Adsorption Potentials of Alfisol on Glyphosate and Cadmium Contaminants

F. B. Okanlawon[1*], O. O. Awotoye[2] and P. O. Ogunbamowo[3]

[1]*Department Wood and Paper Technology, Federal College of Forestry, Ibadan, Nigeria.*
[2]*Department Forestry Technology, Federal College of Forestry, Ibadan, Nigeria.*
[3]*Forestry Research Institute of Nigeria, Nigeria.*

Original Research Article

ABSTRACT

Aims: This study aimed at demonstrating the adsorption capacity as well as the removal of glyphosate and cadmium unto Alfisols.
Place and Duration of Study: Research was carried out in Analytical Laboratory of Department of Chemistry, University of Ibadan, Nigeria. The soil sample was collected from an undisturbed forest land, University of Ibadan, Nigeria.
Methodology: The soil sample was air dried for 72 hours under ambient temperature and allowed to pass through 2 mm sieve before use. All solutions and soil dispersions were prepared using de-ionised water. The pH, organic carbon, particle size, exchangeable cations, cation exchange capacity, available phosphorus and soil total nitrogen were all analysed for in the soil sample following the standard procedures likewise the cadmium and glyphosate adsorption/adsorbent studied.
Results: 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

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Corresponding author: E-mail: Okanlawon.fb@frin.gov.ng, fblawon@yahoo.com;

retention capacity, thus the soil under study is predominantly sandy. A decrease in the equilibrium adsorption capacity was observed when the adsorbent dose was increased from 0.2 – 0.8 g however, with a sharp increase at a dose of 1 g.
An increase in the percentage cadmium removal was observed with increase in pH from 48.80% to a maximum of 91.10% at neutral pH. The result also indicates that increasing the initial concentration of the cadmium ions and glyphosate lead to an increase in the uptake capacity of the soil for both adsorbate. At higher ionic strength of 0.1 M, the peak removal was obtained at initial concentration of 10 ppm which eventually attains equilibrium at other concentration level.
Conclusion: Alfisol can therefore concluded to be an adsorbent provided some conditions like a low cadmium concentration, a neutral pH and a higher adsorbent dosage are adhere too. While glyphosate removal, a pH of 5 and higher ionic strength of KNO_3. is required.

1. INTRODUCTION

The different kinds of pollutants especially heavy metals have attracted attention of scientific community because of serious health hazards associated with them. Hence, heavy metals are refers to any metallic element that has a relatively high density and is poisonous even at low concentrations [1]. Heavy metal pollutants occur in gaseous, liquid or solid forms. They can be created and released due to some human activity or they appear in biosphere due to over-exploitation of resources which leads to unveiling of pollutants from deeper crusts of soil.

However, several factors influence different types of pollutants in the environment. The most important one is the type and strength of interactions of pollutant with soil components. 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 quantity of organic chemicals retained on soil surface and, therefore, the quantity ready to be leached through soil profile until the aquifer [2]. These movements are attenuated by natural processes such as adsorption on soil constituents, as well as chemical and biological degradation.

There is therefore the need for an environmentally sound and friendly cleanup process of evacuating this heavy metals and pesticides from the environment. Adsorption is considered a suitable option due to its relatively new, cost effectiveness, purification and separation potentials. According to Rashed [3] this entails the use of solids to remove substances from gaseous or liquid solutions. Its high efficiency with low usage of chemical sludge and the possibility of regeneration of adsorbents makes it a better options.

The most commonly used adsorbent is activated carbon, some other agrowastes are now been investigated, but for this study, soil matrix specifically Alfisol is been investigated due to its abundance around the Southwestern area of Nigeria. The Alfisols are less leached and have lower acidity than Ultisols and Oxisols, but they exhibit high base saturation [4]. Meanwhile, various factors influence the adsorption capacity potential of adsorbents during the adsorption process. Previous researches have assumed that the efficiency of any adsorbent is strongly influenced by the physico-chemical characteristics of the solutions such as pH, temperature, initial concentration, contact time and also adsorbent dose and these work considered this factors necessary [5].

Thus, this study therefore became necessary so as to predict the mobility and fate of metals and herbicides adsorption characteristics in soil environment and also to understand whether bioremediation is a feasible option for the cleanup of contaminated soil.

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, Oyo State of Nigeria on latitude 70251 – 311N and longitude 3051-5618E and on altitude 228m above sea level. The soil sample was obtained at the depth of 20-40cm. This soil has been characterized as Alfisol by Ewulo et al. [6].

2.2 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.

2.3 Chemicals

Hydrochloric Acid, Potassium Hydroxide, Acetonitrile, Sodium Borate Buffer, Dichloromethane. All chemicals used were of analytical grade and were used without further purification. All solutions and soil dispersions were prepared using de-ionised water.

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 all analysed for in the soil sample following the standard procedures [7].

2.5 Cadmium and Glyphosate Adsorption/ Adsorbent Studies

2.5.1 Effects of adsorbent dosage on cadmium adsorption

About 0.2 – 1.2 g of air-dried soil sample was repeatedly weighed into different pre-cleaned plastic container, 20 ml of 100 ppm of the metal solution was added, the soil solution was shaken with mechanical shaker for 1hour. The solution was centrifuged at 1000 rev/min for 6 minutes and the clear upper solution was removed and analysed with Atomic Absorption Spectrometer [8].

2.5.2 Effects of adsorbate concentration on cadmium and glyphosate adsorption

Cadmium: About 1.0 g of air-dried soil sample was weighed into a plastic container, (1.7, 3.3, 6.3, 13.6, 16.3) and 20 ml of 120 mg L^{-1} cadmium standard solution was added, the solution was made up to 20mL by addition of de-ionized water to cover the concentration range between 0-120 mgL^{-1}. The content was shaken on a mechanical shaker for 1hour to achieve equilibration. The glass tube contents were centrifuged at 1000 rev/min for 6minutes, and the supernatants were withdrawn and analyzed with Atomic Absorption Spectrometer.

Glyphosate: About 1.0 g of dried soil sample was weighed into 20 mL centrifuge glass tubes, (4, 8, 12, 16 and 20) mL of 100 mg L^{-1}glyphosate standard was added and the solution was made up to 20mL by addition of 0.01M KCl. The content was shaken on a mechanical shaker for about 6 hours to achieve equilibration.

The glass tube contents were centrifuged at 1000 rev/min for 6minutes, and the supernatants were withdrawn for derivatization.

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

2.5.3 Effects of pH on the adsorption of cadmium and glyphosate

Cadmium: The effects of pH was studied by measuring 20mL of 120mg/L of cadmium nitrate solution into plastic containers, 1.0 g of air-dried soil sample was added to each solution. The pH of each solution was adjusted to cover the range between 2.0 – 8.0 +0.2 with either 0.1 M HCl or 0.1 M NaOH as the case may be, The contaminated soil was shaken on a mechanical shaker for 240 minutes to achieve maximum level of equilibration, the soil solution was centrifuged at 1000 rev/min and the supernatant was analyzed with AAS.

Glyphosate: The effects of pH was studied by weighing 1.0 g of soil into 20 mL centrifuge glass tubes, then 2 mL of 100 mg L^{-1} glyphosate standard was added followed by 18 mL of 0.1 M KCl. The pH of the mixture was adjusted to various pH (5.0, 6.0, 7.0, 8.0 and 9.0) by the addition of KOH/HCl solutions. The glass tube content was shaken on a mechanical shaker for 6 hours to achieve equilibration.

The glass tube contents were centrifuged at 1000 rev/min for about 6minutes, and the supernatants were withdrawn for derivatization as it was done above.

2.5.4 Effects of Ionic strength on glyphosate adsorption by soil

The effect of ionic strength was studied by weighing 1.0 g of dried soil sample into 20 mL centrifuge glass tubes, 2 mL of 100 mgL^{-1} glyphosate standard was added followed by 18mL of potassium nitrate in three concentrations (0.001 M, 0.01 M and 0.1 M) separately added. The content was shaken on a mechanical shaker for about 6 hours achieve equilibration. The glass tube contents were centrifuged at 1000rev/min for about 6minutes, andthe supernatants were withdrawn for derivatization as done above.

2.5.5 Calculation of the adsorbed contaminants

The amount of contaminant adsorbed at equilibrium was calculated from the following equation [10].

$$qt = \frac{(C0-Ce)v}{m} \qquad (1)$$

Where:

qt - amount of cadmium adsorbed at equilibrium $(mg \cdot g^{-1})$,
Co - initial concentration of the contaminant in liquid phase $(mg \cdot L^{-1})$,
Ce - liquid-phase concentration of the contaminant at equilibrium $(mg \cdot L^{-1})$,
V - volume of contaminant solution (L) and m the mass of the adsorbent (g).

Finally, the adsorption rate was calculated using the following equation:

$$Adsorption\ Rate\ (\%) = \frac{(Ce\ X\ CO\ x\ 100)}{Co} \qquad (2)$$

All experiments were carried out at temperature 28°C and data obtained were used for analysis.

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.

3.2 Effect of Adsorbent Dosage on Cadmium Adsorption

The variation in the amount of cadmium ion adsorbed from a 100 ppm solution of cadmium unto various doses of the soil adsorbent is presented in Fig. 1. A decrease in the equilibrium adsorption capacity was observed when the adsorbent dose was increased from 0.2 – 0.8 g however, with a sharp increase at a dose of 1g. This may be attributed to decreasing surface area that occurs as the adsorbent dose increases [11], thus the equilibrium adsorption capacity Afisol may be a function of its weight. Also, the percentage of cadmium removed increased from 6.48 % to 30.94 % from dosage of 0.2 – 1.0 g before a reduction occurs at a dose of 1.2 g. This is a very slight deviation from that reported by several authors [11,12] for modified kaolinite clay, the increase in the percentage adsorption of cadmium ions with increasing soil dose may be attributed to increased surface negative charge that favours sorbent-solute interaction. Also, the percent cadmium ion removal in this study is lower compared to those reported by Unuabonaha et al. [12] for modified kaolinite clay. This may be due to the nature of the Alfisol soil sample used in this study that has a lower clay content and low cation exhange capacity.

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

3.3 Effect of pH on the Adsorption of Cadmium and Glyphosate onto Alfisol

Figs. 2 and 3 presents the effect of pH of 50 ppm and 100 ppm cadmium ion and glyphosate respectively, varied from pH of 2.0 – 8.0 and 4.0 – 10.0 respectively. An increase in the percentage cadmium removal was observed with increase in pH from 48.80% to a maximum of 91.10 % at neutral pH, this is comparable with that reported by Unuabonah et al. [11] for cadmium adsorption by modified kaolinite clay. However a slight drop was observed at pH of 8 which is projected to remain constant, an indication of the onset of cadmium precipitation and hydrolysis. Also, unlike the effect of adsorbent dose, there was an increase in equilibrium adsorption capacity with a corresponding increase in percentage cadmium ion adsorbed. The increase in the adsorption of metals relative to pH may be attributed to the active sites of the alfisol soil which may become positively charged at very low pH, thereby increasing the competition between hydrogen ion and the metal ion for available adsorption sites because of increased amount of H^+ in solution. However, as pH increases this competition is decrease as these surface active sites becomes more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction and metal ion competition with H^+ becomes reduced [11].

In the case of the effect of pH on the adsorption of glyphosate, an irregular trend was observed, with a maximum removal of 97.38% taking place at pH of 5 with significantly little or no adsorption in the basic regions, also the adsorption capacity decreased significantly from 0.97 to 0.03 mg/g at pH of 5 – 10 further confirming that no adsorption takes place at basic pH.
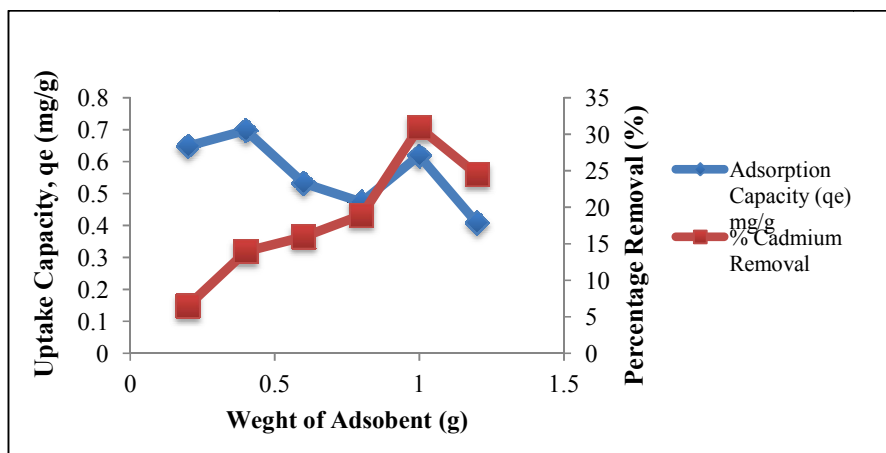

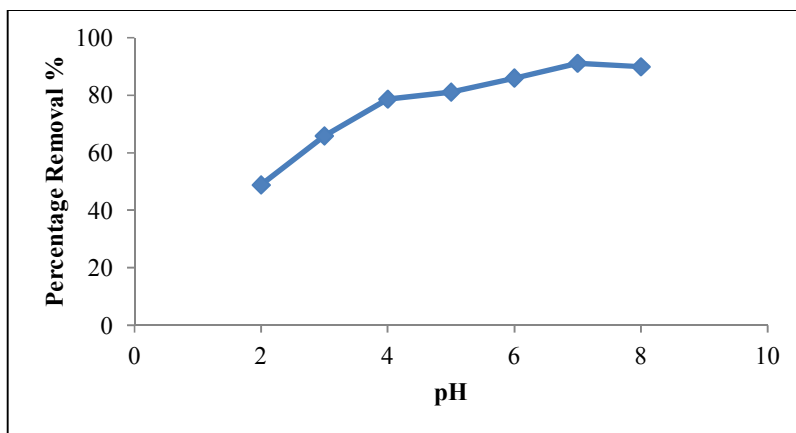**Fig. 1. Effect of adsorbent dose on the adsorption capacity and percent cadmium removal**

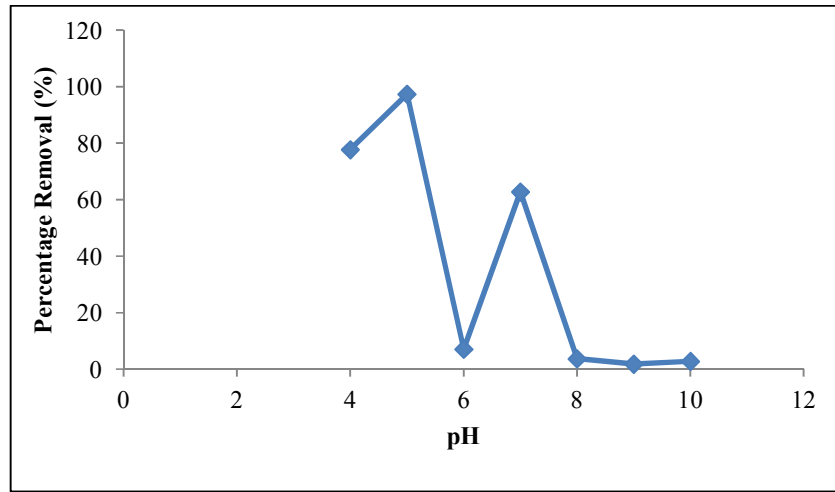**Fig. 2. Effect of pH on cadmium adsorption**

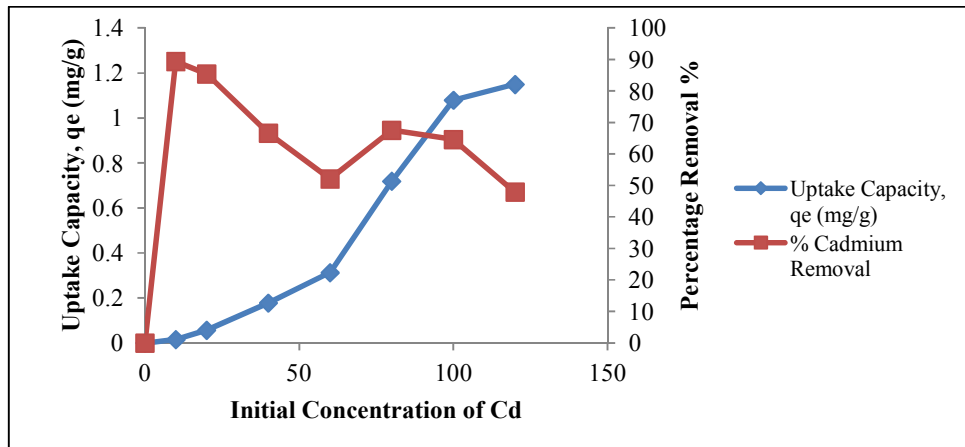**Fig. 3. Effects of pH on glyphosate adsorption**

Fig. 4. Effect of concentration on the uptake capacity and percentage removal of cadmium
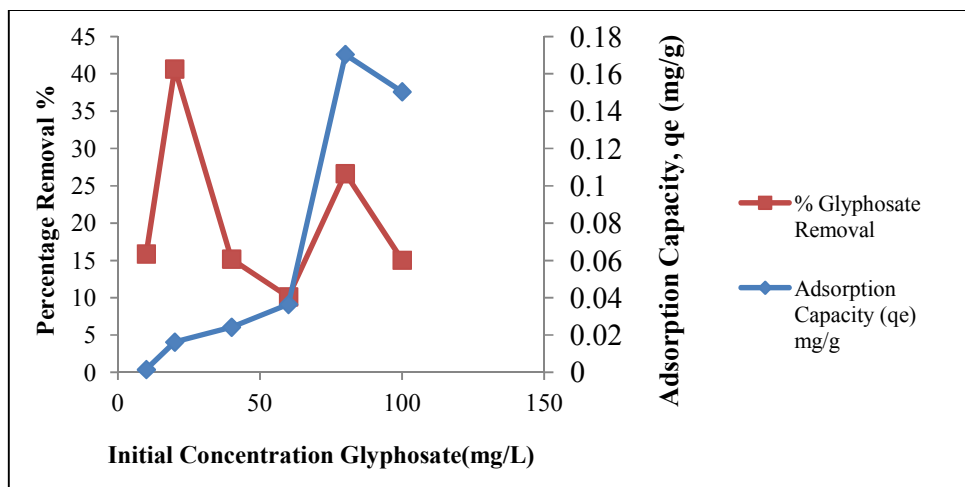

Fig. 5. Effect of concentration on the uptake capacity and percentage removal of glyphosate
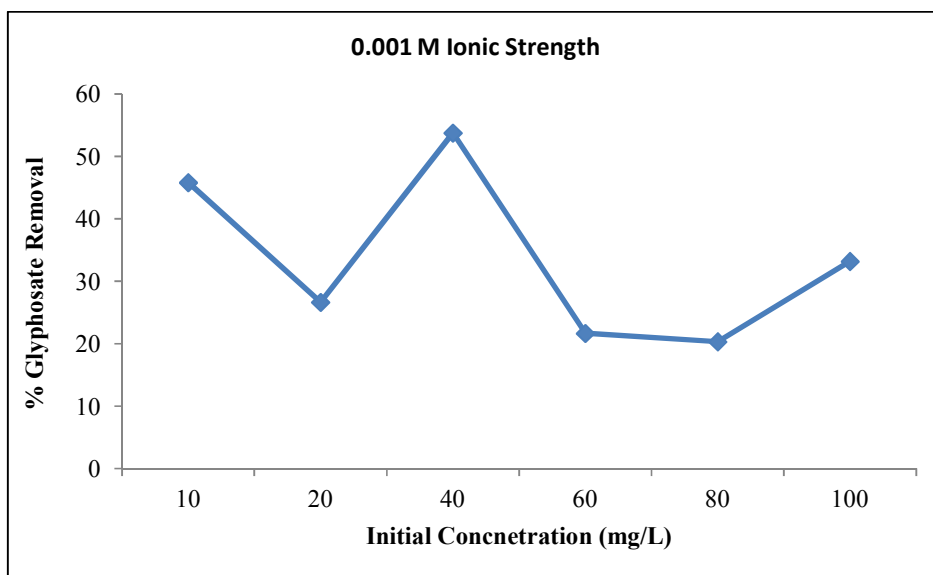
0.001 M Ionic Strength

Fig. 6. Effect of 0.001 M potassium nitrate on glyphosate adsorption

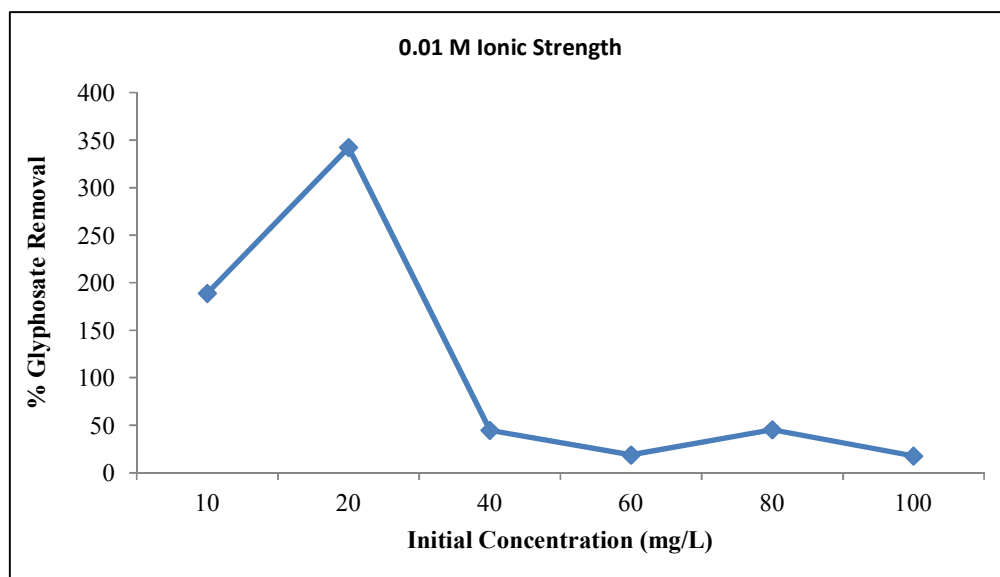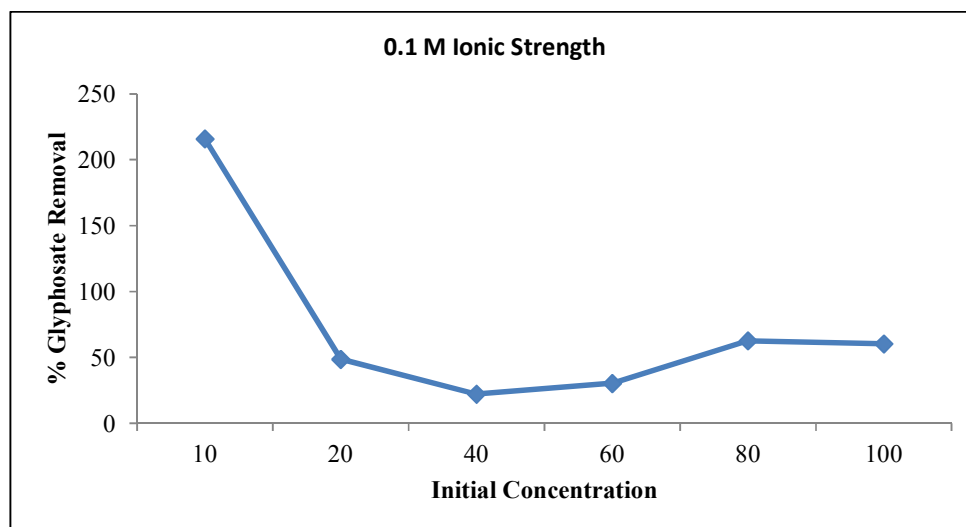**0.01 M Ionic Strength**

Fig. 7. Effect of 0.01 M potassium nitrate on glyphosate adsorption

3.4 Effect of Concentration of Adsorbate on the Adsorption of Cadmium and Glyphosate onto Alfisol

The effect of increase in concentration on the adsorption of cadmium and glyphosate onto Alfisol is depicted in Figs. 4 and 5. The result indicates that increasing the initial concentration of the cadmium ions and glyphosate lead to an increase in the uptake capacity of the soil for both adsorbate. This is in agreement with Unuabonah et al. [11] for the adsorption of lead and cadmium on modified kaolinite clay. This suggests that at lower levels of the cadmium ion and glyphosate, fewer molecules of the adsorbate are available for adsorption. However, lower concentration favours maximum cadmium ion removal with a percentage removal of 89% occurring at a concentration of 10 ppm of the adsorbate. In the case of glyphosate, lesser amount was removed with the optimum concentration of 20 ppm giving a 40.65% glyphosate removal. As in the case of cadmium removal, it appears that higher

Fig. 8. Effect of 0.1 M potassium nitrate on glyphosate adsorption

concentration does not favour removal of glyphosate.

3.5 Effect of Ionic Strength on the Adsorption of Glyphosate

This was studied by preparing the glyphosate solution in different Molarity (0.001 M, 0.01 M and 0.1 M) of KNO_3. Figs. 5 to 7 depict the impact of ionic strength of potassium nitrate on the removal of glyphosate. At higher ionic strength of 0.1 M, the peak removal was obtained at initial concentration of 10 ppm which eventually attains equilibrium at other concentration level.

4. CONCLUSION

This study has demonstrated the adsorption capacity as well as the removal of cadmium and glyphosate unto Alfisols. The soil was found to be slightly acidic with low cation exchange capacity and rich in organic carbon. Investigation of physico-chemical factors shows a decrease in the adsorption capacity of the adsorbent (Alfisol) for cadmium with increase in adsorbent dosage, while the removal capacity increases with increase in adsorbent dose. Neutral pH favours the removal of cadmium giving a peak percentage removal of 91.10% with equilibrium attained at the basic pH range. Similarly the optimum pH for the removal of glyphosate is pH 5 with a maximum removal of 97.38%. Increase in the initial concentration of the adsorbate causes an increase in adsorption capacity of

cadmium and glyphosate; higher concentration does not favour the removal of cadmium and glyphosate with a peak % removal occurring at a concentration of 10ppm and 20 ppm respectively. The effect of the ionic strength on the adsorption of glyphosate shows higher percentage removal taking place at higher KNO_3 ionic strength of 0.1 M and 0.01M.

Alfisol can therefore concluded to be an adsorbent provided some conditions like a low cadmium concentration, a neutral pH and a higher adsorbent dosage are adhere too. While glyphosate removal, a pH of 5, and higher ionic strength of KNO_3.is required. Hence, alfisol can be recommended for both planting and clean up.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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