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Influence of nitrogen-phoshorus-potassium (NPK-15:15:15) fertilizer application on adsorption capacity of pendimethalin in soil

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Abstract
Batch equilibrium method was use to examine the influence of Nitrogen-Phosphorus-Potassium (NPK-15:15:15) fertilizer application on adsorption of pendimethalin (3,4-Dimethyl-2,6-dinitro-N-pentan-3-yl-aniline) in soil. Soil sample taken from the surface horizon of the Federal University of Agriculture Makurdi Teaching and Research Farm was amended with various amount of NPK fertilizer ranging from 5 gram to 30 gram labeled as 5 g NPK, 10 g NPK, 15 g NPK, 20 g NPK, 25 g NPK, 30 g NPK and 0 g NPK (the control/blank sample). The amended soils gave higher values for physic-chemical properties (Table 1) than the un-amended soil except for pH. Effect of parameters such as initial adsorbate concentration, contact time, temperature, adsorbent dose and pH on adsorption, all gave positive correlation with increase amount of NPK-15:15:15 except adsorbent dose and pH which correlated negatively with increased amount of NPK fertilizer.

Keywords: pendimethalin, adsorption, soil, NPK-15:15:15, equilibrium

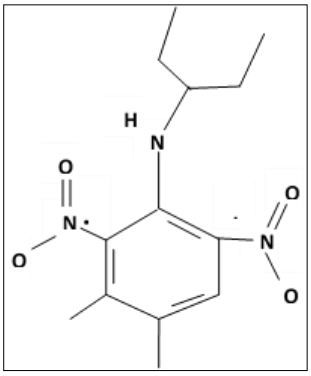
1. Introduction
Herbicides are a group of agrochemical substances known as plant protection products (PPP) that are utilized to specifically, partially or totally control or kill undesirable vegetation, such as weedy plants with the aim to significantly increase crop productivity by protecting the crop (McManus *et al.,* 2014) [1]. Weeds are unwanted vegetation, which are not intentionally planted, but continuously grow in unexpected areas within and around cultivated places (Mensah *et al.,* 2015) [2]. Confronted with aggressive growth of weed, many farmers in Benue, an agrarian state, widely utilize pendimethalin as weed control. Pendimethalin is a selective herbicide used to control annual grasses and broad leaf weeds. It is typically used as a pre-emergent or early post-emergent herbicide in cotton (Williams *et al.,* 2009) [3]. Field dissipation studies have revealed that pendimethalin is persistent, and its half-life is 98 days at 30◦C (Kol *et al*., 2002) [4]. Pendimethalin degrades slowly in aerobic soil and rapidly in anaerobic soil conditions. It is not subject to microbial degradation. Slight loss of pendimethalin can result from photodegradation and volatilization. Pendimethalin adsorbs strongly to organic matter and clay (Kpagh *et al.,* 2016) [5]. Pendimethalin according to Kaleem *et al., 2006* [6] *is* classified as a non-leaching compound. Soil around the Benue valley is low in clay and organic matter content (Sha'Ato *et al.,* 2012) [7]. There is therefore high possibility of leaching and polluting underground water. Pendimethalin is stable to hydrolysis, but is degraded by light in aquatic system. It may be removed from water by its strong tendency to bind to sediment and organic matter. Pendimethalin is absorbed by plant roots and shoots. It is not absorbed by the leaves of grasses. Once absorbed into plant tissues, translocation is limited and it breaks down via oxidation.
Intensive, prolonged cropping depletes soil nutrients hence farmers apply manures to improve soil fertility. Among the substances mostly used by farmers to improve soil fertility is the Nitrogen-Phosphorus-Potassium (NPK-15:15:15) fertilizer. Being a source of nutrient for soil micro-organisms, application of Nitrogen fertilizer according to Shamin and Kiyoshi 2011 [8], from the study on effect of chemical Nitrogen fertilizer application on the release of Arsenic from sediment to ground water in Bangladesh, increases soil microbial activities creating a reducing underground water environment. Pendimethalin, according to result of this work adsorbs better at low pH (reducing condition). Pendimethalin causes cancer, irritates skin, linings of mouth, nose, throat and lungs (OHS, 1991) [9]. Limited information exists in literature on the influence of co-application of Nitrogen-Phosphorus-Potassium (NPK-15:15:15) fertilizer and pendimethalin on adsorption of pendimethalin in soil. Addition of NPK-15:15:15 fertilizer increases soil organic matter content through bio-stimulation. The aim of this study is to examine the influence of Nitrogen-Phosphorus-Potassium (NPK-15:15:15) fertilizer application on adsorption of pendimethalin in soil.

2. Material and Methods
Material
Materials listed here were utilized in the course of the experiment: Distilled water, sodium hydroxide (0.1 M), hydrochloric acid, (0.1 M), Pendimethalin (500 g/L EC). Beakers (250 mL), measuring cylinder (250 mL, 50 mL, 5 mL), analytical weighing balance (Mettler PM 2500), conical flask (250 mL), pH meter (ep$^{(R)}$ pocket-sized), desiccator, spatula, Whatman filter paper (110 mm), 2 mm sieve/shaker. UV-Vis (Jenway 7305) spectrophotometer, mechanical shaker.

Sampling and preparation
Soil samples were taken at the surface horizon (0 - 25 cm) from the Federal University of Agriculture Makurdi Teaching and Research Farm. The whole soil samples were

taken to the Chemistry Laboratory in black polythene bags where they were homogenized, air-dried at room temperature for seven days and then sieved (Kpagh *et al., 2016)* [5].

Pendimethalin



Structure of pendimethalin (3,4-Dimethyl-2,6-dinitro-N-(pentan-3-yl) aniline)

Pendimethalin (as pendilin(R) 500 EC, African Agro Products Ltd, plot 503, Indipendence Road, opposite Bonpai Barrack, Kano state, Nigeria) was purchased from Franken Technology Nigeria Limited, Makurdi and used without purification.

Fertilizer

Nitrogen-Phosphorus-Potassium (NPK 15:15:15) fertilizer was purchased from Benue Agricultural and Rural Development Authority (BNARDA), Makurdi.

Soil amendment

Soil samples in seven plastic containers were amended with 0, 5, 10, 15, 20, 25 and 30 g of NPK fertilizer per kilogram soil at 60% moisture level of water holding capacity and incubated for 30 days at 25 ^{O}C (Bansal, 2010) [10].The physico-chemical properties in table 1 were determined using standard laboratory soil methodology (Kpagh *et al., 2016)* [5].

Determination of physico-Chemical properties of soil

Conductivity measurement was determined by method used by Kpagh *et al., 2016)* [5]. Attrition/Hardness and pH were determined according to method used by Tole *et al.*, (2000) [11]. Cation Exchange Capacity was determined using the Ammonium Acetate (NH_4OAc) method at pH 7. Bulk density was determined using method adopted by Ahmedna *et al* (2000) [12]. Organic matter was determined using the Dichromate method.

Preparation of Stock and Standard Solution

A stock solution of 500 mg/L was prepared by dissolving 1 mL of pendimethalin (500 g/L EC) solution in 1000 mL of distilled water.

Calibration curve

Five working standard solutions of concentrations (10, 20, 30, 40 and 50) mg/L were prepared from the stock solution using dilution equation $C_1V_1 = C_2V_2$. Where:

C_1 = concentration of the working standard solution

C_2 = concentration to be prepared

V_1 = volume of the working standard solution

V_2 = volume of the solution to be prepared

Three mL of each solution was measured into the Uv-vis spectrophotometer cuvettes and the appropriate absorbance taken at 416 nm. (Kpagh *et al.*, 2016 [5]; Mohammed, 2012) [13]. From these measurements the calibration curve was constructed so that the absorbance obtained could be directly converted into the concentration by extrapolating through the linear range (Wuana *et al.*, 2015) [14].

Calibration Curve for adsorption of pendimethalin in soil

Adsorption Experiments

Batch equilibrium method was used in which 10 g of amended and un-amended soil samples were added into seven stopper conical flasks. 10 mL of 50 mg/L pendimethalin solution was added to each soil sample and the volume made up to 100 mL. The suspension was shaken on a mechanical shaker for 80 minutes and left standing for 24 hours at 25^{o}c to attain equilibrium. This was then filtered and the residual pendimethalin in the filtrate determined by UV-visible spectrophotometer. The amount of Pendimethalin adsorbed by soil was determined by subtracting the concentration remaining in the solution after equilibrium from the initial concentration using the equation:

$$q_e = \frac{V(C_0 - C_e)}{W}$$

Where q_e (mg/g), is the amount of Pendimethalin adsorbed per unit weight of soil, C_0 (mg/L), is the initial Pendimethalin concentration, C_e concentration of Pendimethalin at equilibrium (mg/l), V is the volume (mL), W is the weight of soil (g) (Kibami *et al.*, 2015) [15].

Determination of parametric factors

Batch adsorption was carried out to investigate the influence of the following effects on application of NPK 15.15.15 fertilizer on the adsorption of Pendimethalin in soil using 100mL of 50mg/L standard pendimethalin solution except for Initial concentration:

Effect of initial concentration, was studied by contacting 5 g soil with 10, 20, 30, 40 and 50 mg/L into 100mL Pendimethalin standard solutions. Effect of adsorbent dosage was carried out by contacting standard pendimethalin solution with 0.5, 1.0, 1.5, 2.0, 3.5 g soil. Effect of soil pH, determined by contacting 5 g soil with standard pendimethalin solution at pH 2, 3, 5, 7 and 9. Effect of temperature was studied by contacting 5 g soil with standard Pendimethalin solution at 25, 35, 45, 55 and 65^{o}c for 1 hour in a thermostatic water bath. Effect of contact time was studied by contacting 5 g soil with standard Pendimethalin solution for 20, 40, 60, 80 and 100 minutes. Supernatant was analysed spectrophotometrically for the residual concentration of Pendimethalin.

3. Results and Discussion

Table 1: Physico-chemical Properties of Adsorbents

Parameters	S-0g NPK	S-5g NPK	S-10g NPK	S-15g NPK	S-20g NPK	S-25g NPK	S-30g NPK
pH	6.80	6.47	6.21	6.01	6.05	6.06	5.96
E.C (µʃ/cm)	43.0	66.9	64.0	96.8	98.6	101.1	102.1
C.E.C (cmolkg^{-1}) NH_4OAC	8.4	9.0	9.4	9.6	10.2	10.8	10.6
O.C (%)	0.10	1.10	1.06	1.22	1.64	1.06	1.68
Attrition (%)	17.09	22.36	22.50	22.45	23.72	23.72	25.03
Bulk-density (g/cm^3)	0.27	0.46	0.46	0.46	0.46	0.49	0.88
Moisture content (%)	0.20	0.60	0.60	0.60	0.60	0.60	0.80
Surface area (M^{2}g^{-1})	19.64	19.83	19.86	19.86	19.89	19.89	20.07
Porosity (%)	46.80	45.14	45.08	45.03	44.35	44.35	44.39
Sand (%)	69.80	68.92	68.92	68.91	68.88	68.81	67.53
Silt (%)	3.81	3.86	3.90	3.90	4.01	4.01	5.10
Clay (%)	43.55	43.57	44.33	44.33	44.62	44.66	45.05
texture	SL	SL	SL	SL	SL Soil	SL	SL

Where S stands for soil, SL stands for Sandy Loam.

Effect of Adsorbent Dosage

Figure 1. The result shows that adsorption capacity decreases as the adsorbent dose increases from 0.5 g to 2.5 g. This can be explained on the basis of number of sites available for adsorption. The total number of active sites available for adsorption decreases as the adsorbent dosage increases (Itodo and Itodo 2010) [16].

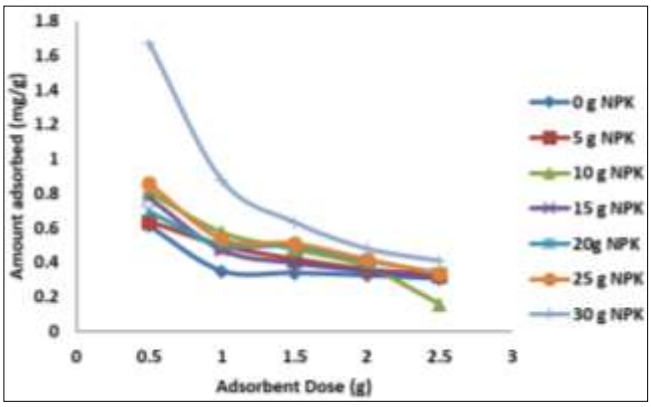


Fig 1: Effect of Adsorbent Dose on Adsorption of Pendimethalin

Effect of Initial Adsorbate Concentration

The result in Figure 2 shows the effect of initial adsorbate concentration on adsorption of pendimethalin in soil. The result implies that adsorption capacity increases with increase in concentration of the adsorbate. This can be explained on the basis of the number of sites available for adsorption. Initially, adsorption was rapid because of the availability of large vacant sites. Thereafter, increasing initial adsorbate concentration results in a greater driving Force to overcome mass-transfer resistance in the phase and the sites are exhausted quickly (Moyo *et al.*, 2017 [17]; Saravanan *et al.*, 2018) [18].

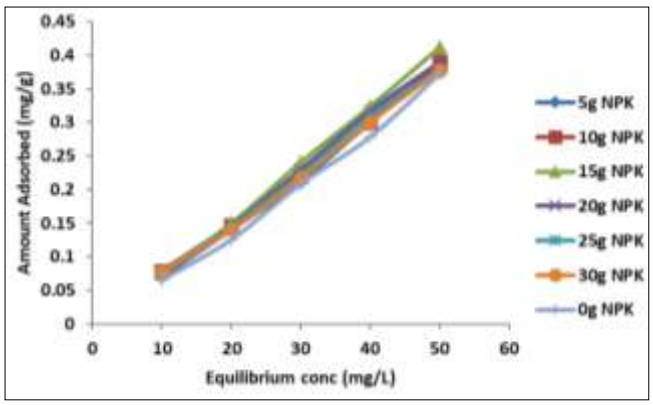


Fig 2: Effect of Concentration on the Adsorption of Pendimethalin

Effect of Temperature

Figure 3 shows the effect of temperature on adsorption of Pendimethalin. The result shows that adsorption of pendimethalin increases with increase in temperature. Girish and Murty, (2014) [19] says that high temperature favours slow diffusion of adsorbate into adsorbent as more adsorbate was required for higher adsorption capacity, indicating an endothermic process. Increased collision between the adsorbate and the adsorbent as the temperature increases also favours adsorption (Kannan *et al.*, 2009) [20]. While adsorption increases with increase in temperature for all the soil samples, the un-amended soil has the least adsorption capacity.

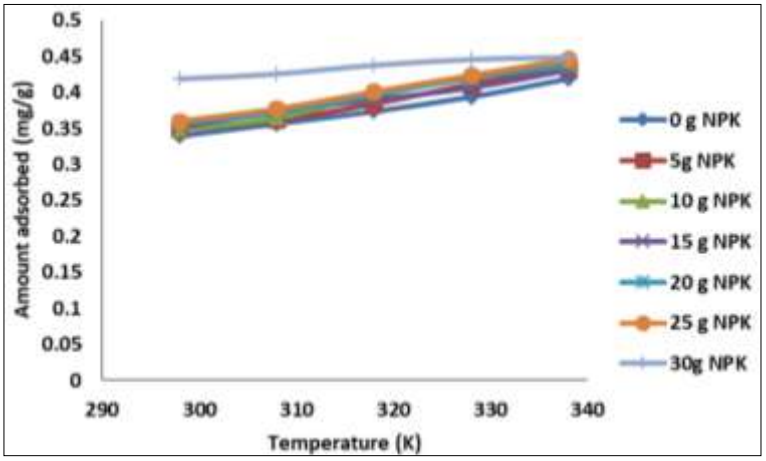


Fig 3: Effect of Temperature on Adsorption of Pendimethalin

Effect of pH

Figure 4 shows the effect of pH. From this result, it can be concluded that adsorption capacity decreases with increase in pH. Similar result was obtained by Filipkowska *et al.*, 2010 [21]. The un-amended soil (0 g NPK) with the highest value 6.80 of pH (Table 1) also had the highest adsorption capacity as seen in figure 3. This result shows that pendimethalin can best be adsorbed under acidic condition (low pH) El-Geundi *et al.*, (2005) [22] obtained similar result from the work: adsorption equilibrium of a herbicide (Pendimethalin) onto natural clay. According to Banerjee and Chattopadhyaya (2013) [23], the effect of pH depends of the nature of the adsorbent and the adsorbate. The environmental effect of this is that the herbicide is not available to be carried in run-off in soil with high acidity. However, if condition changes and the soil become alkaline, there is high risk of possibility of leaching into underground water.

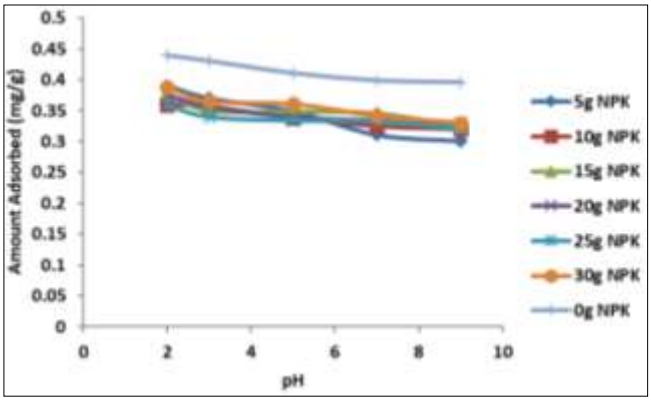


Fig 4: Effect of pH on the Adsorption of Pendimethalin

Effect of contact time

Figure 5 shows adsorption of pendimethalin at different contact time. This result shows that adsorption capacity increases as the contact time increases. The rate of adsorption was very rapid for the first 20 minutes as a result of the fact that the adsorbate has more time to be in contact with the adsorbent (Fathi *et al.*, 2014) [24].

This can be attributed to number of sites available for adsorption on the surface of the adsorbent was sufficient initially, but as time progressed, these sites became gradually saturated Riebe and Bunnenberg, (2007) [25]. Hence the decrease rate of adsorption at 60th minute. The un-amended soil (0 g NPK) has the lowest adsorption rate compared to the amended ones. This can be due to the fact that addition of fertilizer increases soil organic matter. This result also correlates the findings of Bakayoko *et al.*, (2009) [26], Williams *et al.*, (2009) [27].

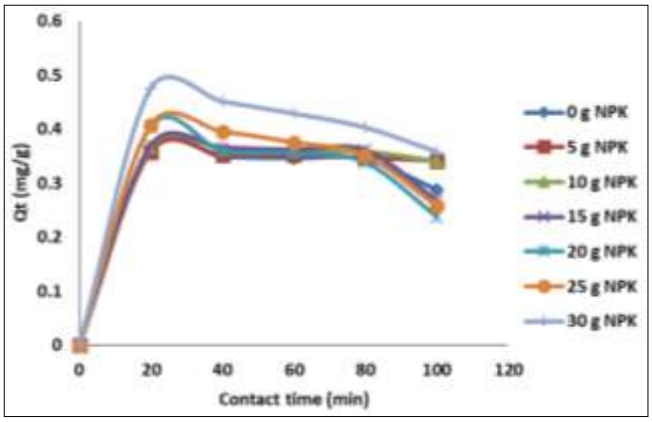


Fig 5: Effect of contact time on the Adsorption of Pendimethalin in Soil

4. Conclusion

The results of the influence of Nitrogen-Phosphorus-Passiun (NPK 15:15:15) fertilizer application on adsorption of pendimethalin in soil, showed that the addition of NPK 15:15:15 served to bio-stimulate the adsorbent as the amended soil showed an increased physico-chemical properties like organic carbon content, electrical conductivity, cation exchange capacity indicated in table 1.0 than the un-amended soil. Adsorption characteristics of pendimethalin unto soil were strongly influenced by initial adsorbate concentration, adsorbent dose, pH, contact time and temperature. The result from statistical test of significance showed that there was no significant difference between the adsorption capacities of the amended soils and the un-amended soil even though the amended soil gave a higher absorbance with increase in contact time. Finally, it is concluded based on the discovery of this study that addition of NPK 15:15:15 fertilizer does not significantly enhance adsorption of pendimethalin in soil.

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