A low-cost adsorbent (wheat plant ash) prepared from agricultural waste for removal of paraquat from aqueous solutions

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A low-cost adsorbent (wheat plant ash) has been prepared using a common agricultural waste (wheat straw) and its physicochemical characteristics, including chemical, physical, mineralogical, and morphological, and adsorption efficacy are investigated. WPA is characterized by SEM (scanning electron microscopy), CHNS(ultimate analysis) analysis, Brunauer–Emmett–Tellersurface area technique, and Fourier transform infrared method. The BET surface area of wheat plant ash was found to be $37 \text{ m}^2/\text{g}$. To evaluate its adsorption capacity, paraquat is chosen as the adsorbate. Batch adsorption is performed by varying adsorbent dosage, initial concentration, and contact time. Experimental data are fitted to both kinetic and isotherm models. Pseudo-first-order and pseudo-second-order kinetic models are applied to experimental data, which indicated that the latter model had the best fit. Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models are then applied to the equilibrium data. The adsorption capacity of WPA for paraquat removal, determined using the Langmuir isotherm, is found to be approximately 241.3 mg/m² at 303 K.

Keywords: Adsorbate, Adsorbent, Adsorption, Paraquat, Wheatplant ash

Paraquat (1-1′-dimethyl-4, 4′-bipiridyl, a biquaternary ammonium compound), is a non-selective contact herbicide that is normally synthesized as a dichloride salt. It is also used as a weedicide in agricultural fields¹. Paraquat (PQ) is cationic in nature, highly solubility in water (620 g/L) , and exhibits high mobility in the environment. It is frequently found in surface and in drinking waters, due to water infiltration from soils contaminated with industrial wastes containing PQ^2 . The common methods adopted to reduce leaching of pesticides into surface or groundwaterare adsorption, membrane technology, oxidation, ozonation, voltammetry and photocatalysis³. Among these methods, adsorption is an extensively implemented technique owing to its inherent advantages such as low cost, easiness in operation, simplicity of design, and insensitivity to toxic pollutants⁴. A variety of adsorbents are used for removal of paraquat, such as bleaching earth, laponite, goethite, waste coffee grounds, activated clay, regenerated clay mineral, clays and organoclays, rice husk ash(RHA), and bagasse fly ash (BFA).

Although advances in agricultural techniques, especially application of synthetic inorganic fertilizers and pesticides, have significantly increased agricultural

productivity, many ofthe chemicals applied are harmful to humans and the environment. Moreover, contamination of nearby waterbodies is another serious problem due to the extensive use of agrochemicals, affecting supplies of potable water and requiring expensive water treatment². Pesticides are a class of persistent organic pollutants that play an important role in crop production and protection. Some pesticides tend to leach through the soil and contaminate the groundwater as well as surface waters and may have adverse effects on human health. Adsorption is one of the best methods for the removal of organic pollutants, and thus, development of new synthetic and economically valuable adsorbents for the removal of organic pollutants may prove invaluable⁵.

Wheat (*Triticum* spp.; Family: Poaceae; subfamily: Pooideae) is primarily cultivated for its grains. In 2013, the total wheat production globally was 713 million tons⁶. Several studies have been conducted on using wastes generated during wheat cultivation as adsorbents: For example, Bulut and Haluk studied adsorption of methylene blue on wheat shells⁷; Ali and Monji prepared adsorbents from wheat bran and studied their efficiency for adsorption

of heavymetals⁸. In a recent study by our research group, WPA was also evaluated for the removal of $2,4$ -D from soil⁹.

In this work, we studied the batch adsorption of paraquat from aqueous solutions on wheat plant ash (WPA) surface. The adsorbed amounts of paraquat were measured in equilibrium. Kinetic parameters were investigated to determine the ratio of reaction time to adsorbed amounts. Various parameters of adsorption were studied in depth such as adsorbent dosage, initial concentration, and contact time. WPA was characterized by X-ray fluorescence (XRF) analysis, proximate analysis, CHNS analysis, Brunauer–Emmett–Teller (BET) surface area analysis, Fourier transform infrared (FTIR), and scanning electron microscopy (SEM). 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 WPA on farmlands and appropriate dosage/hectare is discussed in this paper.

Experimental Section

Preparation of adsorbent

Wheat plant straws were collected from a local farm near Nagpur (Maharashtra, India). They were manually cleaned of dust and soil traces to prevent contamination. Wheat plantremains were sun dried on the farm and burnt in a combustor with grate. Air was circulated via a blower at a low velocity that assists in combustion. The temperature attained by wheat

plantstraw during the process varies at the start and end of the combustion process (range,350–650°C). The residue(i.e., wheat plant ash) thus produced was then cooled and packed in air-tight polyethylene bags. Wheat plant ash was sieved using a BSS 25-mesh sieve to remove larger and unburned particles. Powdered wheat plant ash of size less than 0.3 mm was used for further characterization studies.

Methods and techniques

Surface characteristics, namely, surface area, pore diameter, and volume, were measured using a Micromeritics ASAP2010 instrument. The percentage of chemical composition of wheat plant ash was examined based on surface chemical composition analysis are shown in Table 1, which was performed using an X-ray fluorescence (XRF) analyzer (PW 2403; PANalytical).

Proximate analysis of WPA was performed using gravimetric methods to determine the percentage of moisture content, volatile matter, carbon, and ash content are shown in Table 2. Standard procedures

Table 2 — Kinetic and isotherm models applied for paraquat adsorption using WPA

detailed elsewhere were adapted 10 . 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) (Table 2).

Physicochemical characteristics

Physical properties such as porosity, particle density, bulkdensity, and water-absorption capacity were determined. Porosity, particle density, and bulk density of WPA were determined using the tap-density method. Water-absorption 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 wateradsorption capacity of WPA. The mean particle size of the WPA 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 deionized water. This solution was then diluted according to the condition of each experiment. Properties of paraquat are presented in Table 3.

Batch adsorption

Batch adsorption experiments were performed in a constant-temperature waterbath in which the glass

vials were shaken. The vials contain paraquat solution and predefined quantity of WPA. The samples were then withdrawn aftercertain time and filtered. The supernatant after centrifugation of filtrate was analyzed on an UV–Vis 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) – (3) , respectively.

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

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

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

where C_0 (mg/L) is the initial concentration; C_e (mg/L) is the equilibrium concentration; Vis 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

Understanding the kinetics of adsorption is useful to examine the rate-governing step as well as the mechanisms involved in the adsorption process. The most commonly applied kinetic models are pseudofirst-order (PFO), pseudo-second-order (PSO), Elovich (EL), and intraparticle diffusion $(IPD)^{11}$. The adsorption capacity, which is an important parameter for the selection of an adsorbent, is generally calculated from isotherm models. The parameters and assumptions of isothermal models provide valuable information about the adsorbent–adsorbate interaction, and surface characteristics of adsorbent and its affinity. The well-known isotherms are Langmuir, Freundlich, Temkin,and Dubinin– Radushkevich (D–R) models 12 and these are applied in this paper. The kinetic and isothermal equations used to study the adsorptive removal of paraquat on WPA are presented in Table 4. The model constants are determined from slopes and intercepts of linearized form of equations.

Results and Discussion

Characterization of WPA

Scanning electron microscopy

Scanning electron microscope (SEM) is a kind of electron microscopethat produces a sample image when an electron beam focuses on the sample. The electrons generated interact with the sample and produce various signals that contain information about the sample surface topography and composition.

In this work, high-resolution SEM(JSM6380A; JEOL, Tokyo, Japan) images were obtained to study the morphology and surface characteristics of WPA. SEM images of $5000 \times$ magnification were obtained and surface irregularities of samples were studied (Fig. 1). As can be seen, surface pores are distinctly visible, thus confirming the surface characteristics that are responsible for binding of paraquat onto the WPA surface

Fourier transform infrared spectroscopy (FTIR)

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This offers a significant advantage over a dispersive spectrometer, which is used to measure intensity over a narrow range of wavelengths for a specific period. The functional groups on the ash surface were determined by FTIR (Perkin Elmer Spectrum-1). FTIR spectroscopy also provided valuable insights on the surface chemistry of WPA. Figure 2A,B shows the FTIR spectral images of WPA before and after adsorption.

Characteristic bands of calcium carbonate occur at 770–870 and 1400–1450 cm^{-1} . Bonds between 1100

Fig. 1 **—** Scanning electron microscopy of WPA

and 1300 cm[−]1 are attributed to the presence of cellulosic derivative and CO stretching¹³; additionally, carbonate bonds were also observed on the surface of WPA in this study.

Paraquat shows characteristic peaks at 3055 and 3018 cm⁻¹, which are assigned to the C–H tension mode of the methyl groups on the aromatic ring in the paraquat molecule; additionally, a set of bands between 1641 and 1194 cm⁻¹ is assigned to the C–C tension mode and the C–H deformation mode in the aromatic ring plane¹⁴.

The FTIR spectrum of WPA after adsorption of paraquat is shown in Fig. 2C. As can be seen, the spectrum 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 set of bands can also be seen at 1600 cm^{-1} , which may be assigned to the C–C stretching mode and the C–H deformation mode in the aromatic ring plane¹⁵.

Effect of BMA dosage

The variation in paraquat removal with dosage was studied by increasing WPA dosages from 0.025 to 0.5 g/100 mL, respectively. The experiments were performed at constant concentration (20 mg/L) and time (16h). At a WPA dose of 0.5 g/100 mL, 88.62% removal was achieved (Fig. 3); however, no significant removal was observed at all other ranges, so this dosage was chosen as the optimal value for all studies.

Fig. 2 **―** FTIR spectra: Spectrum Fig. 2A, paraquat; Spectrum Fig. 2B, WPA before adsorption; and Spectrum Fig. 2C, WPA after adsorption.

Effect of initial concentration

The initial concentration of adsorbate was increased from 5 to 40 mg/L at a fixed adsorbent(WPA) dose to study its effect on paraquat uptake at a constant temperature (303 K) and at a contact time (16 h). The maximum removal (88.22%) of paraquat was achieved at the initial concentration (5 mg/L; see Fig. 4). As can be seen, the percentage removal decreased with the increase in the amount of paraquat concentration. Because WPA has limited number of 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, 20 mg/L was chosen as the concentration of paraquat for further studies.

Effect of contact time

To determine the equilibrium time for removal of paraquat on WPA, adsorption studies were performed for different contact times at a constant initial concentration. The results are plotted in Fig. 5 for 20 mg/L initial concentration of paraquat adsorbed on WPA, respectively. The initial uptake on WPA was fast and approximately 58% removal was achieved within 5 min. In the later stages of adsorption, the removal on WPA was slower. It can be seen in Fig. 5 that equilibrium was achieved at 30 min of contact time.

Adsorption kinetic modeling

The results of the effect of contact time on adsorption were analyzed using linearized kinetic

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

models presented in Table 2. The model parameters determined from the slope and intercept of the line for both adsorbents are presented in Table 5. The values of coefficient of determination (R^2) for the PSO kinetic model (Fig. 6) are significantly higher and closer to unity than those for the PFO (Fig. 7) and Elovich models (Fig. 8) for both ashes studied. In addition, the equilibrium capacity predicted by the PSO model for WPA is similar to that obtained in experiments. Therefore, the PSO kinetic model (Fig. 7) best describes the adsorption of paraquat on WPA.

The Weber–Morris plot $(q_tvs t^2)$ of the IPD model presented in Fig. 9 indicates multilinearity for WPA.

Fig. 6 **―** Pseudo-first-order kinetic model for adsorption of paraquat on WPA

Thus, it can be deduced that there exist two or more rate-limiting steps in this adsorption process. The initial stage in Fig. 9 corresponds to the instantaneous adsorption of paraquat on the external surface of WPA. The second part of the plot is ascribed to intraparticle diffusion, which indicates slow adsorption of molecules within the pores¹¹. The third part represents the attainment of adsorption equilibrium. The slopes of the initial two stages of the plot are indicated as k_{d1} and k_{d2} (Table 5), respectively. The rate constants, k_{d1} and k_{d2}

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

Fig. 8 **―** Elovich kinetic model for adsorption of paraquat on WPA

Fig. 9 **—** Weber–Morris plot for adsorption of paraquat on WPA

correspond to external mass transfer and intraparticle diffusion, respectively. In this study, $k_{d1} > k_{d2}$, which indicates that the paraquat molecules are initially adsorbed on the surface because of external mass transfer, and then diffuse inside pores. The value of k_{d2} indicates the rate constant of IPD, whereas the intercept C_2 is related to boundary-layer thickness.

Adsorption isotherm modeling

The isotherm models, namely, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich were applied to the adsorption of paraquat on WPA at 30°C (303K). The isothermal parameters and coefficient of determination (R^2) values for the linear regression model are listed in Table 6. R^2 values close to one indicate the best fitting of Langmuir isotherms (see Fig. 10). The Langmuir isotherm is based on

Fig. 10 **―** Langmuir isotherm model for adsorption of paraquat on WPA

monolayer adsorption with a fixed number of homogeneous adsorption sites. The monolayer adsorption capacity of WPA given by Langmuir isotherm is about 8.928 mg/g. The important characteristics of Langmuir isotherm can be expressed by a dimensionless constant:"separation factor" or "equilibrium parameter". The dimensionless factor was calculated using Langmuir constant. The dimensionless factor is given as

$$
R_{L} = \frac{1}{(1 + K_{L}C_{0})} \qquad \qquad \dots (4)
$$

The parameter R_{L} indicates the shape of isotherm as follows

The value of R_L was used to decide the nature of adsorption. In this study, the values of *RL* were observed in the range between 0 and1 for WPA. This implies the favorability of paraquat adsorption performed at 30°C on WPA.

The Freundlich isotherm model describesthe relation between nonideal andreversible adsorption¹⁶. and can be applied to multilayer adsorption. The Freundlich and Temkin isotherm models assume the heterogeneous surface of the 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 WPA(Fig.11).

Fig. 11 **—** Freundlich isotherm model for adsorption of paraquat on WPA

Fig. 12 **―** Temkin isotherm model for adsorption of paraquat on WPA

The Temkin isotherm (Table 1) contains a factor, A_T , that corresponds to binding interaction between adsorbate and adsorbent at equilibrium, where b_T (Temkin isotherm constant) is related to heat of adsorption. The values of b_T for paraquat removal on WPA are less than that stated for the ion-exchange mechanism (8–16 kJ/mol). Similarly, adsorption energy for physisorption is reported to be less than – 40 kJ/mol¹⁷. Therefore, physisorption of paraquat on WPA is proposed in this study (Fig. 12).

The Dubinin–Radushkevich (D–R) isotherm model is usually applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has been successfully fitted to high soluteactivities and for the intermediate range of concentrations data¹⁸. The D–R model is also used to determine physical or chemical adsorption based on the value of mean free energy E. A value of E between 8 and 16 kJ/mol indicates chemical adsorption, whereas a value of E below 8 kJ/mol indicates physical adsorption⁴ (Fig. 13).

Comparison of adsorption capacity of various adsorbents for paraquat

Table 7 presents a comparison of Langmuir adsorption capacity of various adsorbents for paraquat removal. The adsorption capacities in this table are reported as (i) the quantity of adsorbate adsorbed (mg) per unit mass (g) of the adsorbent and (ii) the quantity of adsorbate adsorbed (mg) per unit surface area $(m²)$ of the adsorbent. Compared with natural (neither chemically modified nor laboratory synthesized), lowcost, and soil-compatible adsorbents, WPA has the

Fig. 13 **—** Dubinin–Radushkevichisotherm model for adsorption of paraquat on WPA.

Table 7 ― 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)	Refs
Goethite	57.6	0.77	13.36	[19]
Waste coffee grounds	1040.3	0.07	0.06	[20]
Activated clay	266	0.06	0.22	[21]
	270	0.05	0.18	
	230	0.04	0.17	
Regenerated clay mineral	101.5	1.31	12.9	[22]
Clays and organoclays	292	0.86	2.94	[23]
	73	2.97	40.68	
	200	3.81	19.05	
WPA	37	8.928	241.3	This study

highest adsorption capacity $(mg/m²)$ for paraquat removal, compared with some of the adsorbents reported in the literature. This indicates that the studied WPA is the most efficient adsorbent for the removal of paraquat from aqueous solutions.

Conclusion

In this study, we have used WPA as an adsorbent for paraquat removal from aqueous solution and determined surface chemical composition of WPA. XRF analysis indicated that WPA contains higher $SiO₂(58.88wt %)$, but Si is unfavorable for adsorption. Therefore, WPA can be used as a source of Si in various industries. The mean particle size of WPA is 0.129 mm, BET surface area was $37 \text{ m}^2/\text{g}$, and PZC was 11.45, which indicates the alkaline nature of the adsorbent. The SEM image of WPA shows regular surface with deep pores exhibiting a repeated pattern.

The equilibrium for paraquat adsorption on WPA surface was practically achieved in 30 min. The pseudosecond-order kinetic model was found to be the best to describe the present system. Adsorption data were applied to four isotherm models, namely, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich. Our result shows that the Langmuir isotherm model has the best fit among these. The Langmuir model confirms monolayer adsorption and WPA's adsorption capacity was found to be 241.3 mg/m².

It is recommended to spread WPA uniformly on land before pesticide application, so that the dual properties of WPA (i.e. yield booster and adsorbent) can be effectively utilized. WPA serves multiple purposes: (i) as an adsorbent for removal of pesticides; (ii) as a soil additive and water enhancer; and (iii) as a micronutrient source for plants.

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