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Adsorption of cationic dye in aqueous solution by chemically modified *Areca catechu* husk

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ABSTRACT

The present investigation is based on utilizing chemically treated *Areca catechu* husk as a low-cost agro-waste adsorbent to replace expensive activated carbon for the removal of Basic red 2 (BR2) dye from water-based solution. Initial experiments have shown that sodium hydroxide treated *Areca catechu* husk provides maximum adsorption of 97.05% compared to the other chemical treatment [distilled washed *Areca catechu* husk (DWAH) 85.34%, sodium carbonate treated *Areca catechu* husk (SCAH) 82.30%, dipotassium phosphate treated *Areca catechu* husk (DPAH) 80.52% and phosphoric acid-treated *Areca catechu* husk (PAAH) 46.33%). Application of Fourier-transform infrared spectroscopy allows identify and characterize unknown components and contamination present on or in the adsorbent. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy analysis was performed with a field emission gun – scanning electron microscopy (FEG-SEM) machine to comprehend surface morphology and elemental arrangement of the husk. Batch experiments were done and optimum adsorption condition of different parameters like pH, rotation per minute, adsorbent dose, initial concentration and temperature as 7, 200 RPM, 10 mg/L, 100 mg/L and 298 K. Four different types of isotherm models were used for study, among these Langmuir isotherm model better suited, with the maximum adsorption potential of 23.87 mg/g. The activation energy was analyzed as 10.23 kJ/mol and thermodynamic analysis indicated the endothermic and spontaneous nature of adsorption. The adsorption kinetics investigation pursued the pseudo-second-order kinetics model. Thus, it can be concluded that *Areca catechu* husk treated with sodium hydroxide is a good alternative, non-conventional, low-cost agro-waste adsorbent for removal of BR2 dye from wastewater and can be an alternative to costly activated carbon.

Keywords: Adsorption; Agro-waste; Basic red 2 dye; *Areca catechu* husk; Isotherm; Kinetics

1. Introduction

A healthy environment is important for the development and growth of any living being [1]. Water pollution caused by dyes is a matter of concern. Dyeing is an essential process used in the textile, dyeing, plastics, paper, ink, leather and cosmetics industries and wastewater from these types of industries contains large quantities of dyestuffs that are considered to be major water pollutants. Currently, more than 10,000 commercially available dyes are present. It is estimated that nearly 1.6 million tons of dyes are produced every year and 10%–15% of this volume is discharged as wastewater into the environment without proper treatment [1–3]. Dyestuffs are non-biodegradable, their complex aromatic structure makes them more stable in temperature, light, microbial attack and oxidation. The growth of zooplankton, phytoplankton and other microorganism living in water bodies are affected by dyes. For humans, they can cause skin allergies, respiratory problems, carcinogenic and mutagenic changes, which can also

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cause cancer and mutation in human bodies and other species. It has been commonly observed in dye using industrial workers [4,5]. The presence of dyes in the aquatic biota is highly noticeable at a low concentration. They absorb and reflect the incoming sunlight and thus interferes with the photosynthesis process of the living plant and the growth of good bacteria living in water bodies [6,7]. Dyes can be classified as anionic, cationic and nonionic dyes, anionic dyes are less toxic than cationic dyes [7]. Hence the human health and the aquatic environment are now under serious threat from untreated dye bearing wastewater discharging from industries to streams, rivers or oceans without proper treatment.

Currently, there are several treatment processes available to remove dyes from wastewater such as sedimentation, chemical coagulation/flocculation, filtration, chemical precipitation, oxidation, advanced oxidation process, ozonation, ion-exchange, reverse osmosis, Fenton process, photo-Fenton process, photocatalytic and electrochemical combined treatment, photo-ferrioxalate system, photocatalytic degradation, biological degradation and adsorption process [8–11].

Nevertheless, from a technical and economic point of view, each of these treatment methods has its drawbacks like inefficient removal, high operational and initial cost, labor-intensive, disposal of toxic sludge, etc. On the other hand, the adsorption process has been found effective, eco-friendly and efficient in dye removal. The adsorption process has been widely and rapidly used over the past decade, due to high efficiency, simple design, easy operation and disposal, regeneration at low cost, no sludge disposal problem, low operational cost, etc [12,13]. Activated carbon is generally practiced as an adsorbent because of its high surface area, adsorption capability and micro-porous structure [3,14]. However, industrial activated carbon is costly to produce, so researchers are looking for alternative low-expensive adsorbents in places of activated carbon. Agricultural bi-products, industrial waste, clay and many more are successfully used because of their good removal efficiency, easy availability with a very low cost [15].

The *Areca catechu* (areca nut) is the seed of areca palm, which generally grows in coastal areas or where the rainfall is high. Tropical Pacific South East, South Asia and parts of East Africa holds the total production of *Areca catechu* nut. India accounts for almost 49.74% of world production, and Assam is India's third-largest producer of areca nuts. The husk is about 10%–20% by weight of the raw nut [16,17]. The main objective of this study is to investigate the removal of Basic red 2 (BR2) dye onto chemically modified *Areca catechu* husk so that it can be used as an alternative to costly activated carbon. Using this waste husk as an adsorbent leads to double advantages such as waste management and a low-cost bio-adsorbent.

2. Material and methods

2.1. Adsorbent preparation and characterization

Raw *Areca catechu* husk used in this investigation was collected from the native market in Silchar, Assam, India. The husks were cleansed with water and dried to eliminate any unwanted material such as dust and dirt. It was then cut into small pieces and sieved it properly through 300 to 500 μm sieve. Further to remove any dust, natural resins and color substance from the husk it was again washed thoroughly with distilled water. The wet sieved husk was then placed over a stainless steel plate and dried at 333 ± 5 K for 24 h in an electric oven. The dry raw *Areca catechu* husk sample was stored in an airtight glass bottle for chemical treatment.

The raw *Areca catechu* husk was chemically modified to improve adsorption by soaking it in a solution of 0.1 M NaOH at a ratio of 1:3 (solid/liquid, w/v) at RPM 200 for 2 h, which remains in solution for 24 h after shaking. After 24 h, the surplus of NaOH was cleaned with distilled water to normalize its pH near 7. Then it was dried for 1 d at a temperature of 333 ± 5 K in an electric oven, and stored in an airtight glass bottle for further experiments. Fourier-transform infrared spectroscopy (FTIR) was done to identify the functional groups present in the adsorbent. Scanning electron microscopy (SEM) study was used to produce sample images with high-resolution and high magnification to understand the surface morphology favorable for dye adsorption.

2.2. Stock solution and batch adsorption studies

Basic red 2 (BR2) dye was used in this study also known as safranin dye having empirical formula $C_{20}H_{19}N_4Cl$, molecular weight 350.8 moL/L, color index number 50240 and λ_{max} is 518 nm. A 1,000 mg/L stock solution was prepared by dissolving 1 g of the BR2 dye in 1 L of distilled water. The desired experimental concentration of BR2 dye was prepared by mixing the required distilled water with the stock solution. The pH of the dye solution if required was adjusted by adding 0.1 M HCl and 0.1 M NaOH solution using an automated pH meter.

Batch experiments have been performed for removal of BR2 dye with sodium hydroxide treated *Areca catechu* husk (SHAH). All the tests were conducted in 250 mL Borosil Erlenmeyer bottles, with 100 mL of known initial concentration dye solution and the required quantity of adsorbent material. The bottles were placed in an incubator shaker at a rotational speed of 200 RPM when the temperature was maintained at 303 K. The effects of pH, shaking speed, initial dye concentration, contact time, temperature and adsorbent dose were also evaluated in these experiments. Every experiment was conducted for almost 120 min. Samples were obtained at regular time intervals and were used to test the concentration of BR2 dye in the solution by double beam UV/Vis spectrophotometer (Chemito, Model 3501/0706). Control experiments were conducted for each type of experiment to check any accumulation of dye on the glassware surface or other losses without adding any adsorbent, no such losses were observed [1,18].

2.2.1. Calculation

The quantity of dye adsorbed per unit *Areca catechu* husk (mg/g) was estimated using Eq. (1):

$$q = \frac{\left(C_0 - C_t\right)V}{m} \tag{1}$$

where C_0 and C_t are the concentration of BR2 dye (mg/L) at time zero and t, respectively, m is the adsorbent mass in solution (g) and V is the total volume of solution (L). For precision and accuracy, all tests were executed two times and mean values were selected [19,20].

2.3. Adsorption isotherm studies

Isotherm studies were done to understand the process of adsorption and interaction between the adsorbent and the adsorbate. It helps to know the basic procedure of the process, whether it is monolayer adsorption or multilayer adsorption. Experiments were performed by raising the adsorbent dose from 1 to 10 g/L after optimization of other variables such as pH, RPM, temperature and initial concentration. There are numerous isotherm models available to analyze the equilibrium of the adsorption process. Among these models, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm models were most widely used by several researchers. The equations of these models are shown in Eqs. (2)–(5), respectively.

Langmuir isotherm model:

$$\left(\frac{1}{q_e}\right)=\left(\frac{1}{Q_0 B}\right)\left(\frac{1}{C_e}\right)+\left(\frac{1}{Q_0}\right) \tag{2}$$

Freundlich isotherm model:

$$\ln(q_e)=\ln\left(K_F\right)+\left(\frac{1}{n}\right)\ln\left(C_e\right) \tag{3}$$

Temkin isotherm model:

$$q_e = B_T \ln\left(K_T\right)+B_T \ln\left(C_e\right) \tag{4}$$

D–R isotherm model:

$$\ln q_e = \ln q_s - \beta\varepsilon^2 = RT\ln\left(1+\frac{1}{C_e E}\right) \tag{5}$$

where C_e and q_e are the concentration of adsorbate at equilibrium (mg/L) and the amount of adsorbate adsorbed at equilibrium (mg/gm), Q_0 and B are the Langmuir maximum adsorption capacity of adsorbent (mg/g) and Langmuir isotherm constant (L/mg), K_F and n are the Freundlich adsorption capacity (mg/g) and adsorption intensity constant, B_T and K_T are the Temkin constant and Temkin adsorption potential (L/g) and q_s, β and E are the theoretical isotherm saturation capacity (mg/g), D–R isotherm constant (mmol^2/J^2) and mean sorption energy, respectively [21,22].

Each adsorption isotherm model gives an important piece of information. For example, if we design a batch system for wastewater treatment, Q_0 from Langmuir isotherm is very essential for removal capacity calculation. From the D–R isotherm model, we can identify the type of adsorption whether chemical or physical. Temkin constant b use to identify either the adsorption is exothermic or endothermic in nature. Therefore isotherms are more important than the removal percentage of dye.

2.4. Adsorption kinetics studies

Kinetic analysis of every chemical process is unavoidable, it is generally used to understand the rate at which it approaches the state of equilibrium condition. In the current study, pseudo-first-order and pseudo-second-order rate kinetic models have been employed to understand BR2 dye's adsorption mechanism behavior on SHAH in terms of time. The equation of these models is shown in Eqs. (6) and (7), respectively.

$$\ln\left(q_e - q_t\right) = k_{p_1} t + \ln\left(q_e\right) \tag{6}$$

$$\frac{t}{q_t}=\frac{t}{q_e}+\frac{1}{k_{p_2} q_e^2} \tag{7}$$

where q_t and q_e are the adsorbed BR2 dye mass at time t and equilibrium (mg/g), and k_{p1} is the pseudo-first-order rate constant (min^{-1}) and k_{p2} is the pseudo-second-order rate constant (g/mg min) [23,24].

2.5. Mass transfer parameter

The adsorption process involves several diffusion phases, in the first phase adsorbate diffuse to the surrounding of the adsorbent from the liquid phase and in the second phase from surrounding to adsorbents surface diffusion takes place, this is commonly known as bulk diffusion and film diffusion, respectively. Then the diffusion into the internal pores of the adsorbent of the adsorbate molecules is called intra-particle diffusion, which is a time-consuming process. Bulk diffusion can easily control by agitating the solution. So, the rate-limiting step of the adsorption process will be film diffusion and intra-particle diffusion [25]. The film diffusion of the adsorbate was studied by Boyd proposed liquid film diffusion model and the diffusion of the adsorbate inside the pores of adsorbent was calculated using the equation offered by Weber and Morris as shown in Eqs. (8) and (9), respectively.

$$q_t = \left(K_{\text{id}} t^{\frac{1}{2}}\right) + C_i \tag{8}$$

$$\ln\left(1-F\right) = -\left(K_{\text{fd}} t\right) \tag{9}$$

where K_{id} is the intraparticle rate constant (mg/g min$^{1/2}$), K_{fd} is the coefficient of mass transfer in the film (cm/min), C_i is the thickness of the boundary layer, F (q_t/q_e) is the fractional attainment of equilibrium [26–29].

2.6. Thermodynamics and activation energy

Activation energy can be explained as the minimum energy requisite by the adsorbate particle to become adsorbed with a certain orientation on the adsorbent surface [30,31]. Arrhenius's empirical equation in its linear form was applied to study the activation energy as shown in Eq. (10).

$$\ln K = -\left(\frac{E_a}{RT}\right) + \ln A \quad (10)$$

where K is the adsorption rate constant (in this situation pseudo-second-order rate constant k_{p2}), T is the temperature in Kelvin, A is the proportionality constant and E_a is the activation energy in kJ/mol [18,21].

3. Results and discussion

3.1. Characterization of Areca catechu husk

3.1.1. SEM analysis

To know the surface morphology and characterization of *Areca catechu* husk, SEM analysis was performed. Fig. 1a shows the SEM images for distilled washed *Areca catechu* husk (DWAH), Fig. 1b shows sodium hydroxide treated *Areca catechu* husk (SHAH) and Fig. 1c shows Basic red 2 dye adsorbed *Areca catechu* husk (BAAH).

From Fig. 1a it can be observed that the surface of DWAH is rough, porous and uneven. These pores and cavity-like structures are heterogeneous in nature and offer a large surface area aimed at adsorption of dye. The surface structure of DWAH changes significantly after chemical treatment, as pores get widen with some extra and larger cavities. During chemical treatment lignin and hemicellulose present on the husk also get removed, it contributes to the extra active surface area. After adsorption of BR2 dye of the pores and active sites of the *Areca catechu* husk were taken by dye molecules and the husk surface becomes smooth with fewer voids.

3.1.2. Energy-dispersive X-ray spectroscopy analysis

Energy-dispersive X-ray spectroscopy (EDAX) analysis was done to recognize the elemental composition or chemical characteristics of *Areca catechu* husk. EDAX spectra of SHAH and BAAH are shown in Figs. 2a and b. Table 1 shows the elemental composition of SHAH and BAAH. From the EDAX spectrum, it is clear that C and O are the major elements of SHAH and a small number of impurities. After adsorption of BR2 dye, the amount of impurities increases with a decrease in major elements. The amount of Cl element increased after BR2 dye adsorption, this is due to

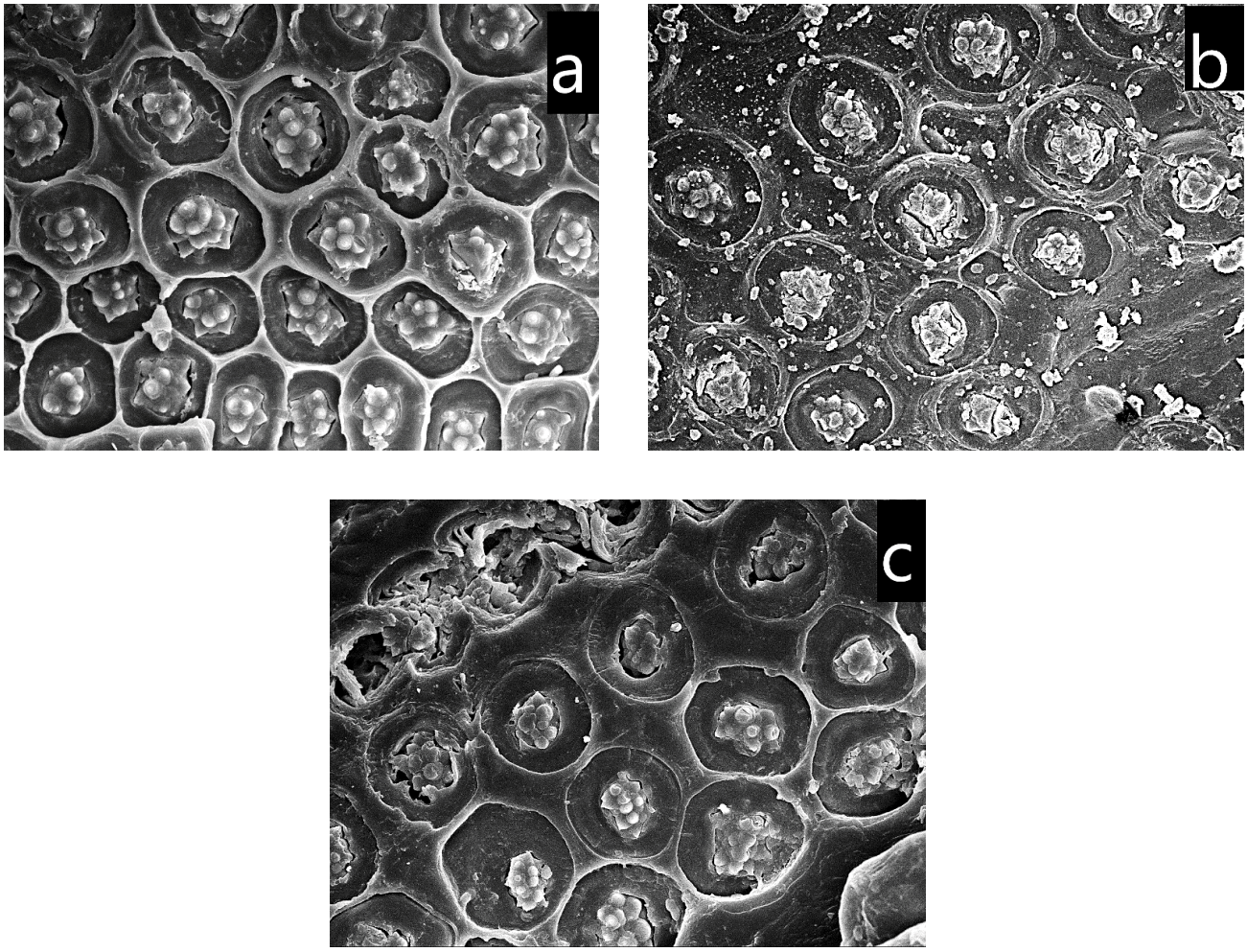

Fig. 1. SEM image (×2,000) of (a) distilled washed *Areca catechu* husk, (b) sodium hydroxide treated *Areca catechu* husk, and (c) Basic red 2 dye adsorbed *Areca catechu* husk.

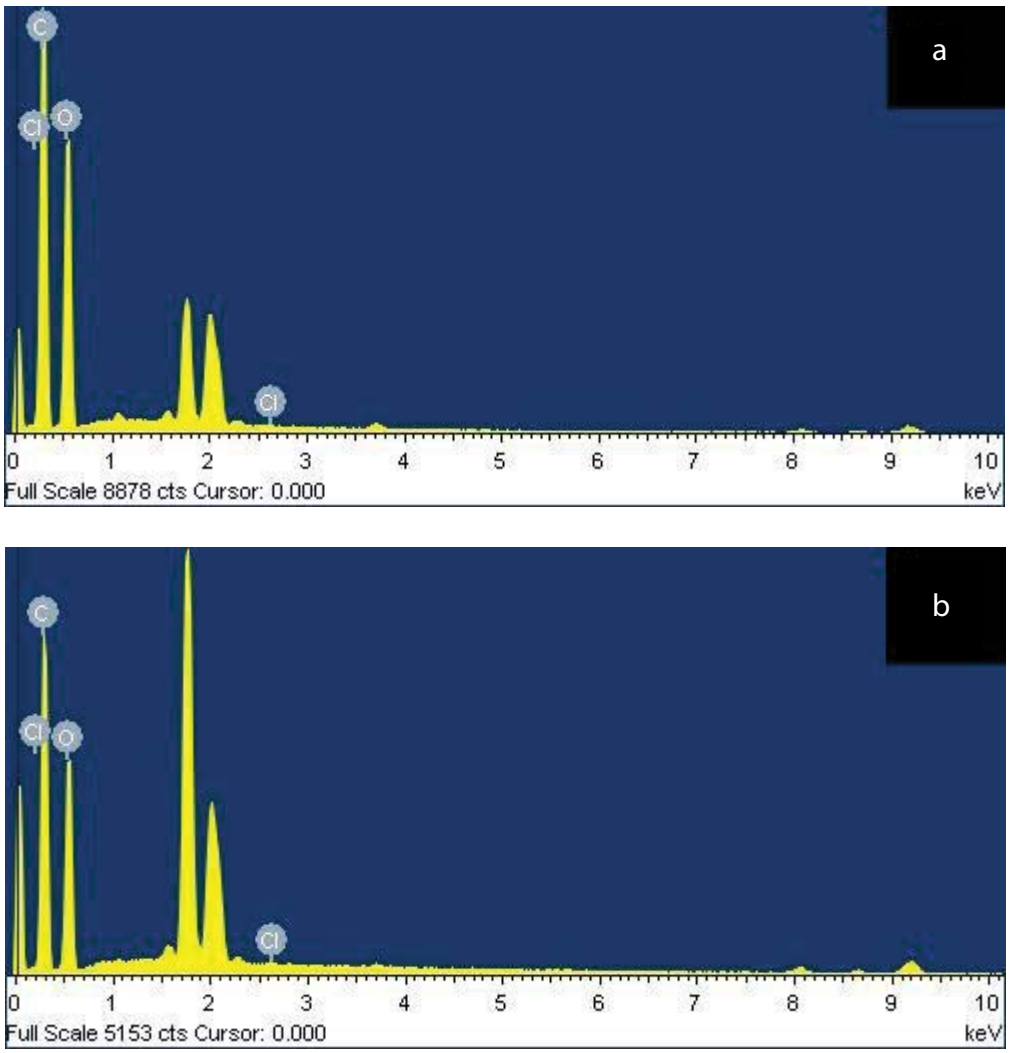

Fig. 2. EDAX image of (a) sodium hydroxide treated *Areca catechu* husk and (b) Basic red 2 dye adsorbed *Areca catechu* husk.

Table 1
Result of EDAX analysis

Element analysis	SHAH		BR2 adsorbed SHAH	
	Weight %	Atomic %	Weight %	Atomic %
C K	48.31	55.47	49.08	56.27
O K	51.62	44.50	50.72	43.65
Cl K	0.07	0.03	0.19	0.07

the Cl element is present in BR2 dye. So it is observed from EDAX analysis that, after the adsorption process, dye molecules remain on the surface of the adsorbent [32–35].

3.1.3. FTIR analysis

To recognize the functional groups and molecular structure of the *Areca catechu* husk FTIR study was performed. Fig. 3 signifies FTIR of DWAH and FTIR of SHAH. The FTIR spectrum scale was between 4,000 and 400 cm^{-1}. The FTIR spectra demonstrate the complex nature of *Areca catechu* husk. The spectra show strong and fine peaks at 3,677.27; 3,656.62; 3,635.57; 3,455.05 and 1,372.31 cm^{-1}, which signifies the existence of –OH or hydroxyl group and a carboxyl group. This may be due to the presence of cellulose on the surface of the *Areca catechu* husk. The peak at 2,920.40 cm^{-1} signifies the C–H stretching and the peak at 1,741.36 cm^{-1} represents the carbonyl group (C=O) due to the existence of hemicelluloses and wax on the husk but the peak at 1,514.38 cm^{-1} belongs to lignin. Again, the peak

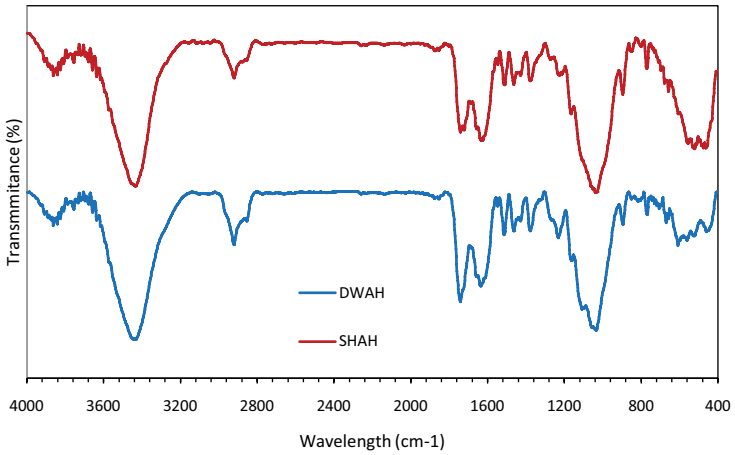

Fig. 3. FTIR of (a) sodium hydroxide treated *Areca catechu* husk (SHAH) and (b) SHAH after adsorption of Basic red 2 dye.

can observe at 1,634.39 cm^{-1} which is due to the existence of hemicellulose. So, FTIR spectra confirm the existence of chemical components such as cellulose, hemicellulose and lignin on the surface of the *Areca catechu* husk.

The FTIR spectra show two major peaks at peak 3,432 cm^{-1} indicating hydroxyl group O–H stretching and at peak 1,741 cm^{-1} presenting carboxyl group C=O stretching. The presence of such a group signifies the presence of cellulose, lignin and hemicellulose. These functional groups are major responsible for the adsorption of BR2 dye from aqueous solution. So, the adsorption process may possibly due to intermolecular H-bonding between O atom present in *Areca catechu* husk and the H atom of BR2 dye or vice versa.

The BET surface area of *Areca catechu* husk before and after chemical treatment was found to be 0.182 and 12.62 m^2/g, respectively. The average pore size of the husk was found at 7.21 nm. The results indicated that after chemical treatment the surface area of *Areca catechu* husk was increased significantly. Therefore, the adsorption of BR2 dye was quite possible for this adsorbent material.

3.2. Batch adsorption studies

3.2.1. Screening study

Screening experiments were performed with distilled washed *Areca catechu* husk (DWAH), sodium hydroxide treated *Areca catechu* husk (SHAH), dipotassium phosphate treated *Areca catechu* husk (DPAH), sodium carbonate treated *Areca catechu* husk (SCAH) and phosphoric acid-treated *Areca catechu* husk (PAAH) to find the most effective and efficient treatment for BR2 dye adsorption. Fig. 4 shows the results of the screening experiment. SHAH gives the best removal of 97.05% compared to

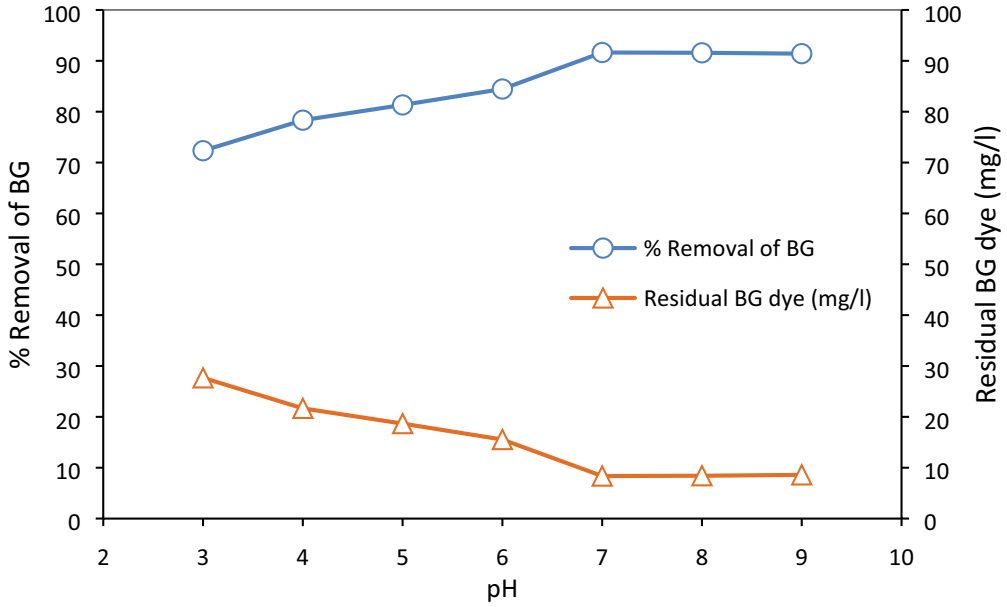

Fig. 4. Effect of pH.

DWAH removal = 85.34%, SCAH removal = 82.30%, DPAH removal = 80.52% and PAAH removal of 46.33%. As per removal efficiency, sodium hydroxide treated *Areca catechu* husk gives the best removal as compares to other pretreatments and hence further experiments were conducted with SHAH.

3.2.2. Effects of pH

The procedure of the adsorption process and the degree of ionization of the adsorbent functional groups are significantly affected by the pH and surface infusion of the adsorbent. A series of tests were conducted to check the influence of pH solution over the adsorption process as final results are shown in Fig. 4. Dye removal efficiency significantly enhances linearly as pH raise from 4 to 7 and a marginal increase was observed from pH 7 to 9. This is due to excess H^+ ions present in the solution and BR2 dye is a cationic dye in nature. So all the dye molecules adsorbed positively charged hydrogen ions and tried to precipitate. Therefore, pH 7 is considered to be the optimum pH level. It can be understood from the pH removal rate that there must be a chemical reaction taking place among the dye molecules and the adsorbent and an electrostatic force of interaction are present.

3.2.3. Effects of RPM

RPM is considered to be another important variable in the adsorption process. The experiments were conducted by altering the speed of the rotary shaker from 125 to 250 RPM. The study was conducted with a 100 mL sample of initial concentration 100 mg/L, pH 7, adsorbent dose 10 g/L and temperature 303 K. From Fig. 5, it is noticed that the removal rate increases proportionally with RPM up to 200, beyond that removal rate slightly decreases. It can be linked to the fact that the magnitude of the separation force develops with a rise in RPM and turn into higher than the binding force at RPM above 200, leading to a rise in desorption and a drop in removal.

3.2.4. Effects of adsorbent dose

The optimum level of adsorbent dose is a significant factor in the adsorption process. The tests were conducted with varying doses from 1 to 10 g/L. The study was conducted with a 100 mL sample of initial concentration 100 mg/L, pH 7, 200 RPM and temperature 303 K. The rate of removal of BR2 dye boost with a rise in the dose as shown in Fig. 6. An increase in dose is proportional to active space and surface area, but at dose 8 g/L and above the removal trend towards equilibrium, so the optimal dose of this experiment was taken as 10 g/L.

3.2.5. Effects of initial dye concentration

The removal percentage of dye molecules is deeply reliant on the initial concentration of dye in the solution. The experiment was conducted with pH 7, 200 RPM, adsorbent dosage 10 mg/L, temperature 303 K and variable concentration of BR2 dye as 50, 100 and 200 mg/L. From Fig. 7, it was observed that the rate of dye adsorption is vice-versa to initial concentration. At a low concentration, all the dye molecules get adsorbed at the active sites of the adsorbent surface and become saturated after some time. However, when the concentration increases with a fixed-dose, there was non-availability of the active sites essential for more dye molecules, resulting in decreased removal but an increase in adsorption capacity. In this analysis, the removal rate of BR2 dye was reduced from 96.96% to 93.37% when the concentration has risen from 50 to 200 mg/L and the sorption capacity increases from 11.18 to 33.34 mg/g

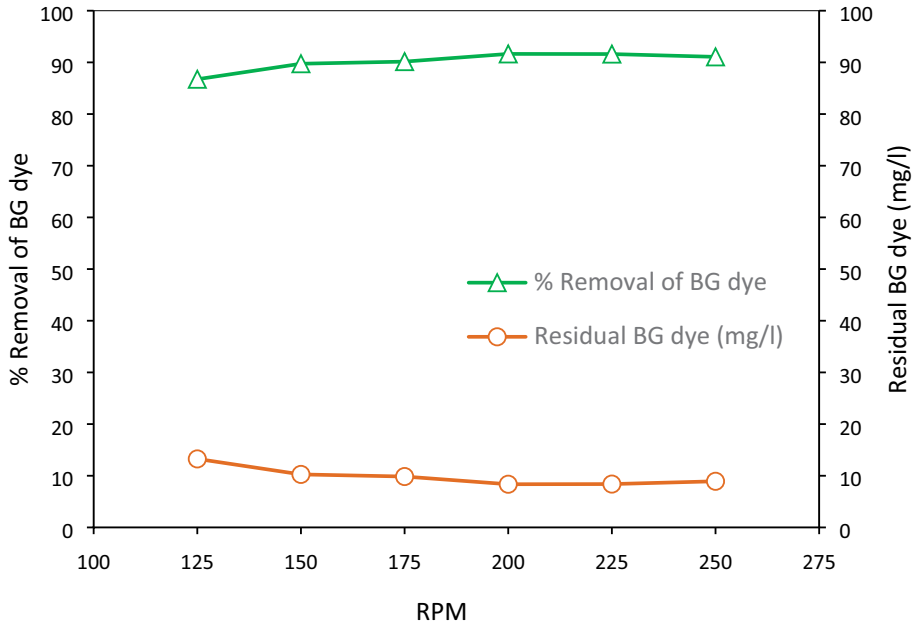

Fig. 5. Effect of RPM.

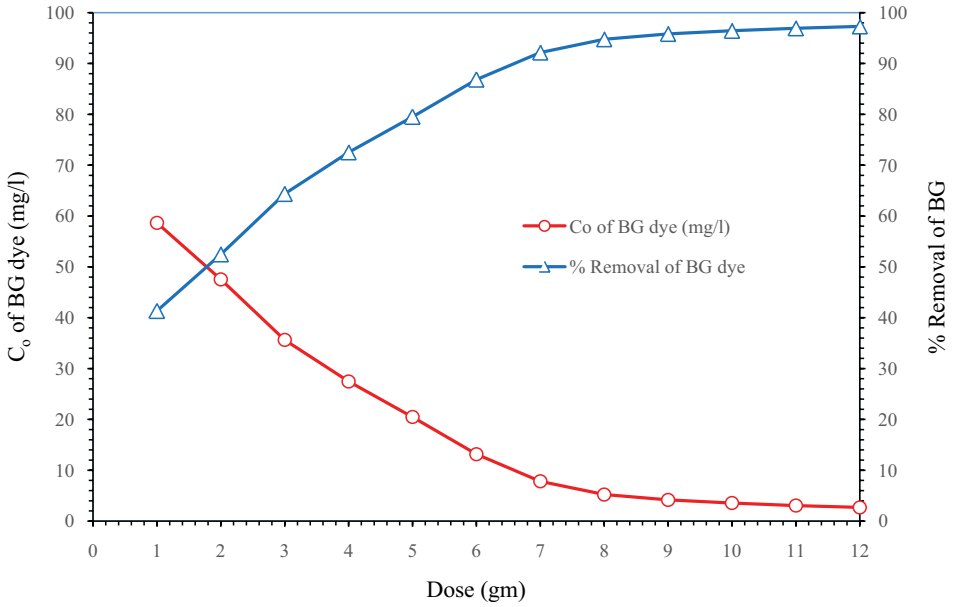

Fig. 6. Effect of adsorbent dose.

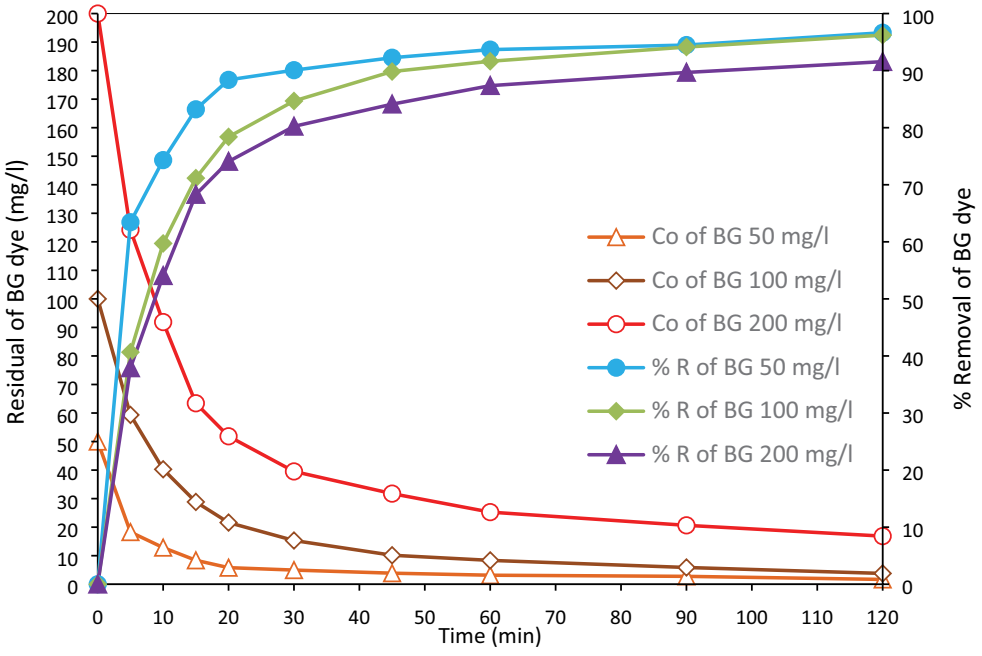

Fig. 7. Effect of initial concentration.

as concentration increases. Nevertheless, as the concentration rises the adsorption capacity increases because of the higher driving force of more dye molecules.

3.2.6. *Effects of temperature*

Temperature effects on SHAH for the adsorption of BR2 dye were investigated with a 100 mL sample for pH 7, dose 10 g/L, RPM 200, initial concentration of 100 mg/L and variable temperature of 303, 313 and 323 K as shown in Fig. 8. It was observed that BR2 dye adsorption also enhances with a rise in temperature, confirming the adsorption process as endothermic. As the temperature rises the adsorption capacity is enhanced due to enlarged surface area and active pores resulting in the more diffusion around the boundary layer grow, but pore diffusion will decrease at a higher temperature as the viscosity decreases with the temperature. The adsorption process involves physical and

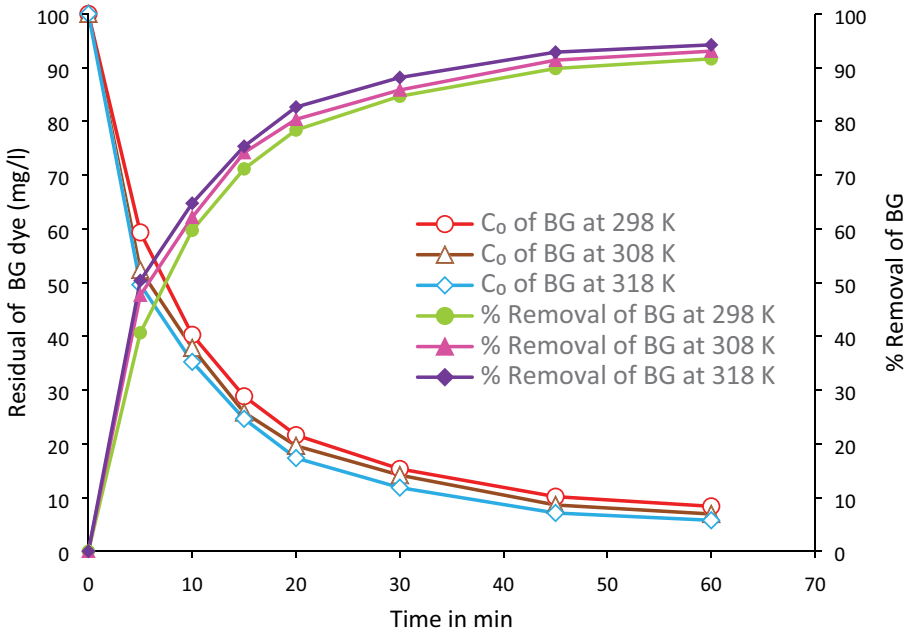

Fig. 8. Effect of temperature.

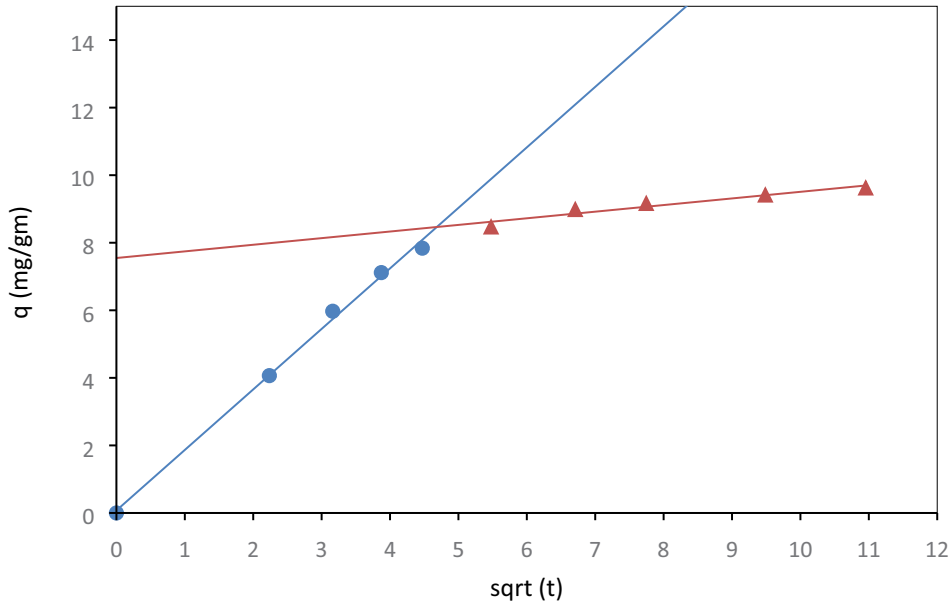

Fig. 9. Test plot for the liquid film diffusion model.

chemical sorption and chemical adsorption occurs due to increased adsorption at an elevated temperature, as is the present study [36,37].

3.3. Adsorption isotherm

Adsorption isotherm analysis was performed with four different models as described in the material and method. All the tests were executed at RPM 200, pH 7, initial concentration of dye 100 mg/L, by changing the dose of SHAH and fixed temperature of 303 K. In Table 2, the values of isotherm models are listed. From the results, as shown in the table, it is evident that the Langmuir isotherm model gives excellent results for a maximum adsorption capacity of 23.87 mg/g with a single layer on the adsorbent surface. Also, the R^2 value of the same isotherm model is 0.982, which lies between 1 and 0 and confirms the process is satisfactory. The value of the Langmuir isotherm constant (b), Freundlich adsorption capacity (K_F) and Temkin constant (B_T) increase with a rise in temperature, confirms the endothermic

Table 2
Results of adsorption isotherms model study

Isotherm model		
Langmuir	Q_{max} (mg/g)	23.87
	b (L/mg)	0.008
	R^2	0.982
Freundlich	K_F (mg/g)	5.546
	n	1.984
	R^2	0.955
Temkin	K_T (L/mg)	1.150
	B_T	7.343
	R^2	0.909
D–R	q_s (mg/g)	18.698
	β (mmol²/J²)	8×10^{-6}
	E (kJ/mol)	8.066
	R^2	0.827

adsorption process. Again from the D–R isotherm model, the valuation of E was obtained as 8.26 kJ/mol, so it can be characterized as a chemical adsorption process [38–41].

3.4. Adsorption kinetic

Kinetic analysis was studied with pseudo-first-order and pseudo-second-order rate kinetic models as discussed earlier. The analysis was done for 25, 50 and 100 mg/L initial concentration. The outcomes of this study are shown in Table 3. From the results, it is clear that adsorption of BR2 dye onto SHAH is better suited with the pseudo-second-order rate kinetic model with an R^2 value of 0.999 compared to the pseudo-first-order model. The value of k_{p2}, which is the pseudo-second-order rate constant raise with a rise in temperature, authenticates the endothermic process [42–44].

3.5. Thermodynamic studies

The thermodynamic parameters, namely Gibbs free energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) were calculated by Van't Hoff equation as shown in Eqs. (11) and (12).

$$\Delta G^\circ = -RT \ln\left(K\right) \tag{11}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

where K is the equilibrium constant of the adsorption process. From Table 4 it is observed that ΔG° value is negative for mentioned temperatures, indicating the favorability of the adsorption process and the process is spontaneous. The values of ΔH° and ΔS° were analyzed from the linear plot between T and ΔG°. The values of ΔH° positive means that the enthalpy is greater than the reactant and ΔS° positive means enhance in the randomness between the solid adsorbent surface and liquid dye solution. Hence, it can be concluded that the nature of the process is endothermic and randomness increases with temperature [45].

3.6. Activation energy

Adsorption of dye molecules on the exterior surface of adsorbent occurs when the dye molecules collide with certain orientation and with minimum energy. The minimal energy that the adsorbate needs to get adsorbed on the adsorbent surface is the activation energy. Arrhenius proposed an analytical interaction, expressed linearly as:

$$\ln K = \ln A - \frac{E_a}{RT} \tag{13}$$

where K is the rate constant of adsorption (present case pseudo-second-order rate constant, k_{p2}), R is the universal gas constant, A is the Arrhenius factor, T is the temperature in Kelvin and E_a is the Arrhenius activation energy (kJ/mol). The value of E_a was calculated as 10.12 kJ/mol by plotting $\ln k_{p2}$ against $1/T$. This value lies in between 83.7 and 8.4 kJ/mol, indicating that the process follows the chemisorption mechanism [46,47].

3.7. Mass transfer and rate-limiting step

Adsorption occurs mainly in film diffusion and pore diffusion, both of these diffusion acts in the series. Fig. 9 shows the plot of Weber and Morris's intraparticle diffusion

Table 4
Result of thermodynamic analysis

T	ΔG°	ΔH°	ΔS°	R^2
(K)	(kJ/mol)	(kJ/mol)	(J/mol)	
293	6.075			
303	8.042	48.26	0.180	0.997
313	9.655			

Table 3
Result of adsorption kinetic models at a different initial concentration

Absorbent		Pseudo-first-order model			Pseudo-second-order model		
C_0 (mg/L)	$q_{e,exp.}$ (mg/g)	$q_{e,cal.}$ (mg/g)	k_{p1}	R^2	$q_{e,cal.}$ (mg/g)	k_{p2}	R^2
50	4.848	1.442	0.043	0.836	4.924	0.096	0.999
100	9.705	6.360	0.045	0.976	10.32	0.013	0.999
200	18.675	7.591	0.032	0.872	19.493	0.008	0.999

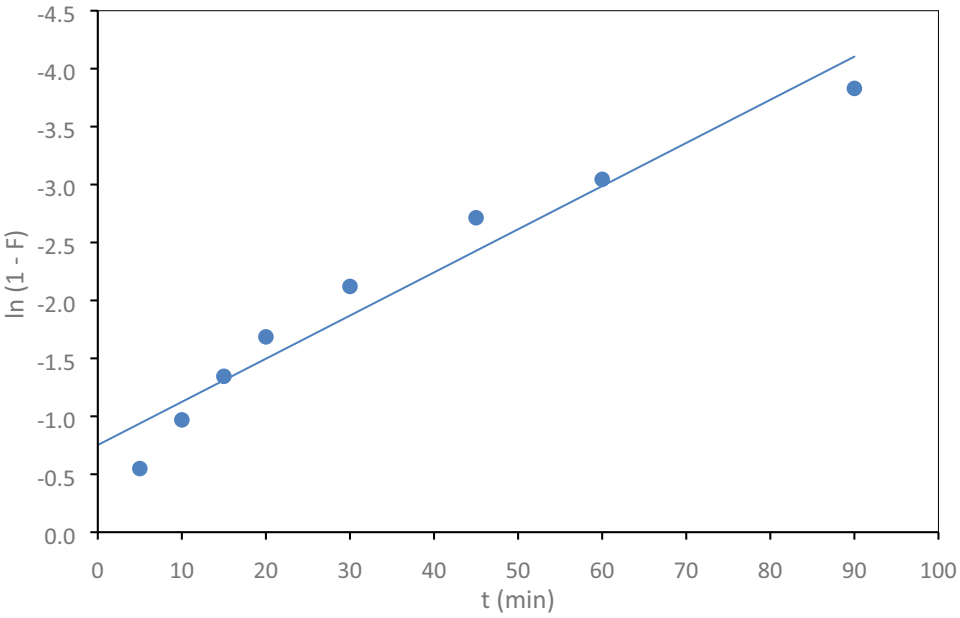

Fig. 10. Test plot for the liquid film diffusion model.

model. In this plot, two straight lines can be identified. The first-line passes through the origin, with time there is some increase in the intercept. This implies that the boundary layer thickness develops with duration. To find the rate of the adsorption process, diffusion of the adsorbate from the fluid phase to the exterior surface of the adsorbent plays a vital role in it. In film diffusion adsorbate comes from the fluid phase to the surface of the adsorbent and in intraparticle diffusion inside the pores of the adsorbent. The lagging step between these steps is the rate-limiting step in the adsorption process. Fig. 10 shows the plot of the liquid film diffusion model. From the plot, it can be noticed that the straight line does not pass through the origin, which means that the liquid film diffusion model has very limited function in this adsorption process. Also, it signifies that both the film and pore diffusion consecutively happening as there is no zero intercept [48–50].

3.8. Adsorption mechanism

The FTIR spectra show several peaks for various functional groups, among them two major peaks at peak 3,432 cm^{-1} indicating O–H stretching of the hydroxyl group and at peak 1,741 cm^{-1} showing C=O stretching of the carboxyl group. The presence of such a group signifies the presence of cellulose, lignin and hemicellulose. These functional groups are mainly responsible for the adsorption of BR2 dye from aqueous solution. In this case, BR2 is a cationic dye and pH tests confirm that the adsorption process supports high pH. Therefore, the adsorption mainly possible due to intermolecular H-bonding between the O atom present in *Areca catechu* husk and the H atom of BR2 dye or vice versa.

The mechanism of adsorption can be understood from the steps which involve in mass transfer parameters. Initially, the BR2 dye molecules migrate to the exterior of the *Areca catechu* husk from the bulk solution. Then, molecules diffuse into the boundary layer of the *Areca catechu* husk, and dye molecules are adsorbed successively at active sites. Finally, molecules move through the *Areca catechu* husk micropores to the inner portions. It can be seen that the initial 30 min the adsorption rate was fast and it reaches an equilibrium state after 120 min. So, it was for sure film diffusion is more predominant and both diffusions are acting in series.

4. Important points from the Basic red 2 dye adsorption process

From this investigation and analysis of various data, the major outcomes of the present study are listed as follows:

- According to the experimental results and analysis, it was found that adsorption of BR2 dye with *Areca catechu* husk increased significantly after chemical treatment with 0.1 M sodium hydroxide and gave maximum removal of 97.05% as compared to DWAH removal = 85.34%, SCAH removal = 82.30%, DPAH removal = 80.52% and PAAH removal of 46.33%.
- Chemical processing improves the surface area of *Areca catechu* husk. Also, SEM analysis shows that the surface of the husk got porous and uneven with more cavities, which helps in the adsorption process.
- FTIR analysis shows that strong hydroxyl groups and carbonyl groups are present on the surface of the husk, which helps it to adsorb BR2 dye. The husk mainly contains cellulose, hemicellulose and lignin.
- EDAX analysis shows that C, O and Cl are the major constituents of *Areca catechu* husk. After adsorption of BR2 dye the percentage of Cl element increase, this is due to the presence of Cl in BR2 dye molecules.
- The dye adsorption efficiency depends upon various parameters and batch experimental studies done to find the optimum level of these parameters. The optimum

level of adsorption parameters are pH 7, adsorbent dose 10 g/L, initial concentration 100 mg/L, agitation speed 200 RPM, and temperature 298 K, respectively.

- Experimental data were better suited in the Langmuir isotherm model with the highest adsorption potential of 23.87 mg/g, it also specifies that the adsorption on the adsorbent surface was monolayer.
- The activation energy was found as 10.12 kJ/mol and the value lies between 8.4 and 83.7 kJ/mol, indicating the adsorption process is a chemisorption process.
- From the thermodynamic study, it was found that the assessment of $\Delta G°$ is negative, which means the process is favorable. The assessment of $\Delta H°$ enthalpy change reveals the endothermic process and it confirms as the adsorption is direct with temperature change.
- Adsorption kinetic study showed that the pseudo-second-order kinetic model is the most suited kinetic model and the sorption was chemisorption. The value of k_{p2} increased with temperature, it also confirms the endothermic nature of adsorption.
- Mass transfer and rate-limiting step study clarify that film diffusion is more dominating compared to pore diffusion.

5. Conclusion

This present study concluded that sodium hydroxide treated *Areca catechu* (areca nut) husk is an effective, inexpensive adsorbent for the removal of Basic red 2 (BR2) dye from a water-based solution. Tests were performed in batch mode and the optimum pH was 7, rotational speed was 200 RPM with the dose of 10 g/L and gave maximum removal of 97.05%. The test data is better defined by the Langmuir isotherm model with the maximum adsorption potential of 23.87 mg/g. The adsorption process is spontaneous and endothermic as the adsorption capacity changes with the rise in temperature. The pseudo-second-order rate kinetic model found best fitted for kinetic analysis. From the literature survey, it is found that the adsorption capacity of *Areca catechu* husk is similar to other adsorbents. Thus, the *Areca catechu* husk is an effective and efficient adsorbent and can be used for industrial purposes for dye-containing wastewater treatment purposes after simple chemical treatment with 0.1 M sodium hydroxide solution and it can be replaced by expensive activated carbon for the removal of Basic red 2 (BR2) dye.

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