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REAL-WORLD MIXED PLASTICS WASTE INTO ACTIVATED CARBON AND ITS PERFORMANCE IN ADSORPTION OF BASIC DYE FROM TEXTILE EFFLUENT

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The char prepared from three different types highly used plastics wastes, i.e., polypropylene (PP), polyethyleneterepthalate (PET), polyvinylchloride (PVC) with HZSM-5 catalyst was activated by CO_2 at 900^{o}C. The prepared plastic waste activated carbon (PWAC) was characterized by SEM, XRD and FT-IR analysis. Experiment was carried out equilibrium, kinetics and thermodynamics of basic green 4 adsorption onto PWAC as function of pH, adsorbent dosage, initial concentration and temperature. The equilibrium adsorption isotherms models of Langmuir, Freundlich, Temkin, Halsey, Jovanovic and Dubinin-Radushkevich were tested for the quantitative description of the dye adsorption. The Langmuir isotherm provided the best fit for dye adsorption onto the prepared activated carbon and the maximum monolayer adsorption capacity of Basic green 4 was found to be 92.73 mg.g^{-1}. The adsorption process well fitted for pseudo second order kinetic model. The activation energy of the system was calculated as 1.434 kJ/mol. Thermodynamic parameters revealed that the adsoption was a physical process, spontaneous and exothermic in nature. The kinetic and isotherm model data was confirmed by linear error analysis.

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Keywords: PWAC; Adsorption; Basic green ; Error analysis; isotherm models; Kinetics; Thermodynamics

1. Introduction

In the present scenario plastics have emerge to be an inseparable part of our society, due to its low cost, light weight, strength to weight ratio, easy processing, durability, etc. Predominantly with the industrial growth in the last 50 years, global consumption of plastic has significantly increased, mainly up to 400 million tons in 2016 [1]. As the consumption of plastics product produce the vast amount of solid waste, pose problem of significant concern [2].The recycling of plastic solid waste is a serious challenge for industrialized countries worldwide and many processes related to treatment plastics waste schemes are incineration and recycling and landfilling [3-5]. Pyrolysis processes consists thermal degradation of plastic waste such as PP, PET add PVC in an N_2 atmosphere to recover the oil and combustible gases out of the polymer waste, although some drawback, such as the usage of the chars produced to be tackled instantaneously. Char produces a value added materials such as carbon adsorbent is one of the most environment friendly ways for recycling these types of waste [6-10]. Many researchers have carried out such work to produce activated carbon from agricultural wastes [11-12] and municipal solid waste. The pyrolysed char residue of the plastics waste can be a good precursor, containing a high percent of carbon to produce selective carbon adsorbent for dye removal from textile effluent [13].

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Adsorption of basic green 4 dye using PWAC adsorbent is generally low-cost and versatile, and illustrate one of the most commonly used methods for removing synthetic dyes from wastewater [14]. The main focus of this study was to evaluate the sorption characteristics of PWAC with basic green 4 from textile industrial effluents. The effects of different parameters such as the pH, the initial dye concentration, adsorption dosage on the adsorption, contact time, and temperature were studied. Few isotherm models were used in this study namely Langmuir, Freundlich, DR, Halsey, Temkin and Jovanovic models. The Langmuir model gives the better fit compared with the other models with the value of correlation coefficient and error analysis.

2. Materials and Methods

2.1. Preparation of the adsorbent (PWAC)

The plastic mixture used for the experiment was composed of 38% polyethyleneterepthalate (PET), 38% polyvinyl chloride (PVC), 19% polypropylene (PP) and 5% HZSM-5 (catalyst was obtained from a Sud-Chemie India Pvt. Ltd) were placed in tubular reactor and heated at 10° C per min to 700 °C for 1h in N_2 atmosphere. 10% carbon yield was obtained after the pyrolysis and residues were powdered with mortar and then washed with 200 ml of concentrated hydrochloric acid for using magnetic stirrer for 1h to remove the inorganic impurities. Finally the residue rinsed with distilled water until the filtrate p^H becomes 7. The final char was dried in a hot air oven at 100°C and it was left to cool over-night. The final activation of char carried out in a specially designed purpose made stainless steel reactor at 800 °C in the presence of CO_2.

2.2. Preparation of adsorbate

Basic green 4 (Malachite green (MG), (CI=42,000, chemical formula $C_{50}H_{52}N_4O_8$, MW=927.03 g/mol) dye was obtained from a nearby textile unit (λ_{max} - 617 nm). Precise quantities of solid dye were dissolved in double distilled water to prepare the stock solutions of Basic green 4. Solutions of various concentrations of dye were obtained by diluting this stock solution. The pH of the prepared solutions was adjusted by using HCl and NaOH solutions strength of 0.01 N.

2.3. Error Analysis

To estimate the best apt of the isotherm models to the experimental data, the optimization technique require different statistical parameters to be well-defined. In this study, the best fit model was appraised by adjusted R^2, the Sum of the Square of the Errors (SSE), the Residual Root Mean Square Error (RMSE) and the chi-square test χ^2 expressed as follows[15-16].

$$\mathrm{SSE} = \sum (q_{e,cal} - q_{e,exp})^2$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{N-2}\sum_{i=1}^{n}(q_{e,exp} - q_{e,cal})^2}$$

$$\chi^2 = \sum_{i=1}^{n}\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}}$$

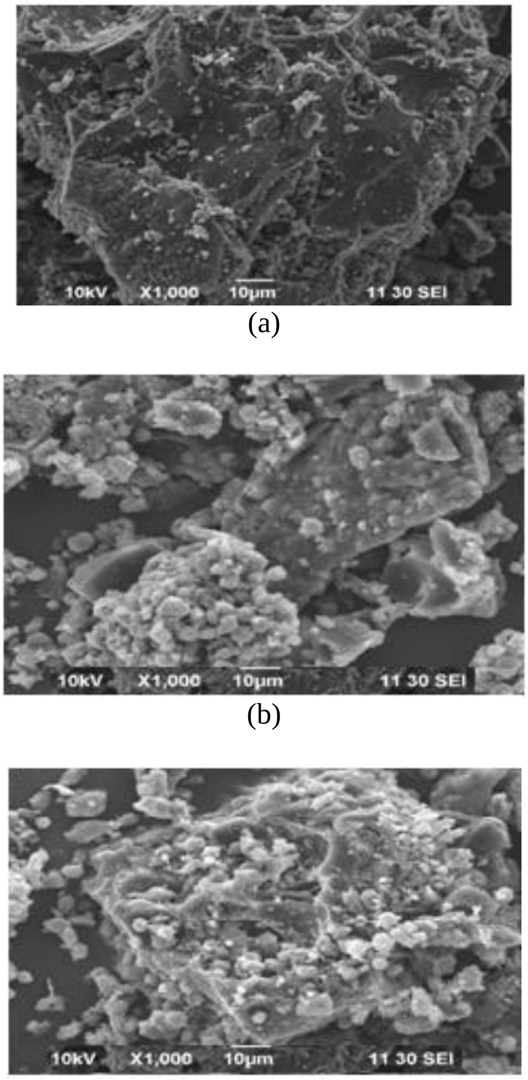
3. Results and discussion

3.1. Characterization of adsorbent

The Morphological characteristics of the samples were studied using JSM-5610LV Scanning Electron Microscope (SEM).The N_2 adsorption-desorption isotherms of activated carbon were measured at 77 K using N_2 adsorption analyzer (Nova, Quantachrome instrument). Fourier Transform Infrared (FT-IR) measurements were carried out using Shimadzu instrument.

3.2. Scanning Electron Microscope analysis

The surface morphology of raw char, activated plastic waste carbon and dye loaded carbon are given in Fig.1a, b&c. From fig. 1a the particles are compact and also ununiformly distributed. The inner carbonaceous phase also becomes fragmented, indicating that the carbon skeleton is severely broken and a “loose sponge” structure is formed during the activating process. The surface of PWAC looks much smoother and pores are irregularly arranged . Small pores can be seen on the inner walls of larger pores and it made difficult to determine individual particle size by SEM [17]. The dye molecules are adsorbed on surface of the activated carbon was shown in fig. 1c.



(a)

(b)

(c)

Fig. 1. SEM image of a) Char b) PWAC and c) dye loaded PWAC

3.3. FT-IR Analysis

The FT-IR spectroscopic study of the raw char, resultant activated plastic waste carbon and dye loaded activated carbon are shown in Fig. 2a, b&c. The peak observed at 3743.83 and 3720.69 cm^{-1} are due to the presence of hydroxyl groups (O–H stretch) on the surface of the material. The skeletal c=c in aromatic ring cause two bands at about 1541.12 cm^{-1} and 1421.54. The peak at 1421.54 cm^{-1} is due to the symmetric stretching of alkene (C=C) group, respectively. The peak obtained at 1220.94 cm^{-1} (C–O stretch) could be attributed to phenol, ester or ether groups. The band at 1093.64 cm^{-1} could also be assigned to alcoholic (R-OH) groups. The peaks found at 798.53 cm^{-1} is due to Si-O or C-O stretching in alcohol, ether or hydroxyl groups and Si-H groups. The band at 675.09 cm^{-1} indicates the alkane C-H bending vibration. Absorption band region at 621.08 cm^{-1} attributed to C=O out of plane vibration. Si–O bending vibrations contributing to the strong absorptions in the 400–600 cm^{-1} region [18]. The absorption band region below 550 cm^{-1} show the Si-O stretching or Si-O-Al stretching may be due to the presence of catalyst. Absorption band at 2300-2400 cm^{-1} could be related to the presence of –COOH group, it was shown in figure 2c.

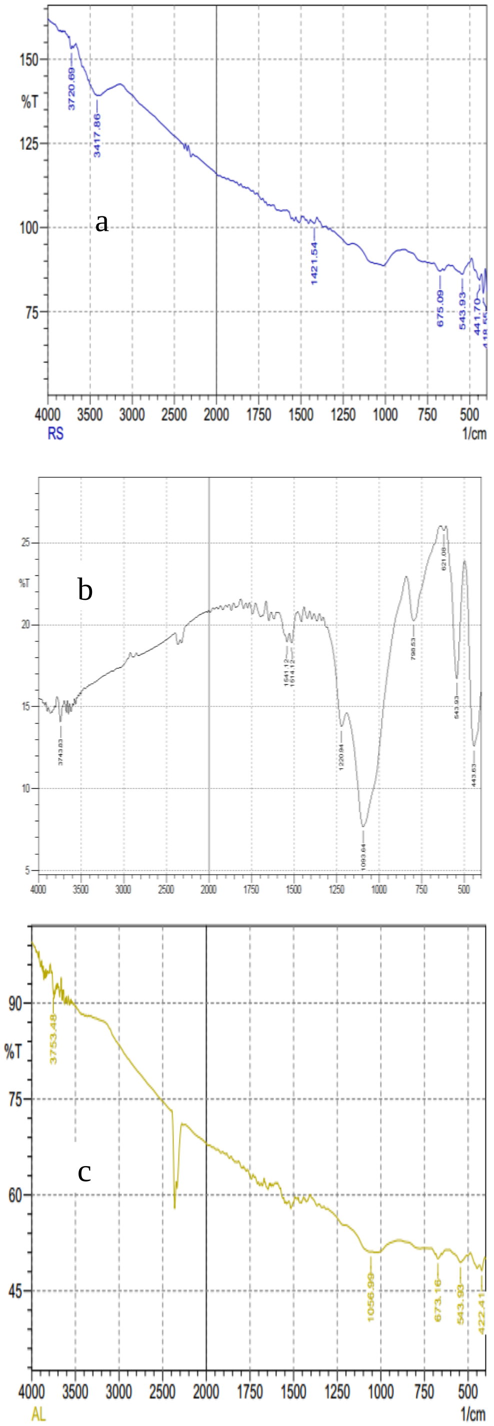


Fig. 2. FT-IR Spectra of a) Raw, b) PWAC and c) dye loaded carbon

4.3 Elemental analysis

The results of the elemental analyses of the raw and plastic waste activated carbon show in fig. 3a and 3b. The raw char contains 52.76% of Carbon, 23.16% of Oxygen, 10.38% of Silicon and 0.88% of Aluminum, 6.35% of chlorine and 6.47% of calcium. The activated plastic waste carbon consist 61.27% of carbon, 22.4% of oxygen, 6.04% of aluminum and 10.29% of Silicon. The pyrolysis and activation distinctly remove the majority of heteroatoms, such as calcium and chlorine from the waste plastic materials, resulting in a significant increase in the carbon content of the activated carbon.

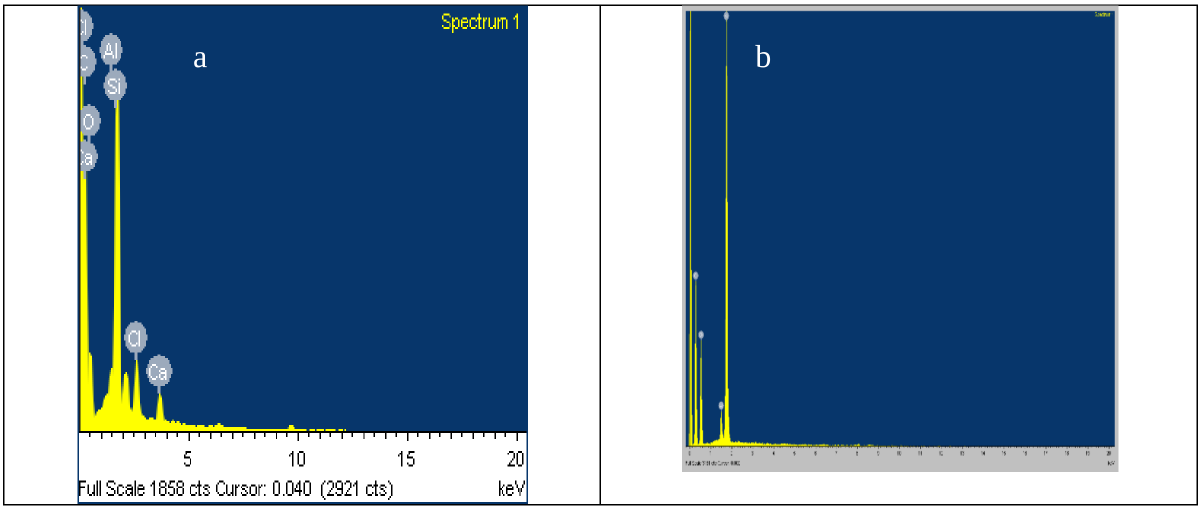


Fig.3. EDAX for a) Char and b) PWAC

3.5. Adsorption Isotherm

The adsorption isotherm describes how adsorbates interact with adsorbents and therefore it is critical in optimizing the use of adsorbents. The adsorption isotherm models relate to the equilibrium concentration of the studied component in the bulk liquid phase and in the adsorbent. Different models have been used to correlate the experimental adsorption data. Some of them consider an ideal behavior of the system, without taking into account the possible sources of non-ideal behavior, like adsorbate-adsorbate interactions in the adsorbed phase. The heterogeneity of the adsorbent surface is the loss of symmetry, clustering or dissociation of the adsorbate and the interaction among the components of the bulk liquid phase. In some cases, the formation of associates the limited solubility of the constituents is in the bulk liquid phase, the irreversibility of the adsorption or even the existence of synergetic effects [19]. The various isotherm models are used to find the best fit of the isotherm model in the adsorption of basic dye onto plastic waste activated carbon. The six isotherm models are used for the present study namely Langmuir, Freundlich, Temkin, DR, Halsey and Jovanovic and equation of the models are given in table (1).

3.5.1. Langmuir Isotherm model

The sorption data were evaluated according to the linear form of the Langmuir isotherm. The plots of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) for basic green 4 are presented in Fig.3 and the linear isotherm constants Q_0, K_L and the error values are presented in Table 2. These isotherms were found to be linear over the whole concentration range studied with extremely higher coefficients of determination (Table 2). The R^2 values suggest that the Langmuir isotherm provides a good model of the sorption system. The sorption constant, K_L and sorption capacity, Q_0, for basic green 4 are higher than other models. The Langmuir data from the other three error analysis methods are presented in Table 2. In all cases, all the error values for any parameter set are lower than the same errors determined for the linear form of the isotherm. The parameter values that are even close to those obtained by linearization are the SSE, RMSE and Chi square. By comparing the magnitudes of the error values together with the range of variation in the isotherm parameters suggests that the Langmuir isotherm provided a good model for the sorption of basic green 4 onto PWAC.

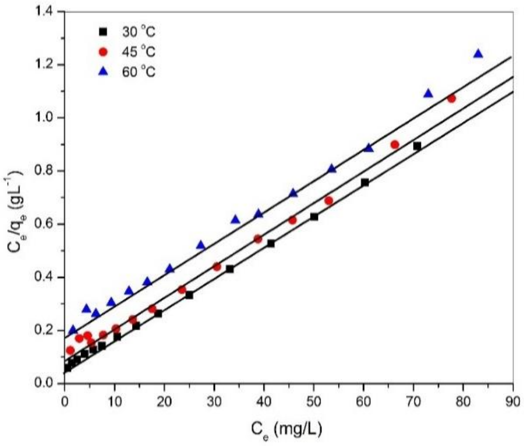


Fig. 3. Effect of Langmuir plot for the adsorption of Basic Green 4 onto PWAC

The essential features of Langmuir adsorption isotherm parameter can be used to predict the affinity between the sorbate and sorbent using a dimensionless constant called separation factor or equilibrium parameter R_L, which is expressed by the following relationship [20-21].

$$R_L = \frac{1}{(1 + bC_0)}$$

The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L=0), linear (R_L=1), unfavorable ($0<R_L<1$), or favorable [28]. The R_L values between 0 and 1 point to favorable adsorption. The R_L value in the present investigation was found to be 0.0307–0.542, signifying that the adsorption of the basic green 4 onto PWAC is favorable.

3.5.2. Freundlich Isotherm model

The constant K_f is an imprecise indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process [29]. If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption [30].The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants K_f and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. However, K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fit and whereas linear regression co-efficient is generally used to determine the validity of kinetic and isotherm models [31]. Specifically, the linear least-squares method and the linearly transformed equations have been usually applied to correlate sorption data where 1/n is a heterogeneity parameter, the smaller 1/n, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when 1/n = 1. If n lies between one and ten, this indicates a favorable sorption process [32]. From the data in table 2, that value of 1/n = 0.4169, 0.4772 and 0.5310 while n= 2.3986, 2.0956 and 1.8831 indicating that the sorption of basic green 4 onto PWAC is favorable, the similar results was obtained by [33]. Fig. 4 shows the linear plot of Freundlich adsorption isotherm model.

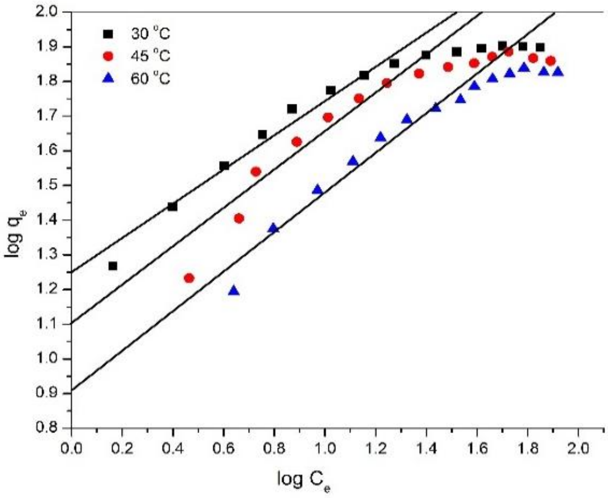


Fig.4. Effect of Freundlich plot for the adsorption of Basic Green 4 onto PWAC

In this case the error parameters are near by the obtained values by linearization, typically provide either the second best fit to the experimental data, based on the SSE, RMSE and Chi square errors. On this basis, Freundlich model gave a reasonable approximation to the optimum parameter. This concludes that the Langmuir adsorption isotherm is best compared with Freundlich isotherm in regression and other parameter values.

3.5.3. Temkin Isotherm

The Temkin isotherm model, also widely used in gas phase adsorption (with its application, rather limited to liquid-solid adsorption equilibrium) assumes adsorption to be characterized by a uniform distribution of binding energies up to some maximum value [34]. The sorption data were analyzed according to the linear form of the Temkin isotherm and the linear plots are shown in Fig. 5. Examination of the data shows that the Temkin isotherm does not provides a close fit to the sorption data, the linear isotherm constants and coefficients of determination are presented in Table 2.

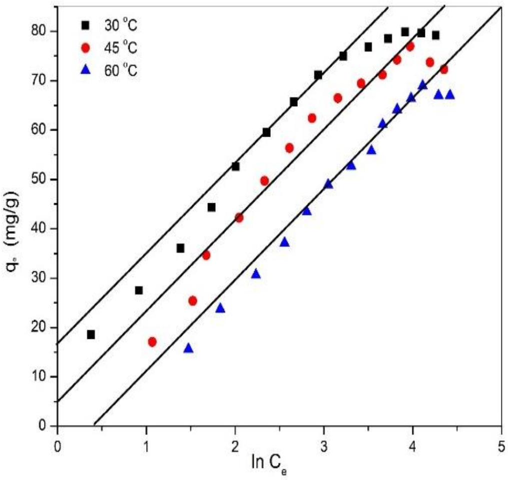


Fig. 5. Effect of Temkin plot for the adsorption of Basic Green 4 onto PWAC

The assumption of the error analysis Temkin isotherm model is not suitable for the adsorption of basic green 4 onto PWAC. β_T(Jmol^{-1})and α_T(L mg^{-1}), which is an indication of the heat of sorption indicating a physical adsorption process [35].

Table 1. List of isotherm models used for the present study

Model	Formula	Reference
Langmuir	$q_e = Q_m \frac{K_L C_e}{1 + K_L C_e}$	[22]
Freundlich	$q_e = K_F\, C_e^{1/n}$	[23]
Temkin	$q_e = \ln K_T C_e$	[24]
Halsey	$\log q_e = \frac{1}{n_H} \log K_H - \frac{1}{n_H} \log Ce$	[25]
Dubinin- Radushkevich	$q_e = q_{DR} \exp(-K_{DR}^2)$	[26]
Jovanovic	$\ln q_e = \ln q_{max} - K_J C_e$	[27]

3.5.4. Halsey Isotherm

Where K_H and n_H are the Halsey isotherm constant and exponent, respectively. This equation is apt for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of the adsorbent.

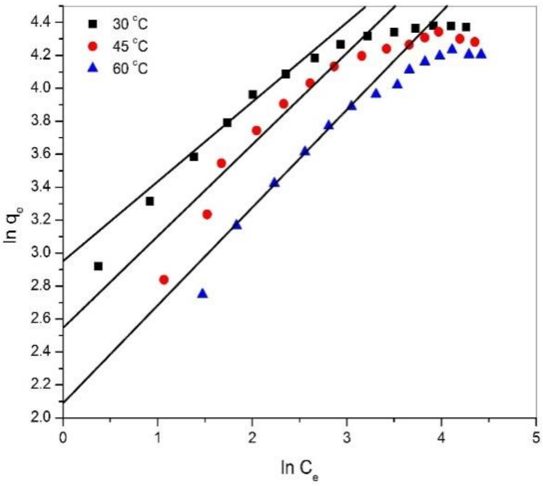


Fig. 6. Effect of Halsey plot for the adsorption of Basic Green 4 onto PWAC

In Fig. 6 shows the Halsey model and also could not describe the sorption of basic green 4 onto PWAC reasonably, because this model also assumes a multilayer behavior for the sorption of a sorbent onto adsorbent and its corresponding SSE, Chi-square and RMSE values in Table 2 coincided with this result. The values of RMSE and χ^2 for the Halsey model are slightly high in comparison with other models.

3.5.5. Dubinin–Radushkevich Isotherm model

The application of Dubinin–Radushkevich isotherm, which was mostly used for gas phase adsorption on activated carbon [36].The Dubinin-Radushkevich (D-R) isotherm model was applied to the data in order to deduce the heterogeneity of the surface energies of adsorption and the characteristic porosity of the adsorbent [37]. One of the unique features of the Dubinin-Radushkevich (DR) isotherm model lies on the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed $\ln q_e$ vs ε^2 the square of potential energy shows in Fig. 7, all suitable data will lie on the same curve, named as the characteristic curve [38].

Table 2. List of different model isotherm parameters and error analysis values

Model	**Isotherm Constants**	**Basic Green 4**		
		30 °C	**45 °C**	**60 °C**
Langmuir	Q_0(mg g^{-1})	86.24	84.03	77.95
	K_L(L mg^{-1})	0.2108	0.1245	0.0843
	R^2	0.9990	0.9900	0.9892
	SSE	0.0010	0.0120	0.0184
	χ^2	0.0040	0.0386	0.0475
	RMSE	0.0296	0.1016	0.1320
Freundlich	n	2.3986	2.0764	1.9602
	K_f(mg g^{-1})(L mg^{-1})$^{1/n}$	17.9227	12.4544	9.1454
	R^2	0.9030	0.8727	0.8745
	SSE	0.1037	0.1374	0.1287
	χ^2	0.0721	0.0956	0.0958
	RMSE	0.3111	0.3575	0.3455
Temkin	β_T(KJ mol^{-1})	16.4434	17.7736	16.9381
	α_T(L mg^{-1})	2.7982	1.3187	0.8596
	R^2	0.9684	0.9450	0.9578
	SSE	260.4087	395.7324	231.2898
	χ^2	5.5276	11.2560	6.0496
	RMSE	15.9862	18.1847	14.9410
Halsey	K_h(mg g^{-1})	1014.8987	188.0819	76.5823
	n	2.3986	2.0764	1.9602
	R^2	0.9684	0.9450	0.9578
	SSE	0.5502	0.7287	0.6828
	χ^2	0.1661	0.2203	0.2206
	RMSE	0.7163	0.8233	0.7955
D-R	K-DR(mol^2 KJ-^{2})	5.834E-06	1.479E-05	3.423E-05
	Q_m(mg g^{-1})	60.81	56.48	52.49
	R^2	0.7391	0.6907	0.7718
	SSE	1.4836	2.2469	1.3169
	χ^2	0.4401	0.7260	0.4112
	RMSE	1.1740	1.3408	0.9913
	E	0.0012	0.0019	0.0029
Jovanovic	q_{max}	1.0395	1.0439	1.0503
	K_J	0.0187	0.0178	0.0164
	R^2	0.4546	0.4663	0.5029
	SSE	3.0938	3.0548	2.7040
	χ^2	1.0899	1.0929	1.0098
	RMSE	1.5452	1.0929	1.4932

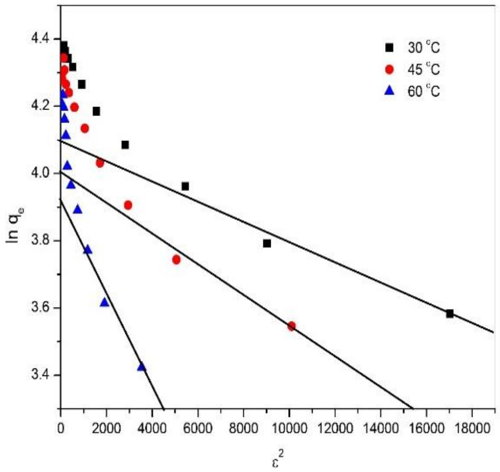


Fig. 7. Effect of DR plot for the adsorption of Basic Green 4 onto PWAC

Dubinin-Radushkevich model provides better fit with experimental data in comparison with Temkin, Freundlich, Halsey and Jovanovic models. The Dubinin-Radushkevich and Langmuir models are almost close together in comparison of their maximum monolayer adsorption capacity show that Dubinin- Radushkevich reveals a better agreement with experimental data. The value of Q_m was 60.81 mg/g which is more close to corresponding Langmuir parameter (Q_0) which is almost nearby (86.24 mg/g) of the adsorption capacity.

The mean adsorption energy (E) was found to be of 0.0012, 0.0019 and 0.0029 kJ/mol at 30 °C, 45 °C and 60 °C, respectively. If the value of E lies between 8 and 16kJ/mol the sorption process is a chemisorption one, while a values of below 8kJ/mol indicates a physical adsorption process. The value of the apparent energy of adsorption less than one indicated for the physisorption plays significant role in basic green 4 onto PWAC [39].Regression parameter R^2 showed (table 2) that this isotherm did not provide a very good fit to the experimental data. Dubinin-Radushkevich model provides poor agreement with experimental data and error analysis in comparison with other model.

3.5.6 Jovanovic Isotherm

In addition the same assumptions contained within the Langmuir model, the Jovanovic model considers the possibility of some mechanical contacts between the adsorbing and desorbing molecules [38].The q_{max} and K_J values are represented in table 2 and the plot was shown in Fig.8. The experimental and error analysis results show that the accordance of the Jovanovic model is not very good compared with other isotherm models.

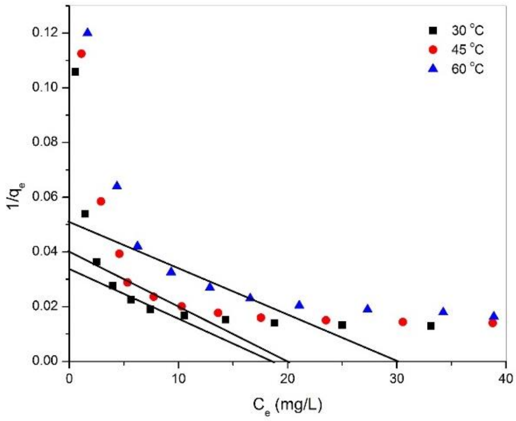


Fig. 8. Effect of Jovanovic plot for the adsorption of Basic Green 4 onto PWAC

3.6.Kinetic modelling for adsorption

The debates on adsorption equilibrium are vital in determining the effectiveness of adsorption; however, it is also essential to identify the types of adsorption mechanism in a given system. In this study four extensively used kinetic different models to predict the adsorption kinetic of basic green 4 on PWAC (pseudo first order, pseudo-second order, Elovich and intra-particle diffusion) models.

3.6.1Pseudo-First order kinetic model

The linearized form of pseudo-first-order model can be expressed as [40].

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

Where k_1 is the first-order rate constant, plots of log $(q_e - q_t)$ versus t Fig. 9 at different temperatures obtained by the experimental data with the Lagergren pseudo-first-order equation provided poor fits to straight lines with very poor R^2 values and large χ^2 values.

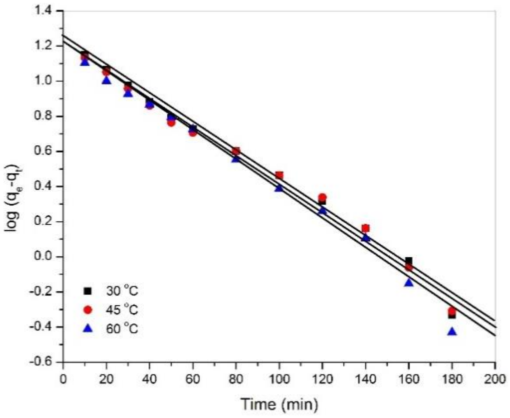


Fig. 9. Effect of pseudo first order plot for the adsorption of Basic green 4 onto PWAC

The high degree of nonlinearity indicates the inapplicability of the pseudo-first-order model for analysing the adsorption kinetics of basic green 4 by PWAC. This inapplicability was further corroborated by the disagreement between the experimental and model-predicted adsorption capacities. An irregularity in the change of pseudo-first-order rate constants with increasing temperature was also observed.

3.6.2. Pseudo-Second-Order Model

The linear form of the pseudo-second-order kinetic model is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

where k_2 $(gmg^{-1}min^{-1})$ is the rate constant of second-order adsorption. Analysis of the experimental data with the pseudo second-order kinetic model provided linear plots of t/q_t versus t. The fittings of the adsorption data with the pseudo-second order kinetic model for various temperatures are presented in Fig. 10. In contrast to the pseudo-first-order model, the pseudo-second-order model fitted the experimental data well, with exceptionally high correlation coefficients ($R^2 > 0.99$) and insignificant χ^2 values.

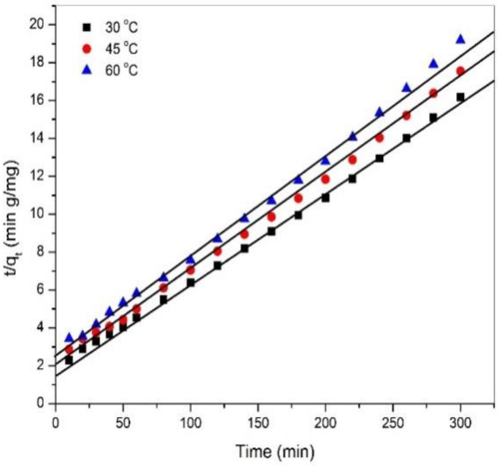


Fig. 10. Effect of pseudo second order plot for the adsorption of Basic green 4 onto PWAC

The very similar values of the adsorption capacities predicted by the pseudo-second-order model and obtained experimentally indicate the good agreement of this kinetic model with the process of basic greed 4 adsorption onto PWAC. The suitability of the pseudo-second-order model for interpreting the kinetic profile of this adsorption process was further confirmed by the regularity in the change in rate constant with the variation of the temperature. It can be observed from Table 1 that the pseudo-second-order rate constant (k_2) decreased as temperature increased. The reason for the decreasing value of k_2 with increasing temperature might be the higher competition of the dye molecules for the surface active sites. This confirms the exothermic nature of Basic green 4 adsorption onto PWAC [41].Thus, in view of these results, it can be concluded that the present adsorption system predominantly follows the pseudo-second-order kinetic model and that the mechanism of the overall process appears to be dependent on both the adsorbate and the adsorbent.

3.6.3. Elovich kinetic model

Elovich equation is one of the useful kinetic models for describing chemisorption. The simplified Elovich model is presented by

$$Q_t = \beta ln\alpha\beta + \frac{1}{\beta}\ln(t)$$

where A is the initial adsorption rate (mg/(g·min)) and B is desorption constant (g/mg) for a particular experiment.

The Elovich model does not predict any definite mechanism, it has been found useful in describing predominantly chemical adsorption on highly heterogeneous adsorbents. For the Elovich kinetic model, the correlation coefficient (R^2 =0.9731) is relatively high, it indicates that the adsorption of basic green 4 onto PWAC is a heterogeneous diffusion process controlled comprehensively by reaction rate and diffusion factor. Furthermore, the higher constant α value shows that chemical adsorption plays a significant role in the adsorption [42]. On increasing the temperature from 30 to 60 °C, the value of desorption constant β have slight significant variation. However, value of α increased as the temperature increased. The value α of and β as a function of solution temperature, on increasing the solution temperature from 30,45 and 60°C, the value of β increased from 0.224 to 0.248 g/mg due to the high availability of surface sites on adsorbent. On the other hand, an increase in the solution temperature from 30°C to 60°C leads to a decrease in the value of α from 1.287 to 0.869 mg/g min. This means that adsorption decreased while desorption increased during increasing solution temperature. However, the experimental data did not give a good correlation for these results at high solution temperature [43].

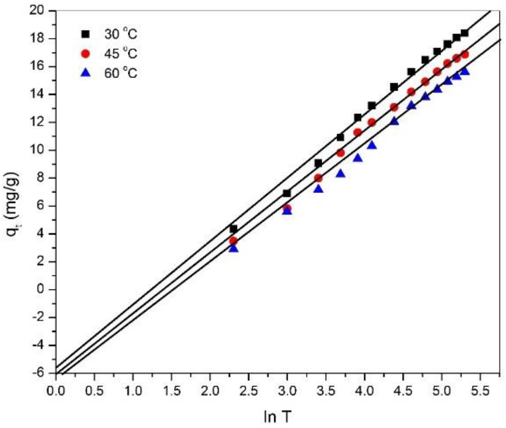


Fig.11. Effect of Elovich plot for the adsorption of Basic green 4 onto PWAC

3.6.4. Intraparticle Diffusion Model

The progress of adsorption can be monitored by the application of intraparticle diffusion model, and the rate-controlling step(s) can be determined. The intraparticle diffusion model is given by the following equation Weber and Morris.

$$q_t = k_{id} t^{1/2} + C$$

where k_{id} ($mg \cdot g^{-1} \cdot min^{-1/2}$) is the intraparticle diffusion rate constant and C ($mg \cdot g^{-1}$) is a constant characterizing boundary layer thickness. k_{id} and C can be determined from the slope and intercept of a plot drawn between q_t and $t^{1/2}$. In a plot of q_t versus $t^{1/2}$ multi-linear correlation can be observed. The first sharp part in the line shows film diffusion or adsorption. The second part is a more advanced adsorption section, that is, where diffusion is the rate-controlling grade. The third part is the equilibrium section, and in this part, intraparticle diffusion starts to slow down because of the very low concentration of the substance remaining in the solution [44]. If the linear section in the second part, that is, the intercept point (C) of the line representing intraparticle diffusion goes through the origin, it is concluded that the adsorption rate controlling step is only intraparticle diffusion. If not, it can be stated that adsorption rate is controlled by more than one mechanism.

To clarify the adsorption mechanism and determined rate controlling step(s), the intraparticle diffusion model was applied to equilibrium data. Graphs of q_t versus $t^{1/2}$ plotted for intraparticle diffusion show that the adsorption process essentially took place in three steps Fig. 12.

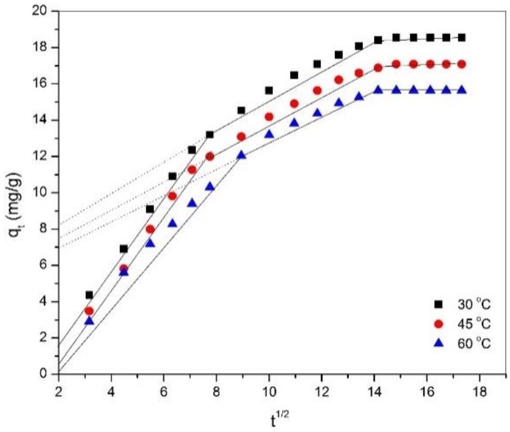


Fig.12. Effect of Intraparticle Diffusion plot for the adsorption of Basic green 4 onto PWAC
Within the first minute, a very fast adsorption takes place in the film layer on PWAC surface.

Then, intraparticle diffusion of basic green 4 molecules toward the pores in inner surface of PWAC starts, which indicates the migration of basic green 4 dye molecules toward the sites where actual adsorption takes place. This step is thought to be the rate-determining or rate-limiting step. However, since none of C constants obtained for intraparticle diffusion approach zero (Table 1), it emerges that adsorption rate is not only controlled by intraparticle diffusion. Therefore, the adsorption rate is controlled by film diffusion along with intraparticle diffusion [45].

Table 3 shows the contribution of adsorption stages to adsorption at the end of adsorption process that has taken place in three stages being film diffusion on exterior surfaces, intraparticle diffusion toward the inside of pores, and equilibrium. The most important point that has to be considered here is that, for all concentrations, film diffusion was completed within the first minute at the end of a very fast process. Moreover, border layer diffusion (film diffusion) that has taken place within the first 1 min contributes the most to adsorption.

3.6.5. Effect of Temperature on the Adsorption of basic green 4 and Adsorption Thermodynamics

To study the effect of temperature on basic green 4 adsorption on PWAC, dye solution with a concentration of 20 mg·L^{-1} and pH of 6 at various temperatures ranging between (30 and 60) °C were treated with 100 mg of PWAC for 3.0 h. The analysed data revels that the adsorption efficiency decreased with increasing temperature, suggesting that basic green 4 adsorption on PWAC has an exothermic nature.

Thermodynamic parameters related to the adsorption process, i.e. Gibb's free energy change (ΔG^o, kJ mol^{-1}), enthalpy change (ΔH^o, kJ mol^{-1}) and entropy change (ΔS^o, J mol^{-1} K^{-1}) were determined by the following equations:

$$\Delta G^0 = -RT\ln K_0$$

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

Thermodynamic parameters can be determined by the adsorption graph plotted as a function of temperature. ΔG^o, ΔS^o, and ΔH^o values were determined from a graph of ln K_0 versus 1/T. It is seen in Table 4 shows that all ΔG^o values are negative; suggesting that basic green 4 adsorption on PWAC takes place spontaneously. A/ΔH^o value of -35.60 shows that the reaction is exothermic and the adsorption advances by physical adsorption [46]. Negative ΔS^o values indicate the randomness in the solid – solution interface [47].

Table 3. List of kinetic and error parameter values for the adsorption of basic green 4 dye onto PWAC

Kinetic Model		**Temperature**		
		30 °C	**45 °C**	**60 °C**
Pseudo-first Order	K_1 (min^{-1})	-0.0166	-0.0163	-0.0175
	R^2	0.9896	0.9886	0.9887
	SSE	2.7699	2.6846	2.2839
	χ^2	5.2731	0.9769	1.7700
	RMSE	1.6570	1.6307	1.5016
Pseudo-second Order	K_2 (g/mg min)	0.0013	0.0012	0.0011
	h	0.5744	0.4771	0.4070
	R^2	0.9986	0.9975	0.9967
	SSE	0.4739	0.8119	1.5039
	χ^2	0.0592	0.1160	0.1705
	RMSE	0.6801	0.9226	1.2989
Elovich	α	1.2873	1.0416	0.8696
	β	0.2249	0.2346	0.2480
	R^2	0.9550	0.8852	0.9731

	SSE	7.2879	6.4434	5.8275
	χ^2	0.5324	0.5498	0.4345
	RMSE	2.9225	2.7587	2.5363
IPD	K_{id}	1.3725	1.3086	1.2459
	R^2	0.9550	0.8852	0.9731
	SSE	39.5724	35.6428	29.7825
	χ^2	4.4810	4.8524	4.3268
	RMSE	6.6879	6.3701	5.6486

Table 4.Thermodynamic and activation energy parameters for the adsorption of basic green 4 dye onto PWAC

Dye	T(K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	Ea(kJ/mol)
Basic Green 4	303	-6.4136	-35.6027	-96.6259	1.4342
	318	-4.6805			
	333	-3.5332			

The negative value of ΔS^o suggests the formation of ordered activated complex and an associated mechanism for the adsorption of dye on PWAC [48].

3.6.6. Activation energy Determination

To estimate the activation energy for sorption of dyes onto PWAC using the Arrhenius equation:

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

where, E is the activation energy (KJ mol^{-1}), k is the rate constant of sorption (g mg^{-1} min^{-1}), A is the pre-exponential factor (g mg^{-1}min^{-1}), R is the general gas constant (J mol^{-1} K^{-1}) and T is the temperature (K).

The plot of lnK vs 1/T is represented in Fig. 7. The energy of activation (Ea) is 1.4342 KJ/mol. lower than 40 KJ/mol, indicating that the process follows physisorption mechanism. The adsorption of basic green 4 dye onto PWAC shows that the rate limiting step in the process is physically controlled [49].on increasing the temperature there is augmentation in the probability of colloiding molecules capturing one another [50].

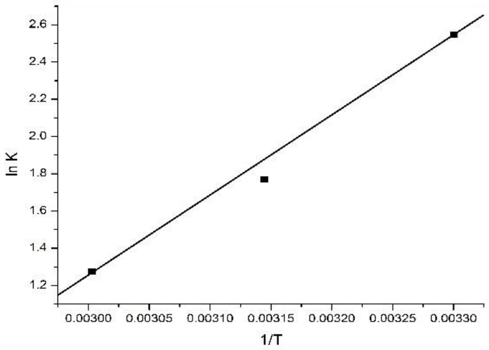


Fig.7. Effect of 1/T vs ln K plot for the adsorption of Basic green 4 onto PWAC

4. Conclusion

This approach provides a novel activated carbon precursor of waste plastic consisting of PP, PET, PVC and HZSM-5 catalyst into high value added PWAC. More importantly PWAC was demonstrated to show the high performance in the uptake of Basic green 4. The experimental data are well represented by the Langmuir isotherm equations to determine the extent and degree of favorability of adsorption compared with other adsorption isotherm models. The Langmuir monolayer saturation capacity was 86.24 mg/g. The results showed that the Langmuir model provides best fit with lowest R^2 and SSE, chi square, RMSE values, since the adsorption curves have a clear saturation plateau. The adsorption of PWAC follows pseudo second order kinetic model. The values of SSE, χ^2, RMSE was very low for pseudo second order model compared with other kinetic models represents the best fit. The negative enthalpy proves that the adsorption of basic green 4 onto PWAC is exothermic in nature.

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