A study on the Adsorption of ammonium in Bentonite and Kaolinite

Poly. Buragohain, Dr. Sredeep.S, and Dr. Nadia . Saiyouri

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 NH₄ through the soil to groundwater and thereby increasing its availability for plants. NH₄ 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.

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 intralayer 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 4087). 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 Wyoming 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 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 1

<table>
<thead>
<tr>
<th>Test</th>
<th>Kaolinite</th>
<th>Bentonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.6</td>
<td>2.65</td>
</tr>
<tr>
<td>pH</td>
<td>6.3</td>
<td>9.5</td>
</tr>
<tr>
<td>Liquid Limit (%)</td>
<td>52</td>
<td>589</td>
</tr>
<tr>
<td>Plastic Limit (%)</td>
<td>35</td>
<td>128</td>
</tr>
<tr>
<td>Plasticity Index (%)</td>
<td>17</td>
<td>461</td>
</tr>
<tr>
<td>CEC (cmol/1kg)</td>
<td>3.68</td>
<td>77.60</td>
</tr>
<tr>
<td>Total SSA (m2/g)</td>
<td>12.56</td>
<td>21.44</td>
</tr>
<tr>
<td>SiO2 (mass %)</td>
<td>39</td>
<td>35</td>
</tr>
<tr>
<td>Al2O3(mass %)</td>
<td>41</td>
<td>18</td>
</tr>
</tbody>
</table>

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 (L), 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.

\[ Q_e = K_F \times C_e^N \]  
(1)

\[ Q_e = (QK_LC_e) / (1+K_FC_e) \]  
(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 NH_4^+
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 NH_4^+ 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 NH_4^+
to overcome the resistances to the mass transfer of NH_4^+
between the aqueous and the solid phases. The various fitting
parameters of the sorption isotherms along with the goodness
of fit (R^2) are listed in table. 2.

![Fig. 1 Adsorption isotherm of bentonite and Kaolinite soil in case of
ammonium salts](image)

It was observed that both the isotherms gave satisfactory
fitting though the best fit was observed for langmuir
isotherm as evident from its R^2 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**

<table>
<thead>
<tr>
<th>Isotherm Model</th>
<th>Kaolinite</th>
<th>Bentonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>K 165.33</td>
<td>380.788</td>
</tr>
<tr>
<td></td>
<td>N 0.37</td>
<td>0.639</td>
</tr>
<tr>
<td></td>
<td>R^2 0.92</td>
<td>0.98</td>
</tr>
<tr>
<td>Langmuir</td>
<td>K 0.0084</td>
<td>0.00045</td>
</tr>
<tr>
<td></td>
<td>Qm 2150.9</td>
<td>23794.09</td>
</tr>
<tr>
<td></td>
<td>R^2 0.989</td>
<td>0.996</td>
</tr>
</tbody>
</table>

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.

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**


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