Use of biomass ashes in agriculture with reference to farming practices in Vidarbha, Maharashtra, India

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As a regular farming practice in India, especially in Vidarbha, biomass ashes (BMAs) are spread on farmland. BMA forms a protective layer on the soil surface and acts as a barrier, thereby preventing direct contact between pesticides and soil. BMA acts: (i) as an adsorbent for removal of pesticides; (ii) as a soil additive and water enhancer, and (iii) as a micronutrient source for plants. In this study, paraquat, a representative chemical was selected to prove the hypothesis that BMAs are the most efficient adsorbents of herbicides used in Vidarbha. The adsorption capacity (mg/m^2) of BFA for removal of paraquat was found to be greater than that reported for natural adsorbents. Based on adsorption capacity, RHA and BFA dosages per hectare of land are recommended for different crops and fruits.

Keywords: Adsorption, bagasse fly ash, biomass ash, paraquat, rice husk ash.

In the recent past, many farmers committed suicide in the Vidarbha region of Maharashtra. According to a report, 3228 farmers in Maharashtra ended their lives in 2015. Of these, 1514 farmers were from Amravati and Nagpur divisions[1]. One reason provided for the suicide is 'crop failure'[2]. Farmers in Vidarbha use pesticides on a large scale to achieve high agricultural productivity. Once the pesticides are sprayed on crops, some portions of the chemicals leach into the soil and enter into the ecosystem. It then moves from one system to another or degrades or in some cases just remains in the same system, either in its original form or as a metabolite. The pesticides used in agricultural applications have sufficient mobility and persistence under suitable conditions, which allows them to leach into the ground and surface waters[3]. Figure 1 shows a typical pesticide run-off.

In the past few years, there has been significant increase in the levels of pesticides detected in groundwater resources. The adverse effects of pesticides on both humans and animals, have now become a topic of intensive discussion, with several reports stressing immediate need to remove pesticides from groundwater resources. Some of the methods introduced for pesticide removal include photocatalytic degradation, combined photo-Fenton and biological oxidation, advanced oxidation process, aerobic degradation, nanofiltration, ozonation, coagulation, fluid extraction, solid-phase extraction and adsorption[4]. Among these methods, adsorption is simple to design and easy to operate for pesticide mitigation. Recent studies have confirmed the use of biomass ashes (BMAs) as effective adsorbents for pesticide removal[5–9]. In India, especially in Vidarbha, BMAs are spread on farmland as a regular farming practice. BMA forms a protective layer on soil surface and acts as a barrier that prevents direct contact between pesticides and soil. It has been hypothesized that as soon as the pesticide comes in contact with BMA, a state of equilibrium is reached almost instantly and the pesticide gets adsorbed on the BMA surface. Thus, the kinetic rate, compatibility with soil, cost and nutritional value of the crop are all major factors to be considered for selecting an adsorbent for field applications.

In this study, we surveyed the most common crops produced and pesticides, especially herbicides applied in the fields in and around the Vidarbha region. Finally,
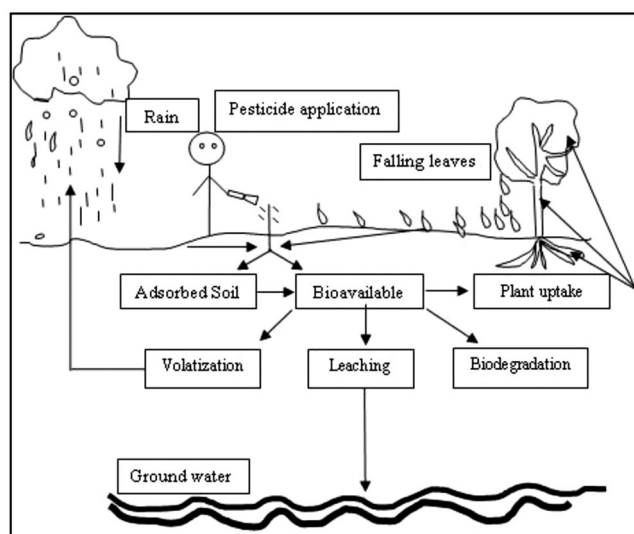

Figure 1. Pesticide run-off.

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paraquat was chosen as the representative herbicide and rice husk ash (RHA) and bagasse fly ash (BFA) were chosen as adsorbents. Both RHA and BFA have high kinetic rate for herbicide removal[8] and offer advantages of low cost and high soil compatibility. Besides, these ashes have also been reported to promote crop yield by about 24%[10]. In this study, we aimed at evaluating the comparative efficacy of RHA and BFA for removal of paraquat through batch experiments for different dosages of RHA/BFA, paraquat concentration, contact time, and particle size of RHA/BFA. Based on the results, RHA and BFA dosages per hectare of land were recommended for different crops and fruits.

Paraquat is one of the most widely used herbicides to control the growth of weeds. It is a contact and pre- and post-emergence herbicide[11]. Several studies have reported the presence of paraquat in water bodies in different zones around the world. According to European standards, the maximum allowable concentration of individual pesticides (including paraquat) in drinking water and surface water is 0.1 μg/l and 1–3 μg/l respectively[12]. In earlier studies, natural adsorbents such as activated bleaching earth, laponite, goethite, waste coffee grounds, activated clay, regenerated clay mineral, clays, and organo clays (sepiolite, bentonite, or illite) were used for paraquat removal[13–19]. To the best of our knowledge, ashes have not yet been explored as adsorbents for paraquat removal. Therefore, in this work, BMA has been used as an adsorbent for the removal of paraquat (herbicide). Further, we have attempted to relate the ash characteristics with its adsorption performance.

Materials and methods

Adsorbent

RHA was supplied by Yash Agro Ltd (Nagpur, India) and BFA was supplied by Wainganga Sugar and Power Ltd (Bhandara, India). The moisture, volatile matter, ash and fixed carbon contents of each ash were determined using the IS:1350 (Part 1-1984) standard method of proximate analysis. The surface characteristics were measured using Brunauer–Emmett–Teller (BET) method and surface area analyser (Micromeritics, ASAP-2010). The elemental composition of each ash was determined using XRF analyser (PANalytical, PW-2403) and Elemental Analyser (vario MICRO cube, Elementar).

Adsorbate

Paraquat (98%) obtained from Sigma Aldrich, was used as an adsorbate. The chemical formula and molecular weight of paraquat are $C_{12}H_{14}Cl_2N_2$ and 257.16 g/mol respectively. We prepared a stock solution of paraquat in deionized water. This solution was then diluted according to the condition of each experiment.

Batch adsorption

The batch adsorption experiments were performed in a constant-temperature water bath by shaking the glass vials. The vials contained paraquat solution and a predefined quantity of RHA/BFA. The samples were withdrawn after a certain time and then filtered. The supernatant after centrifugation of filtrate was analysed on an UV/Vis spectrophotometer (Shimadzu UV-1800, Japan) at 257 nm. The percentage removal and adsorption capacity at any time and at equilibrium (Q_t and Q_e respectively, mg/g) were calculated using eqs (1)–(3) respectively.

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

$$Q_t = \frac{(C_0 - C_t)V}{W}, \tag{2}$$

$$Q_e = \frac{(C_0 - C_e)}{W}V, \tag{3}$$

where C_0 (mg/l) is the initial concentration, C_e (mg/l) the equilibrium concentration, $V(L)$ the volume of adsorbate solution and $W(g)$ is the mass of the 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 modelling

Understanding the kinetics of adsorption helps in examining the rate-governing step and the mechanisms involved in adsorption process. The most commonly applied kinetic models are pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich (EL), and intraparticle diffusion (IPD)[20]. The adsorption capacity, an important parameter for selection of an adsorbent, is generally calculated from isothermal models. The parameters and assumptions of isothermal models provide valuable information on adsorbent–adsorbate interaction, and surface characteristics of adsorbent and its affinity. The well-known isothermal models, Langmuir, Freundlich and Temkin models[21] are applied in this study. The kinetic and isotherm equations used to study the adsorptive removal of paraquat on RHA and BFA are presented in Table 1. The model constants are determined from the slopes and intercepts of linearized equations.

Table 1. Kinetic and isotherm models applied for paraquat adsorption using BMA

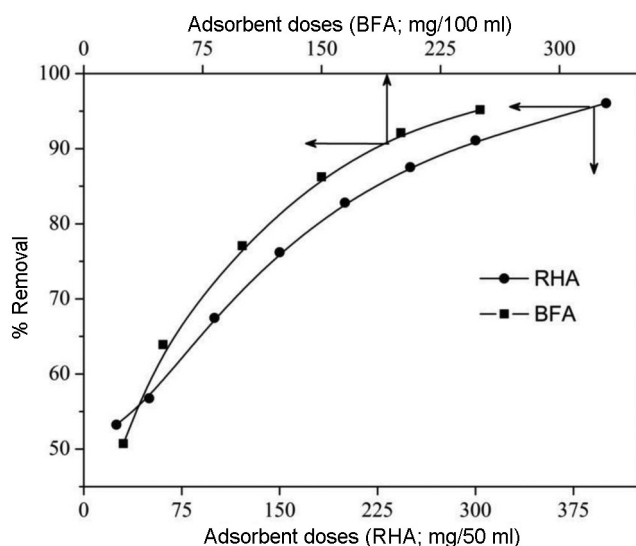|	Linearized form	Plots	Slopes	Intercepts
Kinetic models				
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t) : \mathrm{vs} : t$	$-k_1$	$\ln q_e$
Pseudo-second order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{t}{q_e}$	$\dfrac{t}{q_t} : \mathrm{vs} : t$	$\dfrac{t}{q_e}$	$\dfrac{1}{k_2 q_e^2}$
Elovich	$q_t = \dfrac{1}{\beta} \ln(\alpha\beta) + \dfrac{1}{\beta} \ln t$	$q_t : \mathrm{vs} : \ln t$	$\dfrac{1}{\beta}$	$\dfrac{\ln(\alpha\beta)}{\beta}$
Intraparticle diffusion	$q_t = k_d t^{1/2} + C$	$q_t : \mathrm{vs} : t^{1/2}$	k_d	C
Isotherm models				
Langmuir	$\dfrac{C_e}{q_e} = \dfrac{1}{K_L q_{\max}} + \dfrac{C_e}{q_{\max}}$	$\dfrac{C_e}{q_e} : \mathrm{vs} : C_e$	$\dfrac{1}{q_{\max}}$	$\dfrac{1}{K_L q_{\max}}$
Freundlich	$\log q_e = \log K_F + \dfrac{1}{n} \log C$	$\log q_e : \mathrm{vs} : \log C_e$	$\dfrac{1}{n}$	$\log K_F$
Temkin	$q_e = B \ln A_T + B \ln C_e ; \quad B = \dfrac{RT}{b_T}$	$q_e : \mathrm{vs} : \ln C_e$	B	$B \ln A_T$

Figure 2. Effect of BMA dosage on percentage removal of paraquat.

Results and discussion

Characterization of BMA

The proximate analysis indicated 1.80/6.30% moisture, 6.16/42.46% volatile matter, 89.87/40.16% ash and 2.14/11.0% fixed carbon in RHA/BFA respectively. The percentage of carbon calculated using CHNS analysis was 5.85/47.37, whereas that of silica by XRF analysis was 81.78/36.14% in RHA/BFA respectively. BMAs were found to contain trace quantities of Al_2O_3, K_2O, Fe_2O_3 and CaO, all of which play a significant role during adsorption by imparting surface charges to the BMA surface in an aqueous solution. The BET surface area of BFA was found to be 55 m^2/g, whereas that of RHA was 34 m^2/g. The large surface area of BFA may be due to

high carbon and less silica content. The pore volumes ($4.96 \times 10^{-2} cm^3/g$ and $2.69 \times 10^{-3} cm^3/g$) and pore diameter (46 Å and 81 Å) of BFA and RHA respectively, indicate the presence of shallow pores on RHA and deep pores on BFA. A detailed characterization of RHA and BFA is reported in another study[7].

Effect of BMA dosage

The change in paraquat removal with changes in dosage was studied by increasing the RHA and BFA dosages from 0.025 to 0.4 g/50 ml and from 0.025 to 0.25 g/100 ml respectively. The experiments were carried out keeping concentration (20 mg/l) of paraquat constant for a contact time of 12 h. The results shown in Figure 2 reveal that the percentage removal of paraquat on BFA is more than that on RHA. Therefore, the adsorption capacity of BFA at equilibrium was found to be greater. This is because of higher BET surface area and carbon percentage in BFA than that of RHA. Almost 91% of paraquat was removed on 0.250 g RHA and 0.2 g BFA. However, beyond this range there was no significant change and therefore, the aforesaid dosages were selected as optimum for the next studies.

Effect of initial concentration

The initial concentration of adsorbate was increased from 5 to 70 mg/l to study its effect on paraquat uptake at constant temperature (303 K) for a contact time of 16 h. The optimum adsorbent dosages (0.250 g RHA/50 ml and 0.2 g BFA/100 ml) as noticed in the previous section were selected. It is observed in Figure 3 that the removal (%) of paraquat decreased with increase in concentration of the adsorbate. Since BMAs have limited adsorption

sites, the percentage removal significantly reduced for higher concentrations. However, the equilibrium capacity of each ash was enhanced due to reduced mass-transfer resistance, which was overcome by a concentration gradient at higher concentrations. The equilibrium capacity of BMA improved by approximately 3.4 times when the initial concentration was increased from 5 to 70 mg/l. The increment in equilibrium capacity of BFA was higher than that of RHA, due to the higher surface area of BFA. Approximately 85% (86.2% on RHA, 85.81% on BFA) removal was achieved for 25 and 20 mg/l of paraquat using RHA and BFA respectively. Therefore, the concentrations of paraquat selected for the next set of studies are 25 and 20 mg/l for RHA and BFA respectively.

Effect of contact time

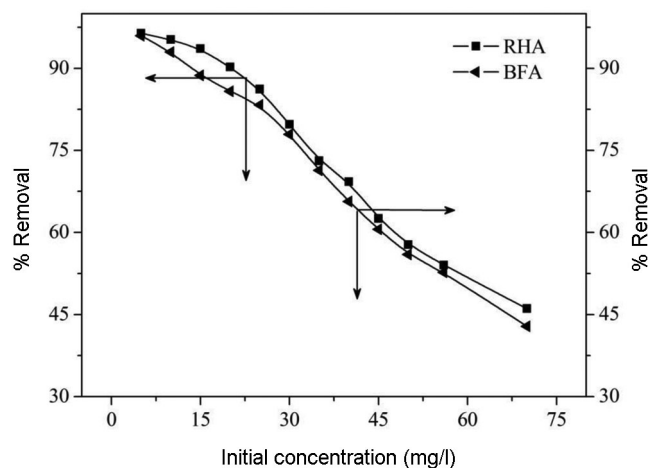To determine the equilibrium time for removal of paraquat on RHA and BFA, adsorption studies were performed

for different contact times at constant initial concentration. The experiment was performed for 0.250 g RHA/50 ml and 0.2 g BFA/100 ml. The results are plotted in Figure 4 for 25 and 20 mg/l initial concentrations of paraquat adsorbed on RHA and BFA respectively. The initial uptake on both ashes was fast and about 50% was removed within the first 5 min. In the later stages of adsorption, the removal on BFA was slower when compared to that on RHA. It can be seen in Figure 4 that equilibrium was reached at 60 min and 300 min of contact time for RHA and BFA respectively. The slower uptake and higher equilibrium time for BFA was due to deeper pores on the surface. However, the opposite trend was observed for RHA due to shallow pores as described in the 'characterization of BMA' section. It was observed that BFA had approximately 3.4 times higher equilibrium capacity than that of RHA.
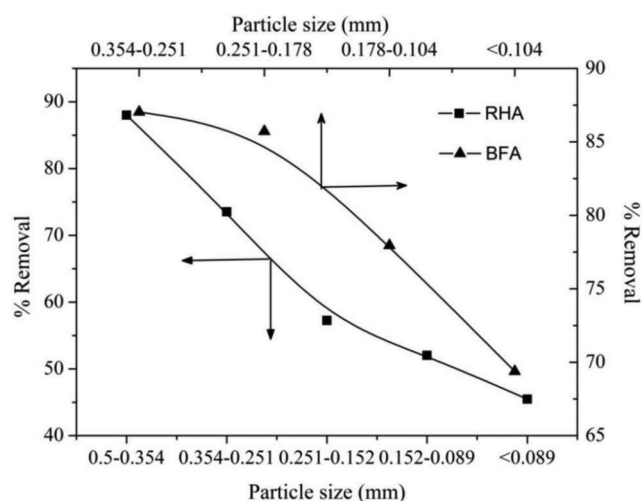

Figure 3. Effect of initial concentration on percentage removal of paraquat.

Figure 5. Effect of particle size on percentage removal of paraquat.

Figure 4. Effect of contact time on percentage removal of paraquat using RHA and BFA.
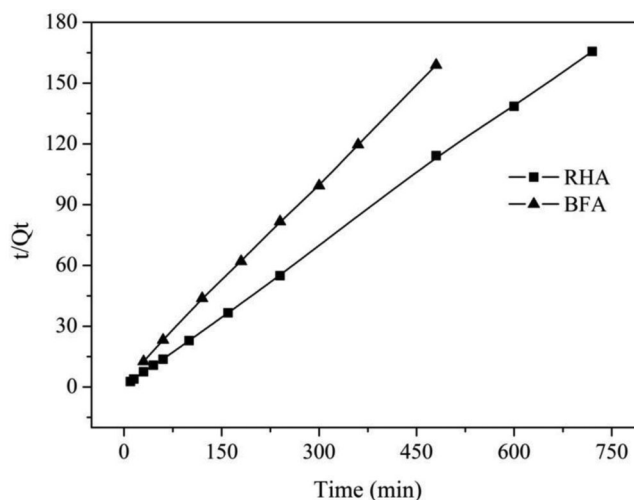

Figure 6. Pseudo-second-order kinetic model for adsorption of paraquat on RHA and BFA.

Table 2. Characteristics of various particle size ranges of BMA

	RHA			BFA	
Particle size (mm)	BET surface area (m²/g)	Silica to carbon ratio	Particle size (mm)	BET surface area (m²/g)	Silica to carbon ratio
0.500–0.354	92.08	6.02	0.354–0.251	98.08	0.12
0.354–0.251	44.37	14.76	0.251–0.178	84.85	0.29
0.251–0.152	26.25	23.60	0.178–0.104	62.58	0.86
0.152–0.089	17.92	28.58	≤0.104	35.50	2.02
≤0.089	13.65	31.83			

Table 3. Kinetic model parameters for paraquat adsorption on BMA

	Pseudo-first-order model				Pseudo-second-order model		
C_0 (mg/l)	q_e exp (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
RHA 25	4.369	0.078	2.062	0.842	0.201	4.329	0.999
BFA 20	2.939	0.017	1.017	0.966	0.387	3.076	0.999

	Elovich model			Intraparticle diffusion model				
	α (mg/(g min))	β (g/mg)	R^2	k_{d1} (mg/(g min$^{1/2}$))	C_1 (mg/g)	R^2_1	k_{d2} (mg/(g min$^{1/2}$))	C_2 (mg/g)	R^2_2
RHA 25	8.094	1.589	0.722	0.278	2.515	0.709	0.010	4.481	0.694
BFA 20	2.579	2.439	0.846	0.086	1.859	0.960	0.014	2.727	0.760

Effect of particle size of BMA

Each BMA was separated into different particle sizes using British standard sieves. Each particle size range, shown in Table 2, was allowed to react with paraquat (25 mg/l for RHA and 20 mg/l for BFA) by constantly shaking for 12 h. It was found that the removal of paraquat is more on bigger particles of RHA and BFA (Figure 5). The behaviour of BMA as an adsorbent has been discussed by us earlier[7]. The possible reason for maximum removal of paraquat for bigger particles is due to the fact that they have smaller silica-to-carbon ratio (Table 2) which indicates larger number of carbon particles present in the ash. As carbon is a better adsorbent than silica, there is maximum removal of paraquat for bigger particles.

The blocking of pores (mesopores/macropores) by submicrometer-scale particles may be a possible reason for lesser surface area of smaller particles. Further, non-porous fines may be present in both ashes, which might have triggered the formation of smaller particle-size. Deokar et al.[7] obtained similar results while studying the removal of 2,4-D on BMA. The present results reconfirm the previously reported findings[7]. The equilibrium capacity of 0.354–0.251 mm particle size of RHA was calculated to be 6.54 mg/g and that of same particle size of BFA was 22.22 mg/g. Therefore, it is suggested that the equilibrium capacity of 0.354–0.251 mm particle size of BFA is approximately 3.4-fold higher than that of RHA, whereas the BET surface area for BFA of the same particle size is approximately 2-fold greater than that of RHA.
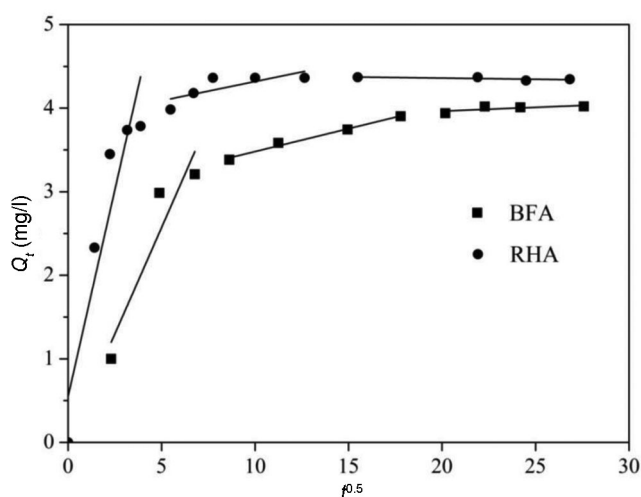

Figure 7. Weber–Morris plot for adsorption of paraquat on RHA and BFA.

Adsorption kinetic modelling

The results of the effect of contact time on adsorption were analysed using linearized kinetic models (Table 1). The model parameters determined from the slope and intercept of the line for both adsobents are presented in Table 3. The values of coefficient of determination (R^2) for the PSO kinetic model are significantly higher and closer to unity when compared to PFO and Elovich models for both ashes studied. In addition, the equilibrium capacity predicted by the PSO model for each ash is similar to that obtained in experiments. Therefore, the PSO kinetic

model (Figure 6) best describes the adsorption of paraquat on BMA.

The Weber–Morris plot (q_t vs $t^{1/2}$) of the IPD model in Figure 7 indicates multilinearity for RHA and BFA. Thus, it can be deduced that there exist two or more rate-limiting steps in this adsorption process. The initial stage in Figure 7 corresponds to the instantaneous adsorption of paraquat on the external surface of the ashes. The second part of the plot is ascribed to intra-particle diffusion, which indicates slow adsorption of molecules within the pores[5]. 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, $k_{d1} > k_{d2}$, 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 modelling

The isotherm models, namely, Langmuir, Freundlich and Temkin were applied to the adsorption of paraquat on BMA at 30°C. The isotherm parameters and coefficient of determination (R^2) values for the linear regression model are listed in Table 4. R^2 values close to one indicate the best fitting of Langmuir and Temkin isotherms, as shown in Figures 8 and 9 respectively. The Langmuir isotherm is based on monolayer adsorption with a fixed number of homogeneous adsorption sites. The monolayer adsorption capacity of BFA given by Langmuir isotherm is about 3.4 times greater than that of RHA. In a previous study[5], the dimensionless factor given by $R_L = 1/(1 + K_L C_0)$ was calculated using Langmuir constant (K_L). The value of R_L was used to decide the nature of adsorption. In the present study, the values of R_L were observed in the range between 0 and 1 for both ashes. This implies the favourability of paraquat adsorption at 30°C on BMAs. The

Freundlich isotherm assumes the heterogeneous surface of adsorbent. In this study, the adsorption intensity factor (i.e. $1/n$) of the Freundlich isotherm is between 0 and 1 which indicates favourable adsorption of paraquat on RHA and BFA. The Temkin isotherm contains a factor, A_T that corresponds to binding interaction between adsorbate and adsorbent at equilibrium whereas Temkin isotherm constant, b_T, is related to heat of adsorption. The values of b_T for paraquat removal on RHA and BFA 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 (ref. 22). Therefore, physisorption of paraquat on RHA and BFA is proposed in this study.

Comparison between different paraquat adsorbents

Table 5 presents a comparison of Langmuir adsorption capacity of various adsorbents for paraquat removal. The
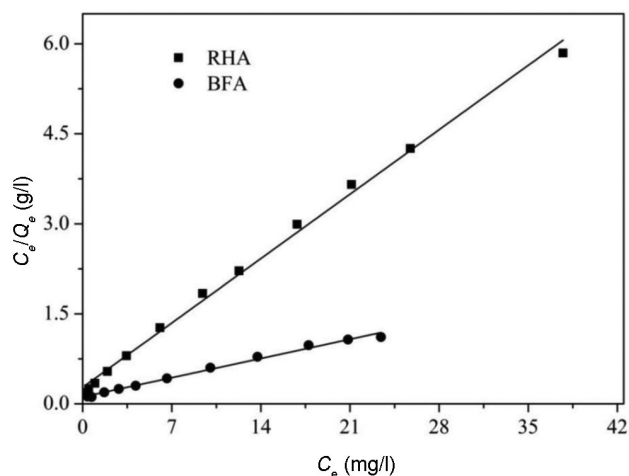

Figure 8. Langmuir isotherm model for adsorption of paraquat on RHA and BFA.
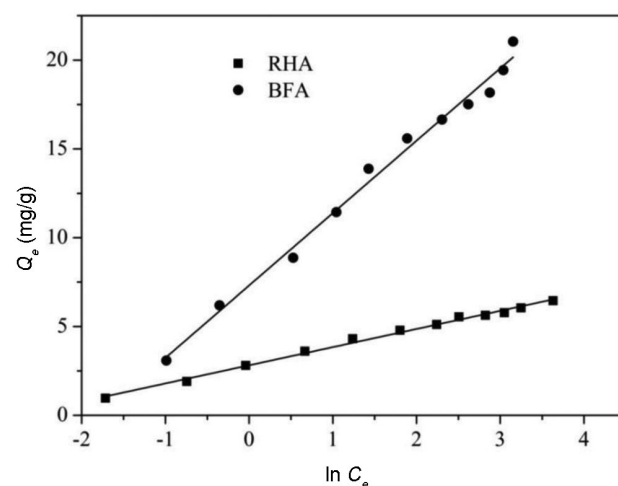

Figure 9. Temkin isotherm model for adsorption of paraquat on RHA and BFA.

Table 4. Isotherm parameters for adsorption of paraquat on RHA and BFA

Isotherm models	Parameters	RHA	BFA
Langmuir	q_{max} (mg/g)	6.53	22.22
	K_L (l/mg)	0.55	0.39
	R^2	0.99	0.99
Freundlich	$1/n$	0.31	0.40
	K_F ((mg/g)/(mg/l)$^{1/n}$)	2.38	0.01
	R^2	0.91	0.92
Temkin	A_T (L/mg)	15.75	6.01
	B (J/mol)	1.02	4.07
	b_T (kJ/mol)	2.42	0.60
	R^2	0.99	0.99

Table 5. Comparison of paraquat adsorption capacity of various adsorbents

Adsorbent	q_{cap} (mg/g)	Surface area (m²/g)	$q_{cap} \times 10^3$ (mg/m²)	Reference
Activated bleaching earth	26.74	268	99.77	13
Laponite	92.57	245	377.83	14
Goethite	0.77	57.6	13.36	15
Waste coffee grounds	0.07	1040.3	0.06	16
Activated clay	0.06	266	0.22	17
	0.05	270	0.18	
	0.04	230	0.17	
Regenerated clay mineral	1.31	101.5	12.9	18
Clays and organo clays	0.86	292	2.94	19
	2.97	73	40.68	
	3.81	200	19.05	
BFA	22.22	55	404	This study
RHA	6.53	34	192.05	This study

adsorption capacities reported in this table are (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 to natural (neither chemically modified nor laboratory synthesized), low-cost, and soil-compatible adsorbents, BFA has the highest adsorption capacity (mg/m²) for paraquat removal. This indicates that the studied biomass ashes (i.e. RHA and BFA) are the most efficient adsorbents for removal of paraquat from aqueous solution.

Agriculture and biomass ashes

Considerable work has been carried out on the use of fly ash[10,23] and biochar[24] in agriculture. The results of these studies have demonstrated the following advantages of using fly ash in agriculture: (i) Increased water-holding capacity of soil; (ii) Saving irrigation water requirement; and (iii) Increased availability of micro nutrients (P, K, Cu, Zn, Mn and Fe) for plants/crops.

Results of field trials confirm that using RHA/BFA on agricultural fields increases crop yield and acts as a supplementary source of P and K. These days farmers use BMA along with coal fly ash. There are many small power generation and co-generation units that use only biomass or biomass in partial amounts with coal. However, handling and disposal of BMA is a solidwaste management issue, with a major portion being disposed in farmlands meant for agricultural purposes.

Agricultural scenario in Vidarbha

Vidarbha comprises two divisions: Amravati and Nagpur. It has 11 districts, namely, Akola, Amravati, Bhandara, Buldana, Chandrapur, Gadchiroli, Gondia, Nagpur, Wardha, Washim and Yavatmal. The crops cultivated in the 11 districts of Vidarbha mainly include soybean,

maize, wheat, rice, cotton, sorghum and sugarcane. Among these, soybean, cotton, rice, maize and wheat are the main crops of the Vidarbha region. Figure 10 shows the annual production of crops in MT in Vidarbha in 2010 (ref. 25). The crop remains, that is, the portion remaining after removing grains/pod, are generally burnt in the field and the ash is spread on the farmland.

We conducted a survey and identified the most commonly used herbicides in this part of India (Table 6). All herbicides listed are acidic in nature. By contrast, the surface of BMA is alkaline in nature. The point of zero charges (pH_pzc) of BFA and RHA are 9 and 8.3 respectively[26,27]. Although the adsorption process depends on many factors such as molecular size, weight of adsorbent molecule, interaction between adsorbate and adsorbent, based on the representative study of paraquat–BFA and paraquat–RHA presented in this work, it can be hypothesized that the listed herbicides and BMAs would prove to be an efficient adsorbent–adsorbate system.

### Recommended dosages of biomass ashes per hectare of land

The Central Insecticides Board and Registration Committee (CIBRC) (Government of India 2015)[28] suggested the use of paraquat herbicide to control weeds in farmland. Table 7 shows the dosages of paraquat/hectare of land for different crops/fruits. During spraying, a large amount of herbicide comes in contact with the soil where it leaches into groundwater or moves with run-off, thereby resulting in contamination of ground and surface water. It is possible to avoid the contamination of water if an adsorbent is added to the soil before spraying herbicide. By doing this, the adsorbent will absorb the herbicide and minimize the contamination of water. Based on Langmuir capacity, we propose the following (Table 7) dosages of RHA and BFA to be added per hectare of farmland. These dosages

Table 6. Commonly used herbicides in Vidarbha

Common name	Structure	Formula	pKa value
2,4-Dichlorophenoxyacetic acid		$C_8H_6Cl_2O_3$	2.73
Glyphosate		$C_3H_8NO_5P$	2.27
Paraquat		$C_{12}H_{14}C_{12}N_2$	4
Quizalofop-*P*-ethyl		$C_{17}H_{13}ClN_2O_4$	0.18
Imazethapyr		$C_{15}H_{19}N_3O_3$	3.9
Fenoxaprop-*P*-ethyl		$C_{18}H_{16}ClNO_5$	0.18
Pyrithiobac-sodium		$C_{13}H_{10}ClN_2NaO_4S$	2.34
Oxyfluoren		$C_{15}H_{11}ClF_3NO_4$	−5 (strongest basic)
Metribuzin		$C_8H_{14}N_4OS$	1.0
Oxidiaryl		$C_{15}H_{14}Cl_2N_2O_3$	6.0
Propaquizafop		$C_{22}H_{22}ClN_3O_5$	2.3
Pendimethalin		$C_{13}H_{19}N_3O_4$	2.8

Table 7. Recommended dosage of RHA and BFA based on Langmuir capacity for cultivation of various crops and fruits

Crop/fruits	Maximum paraquat dosage (kg/ha)	RHA dispersal (kg/ha)	BFA dispersal (kg/ha)
Tea	1.0	153.14	45.00
Potato	0.5	76.57	22.50
Cotton	0.5	76.57	22.50
Rubber	0.6	91.88	27.00
Coffee	0.250	38.28	11.25
Sugarcane	0.500	76.57	22.50
Sunflower	0.400	61.26	18.00
Rice	0.8	122.51	36.00
Wheat	1.0	153.14	45.00
Maize	0.5	76.57	22.50
Grapes	0.5	76.57	22.50
Apple	0.75	114.85	33.75
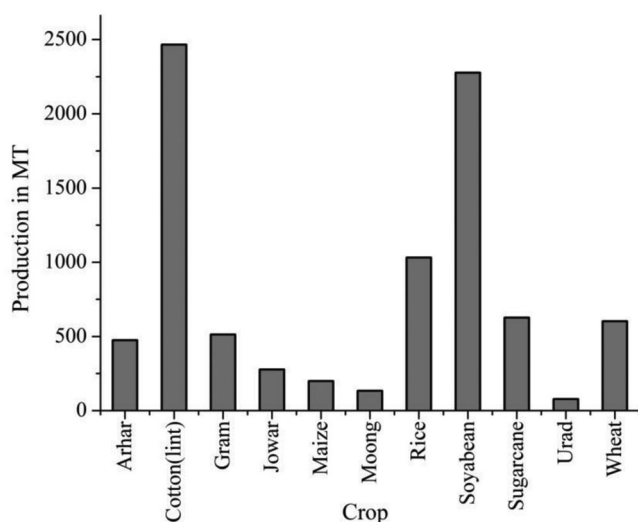
Figure 10. Major crop production in Vidarbha.

may act as a barrier preventing direct contact of herbicide with soil. RHA and BFA have no adverse effects on crops. In fact, direct application of these ashes on land increases crop yield.

Conclusion

The results of the present study show that the equilibrium capacity of RHA and BFA increased by about 3.4 times for increase in concentration from 5 to 70 mg/l. Bigger particles of BMA demonstrated higher adsorption potential due to higher surface area and lower silica-to-carbon ratio than smaller particles which is in confirmation with reported literature[7]. The PSO kinetic model best described the paraquat–BMA adsorption system. The boundary layer and intra-particle diffusion play important roles in controlling the diffusion of paraquat molecules. The application of Freundlich and Temkin isotherms to experimental results confirms the heterogeneous surface of BMA. The adsorption capacity (mg/m^2) of BFA for paraquat removal was found to be greater than that reported for natural adsorbents, which are compatible with farm soil. Specific to the cultivation practice followed in Vidarbha, our survey indicated that all the herbicides used are acidic in nature. By contrast, the surface of BMA is alkaline in nature. Thus, based on a representative study of paraquat–BFA and paraquat–RHA presented in this work, it can be hypothesized that the herbicides used in Vidarbha and BMAs would prove to be an efficient adsorbent–adsorbate system. In general, BMA forms a protective layer on the soil surface and acts as a barrier preventing direct contact between the pesticides and soil. Besides, BMA 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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