

A study on the Adsorption of ammonium in Bentonite and Kaolinite

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Abstract— Adsorption of ammonium on natural soil is important in agriculture as fertilizer and for minimizing groundwater contamination when the waste is disposed. There are several reported studies for quantifying the removal of ammonium by adsorbents such as zeolites. However, there are not many studies that deal with the sorption of ammonium on different type of soils. In the present study, ammonium ion sorption characteristics have been studied on bentonite and kaolinite . The equilibrium sorption characteristics have been mathematically quantified by using the two popular Langmuir and Freundlich isotherms. It was observed that both the isotherms gave satisfactory fitting though the best fit was observed for langmuir isotherm. The initial concentration, and played a pivotal role in the sorption mechanism and also on the removal efficiency. Also higher surface area and CEC yielded higher ammonium retention

Keywords— ammonium, batch equilibrium study, contamination, isotherm ,sorption

I. INTRODUCTION

NITROGEN is one of the essential elements for plants, and lack of N in soils often limits agricultural production.

The frequent use of industrially manufactured nitrogen (N) fertilizers becomes a major source of ammonium in groundwater and surface water (1). The adsorption inhibits the movement of NH_4 through the soil to groundwater and thereby increasing its availability for plants. NH_4 also originate from diverse sources such as landfills, foul sewerage systems and contaminated industrial sites, animal manure, biological N fixation, mineralization from soil organic N. Therefore, decrease of the transformation and moving of N compounds using adsorbent materials as zeolite and betonite is crucial to save ground water and environmental quality in intensive agricultural production. The presence of excess N compounds also causes the environmental destroy, so N compounds play an important role on water pollution. Therefore, the control of them has vital importance. The ammonia and ammonium ions are the more commonly encountered N compounds in wastewater.

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Thus, ammonium has been regarded as a key indicator of groundwater contamination and it is commonly considered during the assessment of pollution risk to groundwater. Moreover it is of concern as it is liable to be found in high concentrations even after centuries since it is not degraded under anaerobic conditions [2]. and its toxicity has been proven [3].

Studies on contaminant retention are important in determining the capacity of soils to respond to the introduction of pollutants into subsurface [2]. To address the soil-contaminant interaction in the subsurface it is essential to know about the distribution of contaminants between solid and solution phases. Most of the reported literature deals with the ammonium adsorption on natural and commercially available zeolites [7]. ; It is felt that more studies are required to quantify the ammonium adsorption in soils, [3] [6]. In the case of clay minerals, it has been found that mixed-layer clays (e.g. montmorillonite/smectite, including bentonite) generally attenuate ammonium more strongly than double layer clays (e.g. illite), which again attenuate more strongly than single layer clays (e.g. kaolinite) .This observation is common in many studies of cation exchange and is related to the respective specific cation exchange capacities of the different clays. It should also be noted that sorption of ammonium to illite and other 2:1-type clay minerals may be an effectively irreversible process since the ammonium ion fits into the intra-layer clay lattice. In soils with considerable illite content, interlayer-fixed ammonium can typically account for 20 to 40% of the total nitrogen. It is found that most of the cases involve natural soils which are a combination of different gradation including clays. Even though there are studies appraising ammonium sorption on clay minerals, further efforts are required to quantify ammonium interaction with natural soils. This would help to understand the relationship between different natural soil properties and ammonium adsorption. Such studies are required for predicting the fate of ammonium and the results can be used for risk assessment for landfills, effluent soak ways, contaminated sites etc where mostly natural soils are present.

In this study, ammonium sorption has been quantified for two different soils (bentonite and Kaolinite) of varying physical characteristics.

II. MATERIALS AND METHODS

In this study two different kinds of soils were used Speswhite Kaolinite and Wooyming Bentonite from France.

Physico-chemical tests such as specific gravity, particle size distribution, Atterberg limits etc. were carried out by following the guidelines provided in the literature (ASTM D 4.08). The total specific surface area (SSA) was determined using ethylene glycol monoethyl ether (Carter et al. 1965) and cation exchange capacity (CEC) has been determined by ammonium replacement method (Horneck et al.1989). The summary of these characterizations is listed in the table. It was observed from XRD that the Speswhite Kaolinite mineralogical components were mainly composed of 94% kaolinite,4% Mica, 1% Montmorillonite, and 1% Feldspar and quartz . Whereas for Wooying Bentonite the mineralogical components were mostly composed of montmorillonite (68 %), quartz, feldspath, calcite, mica. The characteristics are tabulated in table 1.

Ammonium chloride stock solution (1000 mg/l) was prepared by dissolved NH₄Cl (A.R. grade) in deionized water. Solutions at different concentrations were obtained were prepared by adding appropriate amounts of NH₄Cl stock solution to deionized water to obtain ion range of concentrations varying from 10 mg/l to 1200 mg/l. Solid to solution ratio was used as 1:10 and this value was kept as constant in all the sorption experiments. This test is conducted for 24-hours as per ASTM procedure . The resulting solution is subjected to chemical analysis for determining the concentration by using an ion Chromatograph (Metrohm, Switzerland). Each analysis was done three times to ensure repeatability and average of the data the results is used for plotting isotherm.

TABLE I

Test	Values	
	Kaolinite	Bentonite
Specific gravity	2.6	2.65
pH	6.3	9.5
Liquid Limit (%)	52	589
Plastic Limit (%)	35	128
Plasticity Index (%)	17	461
CEC (cmol ⁺ /kg)	3.68	77.60
Total SSA (m ² /g)	12.56	21.44
SiO ₂ (mass %)	39	35
Al ₂ O ₃ (mass %)	41	18

III. ISOTHERMS MODELS

Adsorption and retention capacity of soil is usually modeled by sorption isotherms. The sorption isotherm is defined as the relationship between the contaminant sorbed on the soil (Q in mg/gm) and the soil pore water concentration (C_{eq} in mg/L) at equilibrium. Several sorption isotherm models have been applied to describe experimental data of sorption isotherms. For the sake of convenience for the present experimental work explicit and simple models are preferred and were analyzed with Langmuir (La), Freundlich (F) isotherm, as represented

by equation 1 and 2, respectively [4]. These are the most extensively used isotherms model for bringing out the relationship between adsorbed concentrations (Q_e) versus equilibrium concentration (C_e) of solute species.

$$Q_e = K_F \cdot C_e^N \quad (1)$$

$$Q_e = (QK_L C_e) / (1 + K_L C_e) \quad (2)$$

Where K_F and N are Freundlich constants related to adsorption capacity and adsorption intensity respectively, K_L is the Langmuir adsorption constant related to the binding energy and Q is the maximum contaminant adsorbed by solid (mg/kg).

IV. RESULTS AND DISCUSSIONS

Literature indicates that ammonium equilibrium in solution is largely pH dependent. The investigation for the removal of ammonium ion under about 6 is unlikely attributing this to the fact that increased number of hydrogen ions in solution provides added competition for exchange sites. So considering this we have taken a neutral pH for our analysis. Ammonium adsorption coefficient is a very important proxy to reflect the characteristic of ammonium adsorption on soils. The equilibrium isotherms of NH₄⁺ are plotted.

It was observed from experimental data as shown in Fig. 1 that an increase in the initial concentration led to an increase in the amount of NH₄⁺ adsorbed by both soils kaolinite and bentonite. This may be attributed to an increase in the driving force of the concentration gradient with the increase of NH₄⁺ to overcome the resistances to the mass transfer of NH₄⁺ between the aqueous and the solid phases. The various fitting parameters of the sorption isotherms along with the goodness of fit (R²) are listed in table. 2.

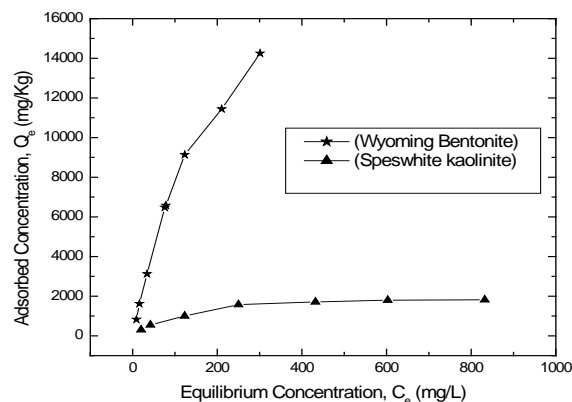


Fig. 1 Adsorption isotherm of bentonite and Kaolinite soil in case of ammonium salts

It was observed that both the isotherms gave satisfactory fitting though the best fit was observed for langmuir isotherm as evident from its R² value of 0.989 and 0.996 for kaolinite and bentonite respectively. Increasing concentration also results in a higher equilibrium capacity being obtained for any

given set of conditions. Initially a sharp increase in capacity can be observed with increasing concentration, reaching a maximum. This maximum value is indicative of the fact that the ion exchange surface is increasingly saturated with the ammonium ion and is reflected by the accompanying reduction in removal efficiency.

TABLE 2

Isotherm Model	Values		
		Kaolinite	Bentonite
Freundlich	K	165.33	380.788
	N	0.37	0.639
	R ²⁺	0.92	0.98
Langmuir	K	0.0084	0.00045
	Q _m	2150.9	23794.09
	R ²⁺	0.989	0.996

This is the maximum amount of ammonium which can be exchanged on to the surface of the material under the experimental conditions and after this point further increases in solution concentration are ineffective in raising the media's capacity. The results as depicted in Fig 3 and Fig. 4 also show that an increase in the initial NH₄⁺ concentration led to a reduction in the percentage removal efficiency of NH₄⁺ ions from aqueous solution. The removal of ammonium ion decreased, showing the process to be highly dependent on the initial concentration, this may lead to a possible saturation of the mono-layer coverage on the surface both bentonite and Kaolinite by the NH₄⁺ ions

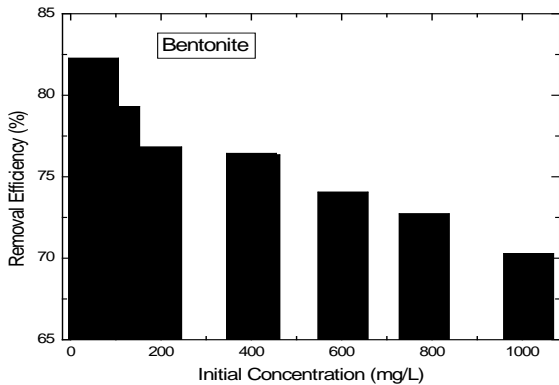


Fig. 2 Removal Efficiency of Bentonite with respect to Initial Concentration.

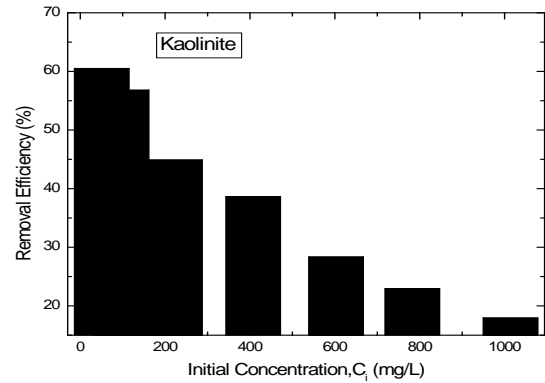


Fig. 3 Removal Efficiency of Kaolinite with respect to Initial Concentration.

V.SUMMARY

To improve the efficiency of N fertilizer application in region, it is essential to understand the fate of ammonium in these soils. Also in soil the availability for plant uptake as nutrient and its leaching process is dependent on the adsorption capacity of the soil. It should be noted that the initial concentration provides an important driving force to overcome all mass transfer resistances between the aqueous and solid phases. Hence, a higher initial concentration of will enhance the sorption process. Further studies are necessary to understand the role of composition and nature of soil components in soils governing the fate of applied ammonium. The analysis of the present investigation also showed that even if ammonium had a lower affinity to be adsorbed from the clayey minerals than the heavy metals, the quantity of ammonium detained by the bentonite is still very high, similar findings were observed by researchers [3]. The preference of adsorption in the soil depends on the type of soil, on the valence and size of the ions adsorbed and on the exchange ions. Ammonium was adsorbed more in bentonite more compared to kaolinite.

It was also noted from the results that the higher surface area and negative charge yielded higher ammonium retention. Adsorption quantity also decreases occurred by the decrease of particle size which could be attributed to the loosening of some active sites. It can be observed from the above figure that Bentonite proved to much better adsorbent than kaolinite

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REFERENCES

- [1] Goodlass G, Halberg N, Verschuur G "Input output accounting systems in the European community -An appraisal of their usefulness in raising awareness of environmental problems." European Journal of Agronomy, 2003, vol 20, pp.17-24
- [2] MikolajkóW J. "Laboratory methods of estimating the retardation factor of migrating mineral nitrogen compounds in shallow groundwater."

- Geol. Quart., Vol **47** no 5, 2003, pp. 91-96. Warszawa
- [3] Pivato A and Raga R "Tests for the evaluation of ammonium attenuation in MSWlandfill leachate by adsorption into bentonite in a landfill liner". Waste Management 26,2006. pp. 123-132
 - [4] Sharma and Reddy. "Geoenvironmental engineering: site remediation, waste containment, and emerging waste management technologies, 2004. John Wiley & Sons, Inc.
 - [5] Vrba J. and RomijnE "Impact of agricultural activities on ground water. "International Contributions to Hydrogeology"1986 vol **5**, pp 89-129. Internat. Assoc. Hydrogeol. Hannover: Heise.
 - [6] Wang M, Liao L, Zhang X, Li Z and Xia Z and Cao W. Adsorption of low concentration ammonium onto vermiculite from hebel province, China .Clays and Clay Minerals, 2011 Vol. 59, No. 5, 459-465.
 - [7] Weber, M. A., K. A. Barbarick, and D. G. Westfall. 1983. Ammonium adsorption by a zeolite in a static and a dynamics system. J. Environ. Qual. 12:549-552.