Adsorption of synthetic dyed wastewater using activated carbon from rice husk

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Abstract

The purpose of this study was to remove dyes from synthetic dyed wastewater using activated carbon derived from rice husk. The initial dye concentration was 45 mg/L. The batch adsorption worked best in an acidic medium of pH 2, adsorbent dosage of 13 g/L and agitation speed of 100 rpm with maximum dye removal of 80% after 10 min. The maximum adsorption capacity of the adsorbent was found to be 2.0 mg/g with a final dye concentration of 10.8 mg/L. The adsorption was found to be a non-spontaneous, endothermic chemisorption process with less disorder which best fitted the Temkin model and followed pseudo-second order. For column adsorption, the highest q_0 corresponds to 12.8 mg/g and the maximum dye removal was above 99.5%. Some of the experimental deductions were confirmed by gas-phase computations [B3LYP/6-31G(d)].

Keywords Adsorption · Activated carbon · Rice husk · Batch · Isotherms · Kinetic models · Column · DFT

1 Introduction

The progress in technology has led to the world achieving new prospects together with pollution problems and environmental disorders. Water pollution is mainly caused by the disposal of domestic, municipal and industrial wastes including textile industry which is considered to be one among the greatest polluters. Textile wastewaters are highly coloured due to unfixed dyes and these dyes must be separated from the wastewater because less than 1 mg/L can be visually detected [1]. These are responsible for aesthetic concerns, hinder light penetration and damage to aquatic microorganisms and they are difficult to eliminate due to their complex structure. Dyes can also

pass through the entire food chain causing biomagnifications [2]. In order to protect the aquatic ecosystem, there are certain stringent discharge standards applicable for industrial effluents.

Adsorption process is considered to be an efficient method to eliminate colours, organic pollutants, odours and oils [3]. Adsorption of dye combines two mechanisms namely adsorption and ion exchange which is controlled by several parameters, such as pH, temperature, dye/adsorbent interaction and contact time among others [4]. The precise nature of the bonding depends on the species involved and is commonly classified as chemisorption or physisorption [5].

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The wastewater treatment method is generally categorized into three main parts; physical, chemical and biological processes [4, 6, 7] which involves four stages namely preliminary, primary, secondary and tertiary treatments [7]. Each of the above mentioned techniques consists of other sub-techniques that differs according to process conditions, chemicals used or removal mechanism. Some of the dye removal techniques are described in Table 1.

Activated carbon is commonly used as an adsorbent which gives a high quality treated effluent and is easy to use. Other advantages of using activated carbon are

that they offer a good removal of a broad range of dyes [3], they can be cheap if low-cost adsorbent is used [2] and it is an environmentally friendly product. Some of the disadvantages include expensive regeneration [16], it cannot be used for disperse and vat dyes, some of the absorbents may be lost [5] and high generation of sludge which can cause difficulty in handling disposal. Ullhyan used activated carbon derived from low-cost adsorbents such as mustard stalk to remove dyes [16]. There are several studies where low cost adsorbents have been used for dye removal such as batch adsorption to remove Reactive

Table 1 Advantages and disadvantages of dye removal techniques

Process	Advantages	Disadvantages
Adsorption on activated carbon	<ul style="list-style-type: none"> • Treated effluent is of a high-quality • Good removal of a broad range of dyes • Good adsorbent • Easy • Cheap if low-cost adsorbent is used 	<ul style="list-style-type: none"> • Regeneration could be expensive, cannot be used for disperse and vat dyes, non-destruction process, some absorbent may be lost • Expensive commercial activation carbon • Disposal problem
Coagulation-flocculation	<ul style="list-style-type: none"> • Economically feasible and simple • Complete removal of dye 	<ul style="list-style-type: none"> • High generation of sludge • Difficulty in handling and for disposal
Electrochemical processes	<ul style="list-style-type: none"> • Non-hazardous breakdown compound • No chemicals required and no generation of sludge 	<ul style="list-style-type: none"> • Sludge of iron hydroxide • High cost of electricity • A direct decrease in dye removal due to relatively high flow rates
Physisorption	<ul style="list-style-type: none"> • Efficiently remove high initial dye concentration and regenerates 	<ul style="list-style-type: none"> • Expensive
Chemisorption	<ul style="list-style-type: none"> • Efficiently remove high dye concentration 	<ul style="list-style-type: none"> • Expensive, difficult to regenerate
Membrane filtration	<ul style="list-style-type: none"> • Removal of all types of dyes • A high-quality treated effluent is obtained • Maximum removal of initial high dye concentrations 	<ul style="list-style-type: none"> • Concentrated sludge generation • Expensive, high pressures and cannot treat large amount of wastewater • Concentration polarisation and membrane fouling
Fenton's reagent	<ul style="list-style-type: none"> • Effective decolourisation of both insoluble and soluble dyes • Cost effective and environmentally friendly, high removal for many brands of dyes, faster reaction and degradation time, no need of complicated instruments 	<ul style="list-style-type: none"> • Usage of Fe^{2+} produced sludge • Generate excess heat, expensive operational cost for high contaminants concentration, high production of iron sludge
Ion exchange	<ul style="list-style-type: none"> • Possibility of regeneration: no adsorbent loss • Effective 	<ul style="list-style-type: none"> • Ineffective for some types of dye, particularly, disperse dyes • Economical restrictions
Photochemical	<ul style="list-style-type: none"> • No sludge production • Reduction of foul odours • Mineralisation of organic compounds, cheap semiconductors 	<ul style="list-style-type: none"> • Formation of by-products • Lower efficiency at high initial dye concentration
Oxidation	<ul style="list-style-type: none"> • Process is rapid and efficient • Simple application 	<ul style="list-style-type: none"> • High cost of energy • Require chemicals
Advanced oxidation process	<ul style="list-style-type: none"> • No sludge generation • Efficient for recalcitrant dyes, • Little utilization of chemicals 	<ul style="list-style-type: none"> • Technical restrictions • By-products formed • Economically unfeasible
Biodegradation	<ul style="list-style-type: none"> • Economically feasible 	<ul style="list-style-type: none"> • Slow process
Irradiation	<ul style="list-style-type: none"> • Effective oxidation at laboratory scale 	<ul style="list-style-type: none"> • Need a lot of dissolved oxygen
Ozonation	<ul style="list-style-type: none"> • Applied in gaseous state • No increase in amount of wastewater and sludge 	<ul style="list-style-type: none"> • Short half-life about 20 min of ozone

Adapted from: Tripathi [8]; Bizuneh [4]; Kumar et al. [7]; Pereira and Alves [9]; Salleh et al. [10]; Wang et al. [11]; Parvathi et al. [12]; Demirbas [13]; Mishra [14]; Babu et al. [15]

Red 195 (RR195) dye using chitosan padded wheat husk and chitosan rice husk under optimised conditions, the efficiency was 79% and 83%, respectively [17]. The use of *Georgenia* sp. CC-NMPT-T3 to degrade and remove RR195 under optimised condition of pH 7.0 and temperature of 40 °C, with an efficiency of 95.93% at 50 ppm within 5 h [18]. Batch adsorption experiment was also carried out to remove Chemazol RR195 using dehydrated beet pulp carbon [19]. At 50 °C and optimum pH of 1.0, the maximum dye capacity was observed to be 58.0 mg/g and equilibrium was reached at 180 min. The adsorption process was spontaneous and endothermic [19]. Cone biomass of *Pinus sylvestris* Linneo was also used to study the biosorption of RR195 from aqueous solution. The maximum pH was 1.0 and the capacity of the biosorption increased from 6.69 mg/g to 7.38 mg/g when the temperature was increased from 20 °C to 50 °C for 200 mg/L dye concentration. The experimental data followed pseudo-second order [20]. There are also reports on the use of activated carbon from rice husk to remove reactive dye [21], methylene blue dye [3] and Janus Green B dye [22].

In view of the above and in continuation with a previous research [23], activated carbon derived from rice husk was used as the adsorbent since it is considered to be an agricultural carbonaceous waste. The primary objective of this study was to investigate the use of the activated carbon from rice husk in removing synthetic dye from wastewater. Within, these objectives, our aims were to; (1) determine the optimum pH, adsorbent dosage, agitation speed for batch adsorption, (2) analyse batch equilibrium isotherms, (3) study the thermodynamics and kinetics of the batch adsorption behaviour, (4) determine the optimum bed height for column adsorption and the results were analysed using Thomas model and (5) calculate the binding energy of RR195 onto pyrene using

B3LYP/6-31G(d) method. The novelty of this study is that actual dye wastewater was prepared and treated while most reports focused on the treatment of dye solution.

2 Materials and methods

This section describes the experimental and computational methods adopted in this research work and the characterisation of the original and treated samples like the pH, level of nitrates, nitrites, phosphates, sulfates, total suspended solids (TSS), biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

2.1 Synthetic dyed wastewater

Synthetic dyed wastewater was prepared by mimicking the hot exhaust dyeing process as illustrated in Fig. 1 at laboratory scale using pre-treated cotton fabric and Sumifix Supra Brilliant Red 3BF known as RR195 [24], an azo dye, as shown in Fig. 2, dyed at 2% shade on mass of fabric and a fabric/liquor ratio of 1:50. According to the fabric/liquor ratio, 20 g/L alkali (sodium carbonate, Na_2CO_3) and 30 g/L salt (sodium sulfate, Na_2SO_4) were added. After the dyeing process, the dyed fabric was removed from the dye bath and was rinsed thoroughly using water and boiled for 15 min followed by cold water. The exhausted dye bath, soaping dye bath and the rinsing water were collected and mixed thoroughly to form the synthetic dyed wastewater.

The optimum wavelength of RR195 dye was determined as a pre-requirement to obtain the calibration curve. Initial dye concentration was measured at the beginning of each experiment using the calibration curve and it was found to be mostly at 45 mg/L.

Fig. 1 Profile of dyeing process

Fig. 2 Structure of RR195 dye [20]

During the dyeing process, according to the fabric/liquor ratio of 1:50, 20 g/L alkali, (sodium carbonate, Na_2CO_3) and 30 g/L salt (sodium sulfate, Na_2SO_4) were added. Na_2SO_4 and Na_2CO_3 were added in order to achieve exhaustion and fixation of dye, respectively. However, Na_2CO_3 is responsible for the increase of the dyebath's pH which resulted in an alkaline wastewater. Sulfate was higher due to the usage of Na_2SO_4 . The effect of sodium carbonate and sodium sulfate on adsorption was not determined.

2.2 Preparation of activated carbon from rice husk

Dried rice husks were used to prepare different types of activated carbon which were tested by performing batch experiments to determine the suitable activation agent, activation time and temperature and particle size. Different activation agents have different effects on the activated carbon due to their intrinsic behaviours during chemical activation which eventually play a significant role in the carbon yield and adsorption performance. 3 kg of rice husk was collected and they were oven dried at 60 °C, for 24 h to remove moisture. After 24 h, the dried rice husks were then reduced to particle size ranging from 28 mesh to 115 mesh. This was performed to increase the surface area offered by the adsorbent for adsorption. They were retained in a sealed air-tight container for subsequent use. They were then subjected to the activation process whereby about 2240 g of activated carbon was obtained from 3 kg of rice husk amounting to about 74% yield. Each test was done in triplicates. For this study, concentrated sulfuric acid, phosphoric acid of 85–88% and orthophosphoric acid of 85% were used. For the trials, the conditions set were original pH of wastewater, adsorbent dosage of 5.0 g/L, agitation speed of 150 rpm and agitation time of 100 min. The trials were performed on granular ACRH of 28 mesh and powdered ACRH of 115 mesh. For sulfuric acid with impregnation ratio of 1:1 (w/v)%, the highest percentage dye removal was found to be 32.1% and 36.8% for

Granular AC (GAC) and Powdered AC (PAC), respectively, at 350 °C for 30 min. The yield was found to be 70.4%. While for phosphoric acid using impregnation ratio of 1:2 (w/v)%, the highest efficiency was found to be at 30 min for both GAC and PAC which gave the highest % dye removal of 36.6% with GAC and 44.0% with PAC. The highest yield was 51% at an activation time of 45 min. For the orthophosphoric acid using impregnation ratio of 2:1 (w/v)%, it was observed that AC prepared at activation temperature of 350 °C showed the highest % dye removal of 45.0% with GAC and 49.0% for PAC. Moreover, the yield was 74.8% which is the highest compared to the others. Thus AC prepared from orthophosphoric acid with impregnation ratio of 2:1 (w/v)%, activation temperature of 350 °C and activation time of 30 min were the most suitable ACRH. It was also the most cost-effective ACRH due to its impregnation ratio, high yield of 74.75% and low activation time.

2.3 Optimum pH

Optimum pH was determined by batch experiments using adsorbent dosage of 5.0 g/L and agitation speed of 150 rpm at room temperature. 1 M HCl and 1 M NaOH were prepared in bulk and were added to adjust the pH dropwise followed by the addition of the adsorbent and this was allowed to run on an orbital shaker for 120 min. The samples were filtered through 90 mm Whatman filter paper and the absorbance was recorded at 540 nm.

2.4 Batch adsorption

Batch adsorption experiments were carried out at optimum pH of 2 in 250 mL conical flask. For each batch process, 200 mL of dyed wastewater was poured into a 500 mL conical flask. The pH of the wastewater was adjusted using 1 M HCl and 1 M NaOH. The conical flask was placed on an orbital shaker. The adsorbent was added to it and the shaker was allowed to run for 120 min. As from this point, samples were taken for 10 and 30 min agitation time since

the optimum time of all the trials were found to be 20 min. The samples were filtered through the 90 mm Whatman filter paper. 10 mL of the filtrate was poured in different spectrophotometer vials. The absorbance of each sample was recorded at 540 nm to determine the optimum adsorbent dosage using constant agitation rate of 150 rpm and optimum agitation speed using the optimum adsorbent dosage as shown in Fig. 3.

The dye concentration on adsorbent was calculated using Eq. (1).

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

where C_o is the initial dye concentration (mg/L), C_t is the residual dye concentration in solution/wastewater at time t (mg/L), V is volume (L) and m is the mass of the adsorbent (g).

The experimental data were analysed using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms. Thermodynamics studies at room temperature and kinetic studies were employed for batch experimental data obtained for different adsorbent dosages and agitation speeds.

2.5 Column adsorption

The column adsorption experiments were conducted in a glass column with a diameter of 5 cm and length of 50 cm. The column was filled with a small layer of cotton and a small layer of granular ACRH at the bottom to prevent drainage of powdered ACRH. Then, the column was mounted up with equal layer of powdered ACRH followed by granular ACRH. The system was set up like a filtration process as shown in Fig. 4.

Fig. 4 Column adsorption set up

The column experiments were performed at optimum pH 2, room temperature, contact time of 10 min and at height of 3, 5 and 7 cm. In order to maintain the contact time of 10 min, the volumetric flow rate for each bed height was calculated by dividing the volume by time. The sample was collected at every 10 min interval for 160 min and the Thomas model was employed to analyse the results. Thomas model was used to investigate the column performance and breakthrough behaviour of RR195 onto ACRH for the column experiments.

2.6 Characteristics of original and treated samples

The treated samples were collected from both experiments at highest dye removal. pH, level of nitrates, nitrites,

Fig. 3 Batch adsorption

phosphates, sulfates, total suspended solids (TSS), biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were determined using standard methods.

2.7 Computational method

Activated carbon from rice husk was modeled as pyrene based on the report by Saleh et al. [25]. Theoretical calculations based on the density functional theory (DFT) method were carried out to determine the binding energy of the dye RR195 onto pyrene. Computations were carried out using Gaussian 09 [26] program package running on SEA-Grid [27–30]. The B3LYP functional in conjunction with the 6-31G(d) basis set for all atoms were employed based on the previous study [25]. Full geometry optimisations on RR195 and pyrene were carried out and verified by frequency computations. RR195 was positioned at five different locations on pyrene and the complex was optimised separately. The binding energy which is the energy needed to disassemble atoms into separate parts was calculated using Eq. (2).

$$\text{Binding energy} = E_1 + E_2 - E_3 \quad (2)$$

where, E_1 , E_2 and E_3 represent the electronic energy of the dye RR195, pyrene and the complex, respectively.

3 Results and discussion

The results of the experimental analysis and calculations are presented in this section.

3.1 Characteristics of activated carbon from rice husk

The pH of the ACRH was 7 as it was carefully adjusted while washing. The moisture contents of the powdered ACRH and granular ACRH were 4.696% and 4.963%, respectively and the bulk density of powdered ACRH was 459.2 kg/m³ while granular ACRH was 181.5 kg/m³. The activated carbon obtained was black in colour as shown in Fig. 5.

3.2 Optimum pH

Figure 6 illustrates the percentage dye removal at different pH with an agitation time of 10 min which is the maximum dye removal after the experiment was conducted for 2 h. It was observed that 64.3% of RR195 was removed at pH 2.0 and as pH increased to pH 12, the efficiency decreased to 48.1%. Previous studies reported that an acidic medium is required for some direct, reactive and acidic dyes such as acid blue 113 and direct blue 80 [31] for different

Fig. 5 (a) Granulated activated carbon (GAC) (b) Powdered activated carbon (PAC)

adsorbents while an alkaline medium is essential for basic dye like methylene blue [32].

The initial pH has a significant role on adsorption capacity as it controls the surface charge of the adsorbent and the degree of ionisation of materials found in the adsorbate [33]. In this study, the ACRH had an initial pH of 7 and increasing the pH promotes alkaline medium of the ACRH which resulted in a net negative charge. Therefore, an increase in pH led to the deprotonation of the surface groups resulting in electrostatic repulsion [32, 33]. At pH 2, there was protonation which eventually led to a net positive charge surface on the activated carbon resulting in electrostatic attraction between ACRH and RR195.

3.3 Optimum adsorbent dosage

From Fig. 7, it can be observed that the percentage dye removal increased from 49.5% to 76.6% with increasing adsorbent dosages, at 13.0 g/L there was a steady point however beyond this point, the curve gave a decreasing trend. The increase in efficiency might be due to greater surface area and greater number of active sites [21]. Aggregation of particles reduced the availability of binding sites for adsorption of dyes which might be the reason for the drop in efficiency [34].

Further, a graph of percentage dye removal versus adsorbent dosage was plotted (Fig. 7) at pH = 2. The R^2 values were greater than 0.95 which indicate good correlation and it can be deduced that 13.0 g/L was the optimum adsorbent dosage.

3.4 Optimum agitation speed

Agitation speed should be enough to ensure that all the binding sites on the surface are easily accessible for dye adsorption [35]. From Fig. 8, it can be observed that the efficiencies increase with increasing agitation speeds from 50 to 100 rpm but decrease from 150 rpm to 300 rpm. This decrease in dye removal can be due to

Fig. 6 Percentage dye removal at different pH **Fig. 7** Percentage dye removal for different adsorbent dosages at pH=2

an increase in the desorption tendency of dye molecules. However, at 10 min, there is a maximum dye removal above 70%. This is because at 50 rpm the ACRH was not spread and was gathered which obscured the active sites of the lower adsorbent's layer and therefore, allowing

only the active sites on the upper layer to adsorb the dye [35].

Increasing the agitation rate from 50 to 100 rpm can diminish the film boundary layer around the adsorbent particles and boosted the mass transfer coefficient of the external film [36] and hence, more dye was adsorbed. Another possibility is that the surface area of adsorbent is available to the whole volume of dye solution while shaking [37].

The efficiencies from 150 to 300 rpm are constant and the effect of agitation has plateaued at 150 rpm for the 10 min samples. The minimum effect pointed out that the external mass is not the only rate-limiting factor [32]. This decrease in dye removal can be due to an increase in the desorption tendency of dye molecules [35]. Hence, it can be deduced that further increase in the agitation speed would not have significant effect. Therefore, the optimum agitation speed was found to be 100 rpm.

3.5 Equilibrium adsorption isotherms

3.5.1 Langmuir isotherm

Langmuir models are valid for monolayer adsorption onto a surface containing a set of distinct localised adsorption active sites with similar adsorption energy, free of the surface coverage and having no interaction between

Fig. 8 Percentage dye removal at different agitation speeds

adsorbed molecules [38]. The monolayer adsorption capacity of the adsorbent and the R_L values were found using Eqs. (3) and (4), respectively.

$$\frac{C_t}{q_t} = \frac{1}{(K_L q_{max})} + \frac{C_t}{q_{max}} \quad (3)$$

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (4)$$

where C_t is the residual dye concentration in solution/wastewater at time t (mg/L), q_t is the dye concentration on adsorbent at time t (mg/g), K_L is the Langmuir constant related to the rate of adsorption (L/mg), q_{max} is the monolayer adsorption capacity of the adsorbent (mg/g) and C_o is the initial dye concentration (mg/L).

When $0 < R_L < 1$, it implies favourable adsorption, $R_L = 0$ indicates irreversible adsorption, $R_L = 1$ refers to linear adsorption and $R_L > 1$ means unfavourable adsorption [22, 39].

Langmuir isotherms are depicted in Figures SI1(a) and SI1(b) for adsorbent dosages and agitation speeds, respectively and the results are summarised in Table SI1. The maximum adsorption capacity of some adsorbents are shown in Table 2. In this study, the maximum adsorption capacity of the adsorbent was found to be 2.037 mg/g at optimum conditions and this shows that the surface of the activated carbon reached its saturation point. Further, both Langmuir isotherms indicate high R^2 values however based on R_L values, the isotherms are not appropriate

since the R_L values are negative due to negative K_L values. Therefore, some modifications are necessary to allocate more freedom in the adsorption and desorption phases [44].

3.5.2 Freundlich isotherm

Freundlich isotherm is an empirical equation which presumes physicochemical adsorption on heterogeneous surfaces [43] implying that binding sites are not comparable and/or independent [19]. The formula used to find the Freundlich constants is given in Eq. (5) [45].

$$\ln q_t = \ln K_f + \frac{1}{n} \ln C_t \quad (5)$$

where q_t is the dye concentration on adsorbent at time t (mg/g), K_f is the Freundlich constant related to the adsorption capacity of the adsorbent, n is the Freundlich constant which gives an indication of how favourable is the adsorption process and C_t is the residual dye concentration in solution/wastewater at time t (mg/L).

A value of $1/n$ closer to 0 implies more heterogeneous adsorption [22], $1/n < 1$ means adsorption capacity is only slightly suppressed at lower equilibrium concentrations [45], $1/n < 1$, $n < 10$ [46] and $n > 1$ implies favourable adsorption [47].

Figures SI2(a) and SI2(b) illustrate the Freundlich isotherm for different adsorbent dosages and different agitation speeds, respectively. The isotherms have high R^2 values. The values of n calculated in Table SI2 were found

Table 2 Maximum adsorption capacity of some adsorbents

Absorbent	Dye	q_{max} , mg/g	References
Activated carbon prepared from rice husk	Methylene blue	333.33	[3]
Activated rice husk	Acid yellow 17	12.98	[40]
NiFe ₂ O ₄ nanoparticles	Anionic dyes of sunset yellow, tartrazine, and Eriochrome black T	72.21, 75.88, 82.04	[2]
Activated carbon produced from fruit juice industry solid waste	Yellow 18	75.76	[41]
Sawdust	Methylene blue	30.11	[42]
Commercial activated carbon		39.09	
Acid activated mustard stalk	Reactive blue 4	25.80	[16]
Physico-chemically treated rice husk	Reactive black 5	8.34	[21]
Iraqi date palm seeds activated carbon	Disperse blue	8.13	[43]
Oxidized multi-walled carbon nanotubes	Janus Green dye	56.00	[33]
Rice husk	Sulfur dye	55.56	[37]
Activated rice husk	Janus Green B	5.88	[22]
Dehydrated beet pulp carbon	Chemazol reactive red 195	58.00	[19]
Rice husk	Direct red-31	129.87	[34]
	Direct orange-26	66.67	
Activated carbon from durian peel	Basic green 4	303.00, 312.50	[31]

to be negative, signifying unfavourable adsorption as reported by Igwe and Abia [48]. High K_F value implies greater adsorption intensity [48] but increasing adsorbent dosage gave a low K_F value and variation in agitation gave nearly constant K_F values. Further, Huang, et al. [49] reported that if neither Langmuir nor Freundlich isotherm fit the data, it implies that there are ion exchange mechanisms.

3.5.3 Dubinin-Radushkevich (D-R) isotherm

D-R isotherm is used to find the characteristic porosity as well as the apparent free energy of adsorption [50] and this is mathematically represented by Eqs. (6) and (7). D-R Model can be applied to distinguish the nature of adsorption by estimating the magnitude of the mean free energy of sorption, E_s [41]. The mean free energy of sorption is calculated by Eq. (8) [50].

$$\ln q_t = \ln q_s - K\varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_t} \right) \quad (7)$$

$$E_s = (-2K)^{-\frac{1}{2}} \quad (8)$$

where q_t is the dye concentration on adsorbent at time t (mg/g), q_s is the theoretical saturation capacity (mol/g), K is the constant related to adsorption energy of porosity factor (mol^2/kJ^2), ε is the Polanyi adsorption potential (kJ/mol), R is the universal gas constant (J/mol/K), T is the temperature C_t is the residual dye concentration in solution/wastewater at time t (mg/L) and E_s is the mean free energy of sorption (kJ/mol).

When $E_s < 8$ kJ/mol, it implies physical adsorption and $8 < E_s < 16$ kJ/mol implies chemical ion exchange adsorption [50]. In ion exchange, cations and anions from the fluid (wastewater) replace dissimilar ions of the same charge initially in the solid. The ion exchanger contains permanently bound functional groups of opposite charge-type.

D-R isotherms are depicted in Figures SI3(a) and SI3(b) and the calculated mean free energy is shown in Table SI3. It can be deduced that adsorbent dosages below 10 g/L followed physical adsorption while adsorbent dosages of 11 g/L to 15 g/L as well as adsorption at different agitation speeds followed chemical ion exchange adsorption.

3.5.4 Temkin isotherm

Temkin isotherm determines the adsorption potential of adsorbent for adsorbates and forecasts a consistent distribution of binding energies over the surface binding

adsorption sites depending on the density and allocation of functional groups both on the adsorbent and dye surfaces [50].

The linearised expression used for Temkin isotherm is given in Eq. (9).

$$q_t = \left(\frac{RT}{b_T} \right) \ln C_t + \left(\frac{RT}{b_T} \right) \ln K_T \quad (9)$$

where q_t is the dye concentration on adsorbent at time t (mg/g), R is the universal gas constant (J/mol/K), T is the temperature which was 298.15 K, b_T is the adsorption potential of the adsorbent and K_T is the binding energy (L/g).

Temkin isotherms are graphically represented in Figures SI4(a) and SI4(b) and a summary of the results is tabulated in Table SI4. The results show high R^2 values implying good linearity for all the adsorbent dosages. A slight decrease is observed in K_T values with increasing adsorbent dosages but the b_T values have an extensive range with highest value at 100 rpm.

3.6 Thermodynamics studies

Thermodynamics of adsorption provides an insight into the mechanism and its adsorption behaviour [41]. The temperature was assumed to be 298.15 K since all experiments were performed at room temperature. The equations for Gibbs free energy [50], enthalpy [51] and entropy [52] are given in Eqs. (10), (11) and (12), respectively.

$$K_T = \exp \left(\frac{-\Delta G^\circ}{RT} \right) \quad (10)$$

$$\Delta Q = -\Delta H \quad (11)$$

$$\Delta G^\circ = \Delta H - T\Delta S \quad (12)$$

where K_T is the binding energy (L/g), ΔG° is the relative Gibbs free energy (kJ/mol), R is the universal gas constant (J/mol/K), T is the temperature which was 298.15 K, ΔQ is the variation of adsorption energy (J/mol) and $\Delta Q = b_T$, ΔH is the relative enthalpy (J/mol) and ΔS is the relative entropy (J/mol/K).

In chemisorptions, adsorption is achieved by endothermic or exothermic processes [39] and the positive enthalpy values imply that the adsorptions are endothermic. The Gibbs free energy is positive which implies that the adsorption is non-spontaneous and negative entropy suggests less disorder. It can also be observed that experiment performed at pH 2, adsorbent dosage 13 g/L and agitation speed 100 rpm had the highest values for the thermodynamic studies. Ghaedi et al. [53] reported that

the adsorption of methyl green onto chemically modified RH was an endothermic process.

3.7 Kinetics studies

Pseudo-first-order and pseudo-second-order were employed in this study whose linearised formulae are given in Eqs. (13) and (14), respectively [52].

$$\log(q - q_t) = \log q_e - \left(\frac{K_1}{2.303} \right) t \quad (13)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

where q is the equilibrium adsorption capacity (mg/g), q_t is the dye concentration on adsorbent at time t (mg/g), q_e is the theoretical equilibrium adsorption capacity (mg/g), K_1 is the rate constant of pseudo-first-order adsorption (1/min), t is the time (min) and K_2 is the rate constant of pseudo-second-order adsorption (g/mg.min).

A graphical representation of varying adsorbent dosages and agitation speeds for pseudo-first-order model are shown in Figures SI5(a) and SI5(b), respectively, and that of pseudo-second-order are depicted in Figures SI6(a) and SI6(b). As observed in Table SI6, the values of q_e for pseudo-second-order decreases with an increase in the adsorbent dosage. The q_e values of pseudo-second-order for adsorbent dosages range from 10 g/L to 15 g/L for all the agitation speeds between 2 mg/g to 3 mg/g and those of pseudo-first-order were fluctuating. It can also be observed that all the R^2 values for pseudo-second-order approach 1. Therefore, it can be deduced that the adsorption follows the pseudo-second-order kinetic model. Pseudo-second-order forecasts the behaviour over the entire series of studies [52] and assumes that chemisorption is the rate controlling step which involves valent forces through allocation or swapping of electrons between adsorbent and adsorbate [54] that is between ACRH and the dye RR195.

3.8 Column experiments

3.8.1 Contact time

The percentage dye removal of an adsorbent may increase or decrease with time and hence the variation may be either positive or negative [6]. In this study, contact time was considered to be 10 min by analysing the batch adsorption experiments and same was applied to column adsorption experiments. The initial fast colour removal was due to the existence of large quantity of vacant sites [21] which were positively charged and therefore, attracted

the anionic dye RR195 resulting in maximum dye removal. With time, the number of active sites dwindled, resulting in reduction of adsorption efficiency [21]. Increase in contact time might cause aggregation of dye molecules making them nearly impossible to diffuse deeper into the structure of the absorbent at its maximum energy sites due to resistance to diffusion [16]. From the batch experiments, it can be noted that at 120 min, equilibrium was almost attained.

3.8.2 Bed height

The trend of percentage dye removal at different bed heights is depicted in Figure SI7(a). Bed heights of 3 cm and 7 cm have an efficiency of 99.14% and 99.96%, respectively. Hence, it is obvious that the removal efficiencies do not change significantly with increase in the bed height at 10 min.

From Figure SI7(b), it can be deduced that the break-through and exhaustion time increase with an increase in bed height which consequently extended the mass transfer zone [42]. Higher bed height possesses more fixation binding sites allowing adsorption of dyes [55]. It also offers a larger service area which increases the volume of wastewater to be treated [42, 52]. Since the rate of adsorption is proportional to the adsorbent's surface area, there is an increase in the solute concentration of the effluent with a decrease in bed height. From Figures SI7(a) and SI7(b), it is concluded that bed height of 5 cm is the optimum bed height and is most economical in terms of cost and efficiency.

3.8.3 Thomas model

The linearised formula of Thomas model is given as Eq. (15) and the column data are depicted in Figure SI8.

$$\ln \left[\left(\frac{C_o}{C_t} \right) - 1 \right] = \left(\frac{K_{Th} q_o W}{Q} \right) - (K_{Th} C_o t) \quad (15)$$

where C_o is the initial dye concentration (mg/L), C_t is the residual dye concentration in solution/wastewater at time t (mg/L), K_{Th} is the Thomas rate constant (L/min.mg), q_o is the maximum column adsorption capacity (mg/g), W is the mass of adsorbent in column (g) and t is the time (min).

From Table SI7, it can be deduced that as the bed depth increases, the value of K_{Th} decreases significantly from 3 cm to 5 cm, however, at 5 cm and 7 cm, it decreases slightly. The value of q_o is also increased considerably from 3 cm to 5 cm. The highest q_o is that of 7 cm corresponding to 12.8 mg/g. The R^2 values of 5 cm and 7 cm bed height can be explained by the fact that from the start of the experiment till 160 min, the column was still

performing efficiently with almost 100% dye removal and hence, there was a long way to go before breakthrough. Therefore, the Thomas model is best fit with 3 cm with a R^2 value of 0.9210.

3.9 Characteristics of original and treated samples

The characteristics of the prepared synthetic dyed wastewater and the treated samples were tested for various parameters and the values are collected in Table SI8. It was found that the principal inorganic pollutants were nitrates, nitrites, phosphates and sulfates, resulting from impurities found in the chemicals used. However, sulfate imparts hardness of water and may be converted to sulfur or hydrogen sulfide depending upon the redox potential of water [37]. TSS was high due to the unfixed dyes, starchy enzymes, colloidal particles or precipitated chemicals. The presence of oxidisable compounds resulted in greater COD values than BOD values [56] as well as due to colloidal matter, since chemicals used or starch found in the cotton fabric could have leached in the dye bath. The ratio of BOD:COD was found to be in the range of 0.2 to 0.35, hence it can be deduced that the wastewater contains a major part of non-biodegradable matter [37].

From Table SI8, it can be deduced that the adsorption of the dye RR195 using ACRH had effectively treated the original wastewater. However, for batch experiments, there are some parameters such as pH and sulfate which should be treated further in order to comply with the norms set.

3.10 Computational chemistry

The structures of the dye RR195 and pyrene are shown in Figs. 9a, b, respectively while all the optimised geometries are illustrated in Figs. 10a–e. The optimised structures at each position are denoted as complex P1, P2, P3, P4 and P5. The calculated binding energies of each complex are summarised in Table 3.

The variation in binding energies indicates that the adsorption was more sensitive towards the nature of the functional group. Activation energy of 5–40 kJ/mol is considered to be physisorption [57]. Complex P3 undergoes chemisorption process as it was reported that chemical adsorption has activation energy between 40 and 800 kJ/mol [57]. This deduction is in accordance with the swapping of electrons which can be observed in Fig. 7c [54]. Furthermore, the binding energy of complex P3 indicates that it undergoes an endothermic chemisorption process [58]. The theoretical findings for complex P3 is in agreement with the experimental analysis whereby at optimum conditions, the adsorption favoured endothermic chemical ion exchange process.

4 Conclusion

1. The optimum conditions for batch adsorption were found to be at pH 2 with an adsorbent dosage of 13 g/L and agitation speed of 100 rpm with highest percentage dye removal of 80% at agitation time of 10 min and at 120 min and the percentage dye removal was nearly plateaued for most of the experiments. The optimal conditions were validated using the verification experiment whereby it was found that they have a relative standard deviation less than 5%. This suggests that the experiments performed were precise and hence can be considered as optimal.
2. Based on the R^2 values ranging from 0.9987 to 0.9994, it was observed that Temkin isotherm has the best fit.
3. At optimum conditions, Dubinin-Radushkevich isotherms indicate that the adsorption followed a chemisorption process with E_s value of 13.36 kJ/mol.
4. The adsorption process was a non-spontaneous, endothermic process with less disorder which followed the pseudo-second-order kinetic model.

Fig. 9 (a) Reactive red 195 dye.
(b) Pyrene

Fig. 10 (a) Complex P1. (b) Complex P2. (c) Complex P3. (d) Complex P4. (e) Complex

Table 3 Binding energy using the B3LYP/6-31G(d) method

	P1	P2	P3	P4	P5
Binding energy (kJ/mol)	3.76	26.55	63.09	−74.47	24.34

- Column adsorption process proved to be an efficient process which treated large amount of synthetic dyed wastewater using limited quantity of activated carbon from rice husk and successfully brought down all values of impurities to permissible limits.
- Computations performed at the B3LYP/6-31G(d) method inferred that the complex P3 had the highest binding energy implying an endothermic chemisorption process.
- For future applications, activated carbon from rice husk possesses good adsorptive characteristics and has good yield of 74.75%. Therefore, large amount of activated carbon can be produced for treating wastewater which will eventually reduce environmental pollution and promotes sustainable development.
- Finally, it can be concluded that the column adsorption process proved to be an effective and efficient process which treated large amount of synthetic dyed wastewater containing reactive red 195 dye up to 99.5% dye removal using a limited quantity of activated carbon from rice husk. In addition to this, from the results of the comparison between batch and column treat-

ment, both process removed impurities from water, however, column adsorption successfully brought down all values of impurities to permissible limits set in the standard for industrial wastewater discharge in Mauritius.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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