Preparation, Characterization and Utilization of Activated Carbon Prepared from Putrescible Vegetable Waste for the Removal of Malachite Green from its Aqueous Solution

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Activated carbon of high adsorption capacities and highly active surface properties were prepared from putrescible vegetable waste material. Chemical activation was done by impregnating the raw material with H_3PO_4 to get phosphoric acid activated carbon (PAAC). Phosphoric acid activated carbon was sieved to different particle sizes and particle size between 125-200 μm was utilized for adsorption studies. Physico-chemical properties of PAAC were analyzed to find out its adsorptive property. Porous nature of the activated carbon before and after adsorption was captured through scanning electron microscope. Surface area for PAAC was found to be 603.7 m^2/g. Spectral studies like Fourier transform infrared spectrometry analysis, X-ray diffraction spectroscopy and SEM elemental analysis were done to characterize the carbon. The adsorption of malachite green from aqueous solution on PAAC was described by Langmuir, Freundlich and Dubnin-Radushkevich isotherms. All the three isotherms revealed that the adsorption of malachite green onto PAAC was favourable. It was found that PAAC follow pseudo second order kinetics for the adsorption of malachite green from its aqueous solution. Intraparticle diffusion model concluded that surface adsorption and it was concurrently operating during the malachite green and PAAC interactions. Results thus revealed that the phosphoric acid activated carbon prepared from putrescible vegetable waste could be effectively employed for cationic dye removal. The present work suggested a novel method for an effective solid waste management and their conversion into value added products.

Keywords: Putrescible vegetable waste, Adsorption, Cationic dye, Malachite green, Isotherms, Activated carbon.

INTRODUCTION

In all the urban and rural areas, huge quantity of solid waste is generated during various activities. These wastes are to be stored, collected, transported, processed and disposed of in an environment friendly manner, so as to keep the environment neat and clean. In spite of incurring huge expenditure, the services that are provided to the solid waste management are not fulfilling the requirement, causing public health hazards and nuisance. Hence, there is a strong need to develop appropriate technology for the proper management of urban as well as rural solid wastes.

Solid waste can be defined as the waste that is not transported by water but that has been rejected for further use. Due to rapid urbanization the amount of solid waste problems is also increasing. Solid waste generated from houses increased significantly in quantity and complexity with the advent of the "throwaway" society and the growth of the packaged and processed food industry. Thus large amount of municipal solid wastes are generated which includes putrescible (biodegradable)[1] solid wastes called garbage and non-putrescible solid wastes called rubbish.

The putrescible solid wastes were particularly generated from home, market places, kitchens in hostels, hotels, marriage halls and also food processing plants. They include food wastes as well as vegetable wastes. It was statistically shown that among various components of solid wastes, vegetable wastes range typically to 17 %[2]. From the food wastes 60-65 % comprises of vegetable wastes.

Vegetable wastes that have been generated from hostels, hotels, marriage halls, *etc*., were mostly thrown out into open spaces. Many research works have been carried out for the proper disposal of vegetable wastes into value added products[3]. Certain processes like vermicomposting[4], incineration[5] and anaerobic digestion[6] were carried out for the conversion of vegetable wastes into useful products. Also conversion of vegetable residues into bio-adsorbents for waste water treatment was also suggested[3].

On the other side, efforts were also made to find an alternate and appropriate technology for the removal of textile dyes from the effluent water. Adsorption onto activated carbon is proven to be very effective in the removal of textile wastes and there is a constant search for highly efficient low cost adsorbent. Such types of adsorbents include groundnut shell[7], peanut hull[8], coconut shell[9], ricinus communis[10], jackfruit peel[11] and citrus reticulata[12].

In the present study, a novel attempt has been made to convert putrescible vegetable waste available free of cost into activated carbon. The main objective of this study was to develop a novel low cost adsorbent from putrescible vegetable waste through chemical activation method and also to study its application to remove malachite green from its aqueous solution.

EXPERIMENTAL

Putrescible vegetable waste (PVW) has been collected from market places, kitchens of college hostels and marriage halls in and around Coimbatore city, Tamilnadu, India throughout the year 2010. During the one year period all types of vegetable wastes and their peel off could be collected. Putrescible vegetable waste was dried in sunlight to remove the moisture content. It was then dried in a hot air oven at 110 °C for 4-6 h. After drying, it was impregnated with a boiling solution of 30 % H_3PO_4 for 1 h and soaked in the same solution overnight. It was kept in hot air oven for 6 h at 120 °C. Excess solution was decanted off and air dried. Then the material was carbonized in a muffle furnace at 450 °C. The dried material was powdered and activated in the muffle furnace at 800 °C for a period of 10 min. Then the material was washed with plenty of water to remove residual acid, dried and powdered. It was then sieved to obtain activated carbon with particle size ranging between 125-200 µm size[13]. The carbon obtained is called as phosphoric acid activated carbon (PAAC) and it was utilized for further studies.

The dye malachite green (MG), a cationic dye was selected as the model compound having m.f.: $C_{50}H_{52}N_4O_8$, m.w.: 927.03 and λ_{max} 617 nm. Its structure is as shown in Fig. 1. Malachite green stock solution of 1000 mg/L was prepared by dissolving it in double distilled water. Working solutions of the desired concentrations were obtained by successive dilution. Dye concentration was analyzed using absorbance values with a UV-VIS spectrophotometer (Model: JASCO V-570). The pH measurements were made using pH meter (Model: LI 610 ELICO). The pH adjustments of the solution were made by 0.1 M HCl or 0.1 M NaOH. The chemicals were of analar grade and all the adsorption experiments were carried out at room temperature of 30 ± 2 °C.
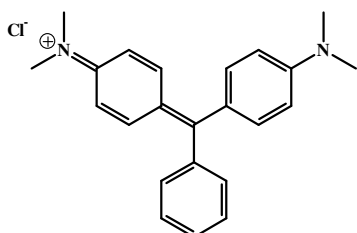

Fig. 1. Structure of malachite green

The batch technique was selected because of its simplicity. The experiments were carried out in a mechanical shaker (KHAN shaker - KEMI make) working at a speed of 150 rpm. Malachite green solution of 50 mL with desired concentrations and initial pH values were used. The adsorbent PAAC (200 mg) were added to each flask and then the flasks were sealed to prevent any change in volume during the experiments. It was agitated for predetermined time intervals at room temperature in the mechanical shaker. Blank samples were run under similar experimental conditions without using adsorbents. After shaking, the adsorbent were separated by centrifugation and the supernatant solutions were estimated by measuring absorbance at maximum wavelengths using UV-visible spectrophotometer (Model: JASCO V-570) at the desired wave length.

The effect of each parameter like adsorbent dose, adsorbent particle size, different dye concentrations and agitation time were studied by fixing the values of other parameters[14]. To correct any adsorption of dye in container walls, control experiments were carried out in duplicate. There was no adsorption by the container walls.

The amount of dye adsorbed by the PAAC was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)v}{W} \tag{1}$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium onto PAAC, C_o and C_e (mg/L) are the initial and equilibrium liquid-phase dye concentration. V(L) the initial volume of dye solution and W (g) the weight of PAAC.

RESULTS AND DISCUSSION

The physico-chemical characteristic of PAAC is given in Table-1. The values show that PAAC has got better porosity, good surface area and also higher iodine number[15]. It concludes that PAAC could be a better adsorbent.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF PAAC

Parameters	Values
Moisture content (%)	4.5
Ash content (%)	8.37
Water soluble content (%)	19.26
Acid soluble content (%)	1.63
Volatile matter (%)	20.5
Iodine number (mg/g)	1101.9
Methylene blue number	525
Bulk density (g/mL)	0.388
Specific gravity	0.98
Porosity	60.4
pH	6.65
pH_{ZPC}	6.87
Electrical conductivity	0.151
Yield (%)	76.48
BET surface area (m^2/g)	603.7
Total pore volume (cm^3/g)	0.7053
Average pore diameter (Å)	46.74
Langmuir surface area (m^2/g)	2469

It was further supported by SEM image of PAAC in Fig. 2. To explore the surface characteristics of PAAC, an FT-IR (Model: FT-IR-2000, Perkin Elmer) analysis was performed in the range of 4000-400 cm^{-1}. IR spectrum PAAC is shown in
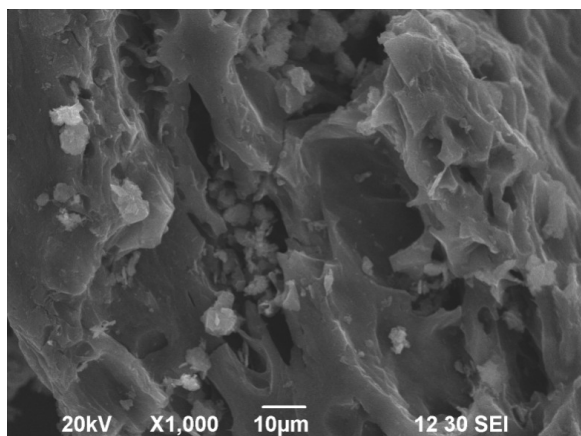
Fig. 2. SEM Image for PAAC before adsorption

Fig. 4. XRD spectra for PAAC

Fig. 3. The peaks 3444, 2918 and 2858 cm^{-1} are ascribed to N-H groups, asymmetric C-H band and symmetric C-H bands of methyl and methylene groups, respectively[16]. The peaks at 2357, 1612 and 1159 cm^{-1} are assigned to C≡C alkyne functionality, C=C vibrational band and C-O band, respectively[17]. All these functional groups are responsible for the enhancement of adsorption properties. X-ray diffraction analysis show broad peaks at 2θ values 23.13, 26.5 and 24.2 which indicate the presence of amorphous form of carbon (Fig. 4). It does not give any major peak which could be due to lack of inorganic substances in the activated carbon[18]. SEM EDX analysis was done to find out the elements present and it revealed that PAAC has carbon 48.66, oxygen 36, phosphorous 13.09, hydrogen 2.1 and sulphur 0.15 by weight percentage.

Effect of adsorbent dosage was carried out at 30 ± 2 ℃ by keeping the volume of dye solution as 50 mL and at a dye concentration of 25 mg/L. The results were shown in Fig. 5. It is evident from the figure that as the dosage of PAAC increases adsorption efficiency also increases. This is due to the availability of more adsorption sites on the surface of the adsorbent[19]. As expected, when the concentration of dye increased the limited capacity of the adsorbent checks any further adsorption of dye and hence the overall removal percentage decreased[20].
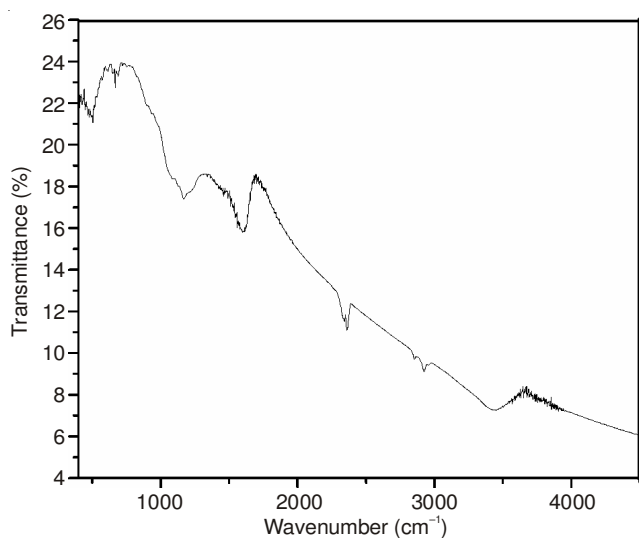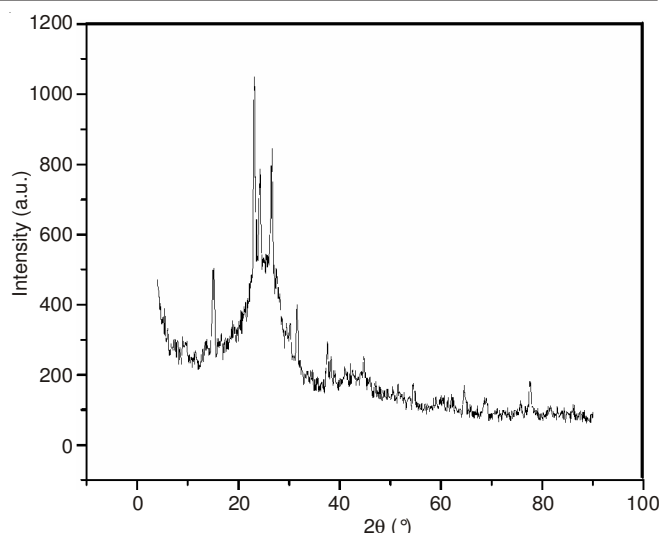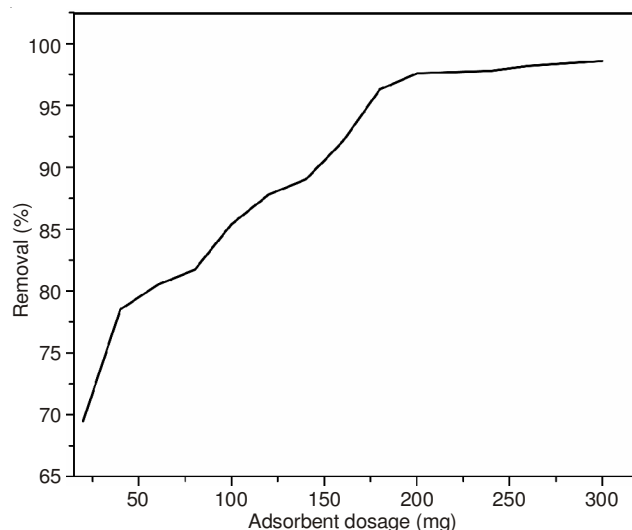

Fig. 5. Effect of adsorbent dosage of PAAC for the removal of malachite green (25 mg/L, pH 7, 30 ± 2 ℃)

Effect of contact time was done with various concentrations and it was shown in Fig. 6. The equilibrium time for the adsorption of PAAC onto malachite green was 2 h. In the process of adsorption, initially dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally, it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time[10].

In aqueous solution ionic dyes release anions or cations. pH influences the adsorption of the charged dye groups onto the surface of the adsorbent[21]. Malachite green being a basic dye produces cations and reduces anions when present in water. As the pH increases the negative charge density on the adsorbents increases leading to more electrostatic attraction of positively charged dye molecules. Due to this reason, at pH 7 maximum adsorption of malachite green onto PAAC took place. At lower pH, due to the accumulation of H^{+} ions on the surface of PAAC, it becomes more positively charged leading to lower adsorption of dye molecules. Fig. 7 clearly shows the effect of pH for the adsorption of malachite green onto PAAC.
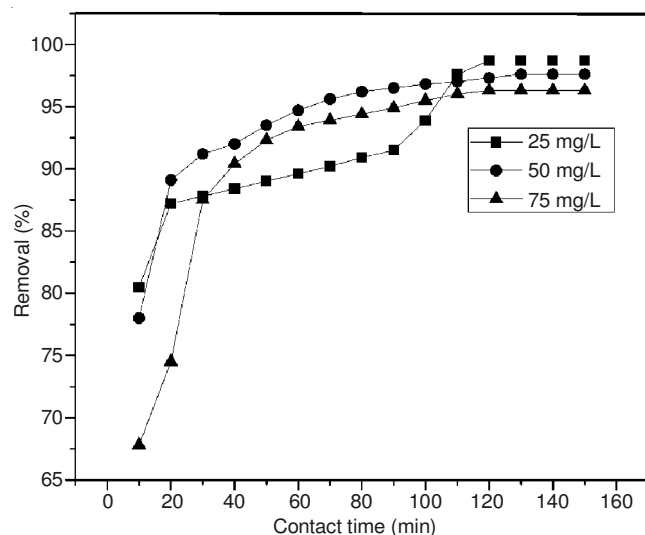

Fig. 3. IR spectra for PAAC

Fig. 6.   Effect of contact time for the adsorption of with malachite green onto PAAC (200 mg) at different concentrations of 25, 50 and 75 mg/L, pH 7, at 30 ± 2 °C
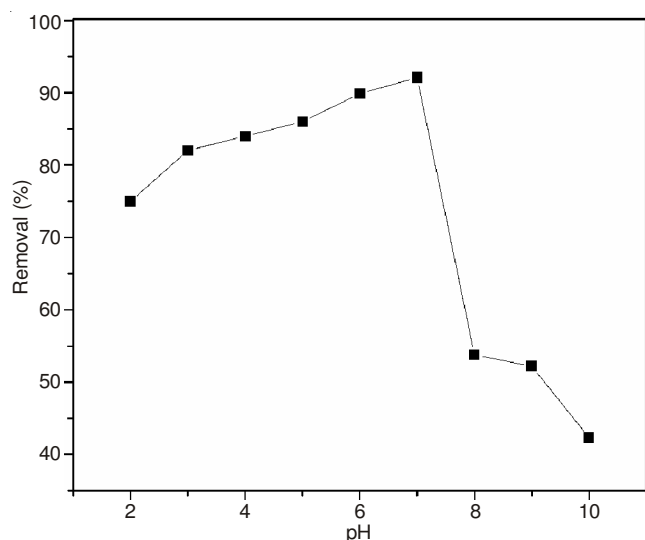

Fig. 7.   Effect of pH on the adsorption of malachite green (25 mg/L, 30 ± 2 °C) onto PAAC (200 mg)

Similar studies were reported in the adsorption of methylene blue[22] and malachite green by fly ash[23].

Adsorption equilibrium data which express the relationship between mass of adsorbate adsorbed per unit weight of adsorbent and liquid-phase equilibrium concentration of adsorbate are represented by adsorption isotherms and provide important design data for adsorption system[24]. The equilibrium data for the removal of malachite green by PAAC were analyzed by Langmuir, Freundlich's and Dubnin-Radushkevich isotherms in the present study.

The Langmuir isotherm plays an important role in the determination of the maximum adsorption capacity of an adsorbent. The form of Langmuir isotherm equation is expressed as follows:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \qquad (2)$$

where Q_m is the theoretical maximum adsorption capacity per unit weight adsorbent (mg/g), K_a is Langmuir adsorption constant (L/mg), C_e and q_e are concentration and amount of dye adsorbed at equilibrium, respectively. The Langmuir isotherm eqn. 2 can be linearized into the following form.

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \qquad (3)$$

A plot of C_e/q_e *versus* C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_a Q_m)$. The results obtained from the Langmuir model for the removal of malachite green onto PAAC is shown in Table-2.

TABLE-2 COMPARISON OF THE COEFFICIENTS ISOTHERM PARAMETERS FOR THE ADOSRPTION OF MALACHITE GREEN ONTO PAAC (200 mg, pH 7, INITIAL DYE CONCENTRATION 25 mg L^{-1})	
Isotherm model	Values
Langmuir isotherm	
Q_m (mg g^{-1})	31.17
K_a (L mg^{-1})	0.0017
R^2	0.9979
Freundlich isotherm	
1/n	0.2969
K_F (mg g^{-1})	0.9595
DR isotherm	
Q_m (mg g^{-1})	17.36
K (mol^2 kJ^{-2})	3.4×10^{-4}
E (KJ mol^{-1})	38.46
R^2	0.9846

The plot of q_e *versus* C_e for the adsorption of malachite green onto PAAC at room temperature according to the non-linear form of Langmuir isotherm model is shown in Fig. 8. Maximum monolayer adsorption of malachite green onto PAAC is 31.17 mg/g which shows that PAAC used in present study has a relatively good adsorption capacity. Correlation coefficient value of 0.9979 further supports the adsorbent (Table-2). A comparison of adsorption capacities of various adsorbents for malachite green is given in Table-3.

Freundlich isotherm is a model based on the distribution of solute between the solid phase and liquid phase at equilibrium. The Freundlich equation is expressed as follows:
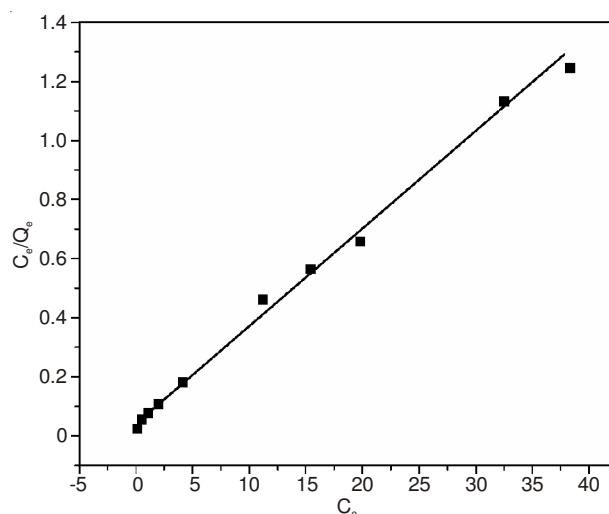
$$q_e = K_F C_e^{1/n} \qquad (4)$$

Fig. 8.   Langmuir isotherm model for the adsorption of malachite green (25 mg/L, pH 7, 30 ± 2 °C) onto PAAC (200 mg)

TABLE-3
COMPARISON OF ADSORPTION CAPACITIES OF
ACTIVATED CARBONS PREPARED FROM VARIOUS
MATERIALS FOR THE REMOVAL OF MALACHITE GREEN

Adsorbent	Q_m (mg/g)	Temp. (°C)	Ref.
Almond shell	1.33	–	30
Lemon peel	3.2-51.7	32	31
Commercial activated carbon	8.27	–	32
Hazelnut shell	8.82	30	30
Coir pith	6.72	–	33
Spent coffee grounds	18.73	–	34
Putrescible vegetable waste	31.17	30	Present work

where K_F is a constant for the system, related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below 1 indicates a normal Freundlich isotherm while 1/n above 1 is indicative of cooperative adsorption. Eqn. 4 can be linearized in the logarithmic form (eqn. 5) and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data, by plotting log q_e *versus* log C_e. The data obtained from linear Freundlich isotherm plot for the adsorption of the malachite green onto PAAC is presented in Table-2 and Fig. 9. The correlation coefficient shows that the Freundlich model is comparable to the Langmuir model. The value for 1/n is lower than 1.0 (Table-2), indicating that adsorption of malachite green by PAAC is favourable.
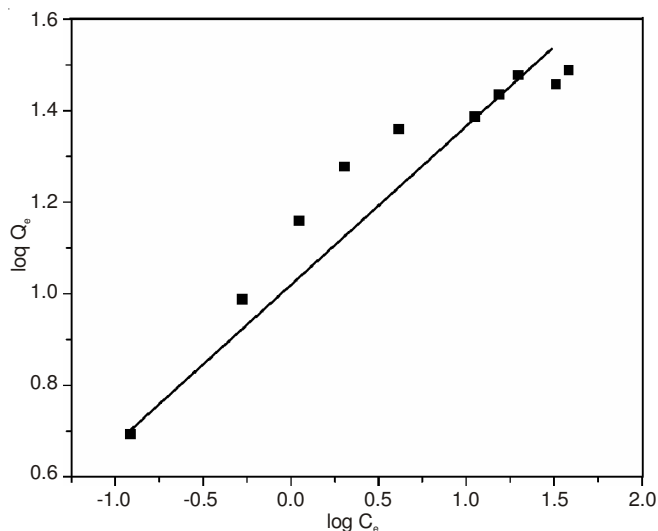

Fig. 9. Freundlich isotherm model for the adsorption of malachite green (25mg/L, pH 7, 30 ± 2 °C) onto PAAC (200 mg)

The energy of activation obtained from Dubnin and Radushkevich isotherm is useful in predicting whether an adsorption is physisorption or chemisorption. The equation

of D-R model is given in eqn. 6 and its linear form is shown in eqn. 7:

$$q_e = Q_m \exp(-K\varepsilon^2) \qquad (6)$$
$$\ln q_e = \ln Q_m - K\varepsilon^2 \qquad (7)$$

where K is a constant related to the adsorption energy, Q_m the theoretical saturation capacity, ε the Polanyi potential, calculated from eqn. 8.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C}\right) \qquad (8)$$

The plot of ln q_e *versus* ε^2 gives the slope K (mol^2/kJ^2) and the intercept which yields the adsorption capacity, Q_m (mg/g). The mean free energy of adsorption (E), defined as the free energy change, when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation:

$$E = \frac{1}{\sqrt{2K}} \qquad (9)$$

The calculated value of Dubnin-Radushkevich parameters is given in Table-2. If physisorption occurs during adsorption process then the energy of activation is less than 8 KJ/mol and if chemisorption occurs it is greater 16 KJ/mol[25]. The values of E which was calculated using eqn. 9 is 38.46 KJ/mol. It was shown in Fig. 10.
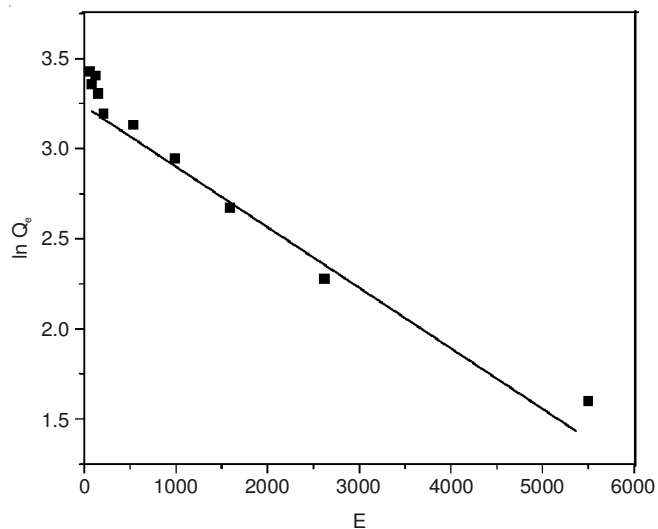

Fig. 10. Dubnin Radushkevich isotherm model for the adsorption of malachite green (25 mg/L, pH 7, 30 ± 2 °C) onto PAAC (200 mg)

Various kinetic studies like pseudo first order, pseudo second order and intra particle diffusion models were analyzed in this study. The pseudo first-order model of Lagergren[26] is based on the assumption that the rate of change of adsorbed solute with time is proportional to the difference in equilibrium adsorption capacity and the adsorbed amount. The pseudo first-order equation is expressed as in eqn. 10

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (10)$$

When the boundary conditions q_t =0 at t = 0, eqn. 10 can be integrated into the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (11)$$

where q_e (mg/g) and q_t (mg/g), are the adsorption capacity per unit weight of adsorbent at equilibrium and at time t (min), respectively. The pseudo first-order rate constant is k_1 (min^{-1}). Linear plot of log ($q_e - q_t$) *versus* t gives the value for rate constant k_1. The correlation coefficients (Table-4) are relatively low for malachite green and it failed to explain the adsorption of malachite green by PAAC with poor fit at various concentrations. This infers that the adsorption of malachite green onto PAAC does not follow first order mechanism.

TABLE-4
KINETIC PARAMETERS OF ADSORPTION OF MALACHITE GREEN ONTO PAAC (200 mg, pH 7, INITIAL DYE CONCENTRATION 25, 50 AND 75 mg L^{-1})

Kinetic models	Initial dye concentration (mg/L)		
	25	50	75
First order kinetic model			
k_1 (min^{-1})	6.49×10^{-4}	1.377×10^{-2}	3.781×10^{-2}
q_e (mg/g)	354.66	72.63	60.91
R^2	0.9892	0.9574	0.8576
Second order kinetic model			
k_2 (g/(mg min))	6.46×10^{-2}	9.04×10^{2}	3.89×10^{-2}
q_e (mg/g)	4.8267	4.9372	5.0289
R^2	0.9983	0.9998	0.9997
h (mg/g min)	1.5051	2.2035	0.9862
Intra particle diffusion model			
k_{diff} (mg g^{-1} min$^{-1/2}$)	7.319×10^{-2}	1.035×10^{-2}	4.229×10^{-3}
C	3.0791	3.814	4.4255
R^2	0.9966	0.9875	0.9905

The pseudo second-order model[27] is based on the assumption that the rate-limiting step involves chemisorption. The equation is represented as in eqn. 12:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{12}$$

When the initial conditions $q_t = 0$ at $t = 0$, after integration, the linear form of the pseudo second-order equation is given in eqn. 13:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{13}$$

where k_2 is the pseudo second-order rate constant (g/g/min). The initial adsorption rate h (mgm/g/min) at $t = 0$ is defined as follows:

$$h = k_2 q_e^2 \tag{14}$$

The straight line plot of t/q_t *versus* t, for the adsorption of MB by both the adsorbents is shown in Fig. 11. From the linear plot the values of h, q_e and k_2 are calculated (Table-4). A very high correlation coefficient value (Table-4) indicates that the adsorption of malachite green onto PAAC follows pseudo second order kinetic model. The rapid uptake of the dye indicates that the rate determining step could be chemisorption in nature[28].

Intra particle diffusion process[29] is the rate limiting step in many adsorption processes. The expression for the intra-particle diffusion model is given by the eqn. 15.
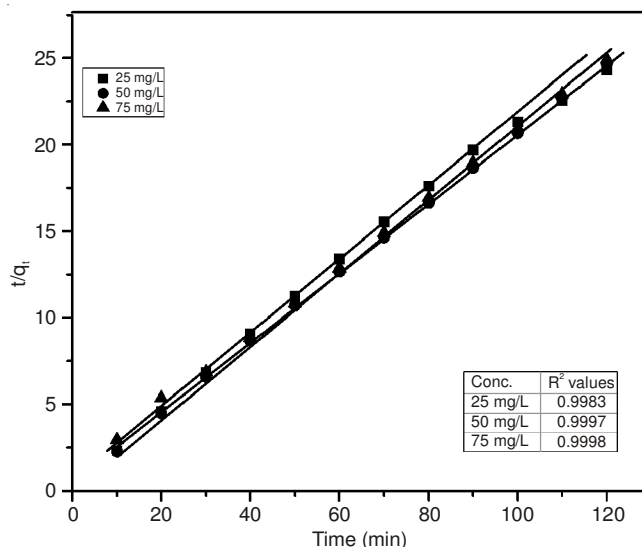
$$q_t = K_{dif} t^{1/2} + C \tag{15}$$

Fig. 11. Pseudo second order kinetic model for the removal of malachite green onto PAAC (25 mg/L, pH 7, 30 ± 2 ºC) onto PAAC (200 mg)

where C (mg/g) is the intercept and K_{dif} is the intra particle diffusion rate constant (in mg/g/min$^{1/2}$). The values of q_t were found linearly correlating with values of $t^{1/2}$ for malachite green at different concentrations (Fig. 12) and the rate constant K_{dif} were directly evaluated from the slope of the regression line. The results are shown in Table-4. The plot of q_t *versus* square root of time would result in a linear relationship and the intraparticle diffusion would be the controlling step if this line passes through the origin. When the plots do not pass through the origin, it indicates some degree of boundary layer control and it further shows that the intra-particle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption. Such plots may present multi-linearity, indicating that two or more steps takes place. The correlation coefficient values for this model range from 0.987-0.9966. Also an increase in C value depicts the abundance of solute in boundary layer[19].
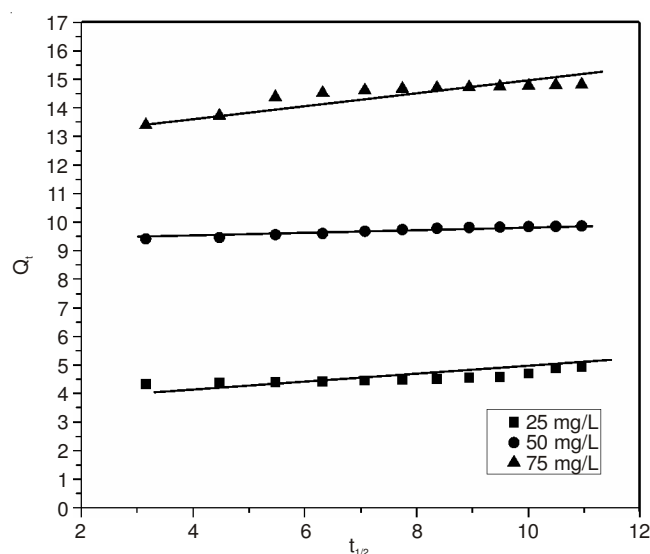

Fig. 12. Intra particle diffusion model for the removal of malachite green onto PAAC (25, 50 and 75 mg/L, pH 7, 30 ± 2 ºC) onto PAAC (200 mg)

Conclusion

The results obtained from the present study suggested the possibility for the conversion of putrescible vegetable waste into phosphoric acid activated carbon for the removal of malachite green from its aqueous solution.

• Phosphoric acid activated carbon prepared from putrescible vegetable waste is a potential low cost adsorbent material.

• The equilibrium adsorption was achieved within 2 h at an optimum pH of 7.

• The experimental results were analyzed by using Langmuir, Freundlich and Dubnin-Radushkevich isotherms.

• Maximum adsorption capacity was given by Langmuir adsorption isotherm.

• Freundlich adsorption constant value indicated that the adsorption of malachite green onto PAAC was favourable.

• The energy of activation obtained through Dubnin-Radushkevich isotherm revealed that the adsorption is chemi-sorption in nature.

• Phosphoric acid activated carbon followed pseudo second order kinetics for the adsorption of malachite green from its aqueous solution.

• Intraparticle diffusion model concluded that surface adsorption and intraparticle diffusion were concurrently operating during the malachite green and PAAC interactions.

• Results thus revealed that the activated carbon PAAC prepared from putrescible vegetable waste could be effectively employed for cationic dye removal. The present work suggested a novel method for an effective solid waste management and their conversion into value added products.

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