University of São Paulo
"Luiz de Queiroz" College of Agriculture

Chemical interaction mechanisms of metals, inorganics anions, organic acids and protein on purified material, artificial soil and cropland soil

Matheus Sampaio Carneiro Barreto

Thesis presented to obtain the degree of Doctor in Science. Area: Soil and Plant Nutrition

Piracicaba
2019

Matheus Sampaio Carneiro Barreto
Agronomist

Chemical interaction mechanisms of metals, inorganics anions, organic acids and protein on purified material, artificial soil and cropland soil

Advisor:
Prof. Dr. **LUÍS REYNALDO FERRACCIÚ ALLEONI**

Thesis presented to obtain the degree of Doctor in Science. Area: Soil and Plant Nutrition

Piracicaba
2019

Dados Internacionais de Catalogação na Publicação
DIVISÃO DE BIBLIOTECA – DIBD/ESALQ/USP

Barreto, Matheus Sampaio Carneiro

Chemical interaction mechanisms of metals, inorganic anions, organic acids and protein on purified material, artificial soil and cropland soil / Matheus Sampaio Carneiro Barreto. - - Piracicaba, 2019.

211 p.

Tese (Doutorado) - - USP / Escola Superior de Agricultura "Luiz de Queiroz".

1. Química do Solo 2. Fenômenos de superfície 3. Cinética química 4. Espectróscopia de absorção de Raios X 5. ATR-FTIR I. Título

To Brazilian society who paid my journey,

I dedicate

ACKNOWLEDGMENT

I must express my huge gratefulness to:

- The University of São Paulo (USP)– Luiz de Queiroz College of Agriculture(Esalq), especially the Graduate Program in Soils and Plant Nutrition;
- The Rutgers University-Newark, greatly the Earth & Environmental Science Department;
- The São Paulo Research Foundation (FAPESP) (grants #2016/05870-1 and #2016/22058-9) for essential financial support;
- The Brazilian Federal Agency for Support and Evaluation of Graduate Education (CAPES) and National Council of Technological and Scientific Development (CNPq);
- My advisor, Professor Luís Reynaldo F. Alleoni, who always trusted and had a commitment to my work;
- My supervisor and co-advisor during my oversea scholarship, Professor Evert Elzinga for the confidence and the "scientific philosophy", which he taught me (Bedankt voor alles!);
- All the staff and the professors of the Department of Soil Science and Centro de Energia Nuclear na Agricultura (CENA) and members of my thesis defense, who contributed to my formation. I thank especially Dr. Marina Colzato, Dr. Débora Ishida, Professora Célia Montes, Professor Pablo Vidal-Torrado, and Professor José Lavres Júnior;
- My safe haven. I thank my family, my parents Betanhia and Antônio, my grandmother Dona Solange, sister Victória, notably my aunt Dr. Monalisa and brother Dr. Victor Augusto for providential help when I arrived in Piracicaba;
- My friends, that as well as a "family" gave me inestimable support. I thank irreplaceable friends Dener e Laisa, for help-hand me even though before I arrive in Piracicaba; dear friends Frederico and Ruan for all assistance not only in amazing but also hard times; the precious time with Adriely in initial steps here; my "little-big" friend Mrs. Huaiyan Zhao (謝謝你的一切。!); Raquel e Mike, Ana, Andréia, Danilo, Marry "Maria", Marina "Gaucha", Xi, and Ernst, for awesome times in US and CA; Will and Bruna, Renato, Michel, Mariana-Olívia, Sarah, Flavio, Judith, Leticia, Joao, Barbara, Alexys, Eloa, M. Regina, Rodrigo "Crok", Josimar, Nicole, Rafael "Chico", Rodolfo-Thaís, Lilian, Acácio, Douglas, Fernando, Mariane, Thaís, Luciana, Matheus, Mayara; my "loooong"- date friends of Bahia: Francisco Chico, Lucas "Formiga", Albervam, Yuri Baleia, Caio César "Boi"; and of Viçosa: Siman, Colocho, Luis Fernando "Bola" Prof. Novais, Prof. Ivo, Prof. Mattielo, and Prof. Weddison;
- Everybody that close or not, helped me to make this possible;
- For provide me strength, hope, patience, faith, and grace, I thank God and all those praying for me.

Certainly because of all of you, when I look back I am sure it was all worthwhile!

For a thousand (million) times, I say THANKS ALL FOR EVERYTHING!

“Parents can only give good advice or put them on the right paths, but the final forming of a person's character lies in their own hands.”

Anne Frank

“To myself I am only a child playing on the beach, while vast oceans of truth lie undiscovered before me.”

Isaac Newton

“If I have the gift of prophecy and can fathom all mysteries and all knowledge, and if I have a faith that can move mountains, but do not have love, I am nothing.”

1 Cor 13:2

CONTENTS

RESUMO

Mecanismos de interação química de metais, ânions inorgânicos, ácidos orgânicos e proteína em materiais purificados, solo artificial e solo cultivado

O solo é um complexo sistema com variadas fases que alojam reações de interfaces que determinam a mobilidade/disponibilidade de nutrientes e contaminantes no ambiente. O entendimento profundo dos mecanismos que regem as reações é um desafio, sendo muitas vezes necessária a utilização de modelos com número reduzido de componentes e de alta pureza, a fim de que se isolem os efeitos de variáveis ambientais como tipo de minerias, pH e tempo. Podem também ser aplicadas sofisticadas técnicas analíticas para elucidar os mecanismos envolvidos. Nesse trabalho, procurou-se avaliar mecanismos de algumas reações químicas que envolvem os nutrientes P e Zn, macromoléculas como proteína e substâncias húmicas, bem como os contaminantes Cd e As; todos eles em matrizes puras ou em amostras de terra de áreas cultivadas e sob vegetação nativa (VN). As principais conclusões foram: (*i*) o complexo de superfície P-hematita em configuração bidentada teve adsorção mais rápida do que a monodentada, sendo a bidentada preferencialmente desorvida pelo ânion citrato, cuja adsorção anterior ao fosfato diminuiu a adsorção de P na superfície da hematita; (*ii*) o As(V) é adsorvido em complexos de esfera interna e externa nas superfícies de hematita e de hausmanita, sendo maior a adsorção na hausmanita, que se mostrou uma opção plausível de filtro para As(V); (*iii*) o processo de adsorção da proteína BSA em hematita teve forte dependência do pH do meio, sendo o pH próximo ao ponto isoelétrico da proteína o que maximizou a adsorção, sendo que houve considerável mudança conformacional nas estruturas secundáriasda BSA após adsorção, o que a tornou menos "empacotada" e mais "desdobrada", (*iv*) o Ca aumentou a adsorção de substancias húmicas nos minerais estudados por meio de complexos ternários "mineral-Ca-substâncias húmicas", e houve preferência de adsorção nas superfícies dos minerais presentes em solos intemperizados, por moléculas orgânicas menos humificadas e/ou de menor peso molecular; (*v*) em pH 4,5 houve menor adsorção de Zn, sendo esse retido preferencialmente em minerais alumino-silicatados, enquanto em valores de pH 6,5 as espécies de Zn ligadas a óxido de Fe e aquele precipitado com P também foram identificadas. Contudo, após seis meses de incubação, essas espécies diminuíram ou desapareceram, sendo as espécies de Zn adsorvidas aos minerais alumino-silicatados dominantes após longo tempo de incubação; (*vi*) Cd e Zn foram adsorvidos rapidamente em solos sob VN ou solos agrícolas altamente fertilizados, sendo que solos agrícolas adsorveram mais esses metais do que o solo sob VN. Porém, apesar da maior adsorção, esses metais ainda foram dessorvíveis por EDTA; (*vii*) a fração de Zn adsorvido à caulinita esteve presente em todas as amostras de solo, independentemente da origem e do manejo, mas o manejo agrícola e o tempo de incubação aumentaram a quantidade de Zn associado a frações de menor mobilidade. Além disso, a espécie de Zn associado ao fosfato esteve presente em solos altamente fertilizados, e a composição mineralógica do solo determinou a distribuição das frações de Zn adsorvido no solo.

Palavras-chave: Fenômenos de superfície; Sistema coloidal; Adsorção; Espectroscopia de absorção de raios-X; Espectroscopia de infravermelho; Mineralogia do solo

ABSTRACT

Chemical interaction mechanisms of metals, inorganic anions, organic acids and protein on purified material, artificial soil and cropland soil

The soil is a complex system with several phases, where abundant interfaces phenomena happen, which determines the mobility/availability of nutrients and contaminants into the environment. The deep understanding of these chemical mechanisms is a challenge, and it is often necessary to use models with reduced numbers of components and high purity, in order to isolate the effects of enviromenmtal variables such as minerals type, pH and time. Also, sophisticated analytical techniques may be used to elucidate the mechanisms involved at atomic and molecular scales. Here, mechanisms of some chemical reactions for some nutrients such as P and Zn, macromolecules such as protein and humic substances, as well as a contaminant such as Cd and As were evaluated, using pure systems, artificial soil or soil samples from cultivated areas. The main conclusions were: (*i*) the previous adsorption with citrate decreased P adsorption on hematite surface. The P-hematite surface complex in bidentate configuration had a faster absorption than the monodentate, and the bidentate was preferentially desorbed by citrate; (*ii*) As(V) was adsorbed on inner and outer-sphere complexes on the hematite and hausmannite surfaces, hausmannite showing a higher adsorption than hematite. The transformation from hausmannite to manganite should increase As(V) adsorption an its stability, thus hausmannite could be a good option as As(V) filter; (*iii*) the adsorption on hematite surface promoted a prominent conformational change in the secondary structures of BSA protein, toward a less "packed" and more "unfolded" protein forms, and the pH near the isoelectric point maximized its adsorption; (*iv*) Ca increased the adsorption of humic substances in the minerals present in weathered soils. Ternary complexes "mineral-Ca-humic substances" were responsible for this increment; and organic molecules less humified and/or with lower molecular weight were preferentially adsorbed on minerals´ surfaces; (*v*) less Zn was adsorbed at pH 4.5, which was preferentially retained in aluminosilicate minerals, while at pH 6.5, more Zn was adsorbed and Zn sorbed on Fe oxide, and Zn-P precipitates were identified. However, after 6 months, these ones decreased or disappeared, and the fraction of Zn sorbed to aluminosilicate minerals incresed; (*vi*) Cd and Zn are rapidly adsorbed on soils under native vegetation or highly fertilized agricultural soils, and agricultural soils adsorb more these metals than soil under native vegetation. These metals, however, were easily desorbable by EDTA; (*vii*) the soil mineralogy determined the main Zn fractions adsorbed on the soil, the fraction of Zn adsorbed to kaolinite was present in all soil samples, regardless of origin and management; agricultural management and time increased the amount of Zn in less mobile fraction, and Zn associated with P was present in highly fertilized soils.

Keywords: Surface phenomena; Colloidal system; Adsorption; X-ray absorption spectroscopy; Infrared spectroscopy; Soil mineralogy

1. GENERAL INTRODUCTION

The soil system is composed of several phases, like each mineral surface, organic compound, water, and gaseous phase. All these individual systems have a singular interfacial region where adsorptions processes occur. The adsorption mechanisms can be investigated from atomic, molecular to macroscopic scale, as well as in-situ process, because of the evolution of instrumental techniques and strategies for individualizing soil players. Hence, these reactions could be analyzed by traditional methods and/or sophisticated technologies such as isothermal calorimetry titration, microscopies (e.g. Force Atomic, Transmission or Scanning Electron) or spectroscopies (e.g. Xray Absorption, Xray diffraction, and Infrared) techniques in combination with interdisciplinary research of biological, chemical, and physical interfaces (Kruse et al., 2015; Lombi and Susini, 2009; Sarret et al., 2013; Sparks, 2006).

Some elements and minerals and organic components have a singular behavior and deserve attention for scientific research. Hematite is an abundant iron oxide in soils and sediments (Schwertmann, 2008), which suggest that it as an appropriated mineral surface to represent highly weathered soils. A significant feature of iron oxides is the high adsorption capacity of oxyanions as phosphate (P), which promotes the low bioavailability of P in some tropical soils (Roy et al. 2016). On the other hand, this high affinity allows the hematite uses for arsenic (As) filter employed in water treatment (Mohan and Pittman, 2007). The mineral hausmannite, as the hematite, also has high As adsorption capacity, but it is metastable at surface environmental condition and could improve As adsorption stability more than hematite-As complexes.

The organic compounds also have impacts in soil process. Citrate has been found in high concentrations in soil porewaters (Clarholm et al., 2015; Nambu et al., 2008). Rhizosphere exudates promote oxyanions' desorption (e.g. P and As), which makes it a model of organic acid in soil. The behavior of humic acids in soils has attracted attention because of climate change mitigation practices related to C soil storage mechanisms (Six et al., 2002). Likewise, some metallic cations have many functions in the soil ecosystem. Calcium (Ca) is a plant/animal nutrient and can enhance organic compounds adsorption on minerals (Sowers et al., 2018). Zinc (Zn) is a nutrient as well, however could be toxic in high concentration, whereas cadmium (Cd) is a harmful metal even in low concentration in soil (Bradl, 2004).

In this study, the chemical interaction mechanisms among metals, inorganic anions, organic acids and biological molecule on purified material, artificial soil, and cropland soil

were investigated by multi-scales spectroscopic techniques. The use of purified material or artificial soil allow as to isolate effects of some environmental variables as pH, ionic strength, surface loading, and aging on specific reactions, for example, the phosphate adsorption on hematite surface or metal fate on soil system after initial adsorption. This approach allows a more detailed and clear description of chemical process. Therefore, we carried out studies from pure materials and artificial soil to real soil sample of cropland and natural areas.

In this study, the hypothesis were: (i) citrate desorbs specific phosphate-adsorbed species, (ii) hausmannite could adsorb higher amount of arsenate and immobilize it in less desorbable forms than hematite, (iii) protein change secondary conformation after adsorbed on hematite, (iv) the presence of phosphate in minerals system drives an increase Zn adsorption as Zn-phosphate phases, (v) calcium improves humic acid adsorption on soil, (vi) cropland soils adsorbs more cadmium and zinc than soils under native vegetation, (vii) agriculture land use promotes different Zn species compared to natural soil, as Zn-phosphate and Zn-carbonate.

The objectives in this study were to evaluate: (i) phosphate and citrate adsorption and competition on hematite surface, (ii) arsenate and citrate adsorption and desorption on hausmannite and hematite surface, (iii) protein adsorption and structural conformation on hematite surface as a function of changes in pH, ionic strength and protein concentration, (iv) the effects of phosphate and pH on Zn adsorption over aging time on artificial soil “clay” fraction, (v) humic acids adsorption improvement due to calcium, on artificial soil “clay” fraction, (vi) adsorption-desorption process of Cd and Zn in soils under native vegetation and in cropland soils, and (vii) zinc chemical fractionation and speciation after adsorption in these soil in soils under native vegetation and in croplands.

References

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interface Sci. 277, 1–18. doi:10.1016/j.jcis.2004.04.005

Clarholm, M., Skyllberg, U., Rosling, A., 2015. Organic acid induced release of nutrients from metal-stabilized soil organic matter - The unbutton model, Soil Biology and Biochemistry. Pergamon. doi:10.1016/j.soilbio.2015.02.019

Kruse, J., Abraham, M., Amelung, W., Baum, C., Bol, R., Kühn, O., Lewandowski, H., Niederberger, J., Oelmann, Y., Rüger, C., Santner, J., Siebers, M., Siebers, N., Spohn, M., Vestergren, J., Vogts, A., Leinweber, P., 2015. Innovative methods in soil phosphorus research: A review. J. Plant Nutr. Soil Sci. doi:10.1002/jpln.201400327

Lombi, E., Susini, J., 2009. Synchrotron-based techniques for plant and soil science: opportunities, challenges and future perspectives. Plant Soil 320, 1–35. doi:10.1007/s11104-008-9876-x

Mohan, D., Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents—A critical review. J. Hazard. Mater. 142, 1–53. doi:10.1016/J.JHAZMAT.2007.01.006

Nambu, K., van Hees, P.A.W., Jones, D.L., Vinogradoff, S., Lundström, U.S., 2008. Composition of organic solutes and respiration in soils derived from alkaline and non-alkaline parent materials. Geoderma 144, 468–477. doi:10.1016/j.geoderma.2007.12.014

Roy, E.D., Richards, P.D., Martinelli, L.A., Coletta, L. Della, Lins, S.R.M., Vazquez, F.F., Willig, E., Spera, S.A., VanWey, L.K., Porder, S., 2016. The phosphorus cost of agricultural intensification in the tropics. Nat. Plants 2, 16043. doi:10.1038/nplants.2016.43

Sarret, G., Smits, E.A.H.P., Michel, H.C., Isaure, M.P., Zhao, F.J., Tappero, R., 2013. Use of Synchrotron-Based Techniques to Elucidate Metal Uptake and Metabolism in Plants, in: Advances in Agronomy. doi:10.1016/B978-0-12-407247-3.00001-9

Schwertmann, U., 2008. Iron oxides, in: Encyclopedia of Earth Sciences Series. doi:10.1002/9783527613229.ch01

Six, J., Conant, R.T., Paul, E.A., Paustian, K., 2002. Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils. Plant Soil 241, 155–176. doi:10.1023/A:1016125726789

Sowers, T.D., Stuckey, J.W., Sparks, D.L., 2018. The synergistic effect of calcium on organic carbon sequestration to ferrihydrite. Geochem. Trans. 19, 4. doi:10.1186/s12932-018-0049-4

Sparks, D.L., 2006. Advances in elucidating biogeochemical processes in soils: It is about scale and interfaces. J. Geochemical Explor. doi:10.1016/j.gexplo.2005.08.105