Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.812526

52 (2014) 6175–6184
September

Adsorptive removal of basic cationic dyes from aqueous solution by chemically protonated watermelon (*Citrullus lanatus*) rind biomass

R. Lakshmipathy, N.C. Sarada*

Environmental and Analytical Chemistry Division, School of Advanced Sciences, VIT University, Vellore, Tamil Nadu 632014, India
Tel. +91 9443630839; Fax: +91 416 2243097; email: ncsarada@yahoo.com

Received 19 April 2013; Accepted 28 May 2013

ABSTRACT

This study presents a study on the potentiality of protonated watermelon rind (PWR), an agro waste, to remove methylene blue (MB), crystal violet (CV), and rhodamine B (RB) dyes from aqueous solution. Protonation of watermelon rind was carried out using hydrochloric acid, and process was evidenced by EDX patterns. The batch experiments were performed systematically by varying contact time, pH, adsorbent dose, initial concentration, and temperature. Effects of salt ionic strength were also studied. Sorption of dyes onto watermelon rind is found to be rapid, and equilibrium has been reached in less than 30 min. The equilibrium data tend to fit better with Langmuir isotherm than Freundlich isotherm. The maximum loading capacity of PWR is found to be 489.8, 104.76, and 86.6 $\mathrm{mg\,g^{-1}}$, respectively, for MB, CV, and RB. Kinetic studies indicate the adsorption process that follows pseudo-second-order model. Thermodynamic parameters including change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) are derived. Desorption of dyes studies was performed with HCl, acetic acid, H_2O, and NaOH. The results suggest that the watermelon rind can be an eco-friendly, low-cost and value-added biosorbent for the removal of MB, CV, and RB from aqueous solution.

Keywords: Watermelon rind; Agro waste; Protonation; Biosorption; Dyes

1. Introduction

Synthetic dyes are widely used in textile, leather, paper, food, pigments, plastics, and cosmetic industries to color the final products. Thus, it ends up in the discharge of large amount of colored dye effluents into water-receiving bodies [1,2]. Discharge of colored dye effluents into natural resources has caused many problems like carcinogenicity, skin allergy, and irritation. Methylene blue (MB) is a toxic dye and causes several health risks in humans upon exposure such as nausea, vomiting, eye injury, and methemoglobinemia [3]. Similarly, crystal violet (CV) is highly cytotoxic and carcinogenic to mammalian cells. It can cause permanent injury to the cornea and conjunctiva [4]. Rhodamine B (RB) causes carcinogenicity, reproductive and developmental toxicity, neurotoxicity, and chronic toxicity toward humans and animals. Thus, it is desirable to remove dyes from industrial effluents [5].

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*Corresponding author.

During the past few years, colored dye effluents are normally treated by physical and chemical treatment process, which are less adaptable, and expensive [6]. It is now well established that for the wastewater treatment, adsorption has several advantages over other methods. Moreover, the ability of adsorption to remove toxic chemicals without producing any toxic byproducts, thereby keeping quality of water undisturbed, has also popularized the adsorption technique in comparison with other techniques [7]. Activated carbon is found to be the most effective adsorbent for the removal of dyes from industrial effluents. But the cost of activation and difficulty in regeneration of spent activated carbon has encouraged researchers to look for alternative adsorbents for the removal of dyes from industrial effluents [8–17]. Biosorption is the "cost-effective technique" for dye removal. Many low-cost agricultural wastes such as peanut husk [18], rice husk [19], and rejected tea [20], fruit peels such as banana peel, orange peel [21], grapefruit peel [22], jackfruit peel [23], custard apple shell [24], and pomegranate peel [25] are used as sorbents for the removal of dyes. The stability and removal efficiency of raw biomass can be further improved by chemical modification and activation. In view of this, several agricultural wastes has been chemically modified and proven to be better sorbents for the removal of dyes. In continuation to these efforts, watermelon rind was chemically protonated and evaluated for the removal of cationic dyes.

Watermelon (*Citrullus lanatus*), being the largest and heaviest fruit, is one of the most abundant and cheap fruits available in India. Watermelon production occupies 6–7% of overall fruit production and is high during summer because of its tropical nature. In the watermelon, red flesh present inside is sweet, edible used for juices and salads, but the outer rind is considered as waste that has no commercial value [26]. Watermelon rind is a by-product from watermelon, which consists of many constituents like proteins, pectin, cetrulline, and caroteniods [27–29]. Due to the presence of hydroxyl and carboxyl groups, watermelon rind is known to bind heavy metals from aqueous solution [30,31]. This study is undertaken to evaluate the application potential of protonated watermelon rind (PWR) biomass as an inexpensive and eco-friendly adsorbent for the removal of CV, MB, and RB from water. The study is further unique as there are no existing reports for the removal of any dyes by watermelon rind. Effect of parameters like pH, adsorbent dose, contact time, initial dye concentrations, and temperature were investigated for the sorption of dyes. Finally, isotherms, thermodynamic, and kinetics as well as the diffusion parameters were evaluated for experimental data.

2. Materials and methods

2.1. Preparation and characterization of adsorbent

Watermelon rind biomasses (WR) were obtained from local fruit market and washed with tap water followed by double-distilled water. After thorough washing, WR was cut into small pieces and dried under sunlight for 72 h to remove moisture content present. The dried WR pieces were washed repeatedly with hot water (70℃) to remove any soluble matter present and dried in oven at 85℃ for 48 h. The oven-dried WR was powdered and sieved through 100 mesh sieve. It is well known that adsorbents from natural resources consists of many alkali and alkaline earth metals such as K^+, Na^{2+}, Mg^{2+}, and Ca^{2+}. These cations are bound to the active sites of adsorbents that results in expose of less number of active sites at the surface of the sorbent for the sorption of dyes from aqueous solution. In order to increase the sorption capacity of dyes onto watermelon rind and to eliminate the competition between dyes and naturally present alkali and alkaline earth metals for surface active sites; WR was chemically protonated using hydrochloric acid. Protonation was carried out by soaking 10 g of WR powder in 250 mL of 0.1 M HCl for 4 h. Later, it was rinsed with double-distilled water repeatedly to remove the desorbed alkali and alkaline metals (e.g. K^+, Mg^{2+}). Thus, the watermelon rind is chemically modified where all weakly acidic sites are occupied by protons [32]. The oven-dried WR after protonation is named as PWR and sieved through 0.150–0.080 mm (100 BSS mesh) sieve and stored in airtight polyethylene bottles for sorption experiments.

The surface functional groups of PWR are determined by FTIR spectrometer (AVATAR 330, Thermo Nicolet). The samples were grounded with KBr, and the prepared translucent pellets are analyzed in the range of 4,000–400 cm^{-1} at 4 cm^{-1} spectral resolution. Scanning electron microscope (SEM) is used to study the surface morphology of PWR before and after adsorption of dyes. Prior to scanning, the biosorbent was coated with a thin layer of gold using a sputter coater to make it conductive. Electron-dispersive X-ray analysis (EDX) was carried out for WR before and after protonation.

2.2. Preparation of dye solutions

MB, CV, and RB dyes are purchased from Merck Co., and the stock solutions are prepared by dissolving exactly 1.0 gL^{-1} in deionized water. The chemical structures and general data of these dyes are represented in Fig. 1 and Table 1, respectively. The initial pH of the dye solution was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

2.3. Adsorption experiments

Batch mode adsorption experiments are carried out in orbital shaker at 150 rpm using 100-mL conical flasks containing 20 mL of dye solutions. Parameters such as pH, adsorbent dose, contact time, initial dye concentrations, and temperature were studied. A blank run containing 20 mL of dye solution without adsorbent is performed to examine the dye adsorption on to the walls of the flask. After each experiment, the samples are centrifuged for 15 min at 3000 rpm, and the concentration of dyes in the supernatant solution was determined by UV–vis spectrophotometer (Hitachi U-2800). The effect of salt ionic strength on the amount of dyes adsorbed onto adsorbent was discussed over NaCl and $CaCl_2$ concentration range from 0.01 to 0.5 mol L^{-1}.

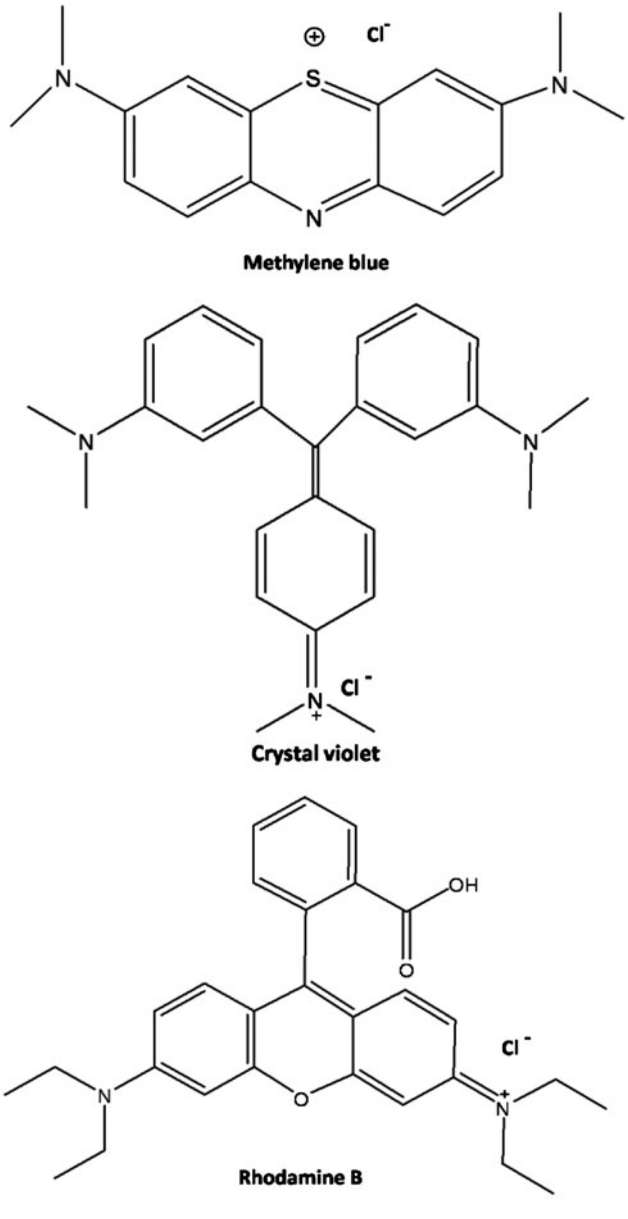

Fig. 1. The chemical structures of three dyes used in present study.

Table 1
General data of three dyes used in present study

Commercial name	CI no.	Mol Wt	λ_{max} (nm)
Methylene blue	52,015	373.88	668
Rhodamine B	45,170	479.02	554
Crystal violet	42,555	407.98	584

Note: CI no. color index number.

2.4. Adsorption isotherms

Adsorption isotherms are used to examine the relationship between dye concentration at equilibrium (C_e) and maximum loading capacity (q_e) of PWR for MB, CV, and RB. The equilibrium data obtained for all the dyes are analyzed with two well-known isotherms the Freundlich and Langmuir models.

Freundlich isotherm is an empirical equation that is based on the sorption of an adsorbate on a heterogeneous surface of an adsorbent. The nonlinear form of Freundlich isotherm is given as:

$$q_e = K_f C_e^{1/n} \tag{1}$$

where K_f and n are Freundlich constants indicate the adsorption capacity and intensity, respectively. C_e (mg/L) and q_e (mg/g) are the equilibrium concentrations, and the amount of dye adsorbed at equilibrium, respectively.

The Langmuir isotherm assumes monolayer adsorption process onto a completely homogeneous surface with a finite number of identical sites. The nonlinear form of Langmuir isotherm is given as:

$$q_e = \frac{V_m b C_e}{1 + b C_e} \tag{2}$$

where C_e is the concentration of dye solutions at equilibrium (mg^{-1}), q_e is the amount of dyes adsorbed per unit mass of adsorbent ($mg\,g^{-1}$), V_m is the amount of adsorbate at complete monolayer coverage ($mg\,g^{-1}$), and b is a constant that relates to the heat of adsorption ($L\,mg^{-1}$).

2.5. Adsorption kinetics

The kinetic experiments are conducted using a procedure similar to equilibrium studies at room temperature. The aqueous samples were drawn at different time intervals, and concentrations of dyes were measured in UV spectrophotometer. To analyze the mechanism and rate of adsorption of dyes onto PWR, experimental data obtained were fitted to Lagergren's pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

The Lagergren's rate equation is one of the most widely used rate equations for the study of the adsorption of an adsorbate from aqueous solution. The linear form of Lagergren's pseudo-first-order equation is given as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where q_e is the amount of metal adsorbed at equilibrium (mg g^{-1}), q_t is the amount of metal adsorbed at time t and k_1 is the first order reaction rate constant. The values of k_1 and q_e can be determined from the slopes and intercepts of ln ($q_e - q_t$) vs. t plots.

The pseudo-second-order kinetic model is the other most widely used model and the expression used in the present study is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 ($\text{g mg}^{-1}\,\text{min}^{-1}$) is the rate constant of pseudo-second-order adsorption. The values of k_2 and q_e can be determined from the plots of t/q_t vs. t.

In order to study the steps of diffusion mechanism, kinetic data are analyzed using Weber and Morris intraparticle diffusion model. The expression is given as follows:

$$q_t = k_{\text{int}} t^{1/2} + C \tag{5}$$

where k_{int} is the intraparticle diffusion rate constant, and C is the intercept related to the thickness of the boundary layer.

2.6. Desorption studies

In order to study the reusability potential of PWR, various dye-loaded PWR is contacted with different desorbing agents. In this study, 0.1 M HCl, 0.1 M acetic acid, distilled water, and 0.1 M NaOH are used as desorbing agents.

3. Results and discussion

Watermelon rinds are known to be rich in alkali and alkaline earth metals such as K^+, Na^+, Mg^{2+}, and Ca^{2+} and trace amount of Zn^{2+} and Fe^{2+}. It has been suggested that the total cation content of a biomass can be considered as a measure of the approximate cation-exchange capacity of an adsorbent material. The total cation content released by WR was 2.102 meq g^{-1} which comprised of 1.282, 0.503, 0.213, and 0.104 meq g^{-1} of K^+, Mg^{2+}, Na^+, and Ca^{2+} ions, respectively. The presence of these cations can greatly influence the sorption capacity due to competition for surface active sites. Hence, it is desirable to remove these cations from WR. In order to remove alkali and alkaline earth metals from WR and to protonate the active sites, 0.1 M HCl has been used as protonate agent. In our earlier study, hydrochloric acid has shown higher desorption percentage of metal ions from WR [30,31]. Hence, 0.1 M HCl is selected as protonate agent. The protonation step opens up many active sites at surface for the sorption of dyes which leads to high sorption capacity of adsorbent. The other add on advantage of protonation process is the removal of natural dyes and water-soluble residues from the WR which might affect the sorption process. Hence, further sorption studies were carried out using PWR for the removal of basic cationic dyes from aqueous solution.

3.1. Characterization of material (PWR)

The sorption of dye ions onto plant materials is attributable to the active groups and bonds present on them. In order to identify the major functional groups present in PWR, preliminary quantitative analysis was done with FTIR spectroscopy. FTIR spectra of PWR displayed a number of peaks pertaining to different functional groups. The broad and intense peak around 3,378 cm^{-1} corresponds to –OH stretching vibrations of cellulose, pectin, and lignin. The peak at 2,917 cm^{-1} attributes to –CH stretching vibrations of methyl and methoxy groups. The peak at 1,728 cm^{-1} corresponds to –C=O stretching of carboxylic acid or esters and asymmetric and symmetric vibrations of ionic carboxylic groups ($-COO^-$), respectively, appeared at 1,621, and 1,421 cm^{-1} [33]. The peak at 1,383 cm^{-1} is assigned to symmetric stretching of $-COO^-$ of pectin [34]. The peaks from 1,350 to 1,000 cm^{-1} can be assigned to stretching vibrations of carboxylic acids and alcohols. It is well indicated from FTIR spectrum of PWR that carboxylic and hydroxyl groups are abundantly presented and as biopolymers these groups act as proton donors. The comparisons of FTIR spectra of protonated and dye-loaded watermelon rinds are presented in Table 2. The shifts in peaks for dye-loaded PWR may be attributed to changes in counter ions associated with carboxylate and the

Table 2
Wave numbers (cm^{-1}) of FTIR peaks of different protonated watermelon rind samples

Functional groups	PWR	MB	RB	CV
–OH stretching vibrations of cellulose	3,378	3,305	3,307	3,304
–CH stretching vibrations of methyl groups	2,917	2,918	2,918	2,920
–C=O stretching of carboxylic acid or esters	1,728	1,737	1,739	1,737
$-COO^-$ asymmetric vibrations of ionic carboxylic groups	1,621	1,598	1,600	1,598
$-COO^-$ symmetric vibrations of ionic carboxylic groups	1,421	1,440	1,435	1,439

hydroxylate anions suggesting that acidic groups, carboxyl, and hydroxyl groups are predominant contributors in dye removal. The removal process can be attributed to negatively charged carboxylate and hydroxylate anions of PWR that can electrostatically interact with the positive charges of dyes.

Elemental analysis was carried out for native WR and for PWR by EDX to confirm the protonation. The EDX pattern of native WR shows the distinct peaks of K^+ and Mg^{2+} ions present in WR. While for PWR, these peaks are found missing which indicates that during acid wash with 0.1 M HCl, desorption of K^+ and Mg^{2+} ions takes place from native WR. The vacant sites originated on the surface of the sorbent are occupied by protons.

3.2. Preliminary adsorption studies

3.2.1. Effect of pH

The value of pH is known as one of the most important factor affecting adsorption capacity of adsorbents. The effect of pH on the adsorption of MB, CV, and RB dyes on PWR was determined by varying the pH from 2 to 11 (Fig. 2). The experimental data showed that solution pH has no effect on adsorption of MB onto PWR, while for CV, adsorption increases with increase in pH and maximum adsorption is observed at pH 8. But in the case of RB, the maximum adsorption takes place at pH 2 and minimum at pH 7. It was also observed that adsorption increases when solution pH was increased (above pH 7). The increase in adsorption appears to be that a change in pH of the solution results in the formation of different ionic species, and different carbon surface charge. At pH values lower than 4, the RB ions are of cationic and monomeric molecular form thus they can enter into the pore structure [35]. At pH value higher than 4, zwitterionic form of RB in water may increase the aggregation of RB to form a larger molecular form (dimer) and unable to enter into the pore. The greater aggregation of the zwitterionic form is due to the attractive electrostatic interactions between the carboxyl and xanthene groups of the monomer [36]. At a pH value higher than 8, preponderance of OH^- generates a competition between $-N^+$ and $-COO^-$ and decreases the aggregation of RB. This causes an increase in adsorption of RB. Similar type of observations has been previously reported for MB [8], CV [2], and RB [37].

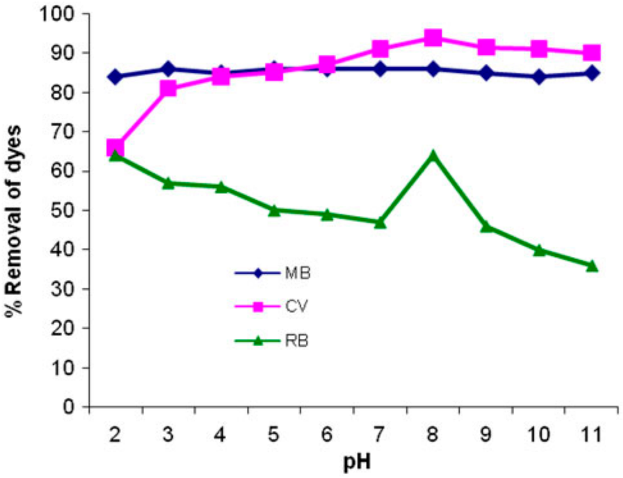

Fig. 2. Effect of pH on sorption of MB, CV and RB ions onto protonated watermelon rind from aqueous solution.

3.2.2. Effect of adsorbent dose

The effect of dosage of PWR on the removal of MB, CV, and RB was studied in various dosages from 0.5 to 5 g/L. The percentage of adsorbed MB, CV, and RB increases with increase in dose, but loading capacity (q_e) was found to decrease. The point of saturation for PWR was found, respectively, at 0.5, 2.5, and 1.5 g/L for the removal of MB, CV, and RB from aqueous solution. At saturation point, removal efficiency was found to be 83, 92, and 57% for MB, CV, and RB, respectively. There was no significant removal of dyes observed above the saturation point due to the establishment of equilibrium between the dye molecules on the adsorbent and in the solution.

3.2.3. Effect of salt ionic strength

It is important to discuss the effect of salt ionic strength on the adsorption of cationic dyes onto PWR. Industrial dyeing effluents usually contain high salt concentration. In order to study the adsorption capability of PWR toward cationic dyes in the presence of ionic salts, salts such as NaCl, $CaCl_2$, and KCl with different ionic strength were used to stimulate the salt ionic in water. The results are summarized in Table 3. From Table 3, it is evidenced that the presence of ionic salts in the solution has greatly influenced the sorption capacity of PWR. Substantial decrease in sorption capacity was noticed with increase in salt ionic strength. Since KCl, NaCl, and $CaCl_2$ can release K^+, Na^+, and Ca^{2+} ions in solution, these ions may compete with cationic dyes for the adsorbent active sites which results in decrease in sorption capacity of dyes. The sorption capacity of PWR decreased to a greater extent in the presence of $CaCl_2$ than NaCl or KCl. This can be attributed to the smaller ionic radius and higher electronegativity of Ca^{2+} ions compared with Na^+ and K^+ ions. Cations with smaller ionic radius are known to be superior for sorption from aqueous solution.

3.3. Kinetics of adsorption

Kinetic experiments were identical for equilibrium studies of MB, CV, and RB. The aqueous samples were taken at preset time intervals and concentrations of dyes were similarly measured. It was observed that removal rate of MB, CV, and RB was extremely rapid in first 10 min and reached equilibrium within 30 min. The rapid removal in first 10 min is due to immediate availability of more number of active sites at surface for adsorption. To examine the rate controlling mechanism of present process, such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order kinetic models was used to test the experimental data of dye adsorption onto PWR.

Table 3
Effect of salt ionic strength on sorption of MB, CV and RB onto protonated watermelon rind (Time-30 min, initial concentration of dyes 50 mg L^{-1}, temperature 30℃)

Salt strength (mol L^{-1})	Salt	Cationic dye loading capacity of PWR (q_e mg g^{-1})		
		MB	CV	RB
0	–	84.7	17.4	16.3
0.1	KCl	77.2	15.9	15.3
	NaCl	76.7	15.7	15.1
	$CaCl_2$	69.8	13.3	13.4
0.2	KCl	65.3	12.4	12.7
	NaCl	65.2	11.9	11.8
	$CaCl_2$	53.7	9.5	10.2
0.3	KCl	53.2	10.3	10.3
	NaCl	49.8	10.1	9.9
	$CaCl_2$	32.6	6.7	6.9

The respective parameters of pseudo-first-order and pseudo-second-order kinetic models for the removal of MB, CV, and RB are presented in Table 4. The low correlation coefficient values and low theoretical q_e values obtained for pseudo-first-order equation indicates that the sorption of dyes did not follow the pseudo-first-order model. The experimental data are observed to fit with pseudo-second-order equation. The obtained correlation coefficients are very closer to 1 for all the dyes; it shows the appropriateness of the model. The theoretical q_e values of all dyes are also very closer to the calculated experimental values. These observations suggest that the removal of dyes onto PWR follows pseudo-second-order kinetic model. According to pseudo-second-order, boundary layer resistance is not the rate-limiting step, the external resistance model cannot adequately describe the adsorption mechanism, and the process controlling the rate may be a chemical sorption involving valences forces through sharing or exchanging of electrons between sorbate and sorbent.

Kinetic data were further analyzed using intraparticle diffusion model in order to study the steps of diffusion mechanisms. A plot of q_t vs. $t^{1/2}$ should result in straight line if the adsorption mechanism follows intraparticle diffusion process only and if the plot shows multi linear plots, it indicates that two or more steps take place. The plots of present process resulted in straight line for MB and CV which suggests that removal of MB and CV follows intraparticle diffusion process. The plot of RB resulted in a two linear plot (Fig. not shown here). The first linear plot is due to the immediate utilization of ample active sites on the adsorbent surface and the second linear plot attributed to very slow diffusion of the adsorbate from the surface site into the inner pores [38]. Thus, initial adsorption of RB by PWR may be governed by intraparticle transport of surface diffusion, and the later part may be controlled by pore diffusion [39]. However, the intercept of the line for all the studied dyes fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of adsorption [40].

3.4. Adsorption isotherms

In order to evaluate the maximum loading capacity of PWR, the sorbents were allowed contacting with

Table 4
Kinetic parameters derived for removal of MB, CV and RB from aqueous solution by protonated watermelon rind ($50\,\mathrm{mg\,L^{-1}}$ at 303 K)

Dye	Experimental q_e (mg g^{-1})	Pseudo first order constants			Pseudo second order constants		
		q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
MB	85.8	0.426	−0.01	0.570	83.30	0.014	1
CV	16.4	0.620	−0.004	0.629	15.87	0.397	0.997
RB	14.6	15.48	−0.01	0.969	14.92	0.112	0.999

varying concentration (50–300 mg/L) of MB, CV, and RB solutions at equilibrium. It was observed that loading capacity increased for all the dyes with an increase in the initial concentration at equilibrium and the maximum loading capacity is found to be 489.8, 104.76 and $86.6\,\mathrm{mg\,g^{-1}}$ for MB, CV and RB, respectively.

The equilibrium data are applied to two well-known isotherms such as Freundlich and Langmuir models. The respective constants determined are listed in Table 5. The correlation coefficients for Freundlich isotherm is found to be low which suggests that Freundlich isotherm might not be applicable to the present system. It was observed the equilibrium data better fit with Langmuir isotherm supported by its correlation coefficients that are closer to one. The theoretical complete monolayer coverage (V_m) based on Langmuir isotherm for MB, CV, and RB onto PWR is calculated to be 500, 100, and $91.74\,\mathrm{mg\,g^{-1}}$, respectively, against 489.8, 104.76, and $86.6\,\mathrm{mg\,g^{-1}}$ found experimentally. Therefore, Langmuir isotherm exhibited as the most appropriate model to describe the equilibrium behavior of cationic dye removal by PWR.

The essential characteristics of Langmuir equation can be expressed in terms of dimensionless separation factor, R_L is given as:

$$R_L = \frac{1}{1 + bC_e} \tag{6}$$

where C_e ($\mathrm{mg\,L^{-1}}$) is the equilibrium concentration of dyes and b ($\mathrm{mL\,mg^{-1}}$) is the Langmuir isotherm constant. The adsorption process as a function of R_L may be described as $R_L > 1$; unfavorable, and $0 < R_L < 1$; favorable, linear, and irreversible for $R_L = 1$ and 0, respectively. The R_L values obtained for MB, CV, and RB at different initial concentrations were found to be between 0.675–0.232, 0.840–0.466, and 0.793–0.370, respectively. It can be seen that all the R_L values obtained are between 0 and 1, showing that the adsorption of MB, CV, and RB is favorable onto PWR.

3.5. Thermodynamics of adsorption

In order to describe the thermodynamic behavior of sorption of MB, CV, and RB onto PWR, at equilibrium, temperature was varied from 303 to 323 K. Thermodynamic parameters including change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were derived from the following equations:

$$K_D = \frac{q_e}{C_e} \tag{7}$$

$$\Delta G^\circ = RT \ln K_D \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

where K_D is the equilibrium constant related to the Langmuir constant b, R is the universal gas constant ($8.314\,\mathrm{J\,Mol^{-1}\,K^{-1}}$), and T is temperature in Kelvin.

The thermodynamics parameters calculated for all the present systems are presented in Table 6. The

Table 5
Freundlich and Langmuir constants calculated for adsorption of MB, CV, and RB onto protonated watermelon rind at 303K

Dye	Freundlich isotherm model			Langmuir isotherm model		
	K_f	$1/n$	R^2	q_{max} (mg g^{-1})	b ($\mathrm{L\,mg^{-1}}$)	R^2
MB	18.1	0.078	0.809	500	0.06	0.983
CV	9.52	0.089	0.772	100	0.03	0.979
RB	10.76	0.094	0.901	91.74	0.01	0.989

Table 6
Thermodynamic parameters derived for adsorption of MB, CV and RB onto protonated watermelon rind (50 mg L^{-1}, 30 min)

Dyes	Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
MB	303	−5.922	−4.353	−1,640
	313	−7.806		
	323	−9.210		
CV	303	−2.473	−1.970	−509
	313	−3.026		
	323	−3.491		
RB	303	1.124	0.286	−877
	313	2.118		
	323	2.878		

calculated ΔG° values of MB and CV were found to be negative which indicates the spontaneous process and the positive values of RB indicate the nonspontaneous process. The increase in negative values of ΔG° with increase in temperature express that the removal process is more spontaneous at high temperature for MB and CV, while for RB, it is vice versa. The negative and positive values of ΔH° indicate exothermic process for MB and CV and endothermic process for RB. The negative ΔS° values for all the dyes indicate the decrease in the randomness of solid–liquid interface during the sorption.

3.6. Desorption and regeneration studies

Desorption and regeneration studies were performed to know the reusability potential of PWR. Desorption of dyes from PWR is studied by using 0.1 M HCl, 0.1 M acetic acid, distilled water and 0.1 M NaOH as desorbing agents. 0.05 g of dye-loaded PWR was contacted with 20 mL of desorbing agents for 30 min at room temperature in a orbital shaker at 150 rpm. The desorbed supernatant solution was subject to UV–vis spectrometer for the residual concentration of dyes. It was found that 0.1 M acetic acid has highest desorbing capacity for all the dyes followed by 0.1 M HCl, distilled water and 0.1 M NaOH (Fig. 3). However, desorbing capacity of 0.1 M acetic acid is found to be 69, 56, and 74% for MB, CV, and RB, respectively.

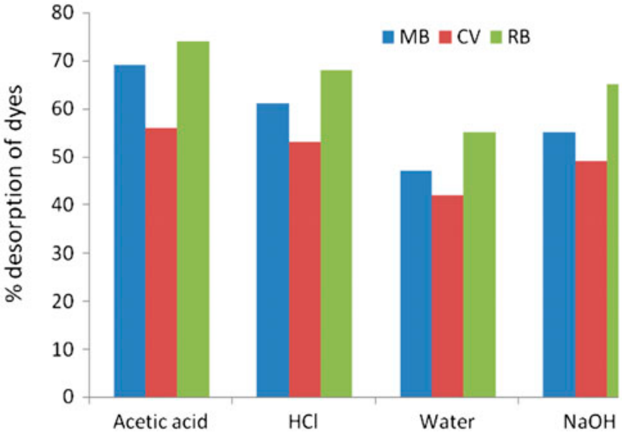

Fig. 3. Desorption of dyes from protonated watermelon rind with different desorbing agents.

Table 7
Comparison of dye loading capacity of watermelon rind with other biosorbents

Sorbent	MB	RB	CV	Reference
Banana peel	20.8	20.6	12.2	[21]
Orange peel	18.6	14.3	11.5	[21]
Grape fruit peel	25	–	254.16[a]	[3,22]
Jackfruit peel	285.73[a]	–	–	[23]
Lemon peel	29	–	–	[41]
Sugarcane dust	3.74	3.79	3.24	[42]
Watermelon rind	489.8	86.6	104.76	Present study

Note: [a]Loading capacities of activated carbon from agricultural sources.

4. Comparison with other low-cost sorbents

The maximum loading capacity of PWR is found to be 489.8, 104.76, and 86.6 mg g^{-1} for MB, CV, and RB ions, respectively. The loading capacity of MB is found to be very high for PWR compared to CV and RB. This is due to molecular size of MB being smaller than CV and RB ions. The high-loading capacity of MB suggests that PWR contains more number of mesoporous sites. The bigger molecular size of the CV and RB ions hinders the entrance into the mesoporous sites resulting in lower adsorption capacity compared to MB. However, the maximum loading capacities of MB, CV, and RB ions are found to be high compared to other sorbents reported in the literature (Table 7). The protonation step has greatly enhanced the sorption capacity of WR which might be an equal competitor to activated carbon.

5. Conclusions

Watermelon rind biomass was chemically protonated by 0.1 M HCl and successfully evaluated for the removal of MB, CV, and RB from aqueous solution. Protonation of rind was confirmed by EDX analysis.

The sorption of dyes onto PWR is found to be rapid and consistent with pseudo-second-order kinetic model. The equilibrium data are well explained by Langmuir isotherm with favorable R_L values for all the dyes. Thermodynamic studies have shown the spontaneous nature of PWR for the removal of MB and CV and nonspontaneous nature for RB. FTIR studies have revealed that hydroxyl and carboxyl ions are involved in uptake of dyes onto PWR. Desorption study suggests that PWR shall be effectively used for one time for the removal of dyes. The presence of ionic salts has great impact on sorption of dyes by PWR. These observations suggest that watermelon rind can prolifically be used as nonhazardous, value added and potential biomass for the removal of basic cationic dyes from aqueous solution in the absence of ionic salts.

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