



Characterization and adsorption study of biosorbents for the removal of basic cationic dye: kinetic and isotherm analysis

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ABSTRACT

Potato peels (PP) and peanut hulls (PH) have been used as biosorbents to remove Methylene Blue (MB) from aqueous solution. By using Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and X ray diffraction (XRD) analysis, PP and PH have been characterized. FTIR analysis confirmed the presence of carboxyl and phenolic hydroxyl groups which constitute the major adsorption sites onto PP and PH. SEM micro photographs indicated the presence of tiny pores on the adsorbent surface responsible for sorption process. XRD showed the presence of crystalline structures in both adsorbents. The effect of different parameters on adsorption was investigated, and conditions were optimized. The equilibrium and kinetics data obtained were analyzed using different models. The adsorption data confirmed second order kinetics and Langmuir Isotherm to be the best fit model for both adsorbents. Thermodynamic studies showed that the sorption process of MB was endothermic and more effective at lower temperatures. The results demonstrated that PH powder has a sufficient potential as an efficient adsorbent material for the removal of basic dyes from textile wastewater. The maximum removal efficiency of PH obtained was 98.1 % and that of PP was 92.7 %.

Keywords: Adsorption; Methylene Blue; FTIR; Isotherms; Kinetics; SEM; Thermodynamics; XRD

1. Introduction

It is necessary to conserve water resources in order to save the planet and future of mankind. Environmental pollution and the water demand have been increasing with the passage of time. The industrial, domestic and agricultural sectors are consuming 22%, 8% and 70% of fresh water respectively which results in the generation of a number of pollutants. Among these pollutants, the important class of pollutants are coloring agents i.e. dyes [1]. According to an estimation, about 280,000 tons of dyes were used globally in textile industries and subsequently were released as textile industrial effluent [2]. The textile industry and its effluent

containing dyes, is considered as one of the main source of water pollution. Most of the dyes discharged and their by-products are carcinogenic and toxic to life forms due to the presence of many carcinogenic compounds, such as various aromatic compounds and naphthalene [1]. It is very difficult to degrade dyeing waste waters due to the stable and very complex structure of dyes [3].

Several technologies have been developed to remove dyes from industrial effluents. The most commonly used methods for the removal of dyes includes membrane filtration [4], catalytic oxidation [5], adsorption [6] and coagulation/flocculation [7]. Among these methods, adsorption has evolved as the optimum choice and cost effective method [8]. To produce high quality of water, dyes can be removed from water and wastewater by sorption of synthetic dyes onto cost-effective and efficient sorbents.

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US Environmental Protection Agency has cited adsorption through activated carbon as one of the best treatment technologies for water and wastewater treatment. However, although activated carbon is considered as the most suitable sorbent for water and wastewater treatment, yet due to its high cost, its extensive use is restricted. To reduce the process cost, efforts have been carried out to find the cheap adsorbents [9]. Different low cost plant materials have been identified as biosorbents for different textile dyes removal i.e. rice husk [10], citrus pectin [11], wheat straw [12], tamarind bark [13] and Bengal gram husk [14] etc. In 2011, Tanyildizi studied adsorption process of reactive dye from aqueous solution by peanut hulls and also the removal of heavy metals by adsorption onto potato peels was investigated by [15]. Nowadays, MB is the most common dye widely used for dyeing wood, silk and cotton [16]. Studies have been carried out for the removal of MB dye from wastewater by using different low cost adsorbents including natural and waste materials i.e. wheat shells [17], tea waste [18], yellow passion fruit peels [19] etc. have been proven to be the potential adsorbents for MB removal. Commodity crops such as peanuts and potatoes generate considerable quantities of hulls and peels each year which have little or no value. PH and PP are high in volume and low in density and are used as animal feed or burned for energy [20] Pakistan ranks 20th and 36th in potato [21] and peanut production in the world respectively. According to an estimate about 3.8 million tons of potato and 0.08 million tons of peanut are produced annually in Pakistan [22]. About 10% of these crops are produced as waste each year that have no or very little value. This leads to explore the adsorption potential of these materials for the of various metal ions and organic compounds [23,24].

Purpose of this research was to characterize and evaluate PH and PP for its removal efficiency for MB. PH and PP are locally available and cheap agricultural wastes. Optimization was carried out to find out optimum contact time, temperature, initial dye concentration, adsorbent dose, pH and particle size. The equilibrium adsorption data of MB on PH and PP was analyzed by Langmuir, Freundlich, Temkin, Dubinin-Raduskevich (D-R) and Flory Huggins models. The kinetic and thermodynamics studies were also analyzed using adsorption models. The research was carried out from 1st September 2016–15th April 2017 at Institute of Environmental Engineering and Research (IEER), University of Engineering and Technology (UET), Lahore, Pakistan.

2. Materials and methods

2.1. Biosorbents

PH and PP utilized in the study were collected from restaurants, cafeterias and houses of Lahore, Pakistan during November to December 2016. To remove dirt particles, biosorbents were thoroughly washed several times with distilled water. To remove moisture, these were dried in oven (Wisewon32) at 35°C for 5 d. Afterwards, these were grounded using pulverizer and finally sieved according to British Standard Sieves (BSS) to get a particle size of 75 μm .

2.2. Adsorbate

The MB used was purchased from Sigma Aldrich. Stock solution of 1000 ppm was prepared by dissolving 1000 mg of $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ in 250 mL of distilled water, and further diluted to 1 L. Standard solutions were prepared by diluting stock solution. All solutions were stored in dark at 4°C due to photo-degradable property of MB.

2.3. Experimental

Batch adsorption studies were carried out for adsorption of MB onto selected biosorbents (PH and PP). In the preliminary step, all experimental work was performed in 250 mL Erlenmayer flasks, by varying one parameter at a time. pH (6–10), contact time (15–45 min), initial concentration (5–60 ppm), biosorbent dose (0.25–3 g), temperature (15–45°C), agitation speed (100–300 rpm), and particle size (53, 75, 160 μm) were optimized. All experiments were repeated thrice and average values of parameters were obtained. Kinetic models (pseudo first order and second order kinetics) were used to find out dynamics of process. Langmuir, Freundlich, Temkin, Dubinin-Raduskevich (D-R) and Flory Huggins were used to explain the relationship between the amount of dye adsorbed and its equilibrium concentration. Non-linear regression methods were used to find out isotherm constants for all five models. Thermodynamic studies were carried out using Van't Hoff equation by calculating thermodynamic parameters i.e. ΔG° (Gibb's free energy change), ΔS° (entropy change) and ΔH° (enthalpy change).

2.4. Characterization of biosorbents

FTIR (JASCO FTIR/4100) analysis of PP and PH was performed to identify different functional groups present in adsorbents. To identify surface morphology of PH and PP before and after adsorption process, SEM ("VEGA 3 SEM") was used. X ray diffraction (XRD) analysis was carried out before and after adsorption using STOE-Theta/Theta Diffractometer System.

3. Results and discussions

3.1. Characterization of adsorbents

The FTIR spectra of PH is shown in Fig. 1a according to spectra, the peak 3350.71 cm^{-1} confirms the presence of alcohols and phenols groups. The peaks 2858.95 cm^{-1} and 2926.45 cm^{-1} specify the presence of carboxylic groups whereas peaks 1055.84 cm^{-1} and 1258.32 cm^{-1} indicate the existence of alcohols and carboxylic groups. The peak 1424.17 cm^{-1} indicates the presence of aromatics and peak 1741.41 cm^{-1} shows the presence of esters and saturated aliphatic [25].

Fig. 1b indicates the FTIR spectrum of PP. The peak 3387.35 cm^{-1} confirms the presence of alcohols and phenols. The peak 1416.46 cm^{-1} shows the presence of aromatics. The peak 1155.15 cm^{-1} indicates the presence of alcohols and carboxylic group. The peaks 765 cm^{-1} and 667.25 cm^{-1} confirm presence of aromatics and 1° and 2° amines. The peaks 1248.68 cm^{-1} and 1043.3 cm^{-1} indicate presence of alcohols, carboxylic, ethers and esters [25].

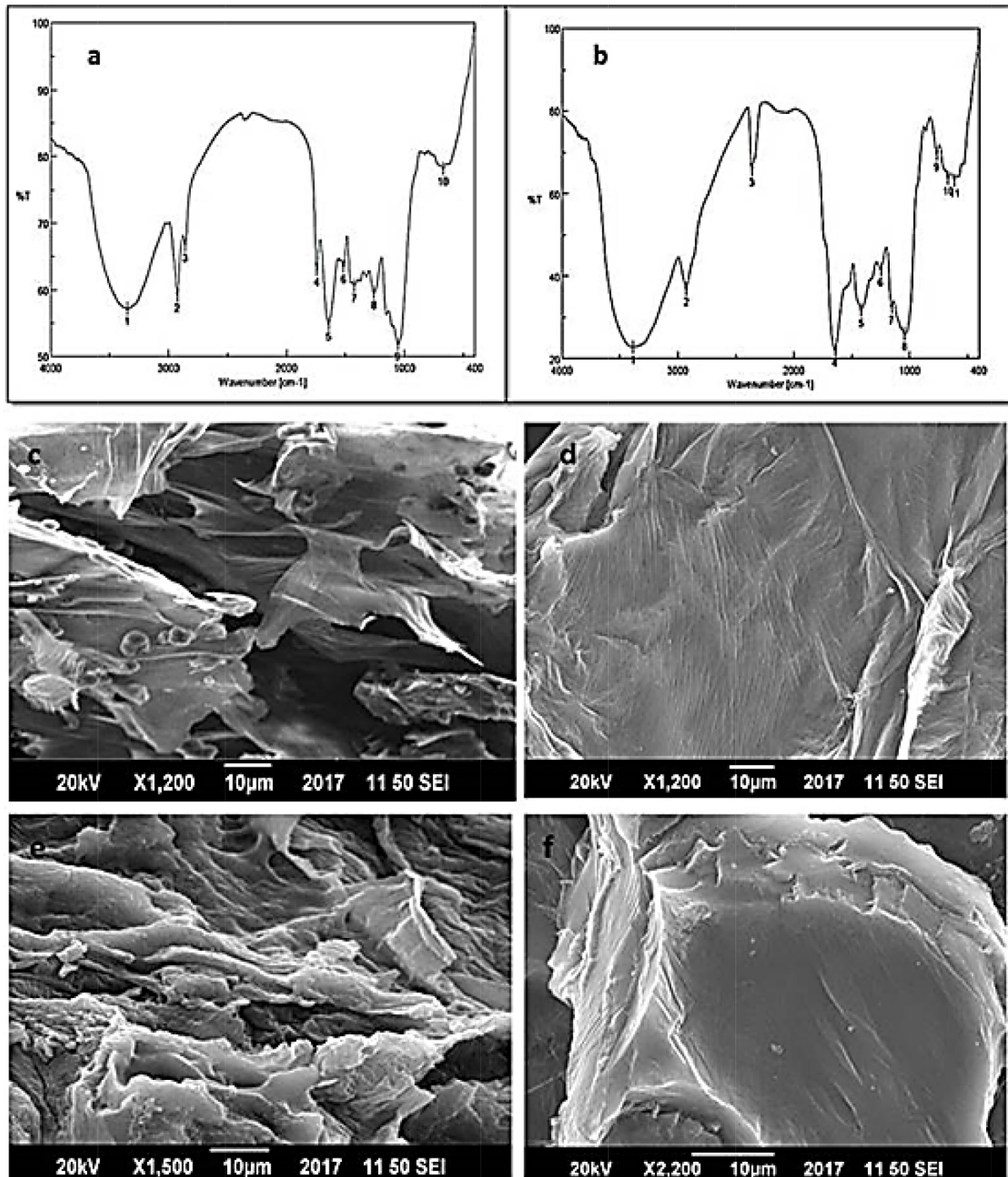


Fig. 1. (a) FTIR spectrum of PH (b) FTIR spectrum of PP, SEM for PH; (c) before adsorption (d) after adsorption, PP; (e) before adsorption (f) after adsorption.

The analysis of Fig. 1a and Fig. 1b shows that alcohols, phenols and carboxylic groups were found common in both PH and PP. Adsorption can take place due to the presence of carboxyl and phenolic hydroxyl groups as these are ionizable and can interact with protons so these functional groups can be the major sites of adsorption for dye removal [26]. Therefore, the common functional groups found in both PH and PP are responsible for adsorption.

Figs. 1c–f show the morphology of PH and PP before and after adsorption phenomenon. For both PH and PP, the surface of adsorbents after dye adsorption is different from the surface of adsorbents before adsorption process. The uneven surfaces of both adsorbents containing fibers promote the active sites for adsorption. In case of PH, the surface is much coarse which further enhance the adsorption capacity of adsorbent compared to PP [26].

XRD analysis was carried out using a diffractometer (STOE-Theta/Theta Diffractometer System) operated at 40 kV and 5 mA. XRD spectrum of both PH and PP indicates typical cellulosic material having different peaks before and after adsorption. Figs. 2a, b show that the absolute intensity of PH was almost doubled after adsorption at the same angles.

3.2. Batch adsorption studies

3.2.1. Contact time

Batch adsorption studies for contact time was carried out using PH and PP powder by varying different contact times at pH 7, 5 ppm of initial dye concentration, 30°C temperature, 0.5 g of dose having particle size of 75 μm and agitating speed of 150 rpm. By increasing the contact time, increasing pattern of adsorption was observed for

both biosorbents till 25 min (equilibrium stage). Further increase in time does not increase the removal indicating that adsorbents surface became saturated and no active site was available for further sorption. Maximum removal efficiency was achieved at 25 min, 88 % for PH and 81.6 %.

3.2.2. Temperature

Adsorption studies for temperature were carried out using PH and PP powder from 15 to 45°C. Maximum removal efficiency of PH was 88% at 30°C and 82.3% for PP at 35°C respectively. Increase in temperature resulted in decrease in viscosity of solution so that the rate of diffusion of the adsorbate molecules increased. As the temperature was increased further, the kinetic energy of dye molecules was also increased which resulted in the reduction of adsorption capacity [27].

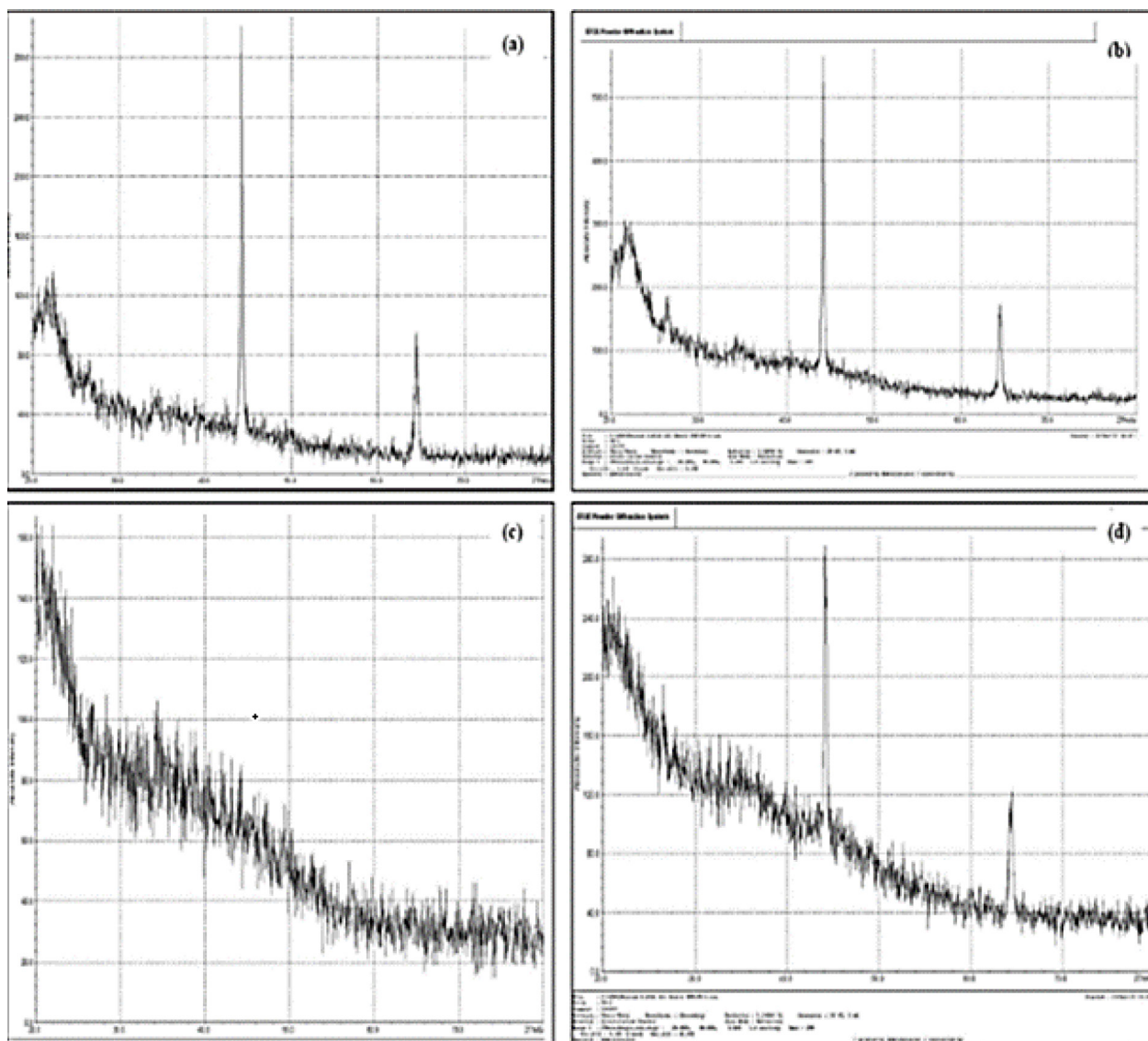


Fig. 2. XRD spectrum of PH; (a) before adsorption (b) after adsorption, PP; (c) before adsorption (d) after adsorption.

3.2.3. Adsorbent dose

Adsorption dose was optimized using PH and PP from 0.25 g to 3 g. Removal efficiency was maximum at 0.5 g for PH (88%) and PP (82.3%). It demonstrates that as the amount of adsorbent (dose) increased, more adsorbent was available for sorption until a saturation point. Moreover; further increasing the adsorbent dose caused an increase in the viscosity of solution leading to the difficulty in dye sorption. Increased biosorbent dose also formed agglomerates thus reducing the effective surface area available to dye molecules [27].

3.2.4. Initial dye concentration

Initial dye concentration was optimized by varying concentration from 10 ppm to 60 ppm. Removal efficiencies were maximum for PH (97.4%) and PP (90.2%) at 40 ppm and 30 ppm respectively. At low concentration, more adsorption sites were available for the dye. However, at high concentration, adsorption sites became fewer and the dye ions took more time in order to reach the last available sites [27].

3.2.5. Effect of pH

Batch adsorption at different pH (from 6 to 10) was analyzed. Removal efficiencies were maximum for PH (98%) and PP (91%) at pH 8. Adsorption of the dye was decreased in acidic range. At lower pH, due to the competition of protons with dye molecules for the available adsorption sites, dye uptake was decreased, hence decreasing adsorption capacity. As the pH was increased, the adsorption of MB onto adsorbents also increased which can be explained by the electrostatic interaction of dye cationic species with the negatively charged surface [28]. Further increase in pH resulted in large numbers of hydroxyl ions that which started attaching directly to the positively charged dye molecules thus reducing its adsorption onto the adsorbent sites [29].

3.2.6. Agitation speed

Equilibrium was obtained at an agitation speed of 150 rpm. Further increase resulted in decrease of removal efficiency due to increased turbulence effect; hence significantly affecting the adhesion of dye molecules onto the adsorbent.

3.2.7. Particle size

Particle size was varied from 53 μm to 160 μm . Maximum removal was achieved with particle size of 53 μm . This was because of the fact that smaller the particle size, greater will be the surface area. The removal efficiency was maximum for PH (98.1%) and PP (92.7%) at 53 μm .

3.3. Equilibrium of adsorption isotherms

Langmuir, Freundlich, Temkin, Dubinin-Raduskevich (D-R) and Flory Huggins isotherms were used to explain

the relationship between the amount of dye adsorbed and its equilibrium concentration.

3.3.1. Langmuir isotherm

Langmuir isotherm refers to development of homogeneous mono-layer of adsorbate on the exterior surface of adsorbent until saturation. This isotherm is effective for formation of mono-layer on the limited number of identical adsorption sites. Linear Eq. (2) of Langmuir isotherm model is given below:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \quad (2)$$

where q_e is the amount of adsorbate per adsorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), Q_o is the maximum adsorption capacity (mg g^{-1}) and K_L is Langmuir constant (L mg^{-1}).

A Langmuir plot of $1/Q_o$ vs. $1/C_e$ gives a straight line with a slope and intercept to compute the values of q_e and K_L [30]. The correlation coefficients shown in Table 1 ($R^2 > 0.99$ for PH and $R^2 > 0.98$ for PP) suggest that the Langmuir isotherm is slightly more efficient for PH than PP. Equilibrium parameter R_L is used to express important characteristics of Langmuir isotherm, given in Eq. (3) [31].

$$R_L = \frac{1}{1 + (K_L C_o)} \quad (3)$$

The value of R_L shows the adsorption nature to be either unfavorable if ($R_L > 1$), linear if $R_L = 1$, favorable if ($0 < R_L < 1$) and irreversible if $R_L = 0$. R_L values obtained for PH and PP were 0.076 and 0.99 respectively showing that adsorbents were favorable for adsorption of MB.

3.3.2. Freundlich isotherm

Freundlich isotherm assumes a logarithmic decline in sorption with the increase in fraction of occupied sites of adsorbent.

$$q = K_F C_e q^{1/n} \quad (4)$$

In Eq. (4), at equilibrium, q is the amount of adsorbent adsorbed (mg g^{-1}), C_e is the amount of adsorbate and K_F and n are Freundlich constants indicating adsorption capacity and adsorption intensity respectively.

$$\ln q = \ln K_F + \frac{1}{n} \ln C_e q \quad (5)$$

Eq. (5) is linear form of Freundlich isotherm. A plot was established between $\ln q$ and $\ln C_e$ and K_F and n were determined. Results obtained for the adsorption of MB on PH and PP are presented in Table 1. Favorable adsorption occurs between n values 1–10. Sorption of MB on PP is favorable under Freundlich assumptions as value of n is 2.25 that is less than 10 and greater than unity. Higher the K_F value more will be the adsorption capacity [32]. So, K_F value was more for PP as compared to PH, indicating more adsorption capacity than that of PH.

Table 1
Isothermic, kinetic and thermodynamic adsorption studies of MB onto PH and PP

Adsorption models		Parameters	PH	PP
Isotherm studies	Langmuir	R ²	0.9917	0.9891
		q _m /mg-g ⁻¹	3.29	4.29
		R _L	0.076	0.92
		ΔG°	-2.22	14.48
	Freundlich	N	0.609	2.25
		K _f mol g ⁻¹	2.3	4.018
		R ²	0.9859	0.9864
		ΔG°	2.059	3.45
	Tempkin	A/L mg ⁻¹	1.53	1.536
		B/KJ mol ⁻¹	3.76	1.80
		R ²	0.9676	0.8625
	D-R	R ²	0.8576	0.6494
		B/mol ² KJ ⁻²	-0.00002	-0.000008
		Q _m /mg-g ⁻¹	2.052	3.329
		E/KJ mol ⁻¹	0.158	0.25
Flory-Huggins		R ²	0.9131	0.6928
		n	13.782	4.8713
		K _{FH} /L mg ⁻¹	0.325	2.867
Kinetic studies	Pseudo first-order kinetic model	B	-13.782	-4.8713
		k ₁	0.0005	-0.0000023
		q _e	1.0957	1.0789
	Pseudo second-order kinetic model	R ²	0.5955	0.555
		k ₂	-0.0032	-0.0167
		q _e	0.1926	0.1959
		R ²	0.653	0.581
Thermodynamic studies	Temperature (K)	ΔG/KJ mol ⁻¹		
	288		-3746.31	-3745.99
	293		-3811.36	-3811.04
	298		-3876.41	-3876.08
	303		-3941.46	-3941.13
	308		-4006.51	-4006.18
	318		-4136.6	-4136.28

3.3.3. Temkin isotherm

Temkin isotherm was used to analyze the potential of adsorption of MB dye onto PH and PP which assumes that decrease in sorption of heat is not logarithmic as that of Freundlich isotherm but it is linear. The linear form is represented in the following equation:

$$q_e = B \ln A + B \ln C_e \quad (6)$$

where B is calculated through the following equation:

$$B = \frac{RT}{b} \quad (7)$$

T (K) indicates absolute temperature, R is the constant of gas (8.314 J⁻¹ mol⁻¹ K⁻¹) and b is related to heat of adsorption. A is the equilibrium constant (min⁻¹) corresponding

to binding energy. Isotherm constants A and B were determined from a plot of q_e versus $\ln C_e$ [33]. Experimental data obtained indicates that Temkin isotherm fits better for PH as compared to PP. The heat (J mol⁻¹) of MB adsorption by PP was found to be less than that for PH, where the correlation coefficient was also less pronounced.

3.3.4. Dubinin-Raduskevich (D-R) isotherm

The linear form of D-R isotherm is represented in Eq. (8):

$$\ln Q_e = \ln Q_D - \beta \varepsilon^2 \quad (8)$$

where ε is calculated by the following equation:

$$\varepsilon = RT \log \left(1 + \frac{1}{C_e} \right) q_D \left(\frac{\mu g}{g} \right) \quad (9)$$

β ($\text{mol}^2 \text{KJ}^{-2}$) is the D-R isotherm constant related to adsorption energy and ε is the Polanyi potential. Q_m is the maximum adsorption capacity (mg g^{-1}). R = gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$) and T (K) = absolute temperature. The adsorption energy can be computed from the following equation:

$$E = (-2\beta)^{0.5} \quad (10)$$

It is reported that when the value of E is below 8 kJ mol^{-1} , the adsorption process can be considered as the physical adsorption. In contrast, if the value of E is located in the range of $8\text{--}16 \text{ kJ mol}^{-1}$, it is the chemical adsorption [34]. From Table 1, it is obvious that energy values were limited within the range of $0.1\text{--}0.3$. It is concluded that the effect of physical adsorption will play a dominating role in the adsorption of MB onto adsorbents.

3.3.5. Flory huggins isotherm

This isotherm is to determine the surface of coverage on adsorbents. The linear form of the Flory-Huggins is given in Eq. (11):

$$\ln\left(\frac{\theta}{C_o}\right) = \ln K_{FH} + n \ln(1 - \theta) \quad (11)$$

where $\theta = \left(1 - \frac{C_e}{C_o}\right)$ is degree of surface coverage, C_o and C_e are the initial and equilibrium concentrations of adsorbate ions, n indicates number of occupied adsorption sites, K_{FH} is the equilibrium constant (L mol^{-1}), K_{FH} and n are calculated by plotting $\ln(\theta/C_o)$ versus $\ln(1-\theta)$. K_F and are related as Eq. (12):

$$K_{FH} = \exp\left(\frac{-\Delta G^\circ}{RT}\right) \quad (12)$$

where ΔG_o indicates standard free energy change, R is the universal constant of gas equal to $8.314 \text{ J (J mol}^{-1} \text{K}^{-1})$ and T is the absolute temperature. ΔG_o values calculated were negative for PH and PP ensuring that the nature of adsorption was spontaneous [35].

3.4. Adsorption kinetic studies

To study the dynamics, the kinetic adsorption data was processed. Pseudo first and second order kinetic models were studied to analyze data by the following equation:

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

where $K_1 \left(\frac{1}{\text{min}}\right)$ = rate constant, $q_e \left(\frac{\mu\text{g}}{\text{g}}\right)$ is amount of adsorbate per adsorbent at equilibrium, $q_t \left(\frac{\mu\text{g}}{\text{g}}\right)$ = the amount of adsorbed adsorbate per unit mass of adsorbent at time t , t = time.

The linear equation of the pseudo-second-order model as given as:

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

where K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is rate constant of the pseudo-second-order adsorption, q_e is amount of dye adsorbed on the solid adsorbent at equilibrium (mg g^{-1}), and q_t is the amount of dye adsorbed on the adsorbent at any time, t (mg g^{-1}). K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) can be calculated from the slope and intercept of the plot of t/q_t against t . The calculated values of K_1 , K_2 , q_e and their corresponding regression coefficient values (R^2) are presented in Table 1. The correlation coefficients for PP and PH were found closer to unity for pseudo-second-order kinetics than for pseudo first order kinetics [36].

From the above results it is clear that the sorption of MB onto PH and PP followed pseudo second-order kinetics due to the value of R^2 which was found closer to unity for both PH and PP.

3.5. Thermodynamic studies

Thermodynamic parameters i.e. ΔG° (Gibb's free energy change), ΔS° (entropy change) and ΔH° (enthalpy change) are calculated by using Eqs. (15)–(17):

$$K_c = \frac{C_{Ae}}{C_e} \quad (15)$$

$$\Delta G^\circ = -RT \ln K_c \quad (16)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (17)$$

where C_e is the equilibrium concentration in solution (mg/L), K_c is the equilibrium constant and C_{Ae} is the solid-phase concentration at equilibrium (mg/L). ΔG° , ΔH° and ΔS° are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the gas constant (8.314 J/mol/K) and T is the temperature (K).

At all selected temperatures, the values of ΔS° for both PH and PP was found 13.0097 while ΔH° for PH was 0.4814 and for PP was 0.8065 . The values of ΔG° are presented in Table 1; the negative signs indicate that process was feasible and spontaneous. With the increase in temperature, ΔG° value was increased showing adsorption process was more favorable at lower temperatures. The positive ΔH° values indicate the endothermic nature of adsorption whereas the positive values of ΔS° ensures that the randomness on the solid-liquid interface was increased [37].

4. Conclusions

Adsorption using wastes to passively remove dyes from aqueous media offers an efficient and cost effective alternative compared to traditional chemical and physical remediation and decontamination techniques. Potato peels (PP) and peanut hulls (PH) were evaluated as adsorbent. FTIR analysis, SEM images and XRD analysis confirmed the adsorption of methylene blue onto these adsorbents. Moreover, these results also explain the

mechanism of removal. Langmuir isotherm showed a better fit than other isotherm models indicating that the process was chemisorption. The adsorption data confirmed second order kinetics. Thermodynamic studies indicated that the adsorption was endothermic and reactions were spontaneous and favorable for both PH and PP. The potential of PH for the biosorption of MB was 98.1% more than that of potato peels (92.7%) optimum conditions. It can be concluded that PH and PP can be used as alternative economic biosorbents for dye removal in wastewater treatment processes.

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Supplementary material

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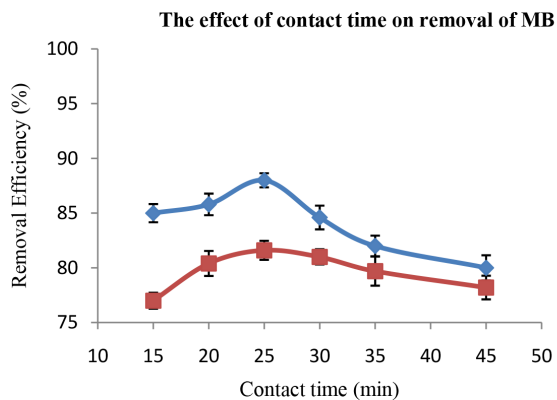


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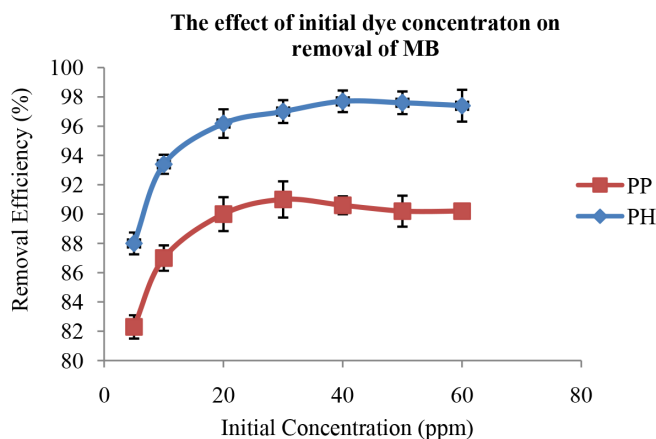


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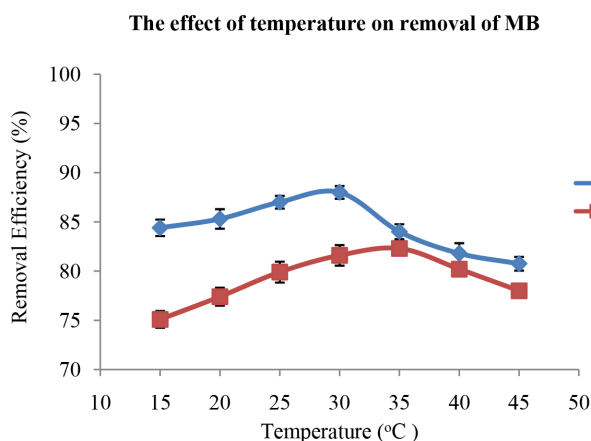


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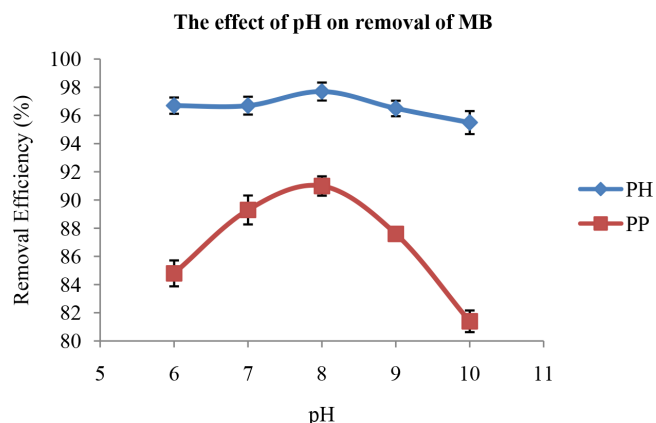


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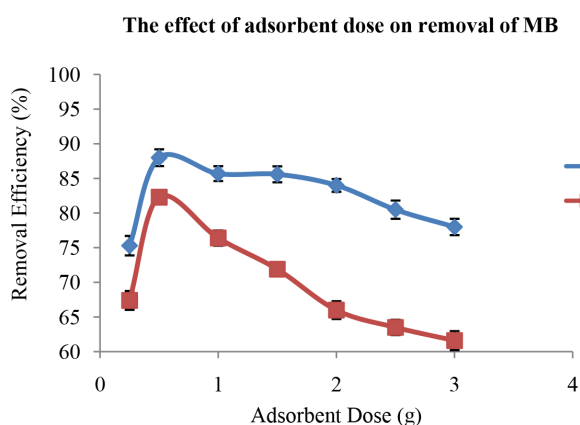


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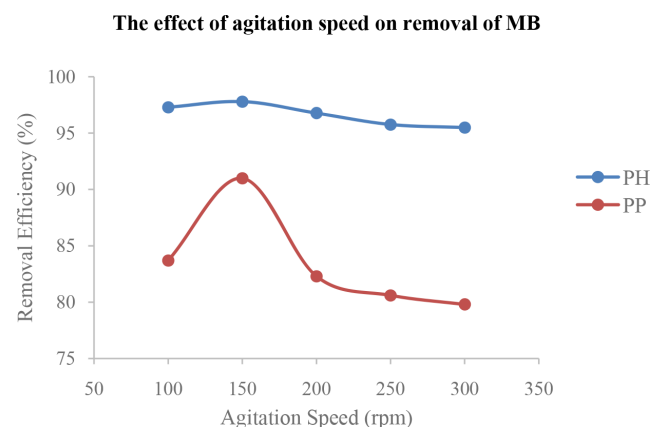


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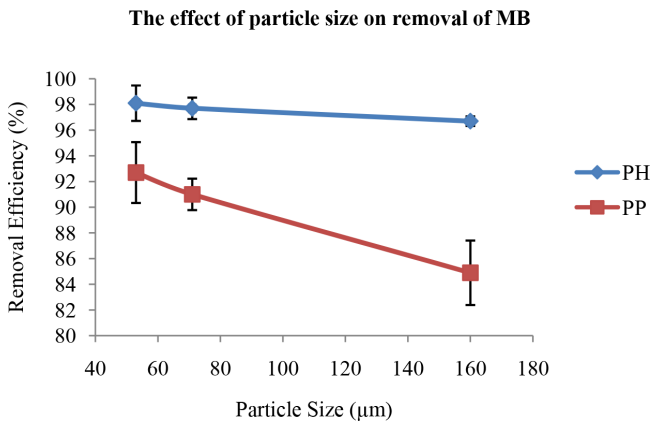


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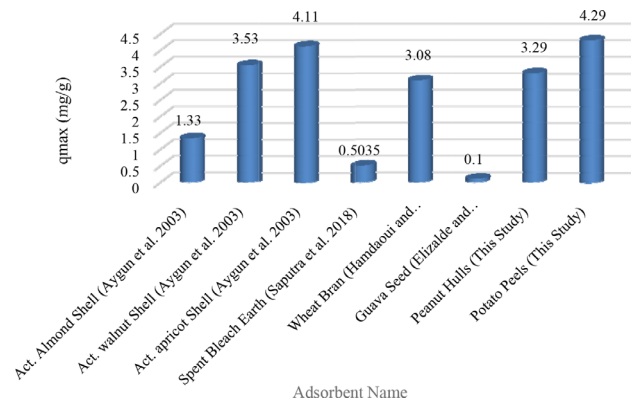


Fig. S8.