Kinetic Studies On Reactive Dye Removal From Aqueous Solution By Using Arecanut Peel

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Received: 10-01-2022 Revised: 19-04-2022 Acceptance: 10-05- 2022 Publication: 31-05-2022.

ABSTRACT
This research aims at finding the effectiveness of Remazole Red RGB dye removal using arecanut peel, an agricultural waste, as an activated carbon. The arecanut peel-activated carbon was prepared in the laboratory by carbonization followed by activation. Adsorption studies were carried out to look for the effect of different experimental scenarios, like different pH values, varying contact times, the initial concentration of dye, and changing arecanut peel carbon dosage, on the removal efficiency of Remazole Red RGB dye from the experimental solution. The equilibrium experimental results were checked for the applicability of the Langmuir and Freundlich isotherm models and the kinetic models. The batch test result was a maximum dye removal of 83% with an initial dye concentration of 5 mg/L at an adsorbent dose of 0.625 g/L at dye pH 4 in a 50-minute time span. For Remazole Red RGB dye removal, the test result is unfavorable for the Langmuir isotherm model but suits well for he Freundlich i isotherm model. The maximum adsorption capacity of arecanut peel carbon on Remazole Red RGB dye was 3.89 mg/g. It was evident that the adsorption process is favorable for the pseudo-second-order rate kinetics. It was seen that intra-particle diffusion is not the only rate-limiting step in this adsorption experimental system; also, regression results show that the linear regression model gives the best outcome. The end result of this study confirms that powder arecanut peel activated carbon was the right option for removing reactive dye from an aqueous solution.

Keywords*:* Arecanut peel, Adsorption, Batch Study, Remazole Red RGB dye, Isotherm, kinetics*.*

I. INTRODUCTION

The main environmental problems originate from the increased global pollution of water bodies by natural chemical compounds and industrial waste [1]. Although the world has witnessed positive effects from increased industry, modernization, urbanization, and advances in technology, the cost we must pay in the future will be far too high [2].
A huge amount of dye from industrial waste water is being released into running water bodies and polluting the natural water bodies. Control measures to treat the dye wastewater are done by the government, users and dye manufacturers [3]. The main use of dyes is in textiles, tanneries, food processing industries etc., in their process to color their manufactured goods [4].
The main characteristics of textile effluents include higher levels of alkaline content, biological oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids (TDS). Adverse effects of dyes on plants and animals include skin irritation, carcinogenesis, decreased photosynthesis in aquatic plants, and disturbing the exquisite balance of the ecosystem [5].
Different treatment methods are adopted for the dye removal from textile waste water; some of them are photocatalytic, electrochemical degradation, ultrafiltration, ion exchange, biological treatment and adsorption on activated carbon. Out of these treatment methods, adsorption looks to be the best option for the removal of colors from dye-bearing wastewater [6].
Numerous conventional and non-conventional adsorbents were used to treat dye-bearing waste water in industrial effluents and researchers are searching for adsorbents that are cost effective, abundantly available and easy to operate [1].
Dyes are mainly classified into anionic (acid dyes), cationic (basic dyes) and non-ionic (disperse dyes) [7]. Remazole Red RGB is highly water-soluble reactive dye that appears as powder [8].
Among the researchers, there has been an increasing concern about developing more efficient, inexpensive and readily available adsorbents from agricultural byproducts. However, for the application in any industry, the selection of adsorbent material is mainly determined by the availability of agricultural products and the applicability of the adsorption method, considering the cost, space and strength of wastewater that can be

treated. Utilization of agricultural wastes for wastewater treatment could be useful in solving the solid waste disposal problems that are faced by farmers and agriculture-based industries (9)
The use of agricultural waste is of high importance since it adds commercial value and reduces the cost of waste disposal, which may play a key role in the economy of our nation.
The main constituents of agricultural waste are cellulose, hemicellulose, and lignin, which are effective adsorbents for a wide range of dyes because of their richness in functional groups such as hydroxyl groups, carboxyl groups and phenols [10].
Arecanut peels (Areca catechu) have no commercial usage and are not eaten by livestock. Moreover, the disposal of unused arecanut peels results in environmental pollution.
The diffusion of Remazole Red RGB dye and arecanut peel adsorption systems at equilibrium conditions is explained by adsorption isotherms and on the basis of isotherm parameters, it is possible to conclude the best type of adsorption process [11].
In the practical implementation of industrial dye wastewater treatment processes, forecasting adsorption kinetics is very crucial and models of kinetic studies help in finding the rate of the process and its controlling step [12]. In this research work pseudo-first-order and pseudo second-order kinetic models were used to examine the well fitted model for the experimental data obtained from the arecanut peel Remazole Red RGB batch adsorption processes.
Few research works were carried out on various low cost agricultural by products for removal of dye bearing waste water from aqueous solution and some of them are Banana Leaves [10]. Sugarcane Bagasse [13] and Pumpkin Seed Hull [14].
The purpose of this study is to find the adsorption capacity of arecanut peel carbon, which is processed from agricultural byproducts for the removal of Remazole Red RGB dye from an aqueous solution in batch adsorption setups at various working conditions.

II Materials and Methodology

A Preparation of adsorbent: Arecanut peel activated carbon was prepared by mixing 4 parts by weight of Arecanut peel thoroughly with 3 parts of concentrated sulfuric acid by weight and keeping it in the hot air oven with the temperature being maintained in the range of 85°C to 100°C for a period of 24 hours. After that, it was washed well to remove excess acid and dried at 101°C. The dried material was processed by thermal activation in the muffle furnace at 600° C for 30 minutes.

***B Adsorbate preparation*:** Remazole Red RGB dye stock solution was prepared by dissolving right quantity (1mg/L) of Remazole Red RGB, a coloring reagent in distilled water. Standard solution was obtained by diluting the stock solution as per the requirement. The same was used throughout the experiment.

C Specification of dye used: Specification of dye used:
Dye – Remazole Red RGB
Type – Reactive dye
Wave length (λ) – 517nm

The adsorption investigation was executed in a batch process by using an aqueous solution of Remazole Red RGB with a concentration range of 1–6 mg/l. The other variable parameters were absorbent dose (0.125–0.75 g/l), contact time (0–60 minutes), and pH of the medium (2–10). The concentrations were determined with the help of a carefully developed calibration curve with a standard Remazole Red RGB dye solution. *D Equilibrium studies:*
The amount of equilibrium adsorption q_e (mg/g) was obtained by

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Percentage of dye removal is calculated by

$$= \frac{C_0 - C_e}{C_0} \times 100$$

Where, Co = initial dye concentration in mg/L, Ce = concentration of dye solution at equilibrium condition in mg/L, V= volume of the solution in liter and W = mass of adsorbent used in gm. The kinetic studies were also carried out using the same procedure.

Sorption amount at any time t ie, q_t (mg/g) was find out by

$$q_t = \frac{(C_0 - C_t)V}{W}$$

Where, Ct = concentration of dye at any time in mg/L.

III Result and Discussions

A Initial dye concentration effect on adsorption

The initial dye concentration effect on the adsorption of Remazole Red RGB dyes onto arecanut peel carbon was evaluated in the range of 1–6 mg/L of the initial dye concentration. The adsorbent dose and the agitation speed were kept at 0.50 g/L and 100 rpm, respectively, for Remazole Red RGB dye at a natural pH (existing pH), for a contact time duration of 60 minutes, and at room temperature (27±2^{o}C). In the case of Remazole Red RGB dye, a maximum removal of 83% at an initial dye concentration of 5 mg/L has been observed, which decreased slightly to 82% with a further increase in dye concentration. Further, the dye removal remained almost constant with an increase in the initial dye concentration. The dye removal is decreased for a further increase in the initial dye concentration, as observed in Figure 1.

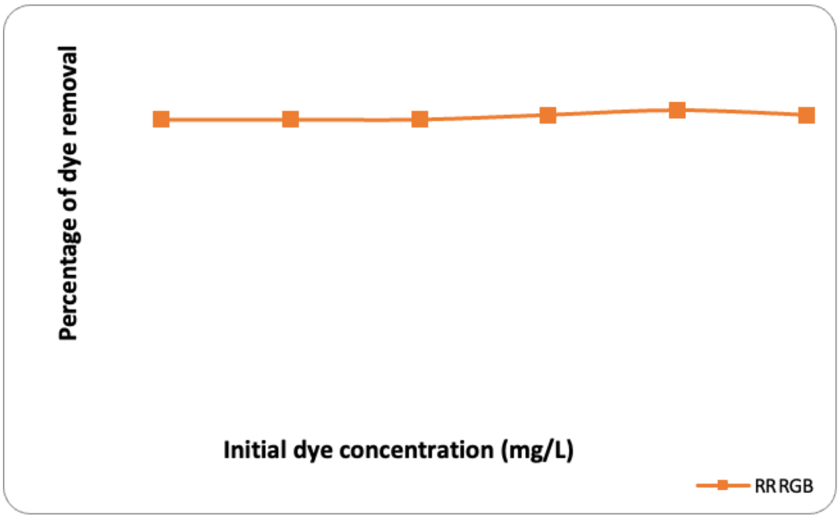

Figure 1: Initial dye concentration effect on 0.5 g/L of arecanut peel carbon

From the Figure 1 it is made out that, at lower concentration percentage of dye removal is high and it goes on decreasing with increase of dye concentration, and then reaches equilibrium condition after long time. This indicates that their presence reduces in immediate solute adsorption due to unavailable active sites required for the high initial concentration of reactive dye.

B Adsorbent dosage variation effect on adsorption process

The effect of adsorbent dose on Remazole Red RGB dye uptake capacity on arecanut peel carbon was tested with different adsorbent doses in the range of 0.125 and 0.75 g/L. Initial dye concentration and agitation speed values were kept at 5 mg/L and 100 rpm for both dyes at natural pH (existing pH) for a contact duration of 60 minutes at room temperature (27±2 oC). The influence of adsorbent dosage on dye removal by arecanut peel carbon on Remazole Red RGB dyes is presented in Figure 2. The removal of dye percentage increases to 83 with an increase in adsorbent dose up to 0.625 g/L of Remazole Red RGB dye, and then it remains almost constant with an increase in adsorbent dose.

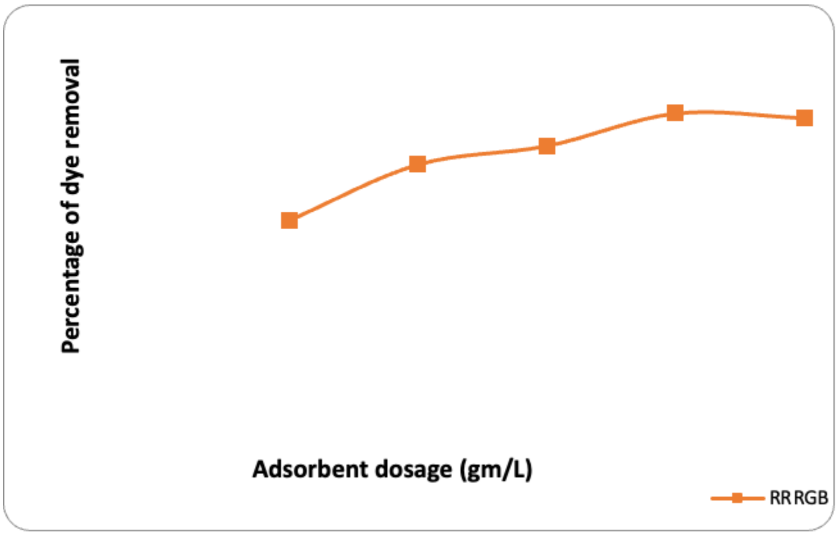

Figure 2: arecanut peel carbon dosage variation effect on dye concentration of 5 mg/L

From the above figure, it is observed that, as the dosage of arecanut peel carbon increases, the dye removal efficiency also increases, while at the same time, the adsorption capacity per unit mass of arecanut peel carbon decreases. This is due to the fact that as the fact that as the arecanut peel dose increases, the number of sites available for adsorption increases, and dye removal efficiency increases.

C Contact time effect on dye removal

The effect of contact time on adsorption of Remazole Red RGB dye onto arecanut peel carbon was investigated in the range of 0-60 minutes. The adsorbent dose of 0.625 g/L for Remazole Red RGB dye is taken. Initial dye concentration and the agitation speed were kept at 5 mg/ L and 100 rpm respectively for both the dyes at a natural pH (existing pH) with room temperature (27±2^{o}C). The effect of contact time on uptake of dye is shown in Figure 3. The removal efficiency is 83 % in 45 minutes for Remazole Red RGB dye and remains almost constant for further increase in contact time.

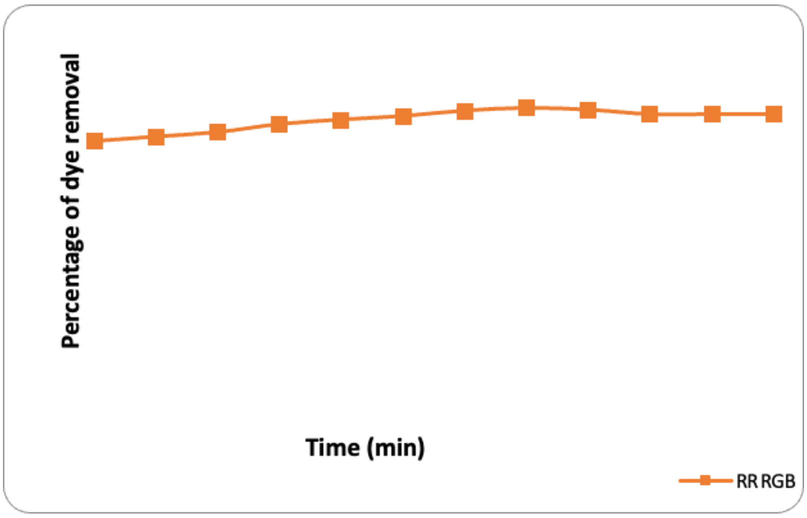

Figure 2: Contact time effect on percentage of dye removal

It could be due to the fact that low cost carbons have macro and micro pores. In the process of dye adsorption, initially the dye molecules encounter the boundary layer effect first and diffuse from boundary layer film onto adsorbent surface, and finally, they diffuse into the porous structure of the low cost carbons.

D pH variation effect on dye removal

The effect of pH 2-10 on adsorption on Remazole Red RGB dye from solutions onto arecanut peel carbon was tested for contact time in the range of 0-60 minutes with 0.625 g/L of arecanut peel carbon for Remazole Red RGB dyes, while keeping initial dye concentration and agitation speed at 5 mg/L and 100 rpm at room temperature (27±2^{o}C).

The percentage of removal of anionic Remazole Red RGB dye by arecanut peel carbon at different pH values for a contact time of 0 - 60 minutes is plotted in Figure 4. The percentage of removal of Remazole Red

RGB dye by arecanut peel carbon increased from 34 to 86 for a decrease in pH of solution from 10 to 2, and the optimum pH value for the maximum dye removal was found to be 4 for the contact time of 50 minutes.

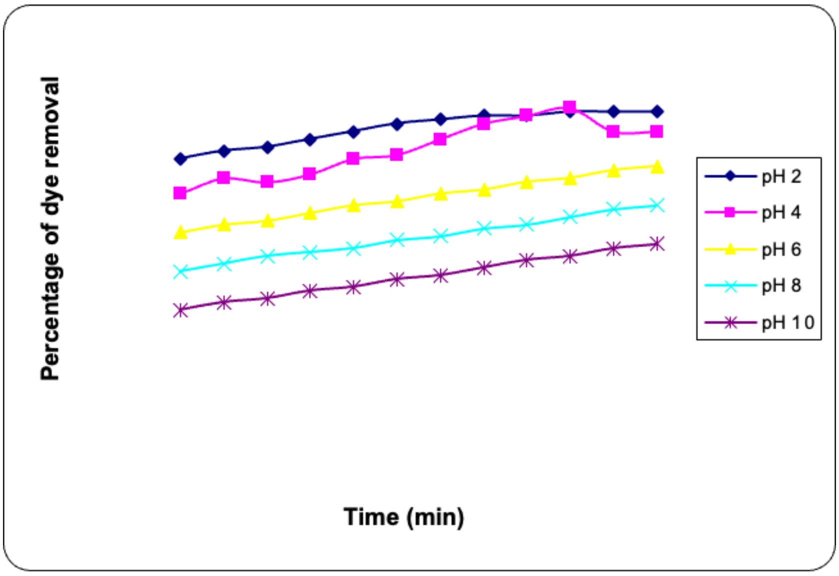

Figure 3: pH variation effect on dye removal onto arecanut peel carbon

Lower adsorption at higher pH values could be due to the abundance of OH^- ions and because of ionic repulsion between the negatively charged surface and the anionic Remazole Red RGB dye molecules; there are also no more exchangeable anions on the outer surface of the adsorbent at higher pH values and consequently the adsorption decreases. At lower pH, more protons will be available thereby increasing electrostatic attraction between negatively charged Remazole Red RGB dye anions and positively charged adsorption sites and causing an increase in the dye adsorption

E Adsorption Isotherms

To assess the efficiency of the Arecanut peel absorbent for Remazole Red RGB dye removal Freundlich and Langmuir isotherms are considered.

The Freundlich isotherm presented in the form of:

$$\log(q_e) = \log k_F + \frac{1}{n}\log(C_e) \qquad (1)$$

Where k_F = adsorption capacity and n = intensity of adsorption and were computed from the slope and intercept of the Freundlich graph of Log Qe versus Log Ce (Fig.5). Where q_e = amount of dye absorbed per unit weight of the arecanut peel absorbent (mg/gm), C_e = Remazole Red RGB dye concentration at equilibrium in mg/L. The value of n between 0 – 10 indicating that adsorption is efficient for this adsorption system (n = 1.707 for this study from Table 1).
The Langmuir isotherm is presented in the form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (2)$$

Where Ce = equilibrium concentration of Remazole Red RGB dye in mg/L, q_e = amount of Remazole Red RGB dye adsorbed at equilibrium condition in mg/g, Q_0 = adsorption capacity of arecanut peel in mg/g and b is the energy of adsorption in L/mg. The values of adsorption capacity of arecanut peel and energy of adsorption were found out from the slope and intercept of the chart Ce/q_e versus Ce (Fig.6). The value of dimensionless factor $R_L = 1/(1+bC_0)$, where C_0 = initial dye concentration. The value of R_L lies between 0 - 1(R_L = 0.062 for this study from Table 2) showing favorable absorption of dye on the arecanut peel carbon.

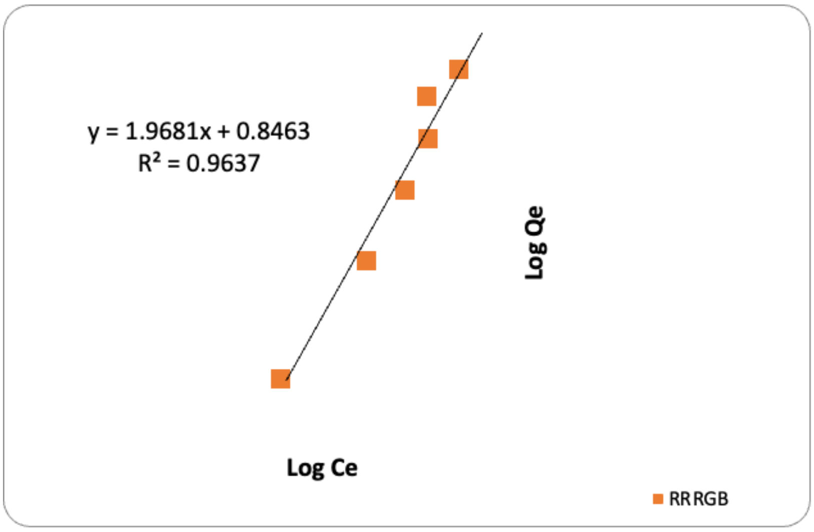

Figure 5: Freundlich isotherms for arecanut peel carbon

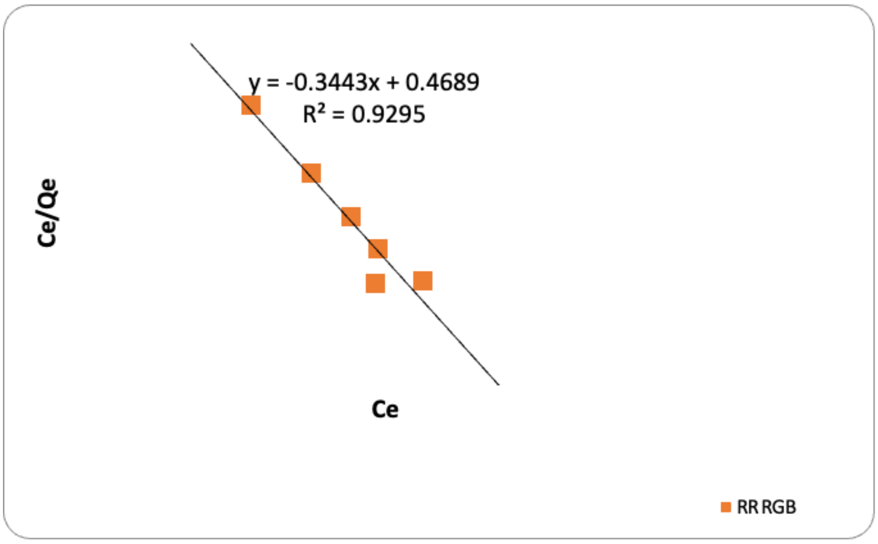

Figure 6: Langmuir isotherms for arecanut peel carbon

Table 1; Parameters of Freundlich for Remazole Red RGB dye on arecanut peel carbon

k_F(mg/g)(L/g)1/n	n	R^2
2.279	0.538	0.963

Table 2: Parameters of Langmuir isotherms for Remazole Red RGB dye on arecanut peel carbon

Qo(mg/g)	b(L/mg)	R^2	R_L
3.89	0.623	0.929	0.186

Table 1 and 2 exhibit the parameters of the two isotherms and the related correlation coefficients. On the basis of R^2 values it can be confirmed that for Remazole Red RGB dye removal the data is unfavorable for Langmuir isotherm model, but fits well for Freundlich isotherm model.
The adsorption capacity of Arecanut peel carbon for the Remazole Red RGB dye (3.89 mg/g).

F Kinetic studies
The expression for pseudo-first-order equation is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (3)$$

Where q_e = quantity of Remazole Red RGB dye adsorbed at equilibrium in mg/g and q_t = quantity of Remazole Red RGB dye adsorbed at any time t in minutes, respectively, and k_1 = rate constant of adsorption in 1/min. Values of k_1 were calculated from the graph of ln ($q_e - q_t$) versus time (Fig. 8).
From the table 3 it is found that qe experimental reading is not same with the qe calculated from the graph. Therefore, first order kinetic model is not favorable for the arecanut peel carbon – Remazole Red RGB batch adsorption system.
The pseudo-second-order kinetic equation is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Where k_2 (g $mg^{-1} min^{-1}$) is the rate constant of second order adsorption. The parameters k_2 and q_e can be obtained from the graph of (t/q_t) versus time (Fig. 9). This model is better to predict the behavior correctly using the whole experimental values adsorption than pseudo-first order model. The correlation coefficient is close to 1.0 (Table 4). The calculated q_e values obtained from this model nearly same as that of the experimental values.

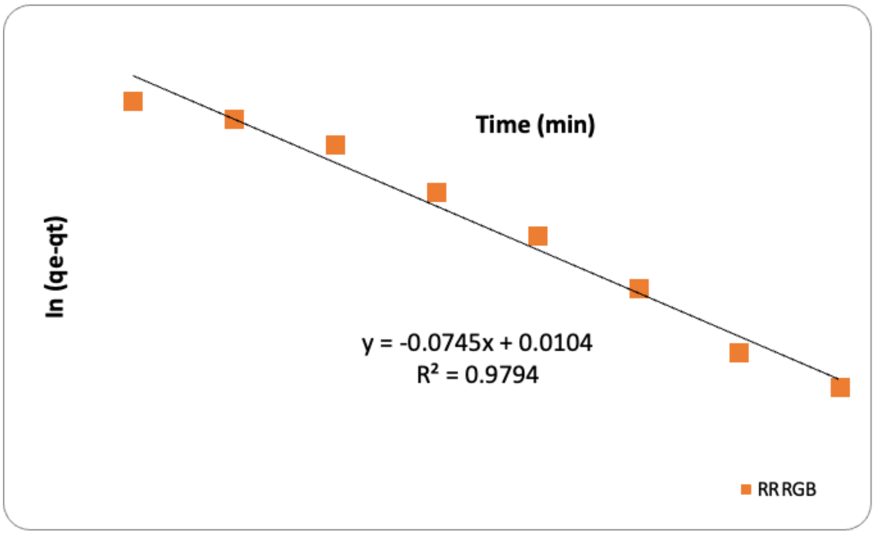

Figure 7: Pseudo-first order kinetic graph for Remazole Red RGB and arecanut peel carbon adsorption processes

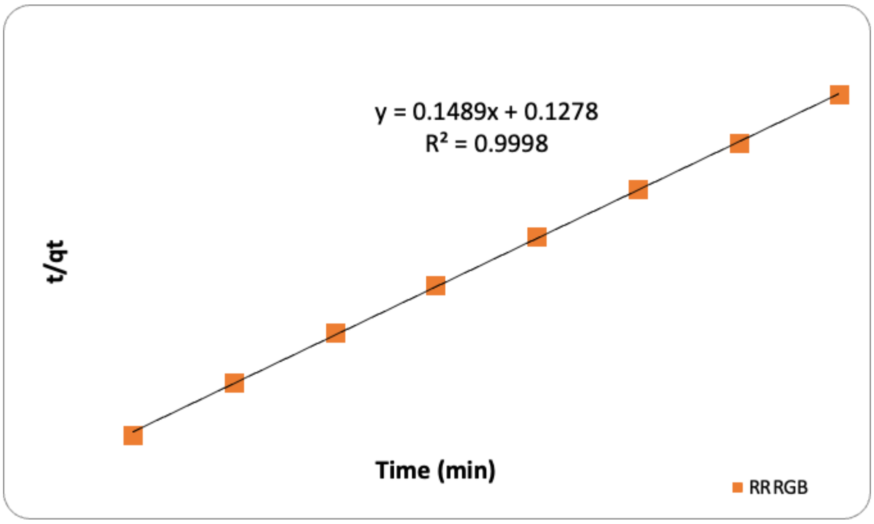

Figure 8: Pseudo-second order kinetic graph for Remazole Red RGB and arecanut peel carbon adsorption processes

Table 3: Pseudo first order kinetic variables of Remazole Red RGB and arecanut peel carbon adsorption processes

q_e exp (mg/g)	k_1(min^{-1})	q_e cal (mg/g)	R^2
6.64	0.0747	1.01	0.979

Table 4: Pseudo second order kinetic variables of Remazole Red RGB and arecanut peel carbon adsorption processes

q_e exp (mg/g)	k_2(g mg^{-1}min^{-1})	q_e cal (mg/g)	R^2
6.64	7.824	6.71	0.9998

The adsorption results (Table 4) confirmed that the adsorption kinetics for Remazole Red RGB dye onto arecanut peel carbon can be fit well with pseudo-second-order kinetic equation. Therefore, in this adsorption system chemical adsorption is control the sorption rate.

G Intra particle diffusion

The intra particle diffusion model is written in the form:

$$q_t = k_p t^{0.5} + C \qquad (5)$$

Where q_t = dye uptake at time t in mg/g, k_p = intra-particle-diffusion rate constant in mg/ g min and C = intercept in mg/g. The graph of qt versus $t^{0.5}$ will give k_p as slope and C as intercept (Figure 9).
The values of the Kp, C and regression coefficients R^2 are tabulated in Table 5.

Table 5: Intra particle diffusion parameters of Remazole Red RGB and arecanut peel carbon adsorption processes

K_p (mg g^{-1} min$^{-0.5}$)	C	R^2
	5.754	0.984

From the results it can be concluded that intra particle diffusion is not only the rate controlling step as the straight line does not pass through the origin and value of C is not equal to zero. The thickness of boundary layer is indicated by the C intercept value. In the arecanut peel – Remazole Red RGB batch adsorption system inter particle diffusion does not control the entire adsorption process.

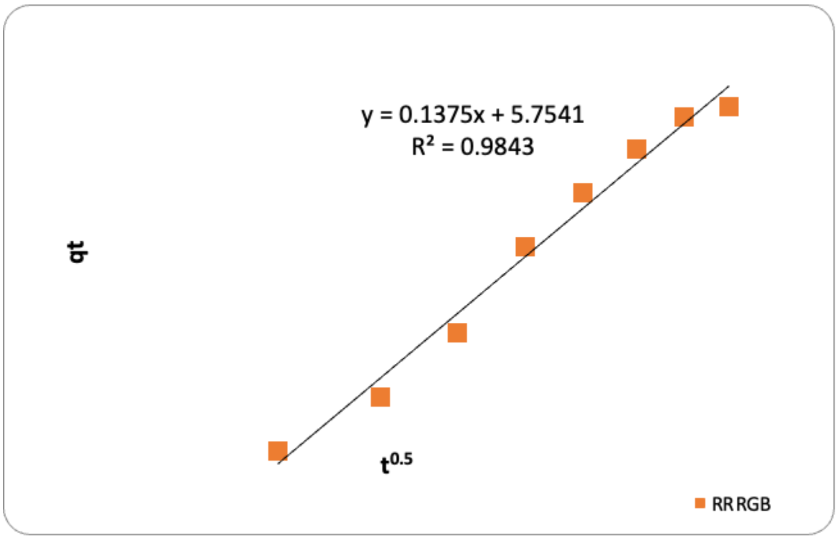

Figure.9: Intraparticle diffusion kinetic model for the adsorption of Remazole Red RGB on arecanut peel carbon

H Regression analysis

The estimated linear model interrelating percentage of color removal with the controlling parameters is expressed in the following Equation 6 & 7 for Remazole Red RGB dye.

Y =A0+A1X1+A2X2 (6)

Y=82.72197+0.304X1-4.9540X2 (7)

Where, X1= contact time in minutes, X2= pH of dye solution and Y= percentage of color removal.

From the model, the most significant controlling parameter of the system affecting percentage of color removal is the pH of the dye solution and the least significant parameter is the contact time for Remazole Red RGB dye for arecanut peel carbon.
From correlation matrix correlation of percentage of color removal to pH is 4.9540 and for contact time is 0.304 for Remazole Red RGB dye adsorption onto arecanut peel carbon.

From the figures the R^2 evaluated as 0.979 Remazole Red RGB dye (Figure.10) adsorption onto arecanut peel carbon. From the result it is observed that the linear regression model gives the best results (R^2 nearly equal to 1).

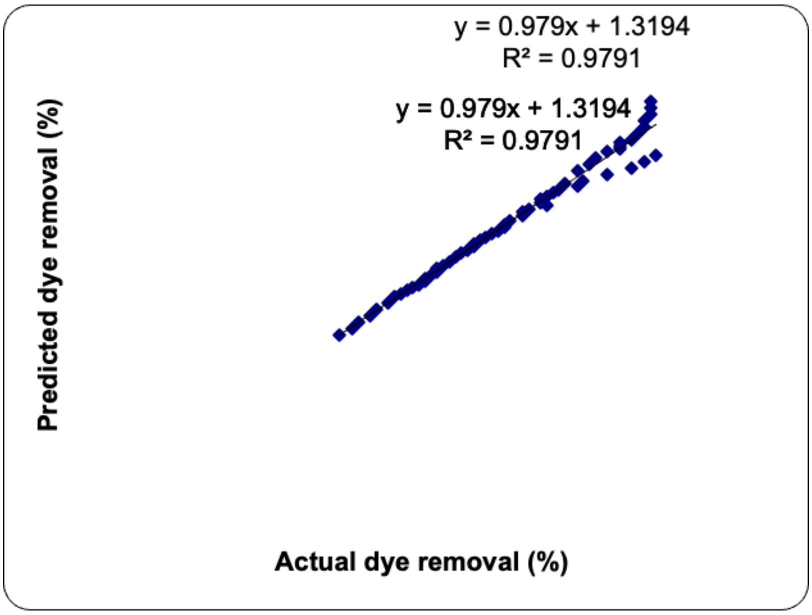

Figure 10: Linear regression plot showing observed and predicted percentage color removal of Remazole Red RGB on arecanut peel carbon

IV Conclusion

From the final results of this study, it can be concluded that arecanut peel and agricultural waste should be used as appropriate materials for the removal of Remazole Red RGB. The removal percentage of Remazole Red RGB dye by arecanut peel carbon is 83% at pH 4 for a contact time of 50 minutes at an initial dye concentration of 5 mg/L at an adsorbent dosage of 0.625 g/L. For Remazole Red RGB dye removal, the data is unfriendly for the Langmuir isotherm model but suits well for the Freundlich isotherm model. The kinetics of the adsorption system were agreeable to the pseudo second-order kinetic model. The intra particle diffusion is not a stage controlling the rate of the complete adsorption process. The outcome of this research showed that the linear regression model gives the best results. The results of the present work disclose that the adsorbent prepared from the arecanut peel removes the reactive dye selected for this analysis, which is very efficient and effective.

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