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The Kinetics, Mechanism and Effect of Contact Time on the Adsorption of Cadmium and Glyphosate to Alfisol

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Authors' contributions

This work was carried out in collaboration among all authors. Author FBO designed the study wrote the protocol and wrote the first draft. Authors FBO and OAA wrote the last draft of the manuscript. Author OAA performed the statistical analysis. Authors FBO, OAO and OAO performed the laboratory experiment. Authors FBO and OAO managed the analyses of the study. Authors OAA and OAO managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

This study was carried out using Alfisol as an adsorbent to adsorb Cadmium and Glyphosate both of which are common inorganic and organic contaminants. The soil samples were air-dried and allowed to pass through 2mm sieve before use while its analysis was done following the standard procedures. The kinetic data were tested with pseudo-first-order and pseudo-second-order models, and it was concluded that both adsorbates adsorption followed the pseudo-second-order kinetics, while the nature and the mechanism of adsorption processes were studied by using an intraparticle diffusion model. A complete linear plot of intraparticle diffusion was obtained for glyphosate which suggests that intraparticle diffusion was the rate-controlling step in its adsorption but the opposite is the case for cadmium adsorption. The peak removal of cadmium occurred after 50 minutes with equilibrium attained over 250 minutes while peak glyphosate removal was achieved after 30 minutes. It can be concluded that Alfisol can be effectively used for the adsorption of both Cadmium and Glyphosate thus showcasing a potential environmental remediation process.

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1. INTRODUCTION

Alfisols are the most common soil type found in West African countries like Ivory Coast, Ghana, Togo, Benin, Nigeria, and Cameroon. They are the most abundant soils in Africa’s sub-humid and semi-arid zones [1]. Alfisols' type of soil is concentrated with the presence of heavy metals, herbicides, and pesticides due to their consistent use which has now become a worldwide environmental problem in recent decades. Organic and inorganic pollutants are mainly man-made and industrial effluents which have constituted a major hazard to human health as well as the surrounding ecosystems.

However, Cadmium, heavy metal of the type inorganic contaminants can be contacted with chemicals that contain cadmium, breathing air, taking drinks such as water and milk, eating foods such as fruits, vegetables, meats, grains and seafood containing cadmium, and also swallowing or touching dust or dirt that contains cadmium. Meanwhile, some chronic diseases like cancers, cardiovascular or neurological diseases accompany the exposure of humans to this heavy metal [2]. On the other hand, Glyphosate is one of the commonly used herbicides, and organic contaminants type is likely to cause environmental problems as they are used in large quantities and are persistent in the environment [3]. It is a white and odorless crystalline solid which is a phosphomethyl derivative of the amino acid glycine (N-[phosphonomethyl] glycine) ($C_3H_8NO_5P$).

Meanwhile, the fate of the different types of pollutants in the environment is influenced by several factors like the type and strength of interactions of the pollutant with the soil components being the most important one. The ability of heavy metals and organic-based herbicides adsorbed by soil and sediment and their tendency to be desorbed are some of the most important factors affecting soil and water contamination. Sorption and desorption are relatively the most studied processes as they determine the number of organic chemicals retained on the soil surface and therefore, the quantity ready to be leached through soil profile until the aquifer [4]. These movements are attenuated by natural processes such as adsorption on soil constituents, as well as chemical and biological degradation.

In the same vein, Alfisol is an adsorbent and its adsorption potential will only be rated or quantified by its kinetics [5]. Hence, kinetic studies of adsorption have great relevance due to applications in the control of environmental pollution. Once the reactions occurring in soil depend on the interactions between the adsorbent and adsorbate and also the conditions of this system, kinetic studies can suggest a possible mechanism for the adsorption and reaction rate, fundamental for understanding the behavior of a pollutant in the soil [6]. The adsorption of the metal ion by adsorbent also depends on the interactions of functional groups between the solution and the surface of the adsorbent. Adsorptions can be assumed to be complete when equilibrium is achieved between the solute of the solution and the adsorbent. However, a specific time is needed to maintain the equilibrium interactions to ensure that the adsorption process is complete.

In this study, attention is focused on the effect of contact time on the adsorption rate of Alfisol, the nature and the mechanism of the adsorption processes.

2. MATERIALS AND METHODS

2.1 Materials

The soil sample was collected from an undisturbed forest land along Parry road in the University of Ibadan, the Oyo State of Nigeria on latitude 70251-311N and longitude 3051-5618E and altitude 228 m above sea level. The soil sample was obtained at the depth of 20-40 cm. This soil has been characterized as Alfisol [7].

2.2 Chemicals

Glyphosate, Potassium Nitrate, Hydrochloric Acid, Potassium Hydroxide, Acetonitrile, Sodium Borate Buffer, Dichloromethane, Cadmium Nitrate, sodium hydroxide. All chemicals used were of analytical grade, and all solutions and soil dispersions were prepared using de-ionized water.

Glyphosate was prepared daily by dissolving it in freshly prepared 0.01M KNO_3 which served as supporting electrolyte.

2.3 Preparation of the Soil Samples for Adsorption

The soil sample was air-dried for 72 hours under ambient temperature and allowed to pass through 2 mm sieve before use.

2.4 Physico-chemical Analyses of the Soil Samples

The pH, Organic Carbon, Particle size, Exchangeable Cations, Cation Exchange Capacity, Available Phosphorus and Soil Total Nitrogen were analyzed in the soil sample following the standard procedures [8].

2.5 Effect of Contact Time on Glyphosate Adsorption by Alfisol

About 1.0 g of soil sample was weighed into a 20 mL centrifuge glass tube, 2 mL of 100 mg L^{-1} glyphosate standard was added followed by 18 mL of 0.1 M Kcl. The contents were blend using a mechanical shaker for (15, 30, 60, 180, and 540 minutes) to achieve various levels of equilibration. The glass tube contents were centrifuged at 1000 revolutions/min for about 6 minutes, and the supernatants were withdrawn for derivatization.

2.6 Derivatization

0.5 mL of borate buffer was added to the supernatant, followed by 0.5 mL of FMOC-Cl solution was added. The mixture was manually shaken to homogenize it. The mixture was left for 2 hours at room temperature to allow appropriate chemical reactions to occur; the resulting solution was mixed with 4 mL of dichloromethane and then centrifuged at 1000rpm for 6 min to separate dichloromethane from water, which is immiscible. The aqueous phase, which contained the derivatized product, was withdrawn and quantified by UV–visible spectrophotometer with the wavelength readings at 298nm [9].

2.7 Effect of Contact Time on Cadmium Adsorption by Soil

1.0 g of air-dried soil sample was weighed into a plastic container; 20 mL of 120 mg/L of cadmium nitrate solution was added. The contaminated soil was thoroughly mixed using a mechanical shaker for (15, 30, 60, 90, 120 180 and 240 minutes) to achieve various levels of equilibration, the soil solution was centrifuged at 1000rev/min and the supernatant was analyzed with Atomic absorption spectroscopy (AAS).

2.8 Kinetic Experiments

The kinetics of adsorption of both Cadmium and Glyphosate was carried out by withdrawing and analyzing the samples at time intervals of every 5 minutes for the first 30 mins and later at every 10 mins until the consecutive residue concentrations became closer [10]. This was carried out separately for four initial concentrations of both contaminants at 300K.

2.9 Calculation of the Adsorbed Contaminants

The amount of contaminant adsorbed at equilibrium was calculated from the following equation [11].

$$qe = \frac{(C_o - C_e)}{m} \qquad (1)$$

Where, qe is the amount of glyphosate adsorbed at equilibrium (mg^{-1}), Co is the initial concentration of the contaminant in the liquid phase (mgL^{-1}), Ce the liquid-phase concentration of the contaminant at equilibrium (mgL^{-1}), V the volume of contaminant solution (L) and m the mass of the adsorbent (g). Finally, the adsorption rate was calculated using the following equation:

$$\text{Adsorption rate } (\%) = \frac{(C_o - C_e)}{C_o} \text{ X } 100 \qquad (2)$$

All experiments were carried out at 28°C.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Adsorbent (Alfisol)

The physicochemical composition of Alfisol soil samples is shown in Table 1. The pH of the soil is slightly acidic with high total organic carbon, while the cation exchange capacity is on the lower side. The textural class of the soil greatly influences its water retention capacity, thus the soil under study is predominantly sandy.

3.2 Effect of Contact Time on the Adsorption of Cadmium and Glyphosate onto Alfisol

Figs. 1 and 2 show the effect of contact time on the adsorption of cadmium and glyphosate respectively. A peak percentage removal of cadmium ion was observed after 50 minutes with a removal of 54% cadmium with equilibrium attained over 250 minutes. For glyphosate, maximum removal was achieved after 30 minutes with a peak value of 88.60% glyphosate removed after which equilibrium was attained over the next 250 minutes. The rapid percentage removal obtained initially for glyphosate may be due to the presence of abundant active sites on the surface of the soil which were later occupied as time progresses, which eventually resulted in the inability of the soil to remove the adsorbate at the later stages of the adsorption process [12]. Also, glyphosate was adsorbed at a faster rate with higher percentage adsorption than cadmium.

3.3 Adsorption Kinetics

The kinetic data for the adsorption of the adsorptions were tested with the well-known kinetic models-pseudo first order and pseudo-second-order model, while the mechanism of the adsorption processes was studied by plotting the data with intraparticle diffusion model and the Morris and Weber plots to predict information about adsorbent/adsorbate interaction (physisorption and chemisorption).

Table 1. Physico-chemical composition of alfisol

Parameters	Value
pH	5.9
Available Phosphorus (mg/kg)	0.97
Total Organic Carbon (g/kg)	9.98
Total Nitrogen (g/kg)	3.73
Exchange Acidity (Cmol/kg)	0.5
Calcium (Cmol/kg)	0.5
Magnesium (Cmol/kg)	0.26
Sodium (Cmol/kg)	0.09
Potassium (Cmol/kg)	0.11
Manganese (mg/kg)	130
Iron (mg/kg)	99.4
Copper (mg/kg)	1.35
Zinc (mg/kg)	0.39
Clay (g/kg)	120
Silt (g/kg)	134
Sand (g/kg)	746
Cation Exchange Capacity	1.46

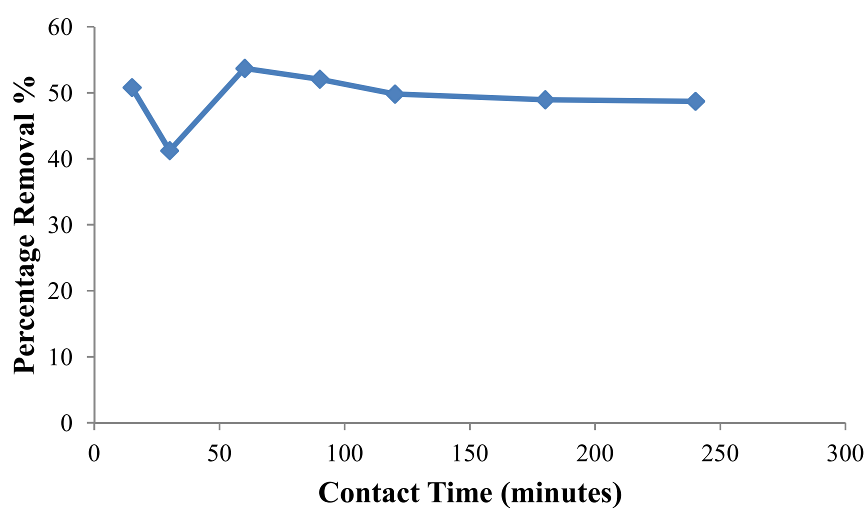

Fig. 1. Effect of contact time on the removal of cadmium

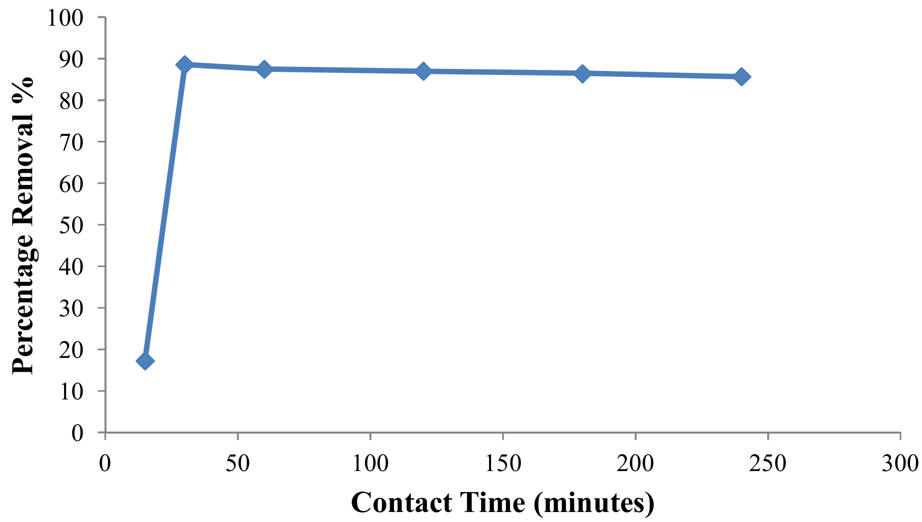

Fig. 2. Effect of contact time on the removal of glyphosate

3.4 Pseudo-First-Order Kinetic

Pseudo-first-order equation was given by [13] to determine the rate constant of adsorption process as:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (3)$$

$$\ln(qe\_qt) = lnqe\_kit \quad (4)$$

Where q_e and q_t are the amounts of the adsorbate adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of adsorption (min^{-1}). Values of k_1 and q_e were calculated from the slope and the intercept of the plots of Log(q_e - q_t) against t.

The adsorption of cadmium and glyphosate did not conform to pseudo-first-order kinetic as the result is of marked deviation from linearity (Table 2).

3.5 Pseudo-Second-Order Kinetic

The linear equation of the pseudo-second-order model is given by the equation

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (5)$$

If the pseudo-second-order kinetic equation is applicable, the plot of *t/qt* against t is linear, then qe and k2 can be determined from both the slope and intercept of the plot. Unlike in the pseudo-first-order data, it can be found that the values for qe for both contaminants were at per but that of k2 varies as in the value of k1 of pseudo-first-order model, the values of r 2 also tend towards linearity showing that the adsorption of cadmium and glyphosate strongly conform to pseudo-second-order kinetic i.e the plot of t/qt against t. This shows that the adsorption of both contaminants is mainly by a simple chemical reaction between the contaminant molecules and the surface functional groups on Alfisol.

3.6 Intraparticle Diffusion Study

This is based on the fact that the uptake of the adsorbate by the adsorbent varies almost proportionately with the square root of the contact time ($t^{1/2}$) according to the following equation:

$$q_t = K_d t^{1/2} + C$$

Where C is the intercept and K_d is the intraparticle diffusion rate constant. From the plot qt against $t^{1/2}$ $K_d$and C were determined from the slope and intercept respectively.

The result of intraparticle diffusion study in (Table 2) therefore shows that intraparticle diffusion was not the only rate-controlling step for Cadmium adsorption, however, in the case of glyphosate adsorption, a completely linear plot was obtained as the plot of qt versus $t^{1/2}$ will pass through the origin suggesting intraparticle diffusion as the only rate-controlling step [14].

Table 2. Result of adsorption kinetics

Kinetic models	Cadmium	Glyphosate
Pseudo first order		
qe (mg/g)	11.8	58.08
K1 (min-1)	6.9 x 10-6	2.3 x 10-5
R2	0.004	0.229
Pseudo second order		
qe (mg/g)	1.17	0.995
K2 (g/mgmin)	0.7	27.5
R2	0.997	0.928
Intraparticle diffusion		
Kd (mg/gmin1/2)	0.0002	0.01
C	1.156	0
R2	0.014	1

4. CONCLUSION

The Adsorption studies for the removal of both Cadmium and Glyphosate by Alfisol had been carried out. The kinetic data were tested with pseudo-first-order and pseudo-second-order models, and it was concluded that both adsorbates adsorption followed the pseudo-second-order kinetics, while the nature and the mechanism of adsorption processes were studied by using an intraparticle diffusion model. The kinetic model that best explains the behavior of cadmium ions and glyphosate in Alfisols is pseudo-second-order kinetics, with a very poor fit for pseudo-first-order kinetic in both cases; this indicates that there is an inclination towards chemisorptions.

From this study, it can be concluded that Alfisol can be effectively used for the adsorption of both Cadmium and Glyphosate thus showcasing a potential environmental remediation process.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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