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Kinetic, Equilibrium, Thermodynamic studies and Quantum Chemical Evaluation on the Adsorption of Methylene Blue dye from Aqueous Solution using Plantain Peel as an Adsorbent

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Abstract

Adsorption capacity of plantain peel was evaluated using batch adsorption studies and quantum chemical calculation. The plantain peel without any modification, was characterized by Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). In batch optimization studies, the maximum adsorption capacity was obtained at the optimum levels of contact time (60 minutes at 14.3884mg/g) adsorbent dose (0.1g at 23.4431mg/g), initial dye concentration (60mg/L at 27.8547mg/g) and pH6 (22.6127mg/g). The mechanism of adsorption, kinetic data were modelled using the pseudo-first-order, pseudo-second-order, Elovich and Intraparticle diffusion. Among the kinetic models studied, the pseudo-second-order equation was the best applicable model to describe the adsorption process of the dye onto the adsorbent employed in this work. Equilibrium isotherm data were also analyzed using the Langmuir, Freundlich, Temkin and Dubinin-Raduskevich isotherms. The Freundlich isotherm model yielded a better result. Isotherm parameters have also been used to obtain the thermodynamic parameters such as Gibb's free energy, enthalpy, and entropy of adsorption. The thermodynamic parameters: change in enthalpy, ΔH = 0.2690 kJ/mol, change in entropy ΔS =-0.0143J/mol. K. The change in Gibbs free energy ΔG = -2483.60 kJ/mol, -2886.50 kJ/mol, -3628.00 kJ/mol, -4516.08 kJ/mol at 303, 313, 323 and 333 K respectively. These results show that plantain peel is a good low-cost adsorbent for the removal of this hazardous dye from wastewater and quantum chemical calculation is also in good agreement with the experimental results. Quantum chemical calculation is found to be one of the best method to determine the adsorption property of any material because of its reliability and simplicity.

Keywords— Adsorption, kinetic, thermodynamic, Isotherms, methylene blue

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1. Introduction

Water is an essential element for the survival of all living organisms. Nowadays, the water sources contaminated by a wide variety of pollutants coming from industrial effluents are a subject of several researchers [1]. Dyes are colored substances that can be applied to various substrates (textile materials, leather, paper, hair) from a liquid in which they are completely, or at least partly, soluble. Man has made use of dyes since prehistoric times, and in fact, the demand and the usage of dyes have continuously increased. However, the presence of dyes even in trace quantities is very undesirable in aqueous environment as they are generally stable to light and oxidizing agents, and are resistant to aerobic digestion [2]. This is partly due to the realization that contamination of aquatic environment by dyes causes reduction in the growth of algae due to obstruction of light required for photosynthesis, which subsequently leads to ecological imbalance in the aquatic ecosystem [3]. Various methods have been studied to remove dyes from wastewaters, including biodegradation [4], electrocoagulation [5], chemical oxidation [6] and adsorption [7]. However, these methods have many disadvantages, as they require expensive equipment and/or a continuous need for chemicals [8]. Therefore, the present study is aimed at testing the efficiency of plantain peel for the adsorption of methylene blue in aqueous solution and possibly proposed the mechanism for the adsorption process.

2. Materials and Methods

2.1 Adsorbent Collection and Preparation

The Plantain peels (PP) were obtained from different restaurants and road side sellers of roasted plantain in Kaduna North LGA of Kaduna state. The PP were first washed with water to remove dirt from its surface. The PP were then rinsed with distilled water to remove dust and impurities deposited on the surface. The PP were air-dried for 14days and then oven-dried at 105 °C for 24 hrs to constant mass. The dried PP were pulverized and sieved to obtain particle sizes of 1-2 mm, stored in an airtight container and labelled Plantain peels (PP).

2.2 Preparation of Congo Red solution

The Stock solution (Methylene blue (MB) dye) was prepared by dissolving accurately weighed 1g of the dye into a 1L to produce 1000 mgL^{-1}using distilled water. The experimental solutions (10-60mg/L of desired concentration were prepared accordingly by diluting the stock solution with distilled water.

2.3 Characterization of the Adsorbent

The surface morphological properties of the adsorbent sample were investigated using Scanning Electron Microscope (Phenom World Eindhoven). Scanned micrographs of adsorbents before and after

adsorption were taken at an accelerating voltage of 15.00 kV and x500 magnification. FTIR analyses of the MB dye, adsorbents before and after adsorption were carried out using Cary 630 Fourier Transform Infrared Spectrophotometer Agilent Technology. The analysis was done by scanning the sample through a wave number range of 650 – 4000 cm^{-1}; 32 scans at $8cm^{-1}$resolution.

2.4 Batch Adsorption Experiment

Batch experiments were carried out to determine the optimum conditions for the equilibrium adsorption of Methylene blue onto PP. The results obtained after the optimization experiments were used to conduct the batch adsorption experiments. Each of these systems was separately run in a 250 cm^3 conical flask differently at 30^0, 40^0, 50^0 and 60^0C respectively. The conical flasks were covered during the equilibration period and placed on a temperature-controlled tightly Innova 4000 incubator shaker for the earlier reported period. After reaching adsorption equilibrium, the content was filtered through Whatman No 1 filter paper. The filtrate was analyzed using Perkin-ElemerUv-visible spectrophotometer [9]. The extent of adsorption was calculated using equations (1) and (2) respectively:

$$Q_e = \frac{(Co-Ce)}{m} \times V \quad (1)$$

$$R_{em}(\%) = \frac{(Co-Ce)}{Co} \times 100 \quad (2)$$

Where Q_e is the adsorption capacity (mg/g), C_o and C_e are the initial and final equilibrium concentration (mg/l) of Methylene blue in solution, V is the volume of Methylene blue in solution (L), and m is the mass (g) of the adsorbent.

3.0 Results and Discussion

Figure 1: FTIR spectral of PP before and after adsorption of MB

The FTIR spectra of PP before and after adsorption on MB is given in Figure 1(a-b). The broad band at $3391cm^{-1}$ is attributed to the stretching vibration of -OH group. The stretching of the -OH group bond to methyl radicals is attributed to the signal at $2877cm^{-1}$. Also, peaks at $2344cm^{-1}$ and $2110cm^{-1}$ are associated with the stretched vibration of alkynes C≡C, while the peak at $1994cm^{-1}$ is ascribed to be C=O group which is affected by minor overlapping with C-C aromatic ring stretched vibrations. The broad peak at $1033cm^{-1}$ is associated to C-O group which confirms the lignin structure of PP. The peaks at $1562cm^{-1}$ and $1402cm^{-1}$ are associated with stretching vibrations of aromatic and C-H in alkane, while the peak at $747cm^{-1}$ and $870cm^{-1}$ are due to stretched vibration of C-O in aromatic, esters and ethers. Figure 1b shows FTIR spectra of PP after adsorption. There was a shift and broadening of adsorption peaks after adsorption. The shift of the -OH peak from $3391cm^{-1}$ to $3272cm^{-1}$ shows the engagement of the -OH group in adsorption. The shift of the carbonyl group peak from $1033cm^{-1}$ to $1011cm^{-1}$ shows

that carbonyl group participated in the adsorption of MB. The presence of these functional groups and their enhancement in adsorption abilities of MB agrees with the findings of another author [10]

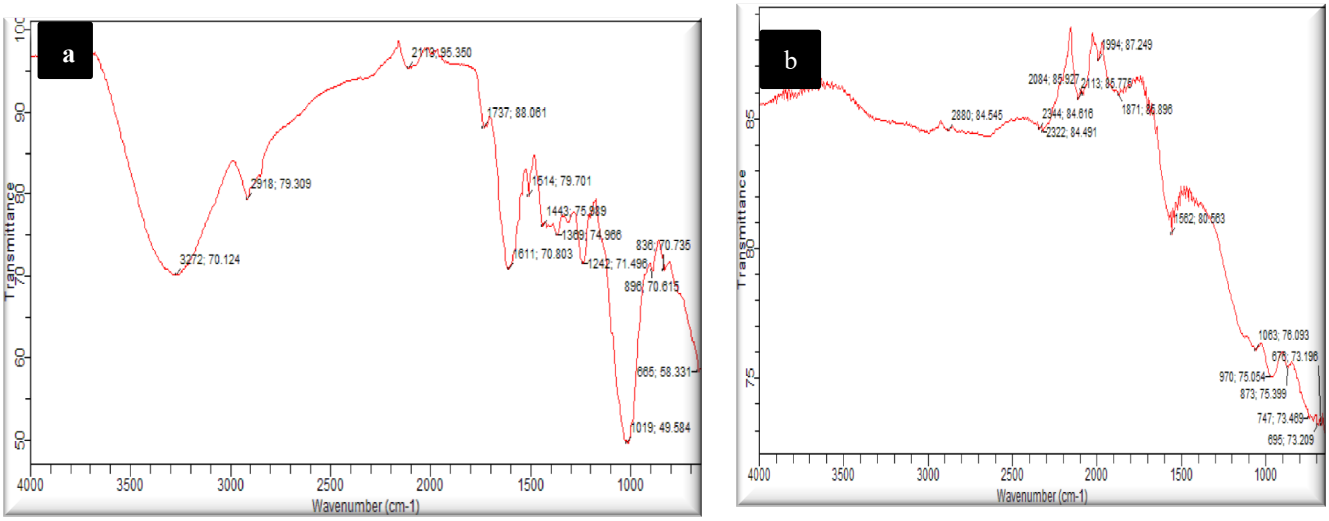

Figure 2: FTIR spectral of PP before and after adsorption of MB

Fig 3(a)-(b) shows the SEM micrographs of PP before adsorption and after adsorption on MB. The micrograph before adsorption showed the surface of PP to be highly rough and irregular which enhances better adsorption [11]. The micrograph after adsorption onto MB shows the morphology of the surface to be rough, heterogeneous and irregular with crevices which enhances better adsorption [12].

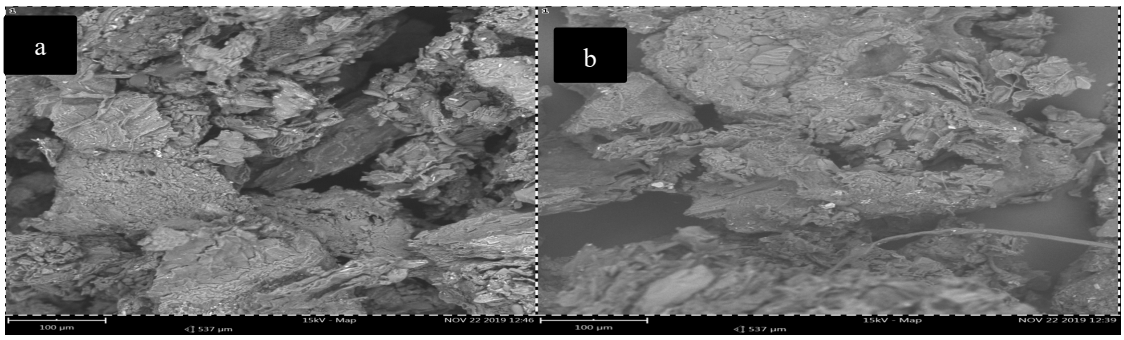

Figure 3. SEM Micrograph of PP (a) before and (b)after adsorption of MB

3.2 Batch Adsorption

The effect of initial dye concentration on the adsorption of MB onto PP is shown in figure 4.2 One of the most important and widely studied aspects of adsorption of organic pollutants to aqueous solution is the effect of solute concentration on adsorption affinity, given that, in theory, this should convey important information about adsorption mechanisms. As the initial concentration was increased from (10-60mg/l), the amount of dyes adsorbed on PP also increased. At low concentration, the available

driving force for transfer of these dye molecules onto the adsorbent particles is low, while at high concentration, there is a corresponding increase in the driving force, thereby enhancing the interaction between the dye's molecules in the aqueous phase and the active sites of the adsorbent. As a result of this, there was an increase in the uptake of MB molecules. Similar results were obtained on kinetics and equilibrium isotherms of pesticides adsorption onto boiler fly ash [15-16].

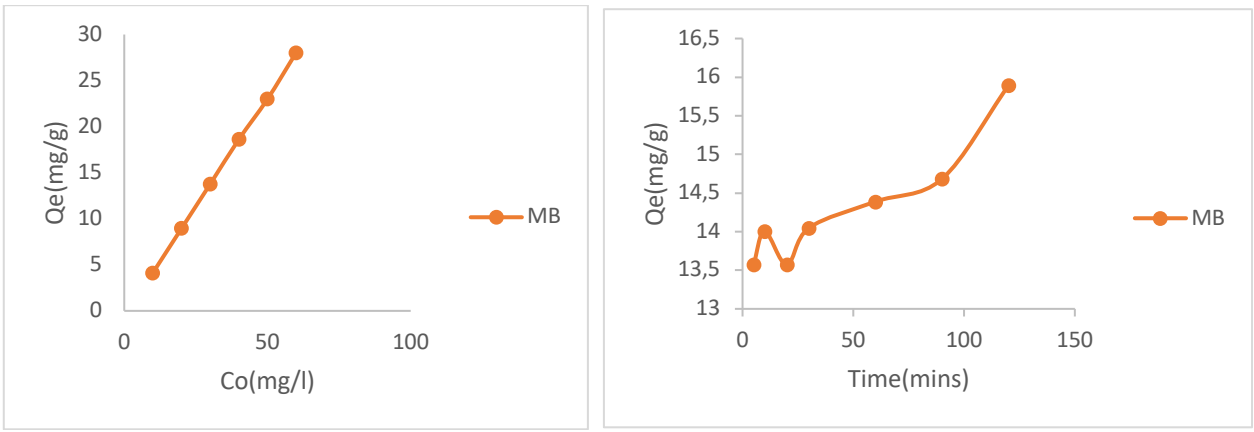

Figure 4.a: Effect of initial dye concentration on the adsorption of MB onto PP is shown in figure

The effect of contact time on the adsorption of MB onto PP shows that the extent of adsorption is rapid in the initial stages (5-60mins) and becomes slow in later stages till saturation is allowed [13] The final dye concentration did not vary significantly after 60mins from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 60mins. It is due to saturation of the active site which do not allow further adsorption to take place. In industries, this contact time is very important for process optimization. This is in agreement with the work of [14]. The initial rapid phase may also be due to the increased number of vacant sites available at the initial stage whereas after 60 minutes decreasing effect is due to vacant surface sites are not easy to be occupied due to repulsive forces.

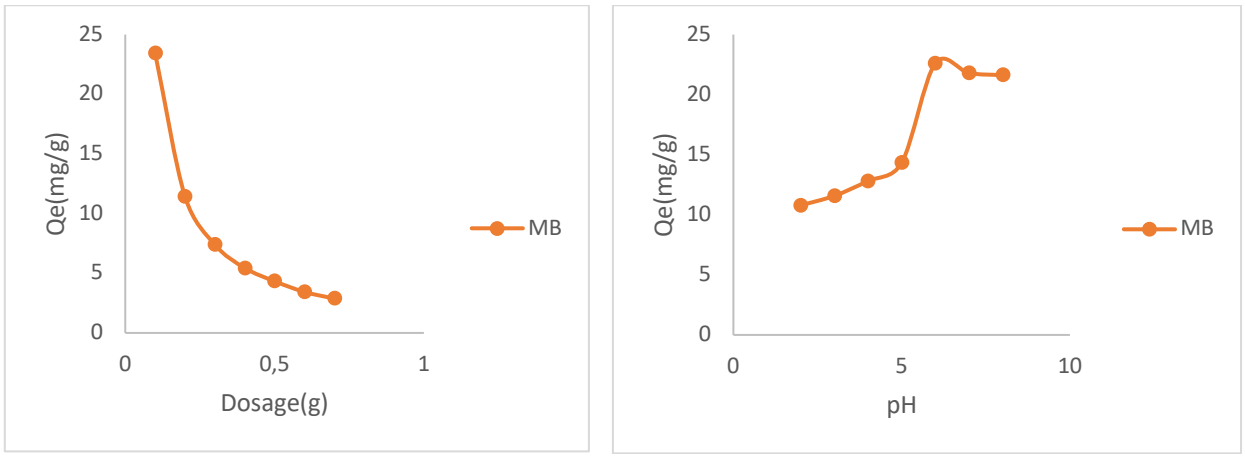

Figure 4.b effect of contact time on the adsorption of MB onto PP

The variation of equilibrium amount of adsorbent dosage was studied by varying amounts of adsorbent dosage from (0.1 to 0.7g) while other parameters were kept constant. It was revealed that the amount of dyes adsorbed first increased with an increase in adsorbent dosage due to increased surface area and more adsorption sites available for binding [17]. The maximum removal for MB dyes was attained at 0.1g given values 93.77% removal. The decrease in adsorption per unit mass with increasing dosage of adsorbent is attributed to possible overlapping of adsorption sites as adsorbent dosage increases which will equally reduce the effective adsorption sites. Similar trends were reported by other authors [18-19]. The effect of pH on the adsorption of MB shows that at high pH values, cationic dyes are adsorbed due to the negatively charged surface sites of the adsorbent. In the present adsorption system, the adsorption capacity of this dye is highest at pH 6 with maximum adsorption capacity of 22.61. This is in agreement with the work of adsorption of dyes by an author [20]

3.3 Adsorption isotherm

Curve fittings to identify best isotherms, for the adsorption of MB on PP was fitted in Langmuir, Freundlich, Temkin and Dubunin- Radushkevich isotherms as shown in Table 1

Table 1. Langmuir**,** Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of methylene blue onto PP

Isotherm	Methylene Blue
Langmuir	
Q_o(mg/g)	134.23
K_L(L/mg)	0.5610
R_L	0.7510
R^2	0.8261
Freundlich	
1/n	2.0567
N	0.4862
K_F	0.6002
R^2	0.9121
Temkin	
A_T(L/mg)	0.3160
b_T	12.670
B	78.560
R^2	0.8512
Dubinin-Radushkevich	
q_s(mg/g)	65.12
K_{ad}(mol^2/KJ^2)	1×10^{-9}
E(KJ/mol)	0.1390
R^2	0.7757

Table 1 shows Langmuir, Freundlich, Temkin Isotherm and Dubinin- Radushkevich constants for the adsorption of MB onto PP. The values of R^2 suggest that the Freundlich isotherm provides the best conformity with experimental data for MB. However, it can be concluded that the process be assumed to be a physical adsorption.

3.4 Kinetic study

The pseudo-second-order kinetic model fits the experimental data quite well. The correlation coefficients (R^2) value of MB was found to be 0.9962 which shows that the experimental and theoretical uptakes are in good agreement. This indicates the applicability of the pseudo second-order kinetic model to describe the adsorption process of MB onto the adsorbent. Table 2 shows the kinetic parameters for the adsorption of MB onto PP

Table 2. Kinetic parameters for the adsorption of MB onto PP

Kinetic Model	Parameters	MB
Pseudo First order	Qe Exp (mg/g)	15.8897
	Qe Cal (mg/g)	4.9000
	K_1 (min^{-s})	0.0080
	R^2	0.0026
Pseudo second order	Qe exp (mg/g)	15.8897
	Qe cal (mg/g)	15.7230
	K_2 (min^{-s})	0.0460
	R^2	0.9960
Elovich	A	1.4214
	B	0.4110
	R^2	0.6464
Intra-particle diffusion	K_3	0.3601
	C	18.4314
	R^2	0.8032

The pseudo-second-order kinetic model fits the experimental data quite well. The correlation coefficients (R^2) value of MB was found to be 0.9962 which shows that the experimental and theoretical uptakes are in good agreement. This indicates the applicability of the pseudo second-order kinetic model to describe the adsorption process of MB onto the adsorbent.

3.5 Thermodynamic study

Thermodynamic parameters give advantageous information about the adsorption nature of this work. The effect of temperature on the adsorption of MB onto PP were studied by varying the temperature from 303 to 333k while keeping all other parameters (pH=6, adsorbent dosage 0.1g, initial MB

concentration=60mg/l, t=60min) at optimized values. The thermodynamic constants such as changes in free energy (ΔG◦), enthalpy (ΔH◦) and entropy (ΔS◦) give useful view about the feasibility and the spontaneous nature of the adsorption process and generally can be obtained from equation (13)

$$\Delta G^{\circ} = -RT \ln K_c \quad (13)$$

$$\ln k_c = -\Delta G^{\circ}/RT = -(\Delta H^{\circ}/RT) + (\Delta S^{\circ}/R) \quad (14)$$

Where R is the gas constant (8.314 J/molK), T is the absolute temperature (K), and k_c is the thermodynamic equilibrium constant and can be obtained from the relation (Calvete *et al.,* 2010):

$$k_c = C_a/C_e \quad (15)$$

Where C_a is mg of MB adsorbed per litter and C_e is the equilibrium MB concentration of solution (mg/L). Both ΔH◦ and ΔG◦ can be obtained from the slope and intercept of van't Hoff plot of lnK_c versus 1/T. The data are tabulated in Table 3. As can be seen on the Table 3, the positive value of ΔH^o indicates that the adsorption of the MB onto PP is an endothermic reaction, and the adsorption occurs easily at higher temperature. The negative ΔS^o indicate decreased randomness at the solid-liquid interface during adsorption of MB [26-28]. The negative values of ΔG^o show the adsorption is thermodynamically feasible and spontaneous. Also, the ΔG^o value increase as the temperature is being increased from 303 to 333 K. The magnitude of ΔH◦ describes the type of adsorption, where the heat of Physical adsorption falls within the range of 2.1–20.9 kJ/mol this suggests that the adsorption of the MB on the PP is physisorption presented in Table 3.

Table 3. Thermodynamic parameters for the adsorption of MB on PP

T(K)	ΔG^o(KJ/mol)	ΔH^o(KJ/mol)	ΔS^o(J/mol.k)
303	-2483.60	0.2690	-0.0143
313	-2886.50		
323	-3628.00		
333	-4516.08		

3.6 Quantum Chemical Studies

Density functional theory is considered as a unique approach to study the reaction mechanism of adsorption process. Table 4 shows calculated quantum chemical parameters of MB molecules. The parameters include the frontier molecular energies (the energy of the highest occupied molecular orbital, E_{HOMO}, the energy of the lowest unoccupied molecular orbital, E_{LUMO} and the energy gap, ΔE), the binding energy (E_B), ionization potential(I), electron affinity(A), global hardness, global softness, the surface area (SA) and surface volume (SV) [29]. E_{HOMO} is responsible for the ability of molecules to donate electron. E_{LUMO} is the measure of the ability of molecules to accept electron. The higher the

E_{HOMO}, the lower the E_{LUMO}, the better the adsorption. Ionization potential is an absolute value of E_{HOMO} which indicates the ability of the molecule to donate electron. Electron affinity (A) is an absolute value of E_{LUMO}. ΔE explains the reactivity of the dyes towards adsorption on the PP surface. The lower the band gap energy, the higher the ionization potential. The energy gap (ΔE) is also an index that is related to molecular hardness or softness. Soft molecules have lower ΔE (and vice versa) hence better adsorption tendency than hard molecule [27]. Therefore, the ease of adsorption is expected to correlate with 2decreasing value of ΔE. From the results presented in table 3.4, the strength of a chemical compound, hence its reactivity can also be assessed by its binding energy (E_B), surface volume (SV), surface area (SA). The higher the values of (SV), (SA), (E_B) for a molecule, the more difficult the compound will be hydrated, protonated or become adsorbed on a surface. Better adsorption of MB is also favoured by lower values of SA and SV. The larger the surface area and surface volume of the adsorbate, the more difficult it will compete to fit into the adsorption matrix of the adsorbent [27-29].

Table 4. Calculated Quantum Chemical Parameters for MB Dyes

Properties	Methylene Blue
E_{HOMO} (eV)	-11.13Ev
E_{LUMO} (eV)	-5.52eV
ΔE (eV)	5.61
Binding energy (kcal/mol)	-358.19
Ionization potential (I) (eV)	11.13eV
Electron affinity (A) (eV)	5.52eV
Global hardness (Ƞ)	-2.81
Global softness (б)	8.33
Absolute electronegativity (χ)	2.3265
Surface area (SA) ($Å^2$)	309.64
Surface volume (SV) ($Å^3$)	297.95

4. Conclusion

PP were used for the removal of methylene blue from aqueous solution using batch adsorption method. The experimental result revealed that the removal of MB was dependent on pH, initial concentration and contact time. The rate of adsorption is always high at the beginning of each experiment. In addition, the higher the initial MB concentration, the higher the amount of MB adsorbed. physisorption mechanism favours the adsorption of MB on PP as the adsorption characteristic was found to follow the pseudo second-order kinetics model and Langmuir adsorption isotherm model with R^2-value 0.999. Thermodynamic studies showed that the adsorption processes were endothermic and mostly spontaneous. Quantum chemical calculated showed how PP can be used as a potential adsorbent for the removal of MB. Therefore; PP can be used as adsorbents for the removal of MB and structurally related herbicides from waste water and industrial effluents.

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