

# Kinetics and Equilibrium Isotherms of Pesticides Adsorption onto Boiler Fly Ash

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## ABSTRACT

The adsorption of two herbicides paraquat dichloride (*N-N*-dimethyl-4,4-bipyridinium dichloride) and glyphosate (isopropyl amine glycine) from aqueous solution onto activated boiler fly ash (BFA) was investigated. Kinetics and equilibrium adsorption was followed by UV-spectroscopy in a batch system and the data were treated according to various rate and isotherm models. The results show that the adsorption capacities is dependent on both concentration and time and the adsorption rate increases rapidly with each specified concentration at initial time of one to ten min and attains equilibrium at about 10 min. Glyphosate was adsorbed more than paraquat dichloride. The adsorption dynamics of the pesticides were well fitted to the pseudo-second order kinetic model, with coefficient of determination of 0.9900 for glyphosate and 0.9714 for paraquat dichloride. The equilibrium adsorption was modeled by five isotherms namely; Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Harkins-Jura. From the coefficient of determination ( $R^2$ ), the Freundlich isotherm gave a better fit for paraquat dichloride (0.9899) while the Harkins-Jura isotherm gave a better fit for glyphosate (0.9719). The apparent energy of sorption or mean biosorption energy was found to be 50.0 and 48.83 KJ/mol for glyphosate and paraquat dichloride, respectively, indicating chemisorptions mechanism. Also, a two way ANOVA without replication shows that the differences in the results of the fitness of the isotherms were not significant. Hence, the use of BFA an agricultural waste in the adsorption of these toxic pesticides from aqueous solution is feasible and could be developed into a cheap, cost effective energy requirement and affordable technology for pesticide clean up from wastewater.

**Keywords:** adsorption, aqueous solutions, boiler fly ash, glyphosate, paraquat pesticides

## INTRODUCTION

Contamination of the environment with pesticides is of great concern. Toxic materials, especially pesticides, are being used in large quantities for many purposes in the environment (Imo *et al.* 2007). These substances are adsorbed in soil environment through natural processes occurring in soil water plant relationships (Mirbagheri and Hashemi-Monfared 2009). Also, pesticide residues in food items have been a concern to environmental and consumer groups of their wide spread use (Darko *et al.* 2007). Pesticides have been widely employed in the control of insects as agricultural pests or as threats to human health through the transfer of dangerous diseases (Ckmaca 2002; Pederson *et al.* 2006; Rawn *et al.* 2006; Arjmandi *et al.* 2010). Although these pesticides facilitate the anthropogenic land use, they have been reported to pose danger to biotic species and seriously damage the human living environment (Sudo *et al.* 2002; Na *et al.* 2006). Several methods had been adopted for the removal of environmental contaminants such as pesticide samples, heavy metals, dyes and so on (Abdel-Ghani *et al.* 2007; Mahvi 2008; Adebisi *et al.* 2011; Basse and Grigson 2011). Adsorption is one of the most important factors that affects fate of pesticide in soils and determines their distribution in the soil/water environment (Kah and Brown 2007). Adsorption as a separation and purification technique has been employed from ancient times to partition and remove certain substances by surface attachment. Hence, adsorption technology is important for the separation and purification of substances and is often the value added step in a process industry.

All pesticides have both benefits and risks (Deer 2004). Pesticides are any substance or mixture of substances used

or applied for the prevention, destruction, repelling or mitigation of any kind of pest (Fieldler and Kpen 1997). Apart from controlling pests and diseases, pesticides when released into the environment are either

(1) Broken down or degraded by the action of solar energy, water or other chemical or microorganisms such as bacteria or

(2) They might resist degradation and thus remain unchanged in the environment or ecosystem for a long period of time. The ability of these pesticides to remain unchanged is called pesticide persistence and is measured by the pesticide half life (Fieldler and Kpen 1997), and the soil adsorption coefficient ( $K_{oc}$ ) (Deer 2004). The larger the  $K_{oc}$ , the more strongly the pesticide is held to soil organic matter and the less likely it will leach. Also, a volatile pesticide gets into atmosphere easily and hence causes much environmental hazard (Arias-Estevez *et al.* 2008).

Pesticides are adsorbed on both organic and inorganic soil constituents, biota's, water bodies and even air thereby contaminating the entire ecosystem and consequently, causing a lot of harm to human and other living organisms. Their relative importance depends on the amount, distribution and properties of these constituents found in soil and the chemical properties of the pesticides (Clausen *et al.* 2001). Persistence of pesticide in soil, which greatly affects its migration behavior in different environmental components, is dependent on its adsorption-desorption characteristics and the downward mobility behavior (Ahmed-Shabeer and Gupta 2011). This necessitates the need to carry out environmental impact assessment for pesticide molecules. For instance, dichlorodiphenyltrichloroethane (DDT) in 1960 was discovered to be preventing many fish eating birds from reproducing and therefore was a strong

militant to biodiversity (Gillion *et al.* 1973).

Organophosphates for examples chloropyrite and most carbamates are known for causing water and soil pollution as well as the contamination of vegetables, fruits, milk, food products and other living organisms (Arjmandi *et al.* 2010). They also cause dangerous health problems depending on the extent of exposure to them. Immediate health effect or acute exposure may cause the following effects in min to hours; changes in rate of heart beat, pimples, increased tears from the eyes, nausea, vomiting, diarrhea, muscle cramps, difficulty in breathing, emotional instability, confusion, seizure, coma and possibly death (Burdick *et al.* 1964). Delayed effects to exposure ranging from days to months may cause damage to nerves, arms and legs, muscle weakness, permanent changes in brain chemistry and behaviours that may lead to problem in brain development (Lucky 1978). Organochlorides and chiral pesticides are known to cause abnormality in the hydrogen bonding system of the biomacromolecules of the body of living organisms (RNA and DNA) and this distortion in hydrogen bonding causes improper cell division in the body of the organism and this leads to mutation and finally cancer and death (Maitland 2000).

As a result of these, many methods have been developed such as leaching, chromatography, volatilization, precipitation, etc. to ensure proper removal of these pesticides contaminants. Leaching pesticides from biological wastes have been modeled by others (Vorkamp *et al.* 1997; Taube *et al.* 2002). Also, models for long-term fate of pesticides in soils are considered in recent years (Scholtz and Bidleman 2007). Many pesticides tend to adsorb strongly to the soil, hence strong sorption, low water solubility and low vapour pressure makes leaching, precipitation and volatilization insignificant pathways for pesticide dissipation (Igwe and Abia 2006). Thus good adsorbents which include fly ash from both industrial and agricultural waste biomass, e.g. cocoa pod husk, groundnut husks, maize cob and husk etc, are being developed for effective and efficient dissipation of pesticide contaminants from soil, underground water and industrial wastewater (Mohan and Hosetti 2002; Igwe *et al.* 2009).

Many researchers have reported the adsorption of pesticides on soil, soil constituents, minerals and activated carbon. The adsorptions of atrazine to clays (Laird *et al.* 1992; Moreau-Kervan and Mouvet 1998) and onto iron oxides (Moreau-Kervan and Mouvet 1998) have been reported. The adsorption of isoproturon to clays (Worrall *et al.* 1996), and to chalk aquifers (Johnson *et al.* 1998), has been investigated. Also, adsorption investigations of the ionic pesticides 2,4-D has been carried out on clays (Weber *et al.* 1965; Hermosin and Cornejo 1993; Sannino *et al.* 1997; Celis *et al.* 1999) and oxide minerals (Celis *et al.* 1999). Muller *et al.* (1998) investigated a method for cleaning water polluted with pesticides. Again, a study was carried out on the sorption of the sparingly water soluble pesticide in various types of soil with different levels of organic matter by Zbytniewski and Buszewski (2002). Also, Lin *et al.* (2011) reported on the biodegradation of cypermethrin by a newly isolated actinomycetes HU-S-01 from wastewater sludge.

Whereas, much research has been devoted to study the sorption of pesticides on soils, soil constituents, minerals and aquifer sediments, not much work has been devoted to the sorption of pesticides on cellulose materials or biomass. Different forms of activated carbon have been employed for the adsorption of different pesticides from aqueous solutions. Granular and powdered activated carbon has been used for adsorption of atrazine, bromoxynil and diuron from aqueous solutions (Baup *et al.* 2002). Also, the adsorption from aqueous solutions of ametryn, aldicab, dinoseb and diuron (Ayranci and Hoda 2005), bentazon and propanil (Ayranci and Hoda 2004), metobromuron (Hoda *et al.* 2009) onto activated carbon-cloth; propanil, 2,4-D and prometon onto black carbon (Qiu *et al.* 2009) and diuron, bromoxynil and ametryn onto wheat residue derived black

carbon (Yang *et al.* 2004) has been reported. Also, in a previous study, ethylenediaminetetraacetic acid (EDTA)-modified maize cob and husk was reported as a good adsorbent for a copper fungicide from aqueous solutions (Igwe *et al.* 2009). Therefore, sorption of pesticides on cellulose biomass and agricultural by-products such as boiler fly ash, maize cob and husk, coconut fibre, etc.; the role of certain parameters and the behaviour of pesticide sorption data to certain isotherm and kinetic equations, deserve further investigations in order to evaluate performance in soil, aquifer or ground water contamination clean-up.

Boiler fly ash (BFA) is abundant in Nigeria and it constitutes a waste problem. The fibre and shell are by-products used as boiler fuel to produce heat for mills and for domestic consumption within the mill. BFA is produced in palm oil mills from the burning of fibre and shell. The porous ash contains about 0.28%-1.33% phosphorus, 1.02-4.31% potassium, 0.39-3.24% calcium and 0.29-2.60 magnesium (Rusnani and Ma 1999). BFA an agricultural waste also constitutes waste disposal problems. This material can be easily processed and acquired. BFA is a renewable agricultural waste available at no or low cost (El Geundi 1991). Most of the reported work on the use of fly ash products is on the removal of heavy metals and has to do with the capability of such material in adsorbing the heavy metals. There are few reports on the specific mode of action of the adsorbents and the extent of adsorption (Wataru and Hiroyuki 1998; Okoronkwo *et al.* 2008). The adsorptive capacities of natural products such as maize cob, sugar cane, sunflower stalks, cocoa pods to cationic dyes have been reported to be significantly higher compared to the anionic compounds (Sun 1997). Therefore, it is necessary to explore the adsorption capacity of BFA to organic compounds such as pesticides.

In this study, two herbicides, paraquat dichloride (*N,N*-dimethyl-4,4-bipyridinium dichloride) and glyphosate (isopropyl amine glycine) were selected for the assessment of the adsorptive properties of BFA as adsorbent and the herbicides rate of adsorption with respect to time and concentration applied. The experimental results were also fitted to some known isotherm models and some kinetic equations.

## MATERIALS AND METHODS

### Materials

All reagents used were of analytical grade and used as purchased without further purification. Doubly distilled-deionized water was used in all dilutions. Trioxonitrate (V) acid HNO<sub>3</sub> (69% w/w) was obtained from BDH chemicals, England. BFA was obtained from a local oil mill in Osisioma Ngwa, Abia State Nigeria. The pesticides used; paraquat dichloride and glyphosate were purchased from Bretmont Ltd. (UK) and Syngenta Crop Protection (Switzerland), respectively. The properties of the pesticides are shown in **Table 1**.

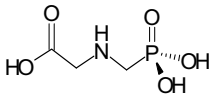
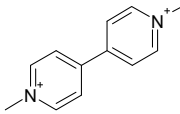
### Adsorbent preparation

The BFA was washed with deionized water and air-dried. The dried BFA was then sieved through a 1000 µm first to remove the big lumps, and then through 500, 250, 150 and 100 µm sizes. The BFA retained on the 150 µm size was used. 250 g of the 150 µm particle size obtained was activated by soaking in 2% (v/v) nitric acid solution. The mixture was stirred and left for 24 hrs after which it was filtered and air-dried ready for use.

### Preparation of pesticide solution

1000 mg/L of each of the two pesticide solutions were prepared by mixing 0.36 mL of the 276 g/L paraquat solution and 0.2 mL of the 500 g/L glyphosate solution and each was made up to the 1000 mL mark in a standard flask. Serial dilution was carried out for each of the above made solutions using deionized water to give 100 mL solution of concentrations 100, 90, 80, 70, 60 and 50 mg/L, respectively.

**Table 1** Properties of pesticides used in the sorption studies.

Parameter	Glyphosate	Paraquat dichloride
Active ingredient	500 g/L isopropyl amine glycine	276 g/L paraquat dichloride
Chemical name	Isopropyl amine glycine	1,1-Dimethyl-4-4-bipyridium dichloride
Molecular formula	C <sub>3</sub> H <sub>8</sub> NO <sub>3</sub> P	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> Cl <sub>2</sub>
Molecular weight	169.07	257.6
Density	1.70	1.25
Melting pt	234°C	300°C
λ <sub>max</sub>	630 nm	630 nm
Water solubility	Soluble	Soluble
Usage	Used as a contact herbicide for control of broad leaf and grassy weeds in plantation crops, fruits, or chards, including non-crop land, aquatic weed control and as defoliant for cotton and hops.	Used as a contact herbicide for control of broad leaf and grassy weeds in plantation crops, fruits orchards, including non-crop land, aquatic weed control and as defoliant for cotton and hops.
Structure		
Soil adsorption coefficient	24,000 (μg/g)	1000,000 (μg/g)
Half life	47 (days)	1000 (days)

### Equilibrium sorption of pesticides onto boiler fly ash

To determine the effect of concentration and time, 100 mL each of the 100, 90, 80, 70, 60 and 50 mg/L solution of paraquat dichloride and glyphosate were put into different conical flasks containing 1 g each of the activated BFA, corked and kept in a constant temperature (30°C) rotary shaker at 100 rpm and constant pH of 7.5 for 10 min. After 10 min, the contents of the flask were centrifuged and the supernatant filtered rapidly into sample bottles using Whatman No 41 filter paper. The experiments were repeated with the other various concentrations for 20, 40, 60 and 120 min contact time. The filtrates were then analyzed for the pesticides using UV spectrophotometer model SP-300 at maximum absorption wavelength (λ<sub>max</sub>) of 630 nm for the two pesticides. The amounts of the pesticide molecules adsorbed (q<sub>e</sub>) in each case were obtained by the difference between the initial concentration (C<sub>o</sub>) and amount remaining at equilibrium (C<sub>e</sub>). All experimental readings were made in duplicates and results presented represent average values of duplicate readings.

### RESULTS AND DISCUSSION

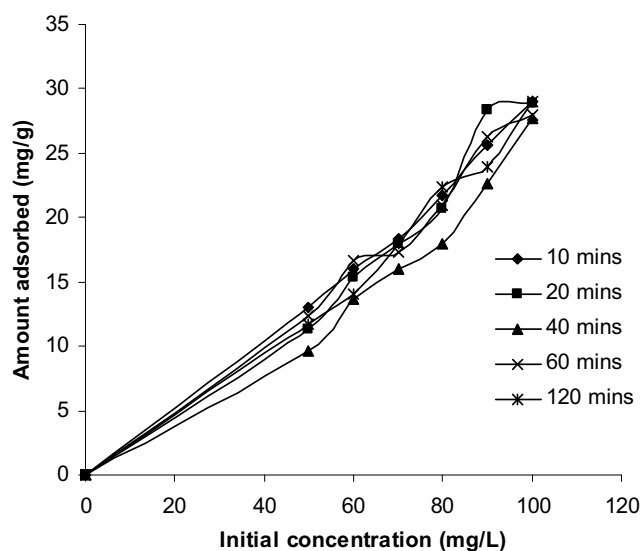
The BFA was soaked in 2% (v/v) nitric acid so as to wash off any soluble biomolecules that may interfere with sorption studies. Also, this helps to activate the BFA by opening up the pores ready for adsorption. The amount of pesticides adsorbed was obtained from a simplified mass balance equation as given below (Ho and Wang 2004):

$$q_e = C_o - C_e \quad (1)$$

where q<sub>e</sub> (mg/g) is the equilibrium amount of pesticides adsorbed, C<sub>o</sub> (mg/L) is the initial concentration of pesticide solution and C<sub>e</sub> (mg/L) is the equilibrium concentrations of pesticide in solution after adsorption. The properties of the two pesticides used in this study were listed in **Table 1**. Both pesticides were used as herbicides for control of broad leaf and grassy weeds in plantation crops, fruits orchards, including non crop land, aquatic weed control and as defoliant for cotton and hops. The density of glyphosate (1.70) was greater than that of paraquat (1.25), whereas, the melting point of paraquat (300°C) was greater than that for glyphosate (234°C). Again, the soil adsorption coefficient (K<sub>oc</sub>) and the high-life (t<sub>1/2</sub>) of paraquat were greater than those of glyphosate.

#### Effect of initial concentration and time

The experimental results showed that glyphosate and paraquat dichloride behaves in a similar way on adsorption to



**Fig. 1** Amount adsorbed (mg/g) as initial concentration (mg/L) is increased for sorption of Glyphosate onto boiler fly ash.

BFA with respect to initial concentration of the pesticides. As the initial concentration was increased, the amount of the pesticides adsorbed on boiler fly ash also increased. **Fig. 1** shows the effect of initial concentration of glyphosate at different time intervals on the amount adsorbed, while that for paraquat dichloride was shown in **Fig. 2**.

For the effect of time, the rate of adsorption increased rapidly with each specified concentration investigated at the initial time of 1 min to 10 min and the peak of adsorption was attained at about 10 min. The effect of time at different initial concentrations on the amount of pesticides adsorbed was shown in **Fig. 3** for glyphosate and **Fig. 4** for paraquat dichloride. It could be seen from these figures that the values obtained at 10 min of 50 mg/L initial concentration for paraquat dichloride and glyphosate were 13.00 and 12.33 mg/L, respectively. After 10 min, the amount adsorbed started decreasing. At 40 min of the same 50 mg/L initial concentration, the amount of paraquat dichloride and glyphosate adsorbed decreased to 9.6 and 9.00 mg/L, respectively. Thus, as time was increased from 10 min to 120 min, the amount of the pesticides adsorbed decreased. Also, it could be seen that as the initial concentration increased, the amount adsorbed also increased hence showing different characteristic lines for the different concentrations.

The amount of glyphosate that was adsorbed was higher than the amount of paraquat dichloride that was adsorbed.

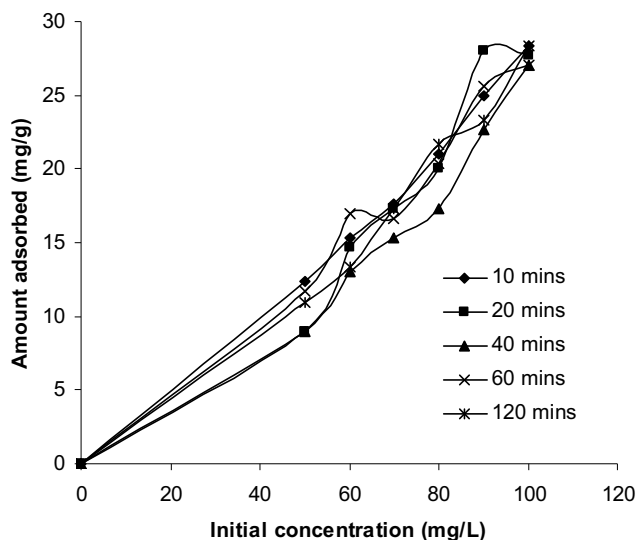


Fig. 2 Amount adsorbed (mg/g) as initial concentration (mg/L) is increased for sorption of Paraquat onto boiler fly ash.

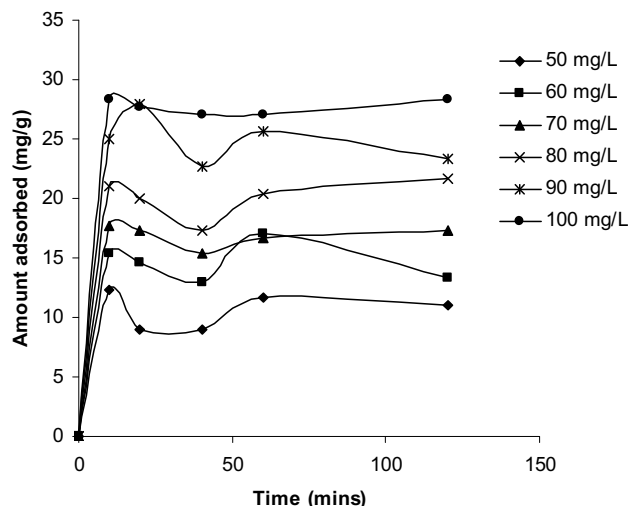


Fig. 4 Amount adsorbed (mg/g) against time (mins) for sorption of Paraquat onto boiler fly ash.

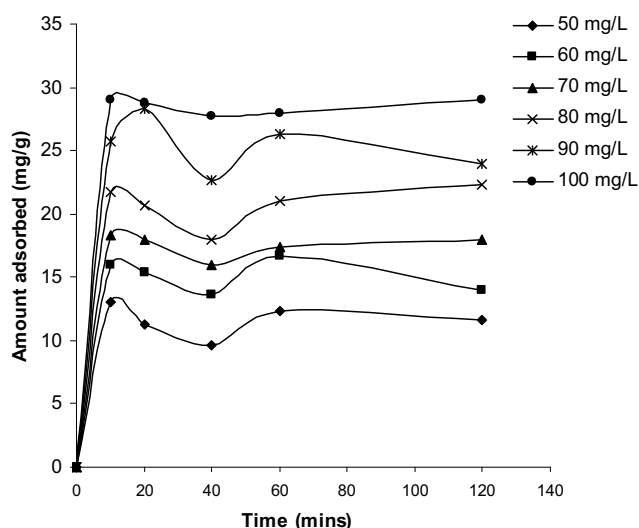


Fig. 3 Amount adsorbed (mg/g) against time (mins) for sorption of Glyphosate onto boiler fly ash.

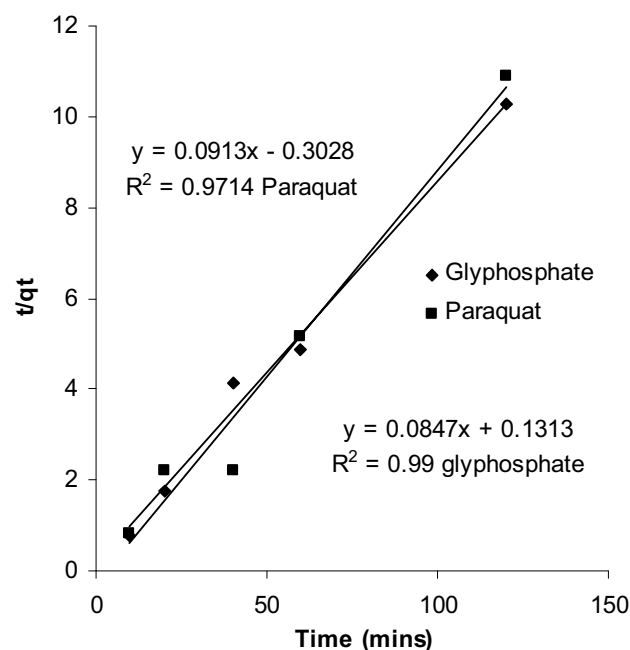


Fig. 5 Pseudo second-order plot for sorption of Glyphosate and Paraquat onto boiler fly ash.

The properties of the pesticides in **Table 1** show that both pesticides are soluble in water. The structures of the pesticides also shown in **Table 1** that both were ionic in solutions but the possible points of attachment hence sorption, for glyphosate was greater than that for paraquat dichloride, hence, the higher sorption capacity for glyphosate. It has been reported that ionic pesticides can interact with surface sites through, for example, electrostatic interactions, ion-exchange reactions or by surface complexation and for these pesticides; adsorption to mineral surfaces may be significant (Brownawell *et al.* 1991; Schwarzenbach *et al.* 1993; Celis *et al.* 1996). Again, the sorption capacity could be linked to the differences in the soil adsorption coefficients for the pesticides. The higher the soil adsorption coefficients, the less likely it will leach and appear in aqueous phase, hence the higher the soil adsorption coefficient the lower the sorption capacity in aqueous solution. Also, the half-life of paraquat dichloride (1000 days) was greater than the half-life of glyphosate (47 days) (Deer 2004).

### Sorption kinetics

Most sorption processes have been reported to take place by a multi step mechanism comprising

(i) Diffusion across the liquid film surrounding the solid particles (a process controlled by an external mass transfer

coefficient),  
 (ii) Diffusion within the particle itself assuming a pore diffusion mechanism (intraparticle diffusion), and  
 (iii) Physical or chemical adsorption at a sorption site.

Two kinetic models were used to test the sorption experimental data. These are the pseudo-first and pseudo-second order kinetic equations. The pseudo first order also called the Lagergren first order rate equation is given as (Ho and McKay 1998):

$$\log (q_c - q_t) = \log q_c - K_1 t / 2.303 \quad (2)$$

where,  $q_c$  and  $q_t$  are the amounts of the pesticides adsorbed at equilibrium and at time  $t$ , respectively (mg/g);  $K_1$  is the rate constant of pseudo-first order equation ( $\text{min}^{-1}$ ). The Lagergren equation did not give any reasonable correlation with the experimental data, hence the plots were not shown and the Lagergren parameters were not calculated. This means that the Lagergren equation did not give any good fit to the sorption experimental data. This confirms that it was not appropriate to use the Lagergren kinetic model to predict the sorption kinetics in the study of pesticides on boiler

fly ash for the experimented sorption period. Also, in most cases in the literature, the pseudo-first order equation of Lagergren did not fit well with the whole range of contact time and was generally applicable over the initial stage (20 to 30 min) of the sorption process (Ho and McKay 1998; Abd El Rahman *et al.* 2006).

The pseudo-second order rate model is expressed as (Ho and McKay 1998; Abd El Rahman *et al.* 2006):

$$t/q_t = 1/h_0 + t/q_e \quad (3)$$

where  $h_0$  the initial sorption rate is given by:

$$h_0 = K_2 q_e^2 \quad (4)$$

and  $K_2$  is the rate constant of pseudo second order equation ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The kinetic plots of  $t/q_t$  versus  $t$  for glyphosate and paraquat dichloride on boiler fly ash are shown in **Fig. 5**. The relation was linear and the correlation coefficients ( $R^2$ ) (glyphosate = 0.9900 and paraquat dichloride = 0.9714) suggested a strong correlation between the parameters and also showed that the ion-exchange chemisorption process was a contributory mechanism which follows pseudo-second order kinetics (Ho and McKay 1998; Abd El Rahman *et al.* 2006). The pseudo second order kinetic constants were calculated as follows for paraquat;  $h_0$  is  $3.30 (\text{mg g}^{-1} \text{min}^{-1})$ ,  $q_e$  is  $10.95 (\text{mg g}^{-1})$ ,  $K_2$  is  $-2.75 \times 10^{-2} (\text{g mg}^{-1} \text{min}^{-1})$ ; and for glyphosate  $h_0$  is  $7.62 (\text{mg g}^{-1} \text{min}^{-1})$ ,  $q_e$  is  $11.81 (\text{mg g}^{-1})$ ,  $K_2 = 5.46 \times 10^{-2} (\text{g mg}^{-1} \text{min}^{-1})$ . Here, at 50 mg/L initial concentration, the calculated equilibrium exchange capacity  $q_e$  was consistent with the experimental data. Also the correlation coefficients were quite high. Therefore, these results show that the pseudo-second order sorption mechanism was predominant and that the overall rate constant of each sorption process appears to be controlled by the chemisorptions process (McKay and Ho 1999; Abd El Rahman *et al.* 2006). These results were similar to that reported by Fontecha-Cámara *et al.* (2008) for the kinetics of diuron and amitrole adsorption from aqueous solutions on activated carbon and Hoda *et al.* (2009) for the removal of metobromuron from aqueous solutions onto high area activated carbon-cloth.

## Sorption isotherms

Adsorption isotherms describes the equilibrium studies that give the capacity of the adsorbent and adsorbate, which is usually the ratio between the quantity adsorbed and that remaining in solution at fixed temperature at equilibrium (Muhammad *et al.* 1998; Jalali *et al.* 2002). Five equilibrium adsorption isotherms were used to fit the experimental data. These were the linear forms of the Langmuir isotherm, the Freundlich isotherm, the Dubinin-Radushkevich isotherm, the Temkin isotherm and the Harkins-Jura isotherm.

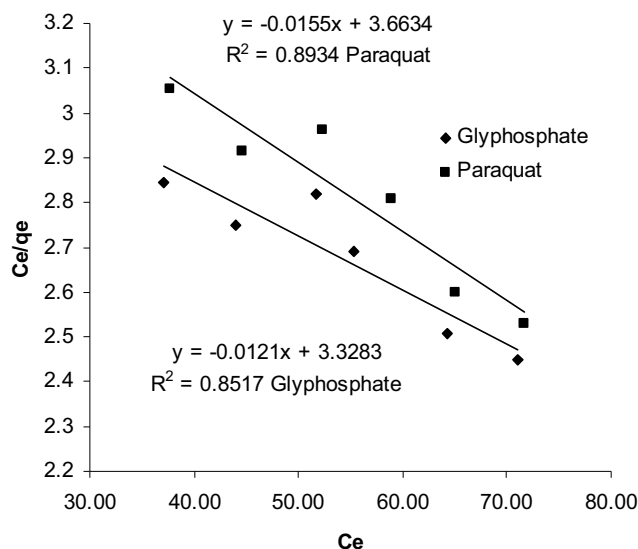
The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface and is given by (Langmuir 1918; Özacar and Sengil 2005):

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (5)$$

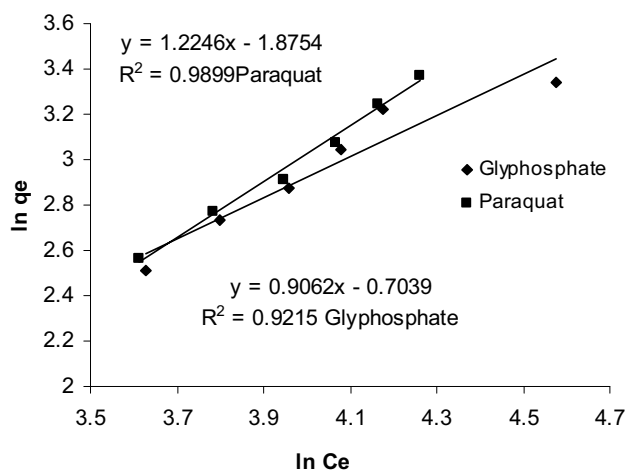
where  $K_L$  ( $\text{L g}^{-1}$ ) is a constant related to the adsorption/desorption energy and  $q_m$  is the maximum sorption upon complete saturation of the biomass surface. The experimental data were fitted into the Langmuir equation for linearization by plotting  $C_e/q_e$  against  $C_e$  and is shown in **Fig. 6**. The Freundlich model was chosen to estimate the adsorption intensity of the sorbate towards the biomass and was represented by (Freundlich 1906; Allen *et al.* 2003):

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (6)$$

where  $K_F$  and  $n$  are the Freundlich constants. The value of  $n$  indicates the affinity of the sorbate towards the biomass. The plot of  $\ln q_e$  against  $\ln C_e$  for the Freundlich isotherm is



**Fig. 6** Langmuir isotherm plot for sorption of Glyphosate and Paraquat onto boiler fly ash.



**Fig. 7** Freundlich isotherm plot for sorption of Glyphosate and Paraquat onto boiler fly ash.

shown in **Fig. 7**. The Dubinin-Radushkevich isotherm was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The model is given by (Dubinin *et al.* 1947; Akcay 2006):

$$\ln q_e = \ln q_D - \beta \varepsilon^2 \quad (7)$$

where  $q_D$  is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface;  $\varepsilon$  is the Polyananyi potential given by:

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (8)$$

and  $\beta$  is related to the free energy of sorption per mole ( $E$ ) of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution given by:

$$E (\text{KJ mol}^{-1}) = (2 \beta)^{-1/2} \quad (9)$$

The Dubinin-Radushkevich isotherm plot of  $\ln q_e$  against  $\varepsilon^2$  is given in **Fig. 8**.

The other two isotherms used to model the experimental data are given as Eq. (10) for Temkin isotherm and Eq. (11) for the Harkins-Jura isotherm (Akkaya and Ozar 2005; Basar 2006; Ozacar *et al.* 2008):

$$q_e = B \ln A + B \ln C_e \quad (10)$$

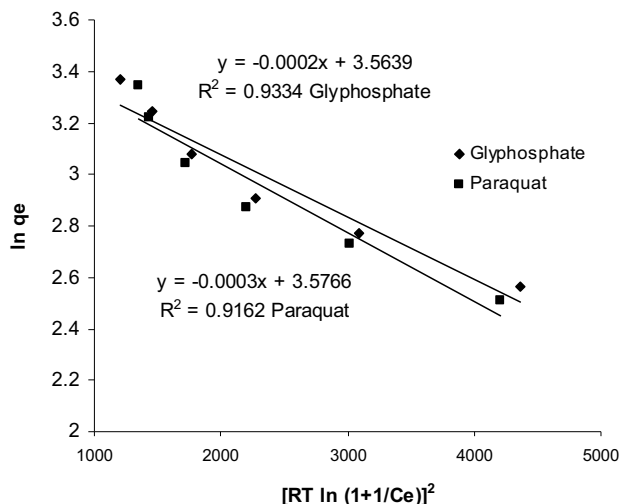


Fig. 8 Dubinin-Radushkevich isotherm plot for sorption of Glyphosate and Paraquat onto boiler fly ash.

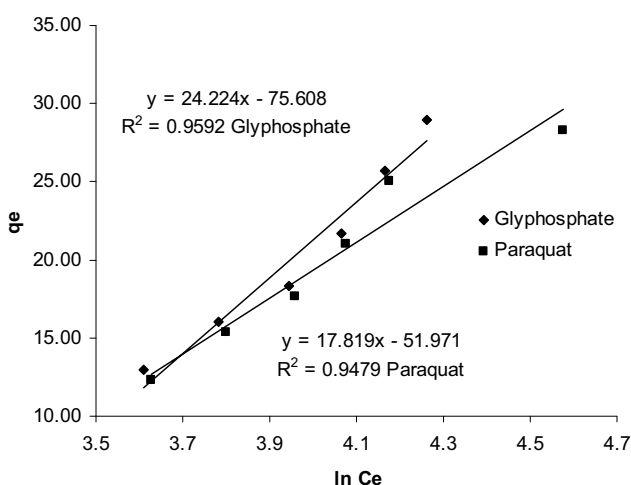


Fig. 9 Temkin isotherm plot for sorption of Glyphosate and Paraquat onto boiler fly ash.

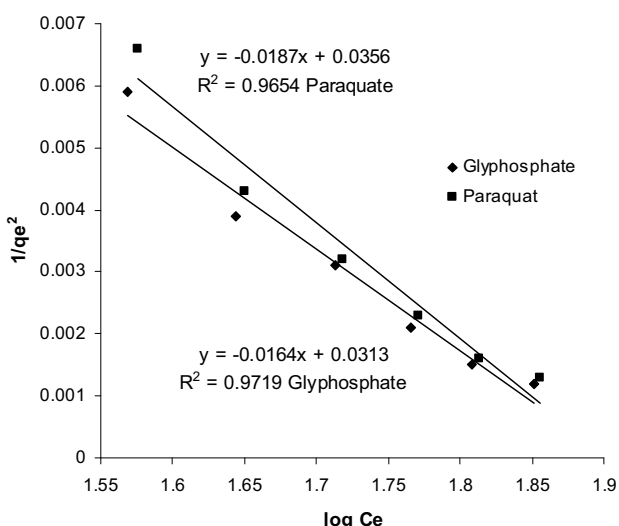


Fig. 10 Harkins-Jura isotherm plot for sorption of Glyphosate and Paraquat onto boiler fly ash.

$$1/q_e^2 = B/A - 1/A \log C_e \quad (11)$$

The plots of the Temkin isotherm are shown in Fig. 9 and that of Harkins-Jura isotherm is shown in Fig. 10.

The adsorption isotherm constants for the various sorp-

tion isotherms were calculated from the slopes and intercepts of the various equations. These are tabulated in Table 2. Also shown in Table 2 are the correlation coefficients for the linear isotherms. The Langmuir constants are negative and the  $R^2$  values are less than 90%. This means that the Langmuir isotherm is not favourable for the sorption of glyphosate and paraquat dichloride on boiler fly ash. The Freundlich constant ( $K_F$ ) for glyphosate (0.50) is greater than that for paraquat dichloride (0.15). This suggests that glyphosate has a greater adsorption tendency for boiler fly ash than for paraquat dichloride. The Freundlich equation parameter  $n$  gave 1.10 for glyphosate and 0.82 for paraquat dichloride. The Freundlich exponent is a measure of the adsorption intensity (Horsfall *et al.* 2004). This indicates that there was a preferential sorption of glyphosate by the boiler fly ash than paraquat dichloride. The Freundlich isotherm exponent ( $n$ ) slightly greater than 1 for glyphosate (1.10) indicates that linear sorption distribution coefficient increases with increasing sorbate concentration (Clausen *et al.* 2001). According to the classification of Giles *et al.* (1960), this type of isotherm is of S-type. This has also been reported for benzoic acid on  $\alpha$ -alumina (Madsen and Blokhus 1994) and for adsorption of 2,4-D on ferrihydrite (Celis *et al.* 1999). The S-shape isotherm implies that the more glyphosate is already adsorbed on the activated BFA, the easier it is for additional molecules to become fixed, probably through hydrophobic pesticide-pesticide interaction (Clausen *et al.* 2001). Other workers have reported the fitness of different isotherms to the sorption of pesticides; for example, the favourability of Freundlich isotherm (Clausen *et al.* 2001; Baup *et al.* 2002; Ayranci and Hoda 2004; Hoda *et al.* 2009; Igwe *et al.* 2009) and Langmuir isotherm (Clausen and Fabricius 2001; Ayranci and Hoda 2004; Igwe *et al.* 2009).

Again, looking at the linear isotherm parameters for the Dubinin-Radushkevich isotherm showed that the D-R isotherm constant was greater for paraquat dichloride (35.75) than for glyphosate (35.30). The apparent energy of adsorption ( $E$ ) gave 50.0  $\text{KJ mol}^{-1}$  for glyphosate and 40.83  $\text{KJ mol}^{-1}$  for paraquat dichloride. It has been reported that physisorption processes usually have adsorption energies less than 40  $\text{KJ mol}^{-1}$ , above which chemisorption processes occur (Ho *et al.* 1995; Horsfall *et al.* 2004). Thus, the energies of 50  $\text{KJ mol}^{-1}$  and 40.83  $\text{KJ mol}^{-1}$  indicate a chemisorption mechanism. This positively confirmed the chemisorption suggested from the result of the pseudo-second order kinetic model (Ho and Wang 2004; Özacar *et al.* 2008). The isotherm constants for the Temkin and the Harkins-Jura model are also shown in Table 2.

Furthermore, the favourability of the adsorption of the two pesticides on boiler fly ash was tested using the essential features of the Langmuir isotherm expressed in terms of a dimensionless constant called separation factor ( $R_L$ ) given by the following equation (Ho *et al.* 2002; Horsfall *et al.* 2004):

$$R_L = 1 / (1 + K_L C_0) \quad (12)$$

where  $K_L$  is the constant from Langmuir equation;  $C_0$  is the initial concentration of pesticide solution ( $\text{mg L}^{-1}$ ). The values of  $R_L$  for the two pesticides under different initial concentration are shown in Table 3. The dimensionless separation factor  $R_L$  indicates the shape of the isotherm as shown in Table 4. Hence, from Tables 3 and 4, the sorption of glyphosate and paraquat dichloride onto boiler fly ash according to the Langmuir equation is unfavourable. This is because all  $R_L$  values ranged above 1.0. This is probably the reason for the negative values obtained for the complete monolayer capacity ( $q_m$ ). It can also be seen that the  $R_L$  values decreases as the initial concentration ( $C_0$ ) decreases, suggesting that the sorption of the pesticides would be favourable at lower initial concentrations. These values of  $R_L$  ( $>1$ ) also confirmed that the Langmuir isotherm could not be used as a favourable isotherm for these pesticides sorption studies on BFA. Other workers have also obtained

**Table 2** Adsorption isotherm constants for the pesticides onto boiler fly ash.

Isotherm type	Glyphosphate	Paraquat
<b>Langmuir</b>		
$q_m$ (mg g <sup>-1</sup> )	-82.65	-64.52
$K_L$ (L mg <sup>-2</sup> )	$-3.64 \times 10^{-3}$	$-4.23 \times 10^{-3}$
$R^2$	0.8517	0.8934
<b>Freundlich</b>		
$n$	1.10	0.82
$K_F$ (Lg <sup>-1</sup> )	0.50	0.15
$R^2$	0.9215	0.9899
<b>Dubinin-Radushkevich</b>		
$q_D$ (mg g <sup>-1</sup> )	35.30	35.75
$\beta$ (mg <sup>2</sup> KJ <sup>-2</sup> )	0.0002	0.0003
$E$ (KJ mol <sup>-1</sup> )	50.0	40.83
$R^2$	0.9334	0.9162
<b>Temkin</b>		
$A$ (L g <sup>-1</sup> )	0.044	0.054
$B$	24.22	19.82
$R^2$	0.9592	0.9479
<b>Harkins-Jura</b>		
$A$	60.98	53.48
$B$	1.909	1.904
$R^2$	0.9719	0.9654

**Table 3** Langmuir dimensionless separation factor ( $R_L$ ) for pesticides sorption on boiler fly ash.

Initial concentration Co (mg/L)	$R_L$	
	Glyphosphate	Paraquat
50	1.223	1.268
60	1.279	1.340
70	1.342	1.421
80	1.411	1.512
90	1.487	1.615
100	1.572	1.733

**Table 4** Shapes of isotherm as given by the Langmuir dimensionless separation factor ( $R_L$ ).

Values of $R_L$	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

$R_L$  values that are either favourable (Ho 2003; Mittal *et al.* 2007) or unfavourable (Igwe and Abia 2003).

### Coefficient of determination

The coefficient of determination  $R^2$  for the five isotherms is also listed in **Table 2**. It can be seen that the Freundlich isotherm had the highest value of  $R^2$  for paraquat dichloride (0.99), while the Harkins-Jura isotherm had the highest value for glyphosate (0.97). The least value of  $R^2$  being the Langmuir isotherm, which gave 0.89 for paraquat dichloride and 0.85 for glyphosate. The significance of the variation in the isotherm models was obtained by considering the pesticides as objects and the  $R^2$  values as variable (Horsfall *et al.* 2004). The significance was then ascertained by using a two-way analysis of variance (ANOVA) without replication ( $P < 0.05$ ) to describe the relationships (i) between the five isotherms in describing the adsorption of the two pesticides on BFA and (2) between the two pesticides for binding sites on BFA. The results are shown in **Table 5**. From

the results in **Table 5**, there was no significant difference in the results obtained from the different isotherm models used in the analysis of the experimental data. Also, the ANOVA results show that the difference in the modeling of the two pesticides was not significant.

### CONCLUSION

Boiler fly ash was successfully used to remove glyphosate and paraquat dichloride from aqueous solution. The experiments show that the removal of these pesticides was both contact time and initial pesticide concentration dependent. Rate of adsorption was always high at the beginning of each experiment with respect to the specified concentration investigated. Also, the higher the initial concentration of pesticides, the higher the amount of pesticides adsorbed. The sorption kinetics data was well-modeled using pseudo-second order kinetic equation whereas; the equilibrium isotherm was fitted to five isotherm equations namely; Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Harkins-Jura isotherms of which the Freundlich isotherm gave a better fit to the sorption process. According to a two-way ANOVA without replication, there was no significant difference in the fitness of the five isotherms to the sorption experimental data. Hence, the use of BFA for the removal of these two pesticides from aqueous solution is feasible, cheap and cost effective because boiler fly ash is a waste and can be obtained at little or no cost. Therefore, development of this adsorbent to be applied in the field will go a long way in reducing the harmful residual pesticides on our waterways, soil, sediments and ground water. It could also serve as a low energy requirement and affordable technology in wastewater treatment.

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**Table 5** Two-way analysis of variable (ANOVA) for the sorption of the pesticides on boiler fly ash.

Source of variation	df	ss	ms	$F_{cal}$	$F_{tab}$
Model	4	0.011817915	0.002954480	4.107	6.39
Pesticides	1	0.000564030	0.000564030	0.784	7.71
Error	4	0.002877585	0.000719396		
Total	9	0.015239530			



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