

Ammonium Adsorption Characteristics of Jasaan Clay Soils under Conservation Agriculture and Conventional Plow-based Production Systems

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ABSTRACT

Knowledge of nutrient adsorption characteristics of soils is important for analyzing nutrient retention for plant uptake and potential losses due to leaching in agricultural crop production systems. This study aimed to characterize and compare the ammonium adsorption behavior of Jasaan clay soils under conservation agriculture production systems (CAPS) and under conventional plow-based (PB) production systems. Soil samples were collected from plots laid in a randomized complete block design for selected treatments T2 (Maize + Stylosanthes – Stylosanthes – fallow) and T5 (Cassava + Stylosanthes – Cassava + Stylosanthes) and a PB system, T6 (Maize-Maize), at the SANREM Research site in Claveria, Misamis, Oriental. Batch adsorption experiments were performed for desorbed soil samples using ammonium solution of various initial concentrations to determine equilibrium concentrations. The adsorption isotherm models such as linear, Freundlich and Langmuir models were then fitted to the experimental data through linear regression analysis. Results showed that the Freundlich and Langmuir adsorption isotherm models best fitted the experimental data for all treatments, with the coefficient of determination R^2 ranging from 0.84 to 0.98 for the Freundlich model and from 0.64 to 0.95 for the Langmuir model. Results also showed that the mean distribution coefficient K_d and the maximum adsorptive capacity of the soils under CAPS were significantly higher ($\alpha=5\%$) than those under PB system. The mean K_d values for treatments T2, T5 and T6 obtained in this study were 1.421, 1.585 and 0.691 L/kg, respectively. On the other hand, the maximum adsorptive capacity values were found to be 2,210.1, 2,441.6 and 1,077.3 mg/kg for treatments T2, T5 and T6, respectively. The results of this study suggest that soils under CAPS have better ammonium adsorption for plant uptake and lower leaching losses than soils under PB systems. Consequently, higher ammonium-nitrogen fertilizer application efficiency can be expected under CAPS than under PB systems.

Keywords: ammonium adsorption, Jasaan clay, soil adsorption capacity, distribution coefficient, conservation agriculture, plow-based system

INTRODUCTION

Most of the farmers in the upland areas of the Philippines continue to practice the conventional plow-based crop production systems. As a result,

soil degradation becomes a problem in these areas as soil disturbances due to plowing result in excessive soil erosion and loss of organic matter. One of the alternative options to address this problem is through conservation agriculture, a biological

engineering technology based on the principles of minimum soil disturbance, continuous mulch cover and diverse crop species (Erenstein *et al.*, 2008). The numerous beneficial effects of this technology have been well documented (e.g. Ella, 2018; Ares *et al.*, 2015). In the Philippines, the soil quality effects of conservation agriculture have been reported in recent years (De Leon and Ella, 2019; Padre, 2016; Ella *et al.*, 2016; Reyes, 2014; Ella, 2014; Tarnate *et al.*, 2014; Ella, 2012). Based on the experimental and modeling research under the Sustainable Agriculture and Natural Resources Management-Collaborative Research Support Program (SANREM-CRSP) in Claveria, Misamis Oriental (Ella, 2014 and Reyes, 2014), it was observed that the soil organic matter at the conservation agriculture production systems (CAPS) plots generally increased through the years while that under plow-based systems generally decreased (Ella *et al.*, 2016). This observation has practical implications on nutrient dynamics in the soil under conservation agriculture and under plow-based systems.

It has long been established that soil organic matter affects adsorption of chemicals in soils. As reported in Fetter (1993), adsorption increases with increasing soil organic matter. Thus, it is important to examine nutrient adsorption characteristics particularly of ammonium in soils under CAPS and plow-based soils to generate additional new knowledge on the impact of conservation agriculture on soil quality. This knowledge may consequently be used for analyzing nutrient dynamics and for determining nutrient retention for plant uptake and potential losses due to leaching.

A number of studies on ammonium adsorption in soils and isotherm modeling in other countries have been reported in published literature. Ranjbar and Jalali (2013) measured and modelled ammonium adsorption in calcareous soils collected

at 0-30 cm using ammonium ion concentration ranging from 10 m/L to 150 mg/L and found out that the average amounts of adsorbed NH_4^+ varied from 8.95 to 35.23%. They also found that the simple linear adsorption and Freundlich adsorption models fitted well with experimental data. In another study by Nanganoa *et al.* (2013), the adsorption potential of fine fractions of sandy clay loam soil for ammonium ion from aqueous solution was examined through kinetic adsorption experiments and they found out that the Freundlich isotherm model fitted well with experimental data. They also observed that equilibrium was reached after 45 minutes. Sharifna *et al.* (2013) performed ammonium adsorption studies on light expanded clay aggregate through batch adsorption experiments and found out that the Freundlich and Langmuir isotherm models fitted well with experimental data. In their experiments, equilibrium was reached after 150 min.

The maximum adsorption capacity of clay soils has also been examined in past studies through batch adsorption experiments and adsorption isotherm modeling and results differed for various soils. For instance, results of adsorption experiments and modeling study by Sharifna *et al.* (2013) on light expanded clay aggregate showed that the maximum monolayer adsorption capacity estimated from the Langmuir isotherm ranged from 0.229 to 0.254 mg/g or 229 to 254 mg/kg. On the other hand, Wang *et al.* (2011) estimated the maximum adsorption capacity of vermiculite, a common layered clay mineral, to be 18 mg/g or 18,000 mg/kg based on Langmuir isotherm model fitted to their experimental equilibrium adsorption data. Hua *et al.* (2010) reported that the maximum ammonium-nitrogen adsorption capacity of silty sand, silty clay and clay estimated from Langmuir adsorption isotherm model ranged from 0.088 to 0.540 mg/g or 88 to 540 mg/kg.

Factors affecting ammonium adsorption such as pH, initial ammonium concentration, soil texture, soil salinity and sodicity among others were also examined by a number of researchers. Kithome *et al.* (1998) in their study of the kinetics of ammonium adsorption and desorption by the natural zeolite Clinoptilolite found that the amount of ammonium sorbed increased with increasing pH and initial ammonium concentration. Nanganoa *et al.* (2013) also studied the effect of pH, contact time, initial concentration and the presence of competing ions. They found that adsorption decreases when the pH is lower than 7.0 or greater than 8.0. Longer contact time and higher initial concentration also led to increased ammonium adsorption. On the other hand, the presence of competing ions also led to decreased ammonium adsorption. Wang and Alva (2000) examined the ammonium adsorption and desorption in selected soils using batch adsorption experiments and concluded that the adsorption capacity of sandy soils is much lower than that of clay and silt loam soils. Awadelkarim and Mahmud (2013) found that increasing salinity leads to decreasing ammonium adsorption in soils while increasing sodium adsorption ratio (SAR) leads to increasing ammonium adsorption. Results of their study on ammonium adsorption in selected soils showed that increasing salinity level from 40 to 80 mmol/L led to a decrease in the mean adsorbed ammonium of from 331 to 263 mg/kg while an increase in SAR from 15 to 25 resulted to an increase in adsorbed ammonium from 256 to 324 mg/kg.

Other factors affecting adsorption of organic compounds onto various natural adsorbent like soils were reported by Delle Site (2001). Among the most notable factors include temperature. In general, adsorption decreases with increasing temperature; however, there are exceptional cases of increasing adsorption with increasing temperature. Lower distribution coefficient values

have been observed at increasing temperatures for most organic compounds whose solubility increases with temperature. Conversely, higher distribution coefficient values can be expected for organic compounds with solubility that decreases with temperature.

The effect of organic matter on adsorption of chemical on soil adsorbents has long been investigated. Fetter (1993) reported that the distribution coefficient K_d is directly proportional to the fraction of organic carbon. Hence, the higher the organic matter content of the soil, the higher is its adsorption capacity. However, Karickhoff *et al.* (1979) found that the adsorption of solute onto mineral surface or organic carbon content of the soil or aquifer almost exclusively takes place onto the organic carbon fraction if it constitutes at least 1% of the soil or aquifer on a weight basis.

While numerous studies on ammonium adsorption in soils have been done in other countries, no such studies have been done for Philippine soils except for the research done by Pineda (2005) and Ella (2005). In their studies, the ammonium adsorption of selected clay soils in Los Baños and Bay, Laguna was characterized through batch adsorption experiments. Results showed that ammonium adsorption was higher in soils with higher organic matter and clay content.

Despite all previous advances, ammonium adsorption studies in soils under conservation agriculture in the Philippines have never been done before owing to the fact that this new agricultural crop production technology, in the strictest sense, has never been practiced in the country. In fact, this biological engineering technology was introduced for the first time in Claveria, Misamis Oriental in 2010 as part of the Sustainable Agriculture and Natural Resources Management - Collaborative Research Support Program

(SANREM-CRSP) project (Ella, 2014; Reyes, 2014). Thus, this study was intended to fill one of the many research gaps and is generally aimed to characterize and compare the ammonium adsorption behavior of Jasaan clay soils under Conservation Agriculture Production Systems (CAPS) and under the conventional plow-based system.

METHODOLOGY

Soil Sampling

Soil samples were obtained from the research site of SANREM in the upland areas of Claveria, Misamis Oriental. The soil type at the site is Jasaan clay, belonging to Ultisol soil order, with soil texture being generally clayey with a mineral composition of Horneblende, Augite, Biotite, and Olivine clay minerals (BSWM, 1983). From soil texture analysis using hydrometer method, the soil is classified as clay with 76.2% clay and 23.3% sand and 0.5% silt on the average. The research site is at an elevation of 684 m above mean sea level (Ella, 2010; Reyes, 2010).

The SANREM research site (Figure 1) contains six experimental treatments (Table 1) in the form of cropping patterns with different cover crops including plow-based system were established and laid out in a randomized complete block design (Ella *et al.*, 2012). Out of the six experimental CAPS treatments being investigated in the SANREM project, CAPS treatments T2 and T5 along with the conventional plow-based system treatment serving as control were selected in this adsorption study. The CAPS treatments T2 and T5 were selected because they are the treatments that have shown the highest increase in soil organic matter content through the years (Ella, 2014). The soil organic matter content was observed to increase to as high as 6.5% and 8.7% for

Table 1. Summary of the CAPS treatments at the SANREM research site

TREAT-MENT	CROPPING PATTERN
T1	Maize+Arachis pinto – Maize+ Arachis pinto
T2*	Maize + Stylosanthes – Stylosanthes-fallow
T3	Maize+cowpea - Upland rice +cowpea
T4	Maize+Rice bean- Maize+Rice bean
T5*	Cassava + Stylosanthes- Cassava + Stylosanthes
T6*	Maize-maize (control)

*- selected for adsorption experiments and modeling



Figure 1. The SANREM research site in Claveria, Misamis Oriental

treatments T2 and T5, respectively, which were relatively higher compared to all the other treatments including the conventional plow-based control. The soil pH did not differ significantly among treatments and had an average of 4.5. Under CAPS treatment T2, the seeds of the main crop corn were dibble-planted while the seeds of the cover crop *Stylosanthes guianensis* were drilled in between the corn rows. In CAPS treatment T5, cuttings of the main crop cassava were planted and the cover crop *Stylosanthes guianensis* seeds were drilled in between. Under treatment T6, the plots were plowed using an animal-drawn moldboard plow and consequently harrowed using animal-drawn toothed harrow and furrowed using the moldboard plow prior to

planting of the main crop corn. No cover crops were grown in between corn under this conventional plow-based treatment.

Three replicates for each of the selected treatments were chosen for the adsorption experiments and modeling. The treatment labels T2, T5 and T6 were maintained in this study for consistency with the other published reports that made use of the same experimental site (e.g. Ella, 2018; Ella *et al.*, 2016; Ella, 2014; Reyes, 2014).

Soil samples, each with a mass of one kilogram, were collected at a depth of 0-15cm from the selected CAPS and conventional plow-based plots using a soil auger. All soil samples were brought to the University of the Philippines Los Baños for adsorption experiments.

Desorption/ Extraction of Cations and Adsorbent Preparation

The soil samples from each of the three replicates under the three treatments were soaked in distilled water placed in 6-L plastic containers. The electrical conductivity (EC) of these soils was monitored using an electrical conductivity (EC) meter until no significant changes in the EC readings were observed. For every EC measurement, the distilled water used in soaking was decanted from the container and replaced with a new one.

After soaking, the soil samples were air-dried for three weeks and then pulverized. The samples were passed through a 0.425-mm standard sieve to remove non-soil materials like plant roots and other impurities. Using an electronic balance, a total of 72 soil samples, each with a mass of 50 g, were prepared for the batch adsorption experiments to represent the 3 treatments and 3 replicates and to cater to the 8 different initial ammonium ion concentrations described in the ensuing sections. These procedures were essentially based on standard methods (e.g. EPA, 1992).

Adsorbate Preparation

Ammonium sulfate powder (RCI Labscan ammonium sulphate) was used as source of ammonium ions for adsorbate preparation. Solutions were prepared by dissolving a known mass of ammonium sulfate in a known volume of distilled water. Stoichiometric computations were done to determine the mass of ammonium sulfate powder needed to be dissolved in a known volume of distilled water to generate the desired ammonium ion concentrations. Eight varying concentrations of ammonium ion NH_4^+ solution (50, 100, 300, 500, 700, 900, 1500 and 2000 mg/L) were prepared. A 500-ml volume of ammonium solution was then prepared for each of the 72 soil samples described in the preceding section.

To facilitate the monitoring of ammonium ion concentration and the determination of equilibrium concentration during adsorption experiments, the relationship between ammonium ion concentration and electrical conductivity was developed. Samples from each of the eight concentrations of the adsorbate prepared were brought to the Central Analytical Services Laboratory of the National Institute of Molecular Biology and Biotechnology (BIOTECH) of UPLB for analysis. The ammonium ion concentration was determined at BIOTECH using titration method. The paired values of EC and ammonium ion concentration were then used to develop the mathematical relationship between the two parameters.

Batch Adsorption Experiments

Batch adsorption experiments were conducted for 72 soil samples soaked in ammonium solution (3 treatments x 3 replicates x 8 initial concentrations of 50, 100, 300, 500, 700, 900, 1500 and 2000 mg/L). A volume of 500 mL of the ammonium solution and 50 g of soil were used in the batch experiments. The electrical conductivity values of the solution in each of the containers were monitored using an EC meter from time zero and every 24 hours thereafter until the readings became relatively constant. The temperature was also monitored. The EC readings were then converted to ammonium ion concentration using the

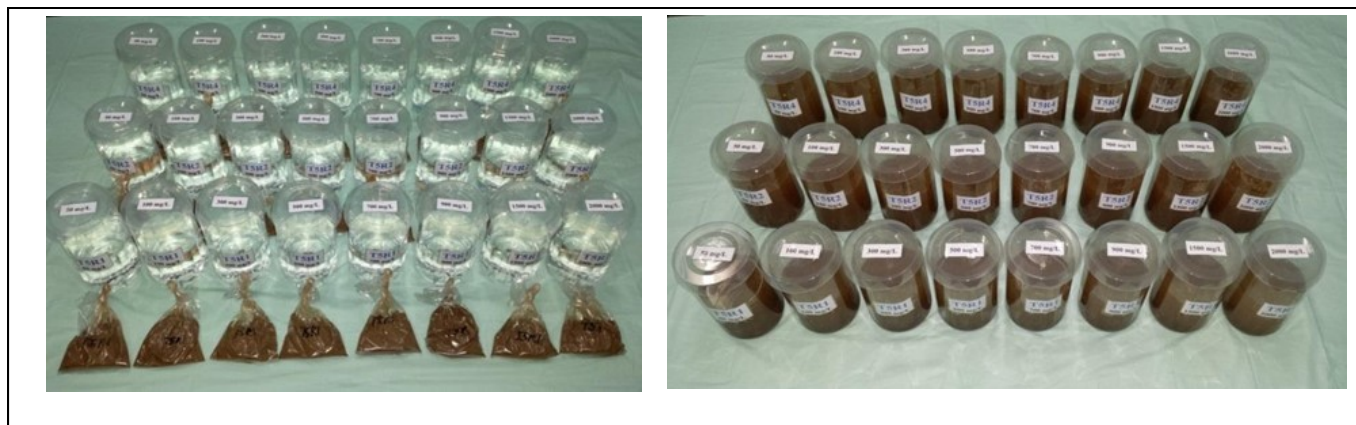


Figure 2. The batch adsorption experiments

developed relationship between these 2 parameters as described in the preceding section. Sample pictures of the batch adsorption experiments are shown in Figure 2.

The percent ammonium adsorbed for each initial concentration was computed using the following equation:

$$\% \text{NH}_4^+ \text{ adsorbed} = \frac{C_i - C_w}{C_i} \times 100 \quad (\text{Equation 1})$$

where:

C_i = initial concentration of NH_4^+ in water, mg/L
 C_w = equilibrium concentration of NH_4^+ in water, mg/L

The mass of ammonium adsorbed per unit mass of soil at equilibrium was computed using the equation:

$$C_s = \frac{(C_i - C_w)}{m} \times V \quad (\text{Equation 2})$$

where:

C_s = equilibrium concentration of NH_4^+ in soil, mg/kg
 C_i = initial concentration of NH_4^+ in water, mg/L

C_w = equilibrium concentration of NH_4^+ in water, mg/L
 V = volume of solution, L
 m = mass of soil, kg

Adsorption Isotherm Data Analysis and Modeling

The paired values of C_s and C_w obtained from batch adsorption experiments were used for adsorption isotherm modeling using the linear, Freundlich, and Langmuir adsorption isotherm models. The linear adsorption isotherm model is given by equation 3.

$$C_s = K_d C_w \quad (\text{Equation 3})$$

where:

C_s = mass of solute adsorbed per unit mass of adsorbent (M/M)
 K_d = distribution coefficient (L^3/M)
 C_w = equilibrium concentration of solute in solution (M/L^3)

The Freundlich adsorption isotherm model is given by equation 4.

$$C_s = K_s C_w^{\frac{1}{n}} \quad (\text{Equation 4})$$

where:

C_s = mass of solute adsorbed per unit mass of adsorbent (M/M)

K_s , n = Freundlich adsorption constants

C_w = equilibrium concentration of solute in solution (M/L³)

The Langmuir adsorption isotherm model is given by equation 5.

$$C_s = \frac{\alpha\beta C_w}{1 + \alpha C_w} \quad (\text{Equation 5})$$

where:

C_s = mass of solute adsorbed per unit mass of adsorbent (M/M)

C_w = equilibrium concentration of solute in solution (M/L³)

α = Langmuir adsorption constant related to binding energy (L³/M)

β = maximum mass of solute that can be adsorbed by the adsorbent or maximum adsorptive capacity (M/M)

In the linear adsorption model, the model parameter K_d was determined through linear regression analysis setting the y-intercept to zero. For Freundlich isotherm model, the model parameters K_s and $1/n$ were determined using linear regression analysis of the logged values of C_s and C_w . For Langmuir model, linear regression analysis was done for the reciprocal of C_s and C_w to determine the model parameters α and β . The goodness of fit for each model was assessed using the coefficient of determination R^2 .

Among the three models, the Freundlich and Langmuir models are the most widely used models for adsorption isotherm modeling. The Freundlich isotherm model assumes heterogeneous surface of the adsorbent and that the active sites and their energies distribute exponentially (Freundlich, 1906; Ayawei *et al.*, 2017; Saadi *et al.*, 2015). On the other hand, the Langmuir isotherm model is based on the following assumptions: 1) monolayer

adsorption, i.e. only a single layer of molecules are adsorbed into the surface of adsorbent, 2) homogeneous surface of the adsorbent and 3) uniform energy for all adsorption sites (Langmuir, 1916; Saadi *et al.*, 2015). Langmuir is a theoretically-based equation while Freundlich is empirically-derived (Ayawei *et al.*, 2017). Both models have proven adequacy for soil adsorption characterization in various studies (e.g. Khajeali *et al.*, 2019; Sharifna *et al.*, 2013; Ranjbar and Jalali, 2013; Nanganoa *et al.*, 2013; Wang *et al.*, 2011; Hua *et al.*, 2010; Gunary, 2006; Dias *et al.*, 2001).

Statistical Analysis of K_d Values and Maximum Adsorptive Capacity

Analysis of variance (ANOVA) was performed to determine if the mean values of K_d and β for each treatment were significantly different from each other at $\alpha=5\%$.

RESULTS AND DISCUSSION

Equilibrium Concentration in Water and in Soil

Adsorption experimental results for the given soil samples showed that almost all the samples reached equilibrium after 7 days and reached an average temperature of 19°C. It was observed that the time required for the ammonium concentration to reach equilibrium was shorter for soils under the plow-based treatment T6, compared to those soils under CAPS treatments T2 and T5. For T6 samples, the change in ammonium concentration in solution became gradual after the 4th and 5th day of soaking while for T2 and T5, EC change became gradual on the 7th day. This indicates that soils under plow-based system (T6) have lower adsorptive capacity than soils under conservation agriculture production systems (T2 and T5). However, a better comparison of adsorption behavior can be made in terms of the distribution coefficient and maximum adsorptive capacity values obtained from adsorption isotherm modeling.

Experimental results also showed that the average %NH₄⁺ adsorbed for all replicates under T2, T5, and T6 were 16.93%, 21.83% and 15.55%, respectively. This suggests that more ammonium ions can be adsorbed in soils under conservation agriculture production systems than in soils under plow-based systems. However, as previously mentioned, a better comparison can be made through adsorption isotherm modeling.

Adsorption Isotherm Modeling

The adsorption model parameters were determined by fitting the adsorption isotherm models to the

experimental data on equilibrium concentration of ammonium in water and in the soil. The average and range of values of the various model parameters for each of the three treatments are given in Tables 2 to 4.

Sample plots of the linear adsorption isotherm models for the three treatments are shown in Figures 3 to 5. It is apparent that the adsorption behavior is generally linear for soils under CAPS treatments T2 and T5 but not for plow-based treatment T6. For T2, the coefficient of determination or explained variance, R², of the linear isotherm model ranged from 0.71 to 0.94.

Table 2. Average and range of adsorption isotherm model parameter values for CAPS treatment T2

ISOTHERM	MODEL PARAMETERS					
	K _d	K _s	N	α	β	R ²
Linear	1.42 (1.37-1.45)	-	-	-	-	0.86 (0.71-0.94)
Freundlich	-	7.68 (6.77-9.32)	1.3 (1.27-1.33)	-	-	0.97 (0.96-0.98)
Langmuir	-	-	-	0.0015 (0.0014-0.0016)	2210.1 (1975.7-2597.4)	0.88 (0.87-0.89)

Table 3. Regular and range of adsorption isotherm model parameter values for CAPS treatment T5

ISOTHERM	MODEL PARAMETERS					
	K _d	K _s	N	α	β	R ²
Linear	1.59 (1.5-1.7)	-	-	-	-	0.73 (0.68-0.76)
Freundlich	-	14.34 (10.25-17.4)	1.41 (1.34-1.46)	-	-	0.96 (0.96-0.97)
Langmuir	-	-	-	0.0021 (0.0017-0.0024)	2441.6 (2336.7-2534.3)	0.93 (0.92-0.95)

Table 4. Average and range of adsorption isotherm model parameter values for PB treatment T6

Isotherm	Model Parameters					
	K _d	K _s	N	α	β	R ²
Linear	0.69 (0.61-0.78)	-	-	-	-	0.10 (0.004-0.22)
Freundlich	-	39.08 (29.26-49.44)	2.20 (2.02-2.30)	-	-	0.87 (0.84-0.90)
Langmuir	-	-	-	0.0042 (0.0034-0.0055)	1077.3 (1034.2-1130.3)	0.81 (0.64-0.91)

For T5, R^2 varied from 0.68 to 0.76. This suggests that the linear adsorption model is adequate to characterize the ammonium adsorption in soils for the selected conservation agriculture production systems. Under plow-based treatment T6, R^2 for the linear adsorption isotherm model was relatively low and ranged from 0.004 to 0.22. This simply implies that the linear adsorption model cannot be used to predict C_s for soils under plow-based systems for any given C_w .

Figures 6 to 8 show sample plots of Freundlich adsorption isotherm models for the three treatments. Based on the coefficient of determination or explained variance R^2 , the Freundlich isotherm model can adequately predict C_s values for all treatments T2, T5 and T6 for given C_w values. For CAPS treatment T2, R^2 ranged from 0.96 to 0.98. For CAPS treatment T5, R^2 ranged from 0.96 to 0.97. For the plow-based treatment T6, R^2 varied from 0.84 to 0.90.

Sample plots of the Langmuir adsorption isotherm models for the three treatments are shown in Figures 9 to 11. It is apparent that the Langmuir model can adequately characterize the ammonium adsorption behavior of soils under the three treatments considered. For CAPS treatment T2, the coefficient of determination or explained variance R^2 ranged from 0.88 to 0.89. For CAPS treatment T5, R^2 varied from 0.92 to 0.95. For the plow-based treatment T6, R^2 ranged from 0.64 to 0.91. All these suggest that the C_s values can be predicted adequately by the Langmuir adsorption isotherm model for soils under the selected treatments for any given values of C_w . More importantly, the Langmuir model can be used to determine the maximum adsorption capacity of the soils studied.

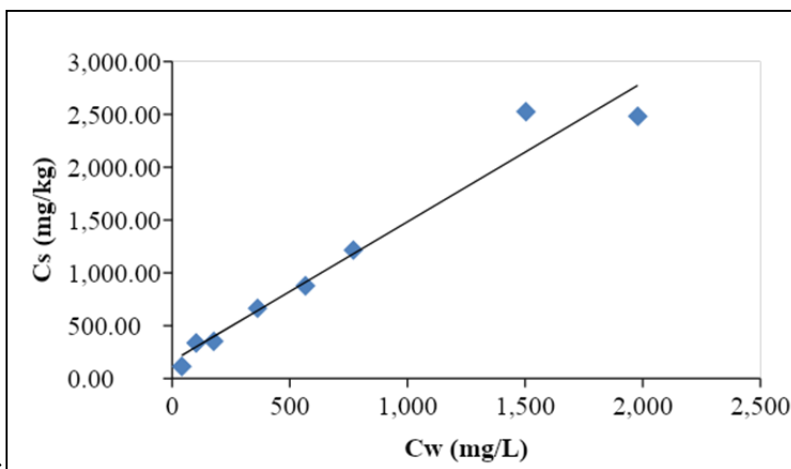


Figure 3. Sample plot of the linear adsorption isotherm model for CAPS treatment T2

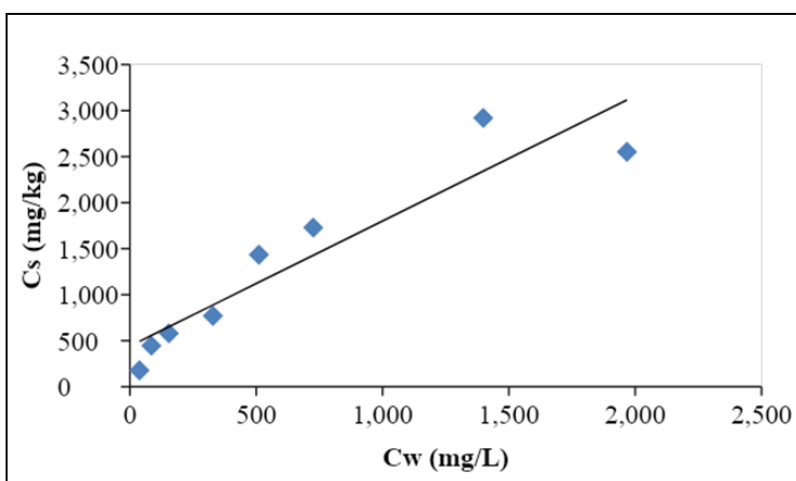


Figure 4. Sample plot of linear adsorption isotherm model for CAPS treatment T5

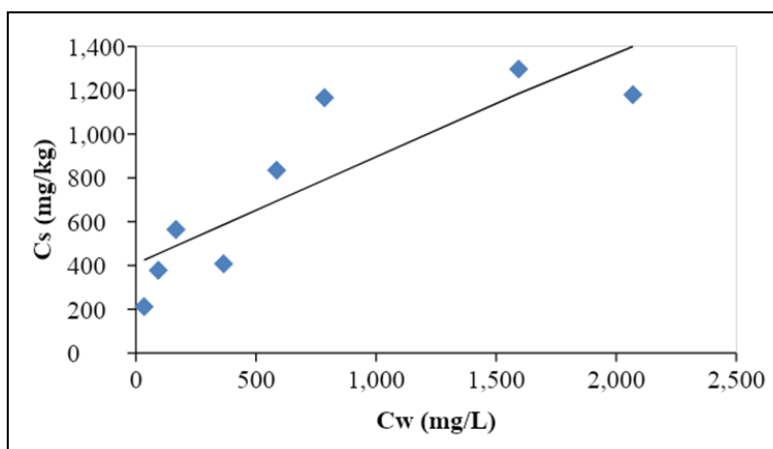


Figure 5. Sample plot of linear adsorption isotherm model for plow-based treatment T6

Overall, the Freundlich and Langmuir adsorption models gave the best fit to the experimental data for all treatments. For CAPS treatment T2, the coefficient of determination R^2 ranged from 0.96 to 0.98 for Freundlich model and from 0.88 to 0.92 for Langmuir model. For CAPS treatment T5, R^2 ranged from 0.96 to 0.97 for Freundlich model and from 0.92 to 0.95 for Langmuir model. For the plow-based treatment T6, R^2 ranged from 0.84 to 0.90 for Freundlich and from 0.64 to 0.90 for Langmuir model. Thus, the NH_4^+ adsorption behavior of soils for all treatments can be best described by both the Freundlich and Langmuir adsorption isotherm models.

The linear adsorption models for all treatments also showed good fit with experimental data for treatments T2 and T5 but not for T6. The coefficient of determination for the linear model for all treatments was also lower than that obtained for Freundlich and Langmuir models. For CAPS treatments T2 and T5, the coefficient of determination R^2 for the linear model ranged from 0.68 to 0.94. For plow-based treatment T6, the R^2 ranged from only 0.004 to 0.22. Thus, the NH_4^+ adsorption of soils under T6 cannot be described adequately by the linear model.

Comparison of Mean Distribution Coefficient Values Among Treatments

Figure 12 shows a graphical comparison of the mean distribution coefficient values (K_d) estimated from linear isotherm models for all treatments.

Table 5. CAPS Treatment / Tukey (HSD) / Analysis of the differences in ammonium distribution coefficient between the treatments with a confidence interval of 95%

CON-TRAST	DIFFER-ENCE	STAND-ARDIZED DIFFER-ENCE	CRITI-CAL VALUE	Pr > Diff	SIGNIFI-CANT
T5 vs T6	0.894	13.504	3.068	< 0.0001	Yes
T5 vs T2	0.165	2.489	3.068	0.104	No
T2 vs T6	0.729	11.015	3.068	< 0.0001	Yes

Tukey's d critical value: 4.339

Table 6. CAPS Treatment / Dunnett (two sided) / Analysis of the differences in ammonium distribution coefficient between the control CAPS Treatment-T6 and the other treatments with a confidence interval of 95%

CATEGO-RY	DIF-FER-ENCE	STAND-ARDIZED DIFFER-ENCE	CRITI-CAL VAL-UE	CRITI-CAL DIF-FERENC-E	Pr > Diff	SIGNIFI-CANT
T6 vs T5	-0.894	-13.504	2.863	0.190	0.000	Yes
T6 vs T2	-0.729	-11.015	2.863	0.190	0.000	Yes

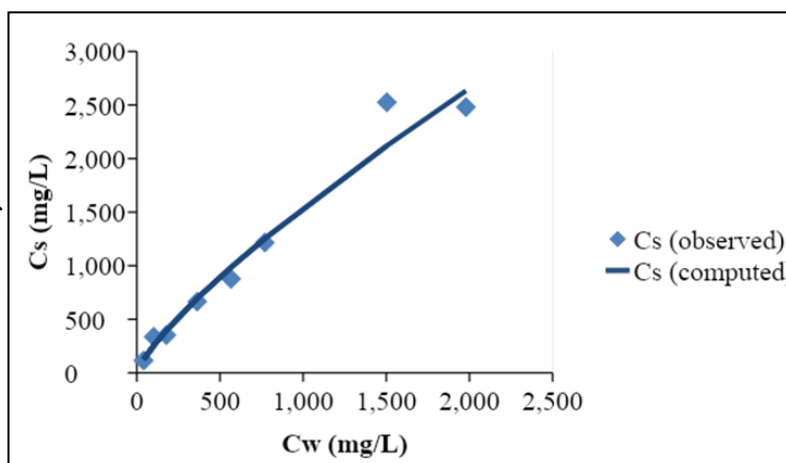


Figure 6. Sample plot of Freundlich adsorption isotherm model for CAPS treatment T2

Using Analysis of Variance (ANOVA), the mean distribution coefficient K_d values for the CAPS treatments T2 and T5 were found to be significantly greater than the K_d values for the plow-based treatment T6 at $\alpha=5\%$. The mean K_d values for the CAPS treatments, T2 and T5, were not significantly different from each other at $\alpha=5\%$. The results of statistical analysis using

Tukey (HSD) and Dunnet (two-sided) tests for comparing mean K_d values are shown in Tables 5 and 6.

The differences in K_d values among treatments are consistent with the differences in observed soil organic matter in the uppermost soil layer. Ella (2014) reported that CAPS treatments T5 and T2, respectively, exhibited the highest and second highest increase in soil organic matter after three years of cropping based on composite soil sampling from the various treatments. On the other hand, the soil organic matter under the plow-based system steadily declined after three years of cropping. However, the differences in K_d values may also be attributed to factors induced by the differences in farming systems other than soil organic matter.

Comparison of Mean Adsorptive Capacity Among Treatments

Figure 13 shows a graphical comparison of the mean adsorptive capacity values of Jasaan clay estimated from the Langmuir isotherm model for all treatments. These values are within the range of reported values of maximum adsorptive capacities of clay soils (e.g. Hua *et al.*, 2010; Wang *et al.*, 2011 and Sharifna *et al.*, 2013). Jasaan clay soils have relatively higher proportion of small-sized particles (<0.002 mm) contributing to greater surface area per unit volume and therefore a relatively high adsorptive capacity.

Based on the results of ANOVA, the mean values of the maximum adsorptive capacity for T2 and T5 were significantly different and higher than that of T6 ($\alpha=5\%$). The results indicate that soils under CAPS have higher adsorptive capacity than those under the conventional plow-based systems. The mean values of maximum adsorptive capacity for T2 and T5 were not

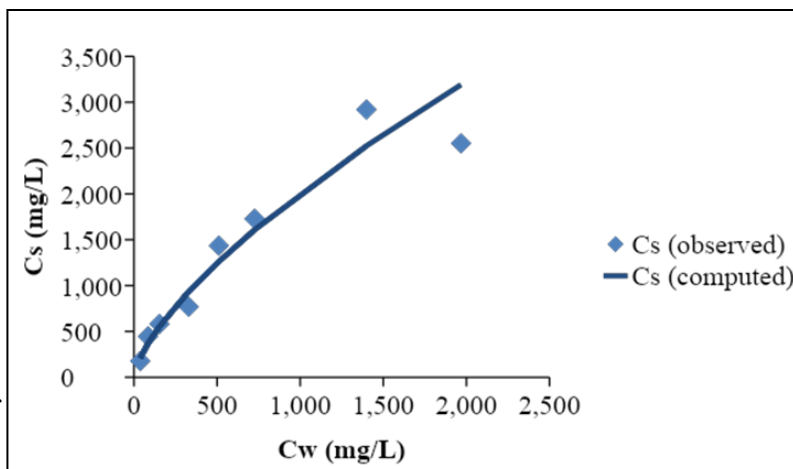


Figure 7. Sample plot of Freundlich adsorption isotherm model for CAPS treatment T5

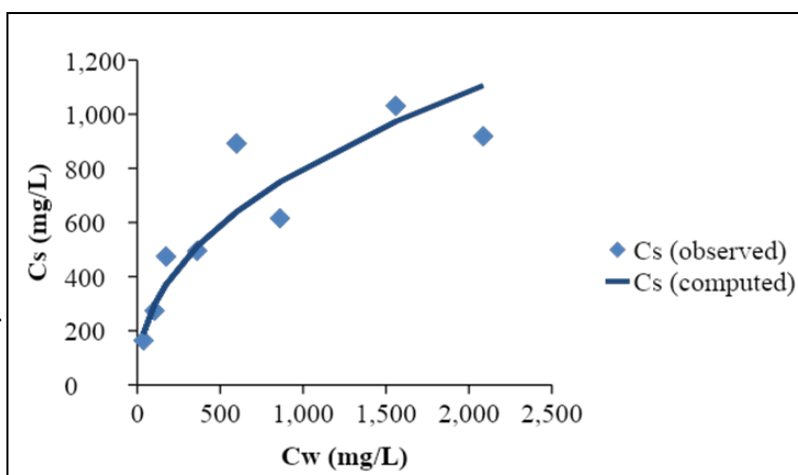


Figure 8. Sample plot of Freundlich adsorption isotherm model for plow-based treatment T6

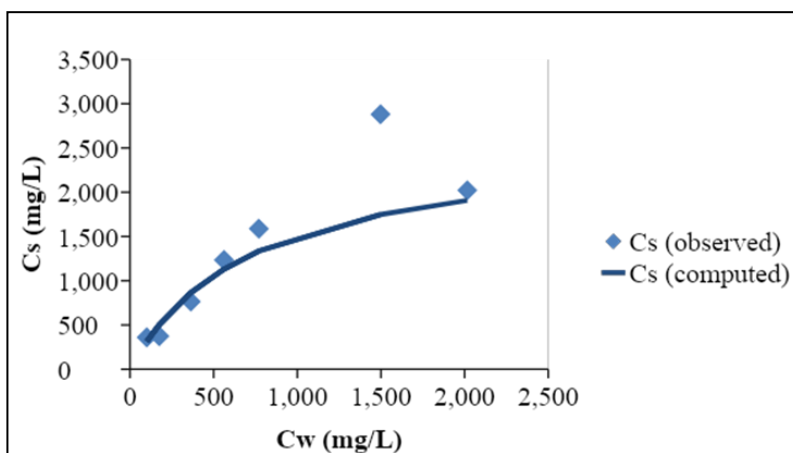


Figure 9. Sample plot of Langmuir adsorption isotherm model for CAPS treatment T2

significantly different from each other. The results of statistical analysis using Tukey (HSD) and Dunnett (two-sided) tests for comparing mean adsorptive capacity values are shown in Tables 7 and 8.

The adsorptive capacity values obtained in this study are within the range of values for soils studies by previous researchers on ammonium adsorption in soils. The maximum adsorption capacity could be as low as 88 mg/kg for silty sand and other soils (Hua *et al.*, 2010) to as high as 18,000 mg/kg for layered clay mineral (Wang *et al.*, 2011).

Implications of the Adsorptive Behavior of Jasaan clay soil under CAPS and PB systems

The results indicate that Jasaan clay soil under CAPS has greater NH_4^+ adsorption than those under the conventional plow-based systems hence a significantly greater amount of ammonium ions can be adsorbed by the soil under conservation agriculture than under plow-based for the same fertilizer application rate. Furthermore, based on the relationship between the distribution coefficient and retardation coefficient, higher distribution coefficient means greater adsorption and retardation thus slower solute or nutrient transport. Less leaching of NH_4^+ can therefore be expected under conservation agriculture production systems than under plow-based systems. These results suggest that soils under CAPS allow longer time for the NH_4^+ containing fertilizer to be retained by the soil for crop uptake than those under conventional plow-based systems thereby maximizing ammonium-nitrogen fertilizer application efficiency. This is

Table 7. CAPS Treatment / Tukey (HSD) / Analysis of the differences between the categories with a confidence interval of 95%

CONTRAST	DIFFERENCE	STANDARDIZED DIFFERENCE	CRITICAL VALUE	Pr > Diff	SIGNIFICANT
T5 vs T6	1364.293	8.139	3.068	0.000	Yes
T5 vs T2	231.515	1.381	3.068	0.407	No
T2 vs T6	1132.778	6.758	3.068	0.001	Yes
Tukey's d critical value: 4.339					

Table 8. CAPS Treatment / Dunnett (two sided) / Analysis of the differences between the control category CAPS Treatment-T6 and the other categories with a confidence interval of 95%

CATEGORY	DIFFERENCE	STANDARDIZED DIFFERENCE	CRITICAL VALUE	CRITICAL DIFFERENCE	Pr > Diff	SIGNIFICANT
T6 vs T5	-1364.293	-8.139	2.863	479.887	0.000	Yes
T6 vs T2	-1132.778	-6.758	2.863	479.887	0.001	Yes

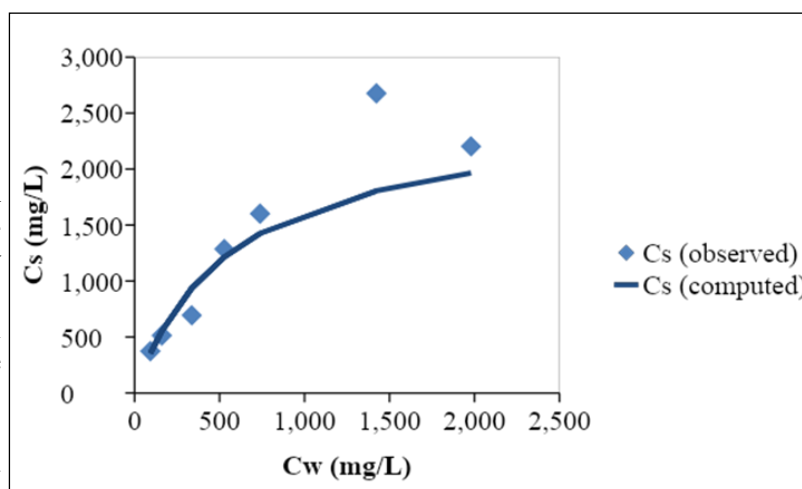


Figure 10. Sample plot of Langmuir adsorption isotherm model for CAPS treatment T5

important not only from the crop production point of view with ammonium being an important plant nutrient but also from the standpoint of environmental protection as the loss of ammonium due to reduced adsorption may pose a threat to groundwater quality especially upon its oxidation to nitrates and the subsequent leaching to the underlying aquifers.

SUMMARY AND CONCLUSIONS

This study aimed to characterize and compare the ammonium adsorption behavior of soils under Conservation Agriculture Production Systems (CAPS) and under the conventional plow-based system. Soils samples were collected from selected CAPS plots of the SANREM Research site in Claveria, Misamis Oriental. Two CAPS treatments T2 (Maize+Stylosanthes-Stylosanthes-fallow) and T5 (Cassava+Stylosanthes-Cassava+Stylosanthes) were used together with T6 (plow-based Maize-Maize) serving as the control. Batch adsorption experiments were then performed and the equilibrium concentration values in the solution for each initial concentration for each treatment and replicate were determined. Based on the equilibrium concentrations in the solution and in the soil, the adsorption isotherms were developed using linear, Freundlich and Langmuir models.

Results of adsorption modeling showed that the Freundlich and Langmuir models can more adequately characterize the adsorption behavior of soils under CAPS and plow-based systems than linear adsorption models. For all treatments, the coefficient of determination R^2 ranged from 0.84 to 0.98 for Freundlich model, from 0.64 to 0.95 for the Langmuir model and from 0.004 to 0.94 for linear model. Results also showed that the mean distribution coefficient K_d and the maximum adsorptive capacity of the soils under CAPS treatments T2 and T5 were significantly higher than those under plow-based system T6 at $\alpha=5\%$. The mean K_d and maximum adsorptive capacity values for T2 and T5 did not differ significantly at $\alpha=5\%$. The mean K_d values for treatments T2, T5 and T6 obtained in this study were 1.421, 1.585 and 0.691 L/kg, respectively. On the other hand, the maximum

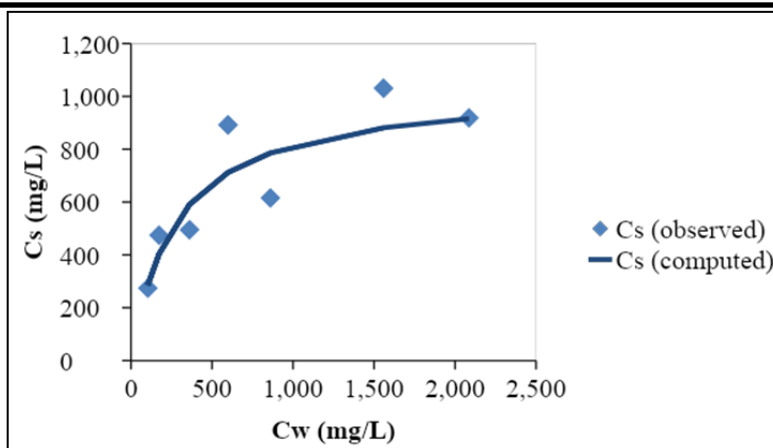


Figure 11. Sample plot of Langmuir adsorption isotherm model for plow-based treatment T6

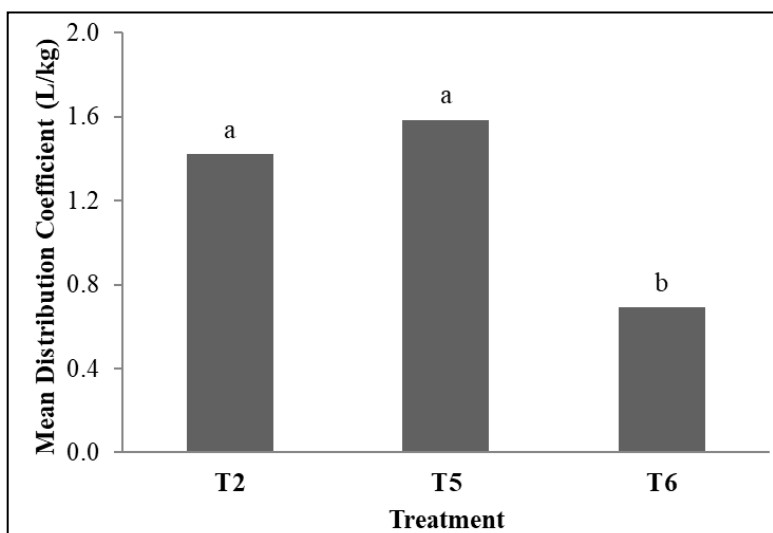


Figure 12. Mean distribution coefficient for all treatments

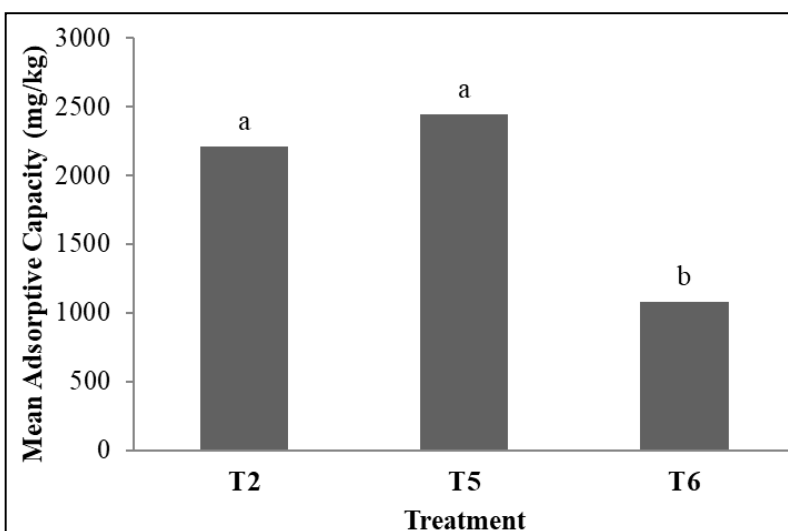


Figure 13. Mean adsorptive capacity values for all treatments

adsorptive capacity values were found to be 2,210.1, 2,441.6 and 1,077.3 mg/kg for treatments T2, T5 and T6, respectively.

The results of this study suggest that soils under conservation agriculture production systems have better ammonium adsorption capacity than soils under plow-based systems. Thus, more cationic nutrients like ammonium can be retained by the soil for plant uptake and less ammonium leaching can be expected under conservation agriculture production systems than under plow-based systems. Consequently, ammonium-nitrogen fertilizer application efficiency can be maximized to a larger extent under conservation agriculture production systems than under plow-based systems.

RECOMMENDATIONS

While this study has provided additional empirical evidence on the positive impacts of conservation agriculture over conventional plow-based systems, particularly on maximization of nitrogen fertilizer application in crop production systems which would prove to be beneficial to resource-poor and marginal farmers, it is recommended that similar studies in other soils in the Philippines under various crop production systems be conducted to further reinforce the findings of this study and that further research towards this end should be given adequate institutional and financial support. Other related studies on the potential benefits of conservation agriculture over plow-based systems should likewise be pursued. On this basis, a paradigm shift in crop production systems in the Philippines from the traditional plow-based, which leads to soil quality degradation, to a soil quality-enhancing conservation agriculture may be considered as a future policy option by the Department of Agriculture.

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