Phosphorus Adsorption and its Relation with Soil Properties in Calcares Soil of Basra City

Najla J. AL-Amiri
Department of soil sciences and water resources, College of Agriculture, University of Basra, Iraq

Abstract
Soil samples from ten different parts in Basra were collected as: Qurna, Medayna, Diar, Hartha, Garmat Ali, Basra University, Brahdia, Tanoma, AbulKhaseeb and Seeba. The physic-chemical properties of these calcareous soil sites were found to be low organic matter and very high ECe and active carbonate. The laboratory work is done by weighting 2.5g. from each soil and put them in 50ml conical flask. Then added phosphorus in form of phosphate mono potassium KH$_2$PO$_4$ on nine levels as follows: (0, 50, 100, 150, 200, 250, 300, 350, 400)µm$^{-1}$. Meanwhile, the treatments were shake and left till equilibrium. After that procedure, it was determined the soluble phosphorus after equilibrium and calculated adsorbed quantity of phosphorus on soil surfaces. The results are tested by linear Langmuir equation and calculation the constants of this equation, ($b$, $k$). The results showed that the greatest adsorption values of Diar and Tanoma soils were greater than other soils. The soil Electrical conductivity, clay and solid carbonat especially active carbonat gave high significant coefficient of ($R^2$) with adsorption maxima of phosphorus ($b$).

Keywords: adsorption, calcares soil, phosphorous, Basra.

1. Introduction
Lower concentration (Wandruszka, 2006). The complex P adsorption isotherm as found in soil due to mixture of various mineral phases are explained using Langmuir equation to understand adsorption process. Adsorption isotherm equation can be used to predicate fertilizer requirement for crops (Gichangi et al., 2008). The nutritional element in soil solution is closely linked to adsorption processes through the physic-chemical characteristics of the soil. This eventually governs the availability of nutrient ions to growing plants. Among the soil properties affecting P sorption capacity are texture, organic matter, soil pH, Aluminum saturation, CEC and CaCO$_3$ content. Knowledge of the relationship of these soil properties with adsorption capacity is therefore necessary in understanding sorption behavior of varied soils. Agbenin and Tiessen (1994) reporting a statistical. Adsorption is net accumulation of chemicals at the interface between solid phase and aqueous solution phase which determines availability of native soil nutrients and the rate of nutrient to be applied to soil as fertilizers (Khan et al., 2010 and Muindi et al., 2015). Understanding of soil phosphorus (P) adsorption chemistry is essential for evolving best fertilizer management practices aimed at enhancing fertilizer (P) use efficiency and environment quality (Mehmood et al., 2010). A survey of the interactions between phosphorus(P) species and the components of calcareous soils shows that both surface reaction and precipitation take place, especially in the presence of calcite and limestone. The principal products of these reactions are dicalcium phosphate and octacalcium phosphate, which may interconvert after formation. The role of calcium carbonate in P retention by calcareous soils is, however, significant only at relatively high P concentration – noncarbonate clays play a more important part at a significant relation between parameters of Langmuir equation and soil properties, such as clay percentage, organic carbon, Fe and Al contents. However, limited work has
been carried out to understand the relationship between the P sorption capacity and soil properties in the research area. The objectives of this study were to determine P adsorption capacity of soil differing in site and develop relationship between P adsorption parameters determined by Langmuir equation and soil characteristics.

2. Materials and Methods

2-1 Soil Samples and basic analytical methods:
Ten soil sites from Basra province namely Qurna, Medayna, Dair, Hartha, Garmat Ali, Basra University, Brahidia, Tanoma, AbulKhaseeb and Seeba selected to study the mechanism of P adsorption. Surface soil samples (0-15 cm) were collected from the ten location, air-dried, ground and passed through a 2mm sieve. The physic-chemical properties estimated according to what is described in Black, 1965.

2-2 phosphorus Adsorption Isotherm:
Phosphorus adsorption isotherm was developed for each soil sample (three replicates) by equilibrating 2.5g air-dried soil with 50ml of KH$_2$PO$_4$ in containing (0, 50, 100, 150, 200, 250, 300, 350 and 400)µg P ml$^{-1}$ shaking for 30 minutes. The soil suspensions were centrifuged then filtered through Whitman No 42 filter paper to obtain a clear solution. Phosphorous in the supernatant was then determined calorimetrically by (Murphy and Riley, 1962) method. The amount of P sorbed was calculated as the difference between the amount of P added and that found after equilibration was considered as adsorbed P. The data were fitted to Langmuir equation. The equation described in its linear form are:

\[ \frac{C}{X} = \frac{1}{K_b} + \frac{C}{b} \]

Where:

- \( C \) = Equilibrium concentration of phosphorus in solution (µPml$^{-1}$)
- \( X \) = µ of P adsorbed (µ P g$^{-1}$)
- \( b \) = Adsorption maximum for Langmuir model (µ P g$^{-1}$)
- \( K_b \) = Bonding energy constant Langmuir model (ml g$^{-1}$)

2.3 Statistical Analysis:
Relationships between P sorption parameters and P sorbed at equilibrium, with selected soil chemical properties were done with simple regression and correlations and tested for significance at \( p = 0.05 \) using the GenStat statistical software (GenStat.2010).

3. Results And Discussion

3.1 Physico-chemical Properties of Soil from ten Sites:
The soils examined varied widely in the chemical and physical properties that commonly affect P sorption (Table 1). Soil texture varied from clay loam to Silty loam. All of the soils site are slightly Alkaline with pH increased from 7.5-7.8 below 30 cm depth. All the soils contain excessive amount of soluble salts with range of electrical conductivity ranged from 1.88 mS cm$^{-1}$ to 43 mS cm$^{-1}$). Soil organic matter (O.M) ranged from 0.84 to 1.27 %. Total carbonate and active carbonate are the dominant present in soil.

3.2 Phosphate Adsorption Isotherms:
The phosphate adsorption isotherms of soil in the Ten study sites were determined by plotting the equilibrium concentration of phosphate (C) against the amount of phosphate adsorbed (X). Comparing the highest amount of phosphate P adsorbed, it is evident that soils in each site had different capacities to adsorb P (Fig. 1). The result of the study showed that Almost all soil samples had the highest value of maximum adsorption, the highest adsorption value was recorded by Seeba. At rate 200.10 µmol ml-1. As for the least adsorption, it was recorded by Qurna and Deir, with the values of 191.88 and 196.01 µmol ml-1, respectively. The graphic representation of the adsorption isotherms of the soils showed that Seeba soil had the highest level of sorbed P, followed by AbulKhaseeb soil while Deir soil had the lowest. This case
was explained on the basis of the high content of carbonate minerals and the high degree of soil interaction (Holford and Mattingly, 1975; Al-Kaysi, 1999; Nfawa, 2002). Also Al-kurani, 2000 and Al-Abaedy, 2001 reported that Iraqi soil has a high adsorption capacity of phosphates and that the active carbonates are the most influential part of phosphate adsorption. A number of researchers have indicated that there is a positive linear relationship between phosphate retention and the carbonate soil content (Afifi and Torrent, 1993 and Sharpley et al. 2003). As for Tisdal et al., 1985 they observed that both adsorption and stabilization occur for phosphorus in calcareous soils and Al-Kurani, 2001 stated that carbonate minerals have an important role in reducing phosphorus availability to the direct formation of calcium and magnesium phosphate compounds.

Fig. 1. Phosphate adsorption isotherm of soils from Ten sites.

Table 1. Physico-chemical properties of soils from the Ten sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>pH</th>
<th>EC (mScm⁻¹)</th>
<th>CEC (cmolkg⁻¹)</th>
<th>OM %</th>
<th>Total Carbonate (g. km⁻²)</th>
<th>Active Carbonate (g. kg⁻¹)</th>
<th>Soil Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qurna</td>
<td>7.50</td>
<td>1.88</td>
<td>19.13</td>
<td>1.22</td>
<td>354.35</td>
<td>110.86</td>
<td>Clay loam</td>
</tr>
<tr>
<td>Medayna</td>
<td>7.59</td>
<td>6.79</td>
<td>22.78</td>
<td>1.25</td>
<td>209.37</td>
<td>70.87</td>
<td>Silty loam</td>
</tr>
<tr>
<td>Diar</td>
<td>7.60</td>
<td>2.78</td>
<td>22.68</td>
<td>1.27</td>
<td>409.09</td>
<td>118.6</td>
<td>Clay loam</td>
</tr>
<tr>
<td>Hartha</td>
<td>7.60</td>
<td>11.0</td>
<td>19.28</td>
<td>1.19</td>
<td>352.47</td>
<td>111.67</td>
<td>Clay loam</td>
</tr>
<tr>
<td>Garmat Ali</td>
<td>7.70</td>
<td>27.4</td>
<td>18.98</td>
<td>0.85</td>
<td>212.49</td>
<td>87.26</td>
<td>Silty loam</td>
</tr>
<tr>
<td>Basra University</td>
<td>7.73</td>
<td>16.01</td>
<td>19.28</td>
<td>1.21</td>
<td>303.12</td>
<td>70.87</td>
<td>Clay loam</td>
</tr>
<tr>
<td>Brahdia</td>
<td>7.50</td>
<td>15.99</td>
<td>27.91</td>
<td>1.24</td>
<td>326.26</td>
<td>112.29</td>
<td>Clay loam</td>
</tr>
<tr>
<td>Tanoma</td>
<td>7.80</td>
<td>26.30</td>
<td>21.0</td>
<td>1.24</td>
<td>405.61</td>
<td>115.5</td>
<td>Clay loam</td>
</tr>
<tr>
<td>AbulKaseeb</td>
<td>7.70</td>
<td>24.01</td>
<td>25.99</td>
<td>1.17</td>
<td>408.74</td>
<td>110.36</td>
<td>Clay loam</td>
</tr>
<tr>
<td>Seeba</td>
<td>7.80</td>
<td>43.11</td>
<td>24.98</td>
<td>1.14</td>
<td>408.79</td>
<td>111.70</td>
<td>Clay</td>
</tr>
</tbody>
</table>

3.3 Langmuir Adsorption Parameters:
The sorption isotherms were examined according to linear form of Langmuir equation. Langmuir adsorption isotherms were plotted by taking C/X against C (Fig.2) Regression coefficients (R²) for the fitted Langmuir P adsorption isotherms were significant for soils from all sites except Deir (Table 2). The R² values were highest 0.680 in Basra University and lowest in Tnoma 0.550. The slope of the plot (1/K) was found less than 0.01 for all the soils. The binding energy was highest in
Seeba 0.0098 ml g\(^{-1}\) and lowest in Dei 0.0063 ml g\(^{-1}\). It was also observed that Basra University soil had the lowest adsorption maximum while Deir, Tanoma had the highest. Studies have shown that Iraqi soil has high adsorption capacity of the phosphate ion, but its binding energy is low. Silivani study, 1993 showed that the study soil (calcic soils) possesses greater ability of adsorption of pyrophosphate compared to orthophosphate, and that the adsorption reaction includes two processes which are adsorption from precedence precipitation, and are accompanied by an increase in the coefficient of stabilization of these soils for both the orto and the pyrophosphate, which reduces the phosphate concentration in the soil solution, which reflects negatively on the availability for plant nutrient. Al-Touki, 1999 obtained a positive correlation relationship between the greater adsorption of lime and the content of both active lime and surface organic matter.

3.4 Relationship between Adsorption and soil properties:

A significant correlation was observed between maximal adsorbed P, for all the added P concentration and soils (Table 3). A positive correlation between EC, Total Carbonate, active carbonat and clay with maximal P was also observed. The results are similar to work reported by other authors (Hoseini and Taleshmikaiel, 2013; Hadgu et al., 2014; Fakher, 2016). Other studies indicate that P retention increases with the ratio of Fe oxidesto CaCO\(_3\) (Castro, 1995 and Carreir and Laitha, 1997). From a practical standpoint it is interesting to consider how P interaction in calcareous soil compare to those in limed acid soils. In cases where substantial amounts of metal phosphates have accumulated in soils of both types due to pedogenesis and / or fertilizer application in excess of plant uptake, calcareous soil are found to contain less surface P than limed acid soils. Ca phosphates predominate in the former, and Al and Fe phosphates in the latter (Khan et al., 2010). Overall, P availability to plants is greater in limed acid soils (Delgado, 2000).

![Fig. 2. Langmuir equation for soils in the ten sites.](image)

<table>
<thead>
<tr>
<th>Table 2. Parameters of the fitted Langmuir adsorption equations with Regression equations.</th>
<th>Qurna</th>
<th>Hartha</th>
<th>Garmat Ali</th>
<th>Basra University</th>
<th>Brahidia</th>
<th>Tanoma</th>
<th>Seeba</th>
<th>Medayna</th>
<th>Diar</th>
<th>Abul Khaseeb</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (µmol/ml(^{1}))</td>
<td>0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
<td>1</td>
<td>1.2</td>
<td>0</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>C (µmol/ml(^{1}))</td>
<td>0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
<td>1</td>
<td>1.2</td>
<td>0</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>
Much has been learned about P mobility in calcareous media over the last five decades, but some gaps in understanding remain. Many of these occur at the molecular level of P interaction with subsurface species, including the detailed mechanism of P desorption under the influence of organic species (Wandruszka, 2006). The results also revealed differences in P adsorption among soils from the study sites. The differences in the P adsorption maxima of the studied sites indicate that use of blanket P fertilizer recommendations for the whole Basra city may affect crop yields most sites. Additionally, the study identified soil salinity, total carbonate and active carbonate as some of the factors that influence P availability. There is therefore, need for more intensive studies to understand the role and interactions of soil properties on P availability in the study area.

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