Groundnut plant ash: Characterisation and adsorption efficacy study for removal of paraquat dichloride

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For the first time combustion residue of agricultural waste i.e. groundnut plant is characterized in detail and explored as an adsorbent for removal of chlorinated herbicide, paraquat. The study investigates the chemical, physical, mineralogical, and morphological characteristics of GPA (Groundnut Plant Ash) adsorbent produced using groundnut plant. GPA has been characterized using the Fourier Transform Infrared (FTIR) spectroscopy to determine the functional groups, and Scanning Electron Microscopy (SEM) to examine the surface morphology of the carbon. Batch adsorption is performed by varying adsorbent dosage, initial concentration and contact time. Result shows that the kinetic models mainly the pseudo-second order and Elovich model had the best fit. The equilibrium data are analyzed using different isotherm models. The adsorption capacity of GPA for paraquat removal is found 265.71 mg/m^2 which is the highest reported value.

Fabaceae is the family of Groundnut (Arachishypogaea). It's generally used for its nuts, peanuts and is also used in cosmetics, plastics, dyes, and paints. When biomass is burned in the presence of oxygen, ash is produced. There are many important constituents present in ash which are useful for soil modification[1]. These constituents ultimately increase the micronutrient, water holding capacity, texture, bulk density, pH and biological properties of soil. The biomass ash has nominal amount of heavy metals that are highly useful for its utilization in the remediation of soil. The production of ground plant seed was reported to be 45.654 million tons[2]. It has been previously reported that ash addition will absorb the pesticides as well as improve the fertility of soil[3]. Literature reports indicated that the constituents in biomass ashes can be useful as a bio fertilizer[4].

Pesticides are a class of persistent organic pollutants that play an important role in crop production and protection. Some pesticides have a tendency to leach through the soil profile and contaminate the ground water as well as surface water and may have adverse effects on human health[5].

Paraquat (1, 1-dimethyl-4, 4-bipyridinium dichloride) is one of the globally used herbicides since many years. Its major use is to control growth of broad leaf weeds, grasses in plantation crops and in fruit orchards[6]. The high water solubility of paraquat (620 g/L) has enhanced the risk of contamination of water during its use in agriculture. In fact, many studies have revealed its presence in surface and drinking waters. According to European standards, the lethal dose of paraquat for human being is 35 mg/kg[7], the maximum allowable concentration for individual pesticides (including paraquat) in drinking water is 0.1 μg/L and 1–3 μg/L in surface water[5]. Therefore, the removal of paraquat from water has become great necessity as far as water pollution is concerned[8]. Previously, numbers of methods have been reported in literature for removal of pesticides from water[3]. In previous studies, natural adsorbents such as activated bleaching earth, laponite, goethite, waste coffee grounds, different clays, RHA and BFA were used for paraquat removal. Adsorption is attractive due to its relative simplicity of design, operation and scale up, high capacity, favorable rate, and low cost[5].

In this work, an attempt has been made to characterize GPA in detail as well as to remove paraquat from aqueous solutions. Kinetic parameters were investigated to determine the ratio of reaction time versus adsorbed amounts. This study focuses on the use of locally available ash as a source of micronutrient supply as well as an adsorbent for pesticide removal. The significance of applying GPA on farmlands and appropriate dosage/ hectare is discussed in this paper (Table 1).

Property	Value
Chemical formula	$C_{12}H_{14}C_{12}N_2$
molecular weight	257.16 g/mol
Solubility in Water	In water 700 g/L (20°C).
Appearance	Colorless, hygroscopic crystals (pure).
Density (g cm-3):	1.25 g/cm^3

Experimental Section

Preparation of adsorbent

Groundnut plants were collected from a local farm near Nagpur, India. The plant remains were manually cleaned to remove dust and soil traces to prevent contamination. Groundnut plants remains were sun dried and burnt in a combustor with grate. Air was circulated by blower at a low velocity that assists combustion. The temperature attained by groundnut plants during the process varies at the start and end of the combustion process with a range of 350–650°C. The residue groundnut plant ash (GPA) thus produced was then cooled and packed in airtight polyethylene bags. Groundnut plant ash was sieved using British standard sieve (25-mesh) to remove larger. Powdered groundnut plant ash of size less than 0.3 mm was used for further characterization.

Methods and techniques

The surface characteristics, namely surface area, pore diameter, and pore volume were determined using Nitrogen adsorption-desorption isotherm and Brunauer–Emmett–Teller (BET) method (Micromeritics ASAP2010). The chemical composition of GPA was determined using X-ray fluorescence (XRF) analyzer (PW 2403; PAN analytical). Proximate analysis of GPA was carried out using gravimetric methods to determine the percentage of moisture, volatile matter, ash and fixed carbon. Standard procedures detailed elsewhere were adapted[9]. Ultimate analysis (CHNS analysis) was carried out, using the vario MICRO cube model (elementary), to determine the composition of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S).

Physical properties such as porosity, particle density, bulk density and water-absorption capacity were determined. Porosity, particle density, and bulk density of GPA were determined using the tap density method. Water adsorption capacity is the ability of ashes to hold water per gram of ash. About 1 g of ash was added to 50 mL of water. The mixture was allowed to react for 3 h, and the remaining water was decanted and measured. The difference between the initial and final volumes of water gives the water-adsorption capacity of GPA. The mean particle size of the GPA was determined by sieve shaking.

Adsorbate

Paraquat (98%), as obtained from Sigma Aldrich, was used as an adsorbate. We prepared a stock solution of paraquat in mili-Q water. This solution was then diluted according to the condition of each experiment.

Batch adsorption study

The batch adsorption experiments were carried out in a constant-temperature water bath in which the glass vials were shaken. The vials contain paraquat solution and predefined quantity of GPA. The samples were then withdrawn after certain time and filtered. The supernatant after centrifugation of filtrate was analyzed on an UV/V is spectrophotometer (Shimadzu, Model UV-1800, Japan) at 257 nm. The percentage removal, adsorption capacity at any time and at equilibrium (Q_t and Q_e, respectively, mg/g) were calculated using equations (1), (2), and (3), respectively.

$$\%\text{Removal} = \left(\frac{C_0 - C_e}{C_e}\right) \times 100 \qquad \dots (1)$$

$$Q_t = \frac{(C_0 - C_t)V}{W} \qquad \dots (2)$$

$$Q_e = \frac{(C_0 - C_e)}{W}V \qquad \dots (3)$$

where C_0 (mg/L) is the initial concentration, C_e (mg/L) is the equilibrium concentration, V (L) is volume of the adsorbate solution, and W (g) is the mass of adsorbent. The effects of adsorption parameters such as adsorbent dosage, adsorbate concentration and contact time on paraquat removal were studied. Results reported are an average of triplicates.

Adsorption kinetic and isotherm modeling

In order to examine the mechanism of adsorption process and to identify the rate controlling steps, the pseudo-first-order (PFO), pseudo-second order (PSO), Elovich (EL) and intra-particle diffusion (IPD) models were applied to batch experimental data. The linearized form of PFO, PSO, EL and IPD models are presented by the equations (4),(5), (6) and (7) respectively.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad \dots (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \dots (5)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad \dots (6)$$

$$q_t = K_d t^{\frac{1}{2}} + C \qquad \dots (7)$$

where, k_1 is pseudo-first-order rate constant (min^{-1}), q_e and q_t are the amount of solute adsorbed per unit adsorbent at equilibrium and at any time (mg/g), k_2 is pseudo-second-order rate constant [g/(mg min)], [mg/(g min)] corresponds to the chemisorption rate at zero coverage, β is related to the extent of surface coverage and activation energy for chemisorption (g/mg), k_d is the IPD rate constant [mg/(g min$^{1/2}$)].

The adsorbent capacity which is an important parameter for the selection of an adsorbent was determined using the isotherm models. The isotherm parameters provide valuable information about the adsorbent–adsorbate interaction, and surface characteristics of adsorbent and its affinity. The well-known isotherms are Langmuir, Freundlich, and Temkin models [10] given in equation (8), (9) and (10) respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad \dots (8)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad \dots (9)$$

$$q_e = B\ln A_T + B\ln C_e \qquad \dots (10)$$

$$B = \frac{RT}{b_T} \qquad \dots (11)$$

where, K_L is Langmuir constant (L/mg), q_{max} is Langmuir maximum monolayer capacity (mg/g), K_F (mg/g) (L/mg) $^{1/n}$ is Freundlich constant, n is Freundlich adsorption intensity, R (8.314 J/mol K) is Universal gas constant, T is Temperature (K), b_T is Temkin constant related to heat of sorption (J/mol) and A_T is Temkin equilibrium binding constant (L/g). The kinetic and isotherm equations used to study the adsorptive removal of paraquat on GPA. The model constants are determined from slopes and intercepts of linearized form of equations.

Results and Discussion
Characterization of GPA

The proximate analysis of GPA presented the following composition: 87.79% ash, 10.81% volatile matter, 0.91% fixed carbon and 0.47 % moisture. The high ash content reflects the inorganic nature of GPA. The presence of carbon was also confirmed by CHNS analysis, which indicated the following composition: 3.57 % carbon, 0.354 % hydrogen, 0.12 % nitrogen and 0.12 % sulphur. The BET surface area was found to be 7 m^2/g. Physical properties such as porosity; particle density, bulk density, and water-absorption capacity are shown in Table 2.

The chemical composition indicated that GPA is a source of many elements such as Al, Si, Ca, Mg, and K, all of which act as supplementary nutrients to the soil. XRF analysis of GPA obtains the following composition: 28.01% SiO_2, 10.6% Al_2O_3, 5.73% K_2O, 14.63% Fe_2O_3 and 11.21% CaO along with few other oxides.

Scanning electron microscopy (SEM)

SEM of GPA shown in Fig. 1 reveals the surface texture and porosity. It shows very fine particle size to

Table 2 — Properties of GPA

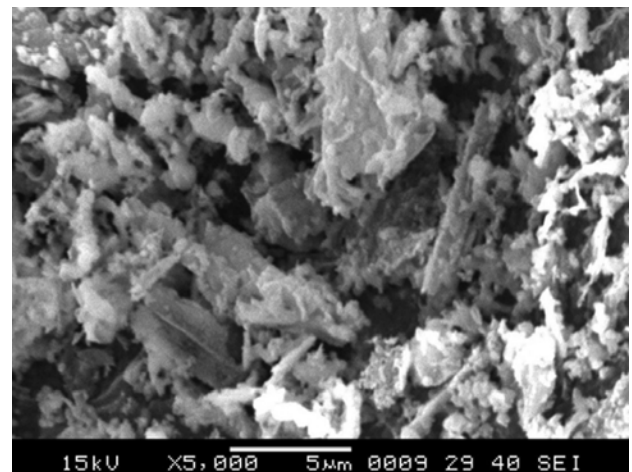| Parameter	Value (GPA)
(BET) Surface area (m^2/g)	7
Moisture content (%)	0.47
Volatile matter (%)	10.81
Ash	87.79
Fixed carbon (%)	0.91
C (%)	3.57
H (%)	0.354
N (%)	0.12
S (%)	0.119
Point of zero charge	12.4
density (g/cc)	1.72
Bulk density (g/ml)	0.3
Porosity %	82.11
Water absorption capacity (ml/g)	0.2
Mean particle size (mm)	0.096

Fig. 1 — Scanning electron microscopy of GPA

the order of a millimeter or less and that there are pores of varying sizes within the particle.

The chemical structure of the adsorbent is crucial in understanding the adsorption process. The FTIR technique is an important tool to identify the characteristic functional groups which are significant in adsorption process. The FTIR for GPA before and after adsorption is given in Fig. 2.

Calcium carbonate characteristics band occur at 770–870 and 1400–1450 cm^{-1}, and bonds between 1100 and 1300 cm^{-1} attributed to presence of cellulosic derivative and presence of CO-stretching bond. Paraquat shows characteristic peaks at 3055 and 3018 cm^{-1}, assigned to the C–H tension mode of the methyl groups on the aromatic ring in the paraquat molecule; and bands between 1641 and 1194 cm^{-1} assigned to the C–C tension mode and the C–H deformation mode in the aromatic ring. After adsorption, FTIR spectrum of paraquat is shown in Fig. 2C. The FTIR spectrum of the paraquat–exhibits band characteristics of paraquat centered at 3133 cm^{-1}, assigned to the C–H stretching mode of the methyl groups on the aromatic ring in the paraquat molecule. A characteristic band can also be seen at 1600 cm^{-1} that is assigned to the C–C stretching mode and the C–H deformation mode in the aromatic ring plane[11].

Effect of GPA dosage

The effect of adsorbent dosage on removal of adsorbate for 25 mg/L concentration was observed. The graph shows the percentage removal of paraquat against the adsorbent dosage. The variation in paraquat removal with dosage was studied by increasing GPA dosages from 0.1 to 2.5 g/50 mL respectively. The experiments were carried out at constant concentration (25 mg/L) and time (16 h). The results shown in Fig. 3 express approximately 87 % removal using 1.2 g GPA per 100 mL solution. For further dosages, the removal is not significantly improved. This ensures greater removal of adsorbate, due to the initial availability of more vacant site for adsorption, and therefore, the aforementioned dosages were selected as optimum for next studies.

Effect of initial concentration

The effect of initial concentration of paraquat on percentage removal was studied by varying the concentration from 5 to 40 mg/L at constant dosage (optimum dosage). The experiments were performed at constant contact time (16 h) and temperature (303 K). Results presented in Fig. 4 indicate that the removal
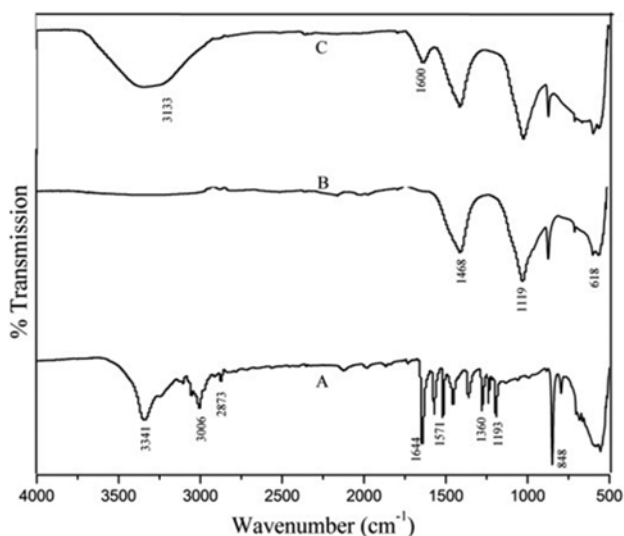

Fig. 2 — FTIR spectra: Spectrum A, Paraquat; Spectrum B, GPA before adsorption and Spectrum C, GPA after adsorption.
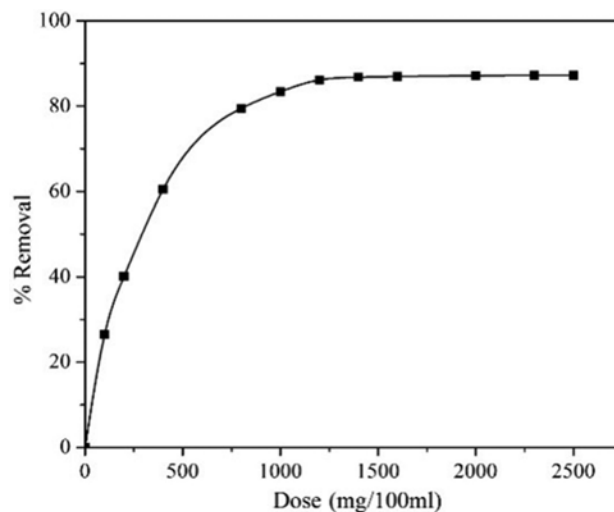

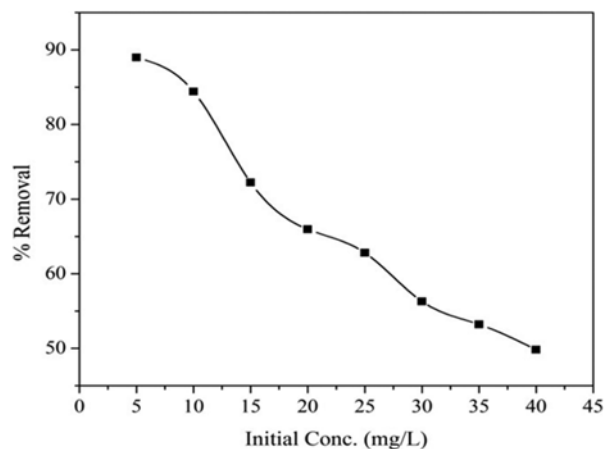Fig. 3 — Effect of GPA dosage on % removal of paraquat

Fig. 4 — Effect of initial concentration on % removal of paraquat

of paraquat is significantly decreased with increasing concentration. Because GPA has restricted adsorption sites, the percentage removal is significantly reduced for higher concentrations. However, the equilibrium capacity of ash is better due to reduced mass-transfer resistance, which is overcome by a concentration gradient at higher concentrations. Therefore, the concentrations of paraquat selected for next study was 20 mg/L.

Effect of contact time

The effect of contact time is studied to determine the equilibrium time for the removal of paraquat on GPA. Adsorption experiments were carried out for different contact time at a constant initial concentration (20 mg/L) and adsorbent dosage (1.2 gm/50 mL). The Fig. 5 shows that the initial uptake on GPA was fast and about 50% removal was achieved within the first hour. In the later stages of adsorption, the removal on GPA was slower. It can be seen in Fig. 5 that equilibrium was reached at 480 min of contact time GPA. There is no significant change in removal after these durations of time. A more number of vacant sites on surface are available for removal during the early stage of adsorption. The removal of paraquat is higher initially because a larger surface area is available for adsorption.

Adsorption kinetic modeling

The results of effect of contact time on adsorption were analyzed using linearized kinetic models. The model parameters determined from slope and intercept of line for adsorbents GPA are presented in Table 3. The values of coefficient of determination (R^2) for both the PSO kinetic model and Elovich models are significantly higher and closer to unity than the PFO (Fig. 6). In addition, the equilibrium capacity predicted by the PSO model for GPA is similar to that obtained in experiments. Therefore, the PSO kinetic model (Fig. 7) is best to describe the adsorption of paraquat on GPA.

PFO and PSO models are not able to identify the diffusion mechanism, therefore intraparticle diffusion model proposed by Weber and Morris was applied. The Weber–Morris plot (qt vs t½) of the IPD model in Fig. 8 indicates multilinearity for GPA. Thus, it can be deduced that there exists two or more rate-limiting steps in this adsorption process. The initial stage in Fig. 8 corresponds to the instantaneous adsorption of paraquat on the external surface of the GPA. The second part of the plot is ascribed to intraparticle diffusion, which indicates slow adsorption of molecules within the pores. The third part represents the attainment of adsorption equilibrium. The slopes of the initial two stages of the plot are indicated by k_{d1} and k_{d2} (Table 3) respectively. The rate constants, k_{d1} and k_{d2} correspond to external mass transfer and intraparticle diffusion, respectively. In this study, $k_{d1} > k_{d2}$, this indicates that the paraquat molecules are initially adsorbed on the surface and then diffuse into the pores. . The value of k_{d2} indicates the rate constant of IPD, whereas the intercept C_2 is related to boundary-layer thickness.
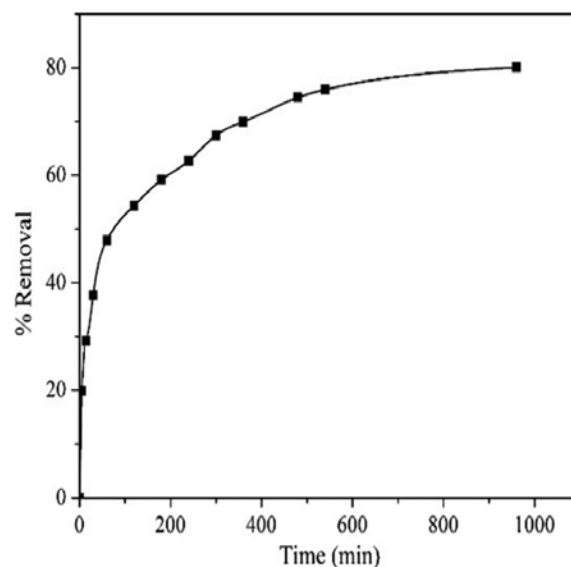

Fig. 5 — Effect of contact time on % removal of paraquat using GPA.

Table 3 — Kinetic model parameters for paraquat adsorption on GPA

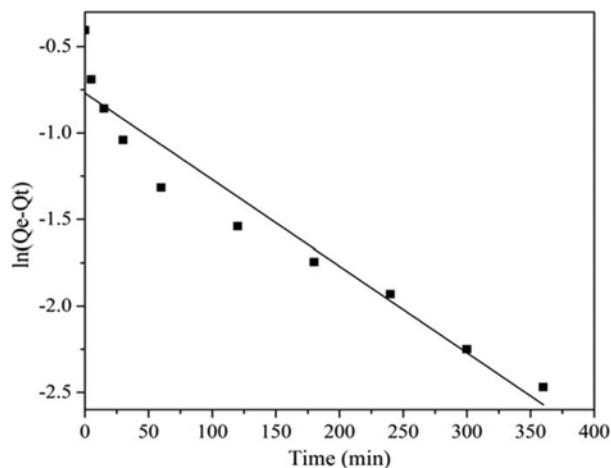| C_0 (mg/L)	Pseudo-first order model				Pseudo-second order model			Elovich model			Intraparticle diffusion model					
	$q_e$expt (mg/g)	k_1 (min^{-1})	$q_e$cal (mg/g)	R^2	k_2 [g/(mg min)]	$q_e$cal (mg/g)	R^2	α [mg/ (g min)]	β (g/mg)	R^2	k_{d1} [mg/(g min$^{1/2}$)]	C_1 (mg/g)	R_1^2	k_{d2} [mg/(g min$^{1/2}$)]	$C2$ (mg/g)	$R2^2$
GPA (20ppm)	0.667	0.005	0.463	0.936	0.037	0.677	0.993	0.085	10	0.993	0.0057	0.015	0.981	0.016	0.268	0.993

Fig. 6 — Pseudo-first-order kinetic model for adsorption of paraquat on GPA
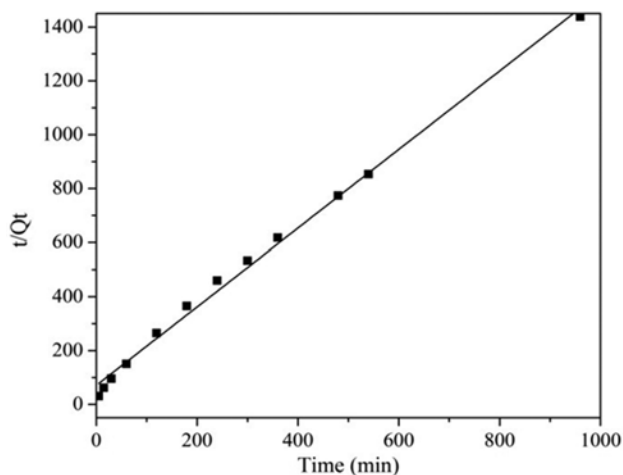

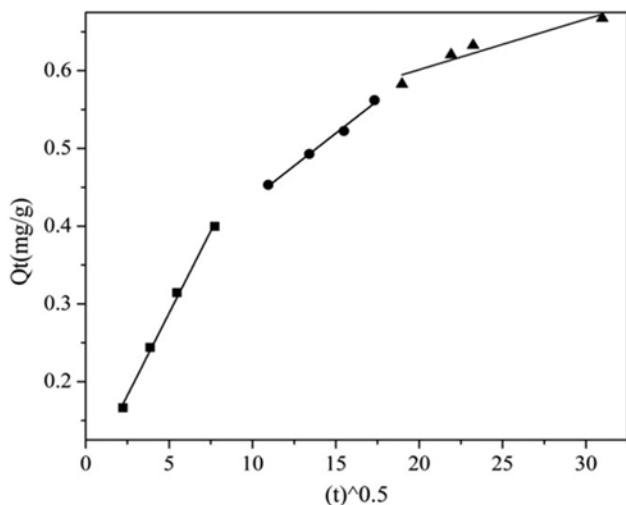Fig. 7 — Pseudo-second-order kinetic model for adsorption of paraquat on GPA

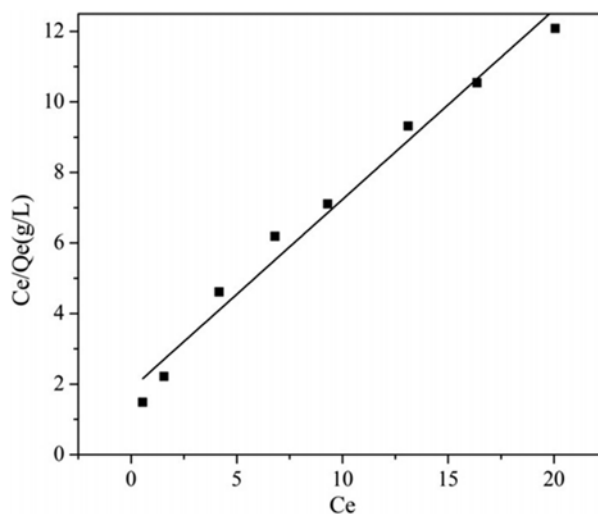Fig. 8 — Weber–Morris plot for adsorption of paraquat on GPA

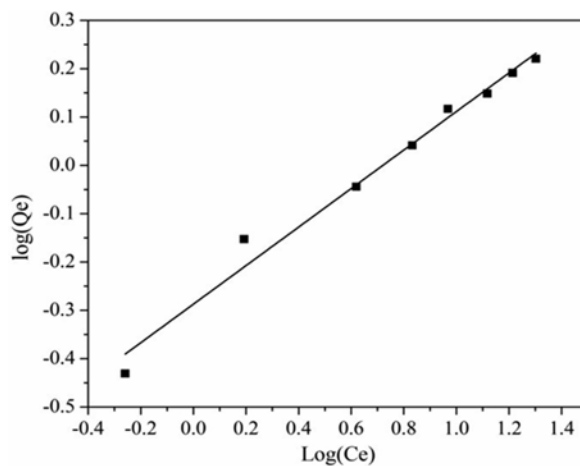Fig. 9 — Langmuir isotherm model for adsorption of paraquat on GPA

Fig. 10 — Freundlich isotherm model for adsorption of paraquat on GPA.

Adsorption isotherm modeling

Adsorption isotherms are required for the design of adsorption systems. Data obtained from isotherms notify about the amount of adsorbent necessary for removing a unit mass of impurity under the system conditions. The isotherm models, namely, Langmuir, Freundlich, and Temkin were applied to the adsorption of paraquat on GPA at 303 K is shown in Fig. 9, 10 and 11. The values of isothermal parameters and coefficient of determination (R^2) for the linear regression model are listed in Table 4; R^2 values close to one indicate the best fitting of Langmuir and Freundlich isotherms, which are shown in Fig. 9 and 10, respectively. The Langmuir isotherm is based on monolayer adsorption with a fixed number of homogeneous adsorption sites[10]. The monolayer adsorption capacity of GPA given by Langmuir

isotherm is about 265.71 mg/m^2. The essential factor of the Langmuir isotherm is expressed by 'RL', which is a dimensionless constant. It is also known as equilibrium parameter or separation factor. The dimensionless factor

Fig. 11 — Temkin isotherm model for adsorption of paraquat on GPA.

was calculated using Langmuir constant. The dimensionless factor given by

$$R_L = \frac{1}{(1+K_L C_0)} \qquad \text{... (12)}$$

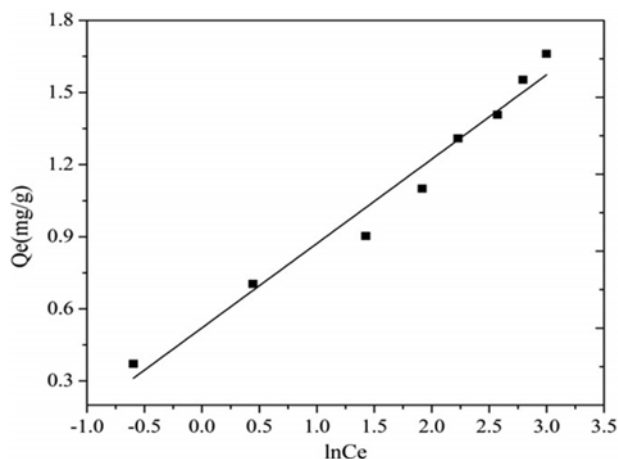The value of R_L was used to decide the nature of adsorption[3]. In this study, the values of R_L were observed in the range between 0 and 1 for GPA. This implies the favorability of paraquat adsorption performed at 30°C on GPA.

Freundlich adsorption model is established for multilayer adsorption on heterogeneous surfaces of adsorbent· In this study, the adsorption intensity factor (i.e. $1/n$) of Freundlich isotherm is between 0 and 1, which again indicates favorable adsorption of paraquat on GPA[12].

Temkin isotherm confirms the exothermic nature of adsorption. It contains a factor, A_T that corresponds to binding interaction between adsorbate and adsorbent at equilibrium where as Temkin isotherm constant, b_T is related to heat of adsorption. The values of b_T for paraquat removal on GPA are less than that stated for ion-exchange mechanism (8–16 kJ/mol). Similarly, adsorption energy for physisorption is reported to be less than –40 kJ/mol[5]. Therefore, physisorption of paraquat on GPA can be proposed in this study.

Comparison of adsorption capacity of various adsorbents for paraquat

A comparison of Langmuir adsorption capacity of various adsorbents for paraquat removal is shown in Table 5. The adsorption capacities in this Table 5 are reported as (i) the quantity of adsorbate adsorbed (mg)

Table 4 — Isotherm parameters for adsorption of paraquat on GPA

Isotherm models	Parameters	GPA
Langmuir	q_{max}(mg/g)	1.862
	K_L (L/mg)	0.288
	R^2	0.981
Freundlich	n	2.512
	K_F [(mg/g)/(mg/L)$^{1/n}$]	0.516
	R^2	0.983
Temkin	A_T (L/mg)	4.418
	B(J/mol)	0.35
	R^2	0.972

Table 5 — Comparison of paraquat adsorption capacity of various adsorbents

Adsorbent	Surface area (m^2/g)	q_{cap} (mg/g)	$q_{cap} \times 10^3$ (mg/m^2)	Ref No.
Activated Bleaching Earth	268	26.74	99.77	[13]
Laponite	245	92.57	377.83	[14]
Goethite	57.6	0.77	13.36	[15]
Waste coffee grounds	1040.3	0.07	0.06	[16]
Activated clay	266	0.06	0.22	[17]
	270	0.05	0.18	
	230	0.04	0.17	
Regenerated clay mineral	101.5	1.31	12.9	[18]
Clays and organoclays	292	0.86	2.94	[19]
	73	2.97	40.68	
	200	3.81	19.05	
BFA	55	22.22	404	[5]
RHA	34	6.53	192.05	[5]
GPA	7	1.86	265.71	This study

per unit mass (g) of the adsorbent and (ii) the quantity of adsorbate adsorbed (mg) per unit surface area (m^2) of the adsorbent. Compared with natural (neither chemically modified nor laboratory synthesized), low-cost, and soil-compatible adsorbents, GPA has the highest adsorption capacity (mg/m^2) for paraquat removal. This indicates that the studied GPA is the most efficient adsorbents for the removal of paraquat from aqueous solution.

Conclusion

The equilibrium data applied to different isotherm models Langmuir and temkin isotherm indicate exothermic nature of adsorption.

1. The equilibrium time for Paraquat adsorption on GPA surface was practically achieved in 480 min.

2. The pseudo-second-order kinetic and Elovich kinetic models were found to be the best to describe the present system.

3. The maximum adsorption capacity (q_{max}) was obtained 265.71 mg/m^2 for paraquat.

4. The Freundlich isotherm fits better than the Langmuir and Temkin.

5. It is recommended that GPA is spread uniformly on land before pesticide application, so that the dual properties of GPA (i.e. yield booster and adsorbent) can be effectively utilized.

6. GPA serves multiple purposes: (i) as an adsorbent for removal of pesticides; (ii) as a soil additive and water enhancer; (iii) as a micronutrient source for plants.

Acknowledgement

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