

## Abstract

**Name:** Seiam Hassan Abd El-Ghany Seiam

**Title of the thesis:**

*Chemical behavior of phosphorus in some Egyptian soils*

**Degree of Doctor of philosophy, Cairo University, Faculty of science, Department of chemistry 2009.**

The current of this work aims to throw light on some factors affecting phosphate adsorption in some Egyptian soils and the role of organic anions to decrease and/or inhibit this process. To fulfill these purposes, seven representative soil samples (0-30 cm depth) collected in this investigation. The tested soils have different chemical and physical properties and represent to the different abundant Egyptian soil textures (loamy, sandy, calcareous, and clay). An incubation experiment-for six months- was carried out at 30°C at rate of P concentrations of 0, 10,20,30,...,90 mg P/kg as  $\text{KH}_2\text{PO}_4$ . The investigated soils were found to have a moderate agreement with the linear **Langmuir** isotherm equation where their correlation coefficients were 0.500 , 0.618 , 0.521 , 0.101, 0.687, -0.235 , and 0.787, respectively, and for **Freundlich** isotherm equation the corresponding values of their correlation coefficients were 0.800, 0.867, 0.925, 0.524, 0.825, 0.858, and 0.853, respectively, whereas for the **Temkin** isotherm equation the corresponding correlation coefficients were 0.659, 0.752, 0.813, 0.293, 0.729, 0.899, and 0.775, respectively. Generally, **Freundlich** equation gave the best fit for the equilibrium P adsorption data than did the **Langmuir** and **Temkin** equations at range of P concentration of 0-90 mg P/l. The observed moderate values in their correlation coefficients of soils with the linear **Langmuir** isotherm equation are may be due to the presence of  $\text{CaCO}_3$  contents in relatively amounts in these soils. Where,  $\text{CaCO}_3$  has two or more adsorbing sites having widely different affinity to sorb phosphate groups. Concerning **Langmuir** isotherm equation the **MBC**(maximum buffering capacity) values were found to have an opposite trend with the  $X_m$  (adsorption maximum) values. Studying the effect of phosphate adsorption on pH of soil solution, the data showed that the pH of soil solution decreases with increasing the amount of P sorbed into soil surfaces. This may be attributed to the higher positive charge of clay mineral and the lesser competition of hydroxyl ions with phosphate into clay surfaces. The amount of adsorbed P was found to increase with increasing the time of incubation, that is probably due to the presence of  $\text{CaCO}_3$  in high content and the higher pH values which ranged between 7.04 and 8.71 whereas the Ca-P compound are the dominant precipitates than that for Fe and Al ones. Fractionation analysis of soils by **Chang** and **Jackson** method showed that the abundance of different P fractions was in the order of : Ca-P > Al-P >  $\text{NH}_4\text{Cl}$ -P > Fe-P > citrate-dithionate -P (CDP) in the treated and untreated soils. Treatment of the investigated soils- after removing of their organic matter by using concentrated  $\text{H}_2\text{O}_2$ - by different types of organic anions (citrate, oxalate, and tartrate) was found to reduce and/or inhibit the adsorption of P. This may be attributed to that at high pH values the carboxylate group of the organic anion has a negative charge high enough to compete phosphate group on active sites. The obtained results declared that the ability of organic anions to decrease phosphorus adsorption on soil surfaces followed the sequence: citrate > oxalate > tartrate.

**Key words:** Phosphorus-  $\text{CaCO}_3$ - adsorption- pH- Organic anions- Langmuir- Freundlich- Temkin- Fractionation -Chang and Jackson method

**Supervisors:**

1-Prof. Dr. Said Abd El- Rahman Mostafa

2- Prof. Dr. Ahmed Taher Abd El-Sadik

**Chairman of Chemistry Department:**

## Contents

<b>1- Introduction.....</b>	<b>1</b>
<b>2- Review of literature.....</b>	<b>3</b>
<b>2.1. Types of phosphorus in soil.....</b>	<b>3</b>
<b>2.2. Available phosphorus .....</b>	<b>4</b>
<b>2.3. Adsorbed phosphorus.....</b>	<b>6</b>
<b>2.4. Determination of phosphorus in soil.....</b>	<b>20</b>
<b>2.4.1. Detemination of P using the Inductive Coupled Plasma             Technique.....</b>	<b>21</b>
<b>2.4.2. Detemination of P using colorimetric methods.....</b>	<b>21</b>
<b>2.5. Technique and extraction for measuring available P in soil.</b>	<b>23</b>
<b>2.5.1. Main principles for P extraction.....</b>	<b>25</b>
<b>2.5.1.1. Olsen's extractants.....</b>	<b>25</b>
<b>2.5.1.2. Bray extractant.....</b>	<b>26</b>
<b>2.5.1.3. Mehlich No.1 extractant.....</b>	<b>26</b>
<b>2.5.1.4. Mehlich No.3 extractant.....</b>	<b>27</b>
<b>2.5.1.6. Morgan extractant.....</b>	<b>28</b>
<b>2.5.1.7. Ammonium bicarbonate- DTPA (AB-DTPA)                 extractant.....</b>	<b>28</b>
<b>2.5.1.8. Troug extraction.....</b>	<b>28</b>
<b>2.5.1.9. Acetic acid-extraction.....</b>	<b>28</b>

<b>2.6. Phosphorus fractionation.....</b>	<b>29</b>
<b>2.6.1. Modification of P-fractionation.....</b>	<b>29</b>
<b>2.6.2. Implications of P-fractionation.....</b>	<b>30</b>
<b>3. Materials and methods.....</b>	<b>36</b>
<b>3.1 Reagents and Indicators.....</b>	<b>36</b>
<b>3.2. Soil samples.....</b>	<b>39</b>
<b>3.3. Preparation of solutions.....</b>	<b>39</b>
<b>3.4. Spectrophotometric method for the determination of</b>	<b>48</b>
<b>available phosphorus in soils.....</b>	
<b>3.5. Soil phosphorus fractionation procedure.....</b>	<b>49</b>
<b>3.6. Determination of different types of extracted phosphorus</b>	<b>50</b>
<b>3.7. Determination of some soil chemical properties.....</b>	<b>51</b>
<b>3.8. Experimental design.....</b>	<b>55</b>
<b>3.9. Statistical analysis and calculation methods.....</b>	<b>57</b>
<b>4. Results and discussion.....</b>	<b>58</b>
<b>4.1. Introduction.....</b>	<b>58</b>
<b>4.1.1 Phosphorus adsorption isotherm curves.....</b>	<b>58</b>
<b>4.1.2. Langmuir adsorption isotherm equation.....</b>	<b>59</b>
<b>4.1.2.1. Description of conventional Langmuir indices of</b>	
<b>investigated soils.....</b>	<b>65</b>
<b>4.1.2.2. Interrelationships between P adsorption indices.....</b>	<b>67</b>
<b>4.1.3. Freundlich adsorption isotherm.....</b>	<b>68</b>

4.1.4. Temkin adsorption isotherm .....	74
4.2. Effect of phosphate adsorption on pH changes.....	79
4.3. Effect of incubation period on phosphate adsorption.....	83
4.4. Fractionation of different phosphorus forms.....	88
4.5. Effect of organic anion on phosphate adsorption.....	94
4.5.1. Comparison between citrate, oxalate, and tartarate anions effect on phosphate adsorption.....	98
4.5.2. Fitting IR charts for adsorption phenomenon.....	101
5.Summary.....	106
6.References.....	111