudo First order			
	k_1	0.0126	0.0235
	R^2	0.4271	0.1756
Pseudo Second order			
	k_2	0.01501	0.01553
	R^2	0.9998	1
Intraparticle diffusion			
	K_{diff}	0.2318	0.1159
	R^2	0.5742	0.5876

CONCLUSION

The research findings revealed the adsorption capabilities of the substrate and that the adsorption process may involved pseudo second order kinetics as contained in table 1.

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