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Lithium adsorption on amorphous aluminum hydroxides and gibbsite

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Abstract

Lithium (Li) adsorption on both amorphous aluminum hydroxides and gibbsite was studied. For the amorphous $Al(OH)_3$ the adsorption was found to be pH dependent. Generally, 1.6 times more Li was adsorbed at initial pH value 8.0 compared with pH value 6.50. Gibbsite adsorbed 11.6 to 45.5 times less Li quantities compared with amorphous $Al(OH)_3$. Lithium adsorption was not depended on equilibrium times. It remained stable for all equilibrium times used. Lithium quantities extracted with 1N CH_3COONH_4 pH 7 , represent the physical adsorption, while the remaining Li that was adsorbed on $Al(OH)_3$, represents the chemical adsorption. During the desorption process 19% of Li extracted with NH_4^+, represents the physical adsorption, while the remaining 81% of Li, which was adsorbed represents the chemical adsorption. In gibbsite, 9.6% of Li represents the physical adsorption and 90.4% the chemical one. The experimental data conformed well to Freundlich isotherm equation.

Keywords: Adsorption, aluminum hydroxides, desorption, lithium

Article Info

Introduction

Lithium is trace metal and one of the alkali metals. It belongs to the IA group of the periodic table 1. Lithium occurs in basaltic tuff, rhyolite, mica schist, sedimentary rocks, gneisses, marble, calcareous rocks and in low amounts in limestones and ultra basic rocks. Lithium concentrations in the soils are 20 to 30 mg kg^{-1}. Soils derived from granitic – syenitic parent material have the highest concentration. Also it is found in minerals, irrigation waters and rivers as well as in sea or oceans. Lithium is much more mobile in soils than Rb and Cs. It is held within the structure of clay minerals produced during soil weathering, e.g. gibbsite, and it is not available to plants. Lithium is adsorbed to the soil solid phase, especially illites (Helmke and Sparks, 1996). According to Pistiner and Henderson (2003), Li is adsorbed by secondary minerals (smectite) by physisorption and onto ferrihydrite or gibbsite surfaces by chemisorption. Soils with excessive levels of organic matter have low Li concentration (3-4 mg kg^{-1}). Of the alkali elements, Li is the most toxic to plants (Bradford, 1966). Lithiophorite $[(Li,Al)MnO_2(OH)_2]$ is commonly found in weathered zones of Mn deposits and in certain acid soils (De Villiers, 1983). The formation of this compound requires a relatively large concentration of Al^{3+} (Golden et al., 1993). Brümmer (1986) suggested that the adsorption of heavy metals by goethite comprises three different steps: first, surface adsorption (physical adsorption), second, diffusion into goethite particles and third, adsorption and fixation at positions within the mineral particles (chemical adsorption). These steps are able to describe the adsorption process of amorphous $Al(OH)_3$.

Metal cations adsorption on poorly crystalline or microcrystalline materials such as allophanes, imogolite and Al-hydroxide gels occurs at discrete surface sites, Al-OH groups. Amorphous $Al(OH)_3$ aging with time, increased the crystalline state of these materials and decreased the adsorption ability of the gels.

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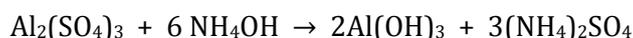Tel.: +302310998717   E-mail address: kprodrom@agro.auth.gr

The objective of this study is to investigate Li adsorption on amorphous aluminum hydroxides at different pH values, as well as on well crystallized gibbsite.

Material and Methods

Aluminum hydroxide was precipitated stoichiometrically according to reaction,

$$Al_2(SO_4)_3 + 6\,NH_4OH \rightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$$

in a series of 50 ml centrifuge tubes. The tubes were stoppered, shaken for 15 min and centrifuged at 5,000 rpm for 10 min. Then, they were washed with distilled water once (pH ~ 8.0) and twice (pH ~ 6.50). The obtained gels did not appear to be crystalline to X-ray analysis. Figure 1 gives the electron images of amorphous $Al(OH)_3$.

Well crystallized $Al(OH)_3$

Gibbsite was obtained from BDH Chem. Ltd. Figure 2 shows the x-ray diffractogram from gibbsite.

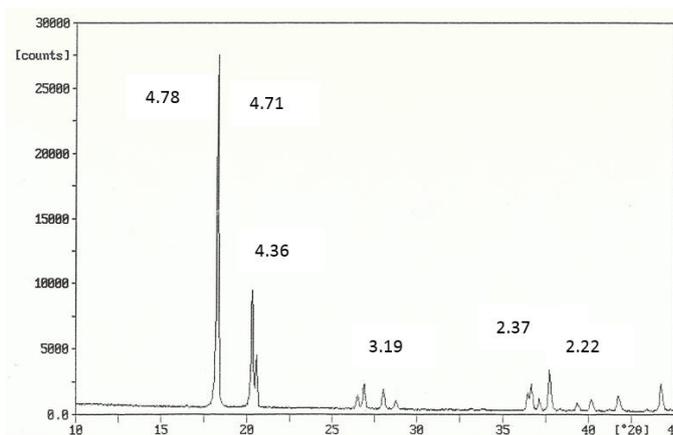

Figure 1. Electron (SEM) image of amorphous $Al(OH)_3$

Figure 2. X-ray diffractogram obtained from gibbsite

Adsorption experiments

Samples of $Al(OH)_3$ were treated with Li solutions of different concentrations (10, 20, 40, 60, 80, 100, 120 and 160 ppm). The samples were shaken for 30 min and equilibrated with Li solutions for 0.5, 2, 24, 48, 72, 120 and 240 hours periods at a temperature of 25 ± 0,2°C. After centrifugation at 6,000 – 7,000 rpm for 10 min the supernatant liquids were filtered into volumetric flasks. Aliquots of the clear supernatant were analyzed for Li by flame photometry. The adsorption experiment took place at two different pH values 6.50 and 8.0 after the $Al(OH)_3$ precipitation.

The gibbsite sample was equilibrated with Li solutions for 24, 48, 72, 120 and 240 hours during the adsorption process, because the adsorption ability of this material is very small for 0.5 and 2 hours. All the determinations were done in triplicate.

Desorption process

After the adsorption process, the samples of $Al(OH)_3$ were equilibrated with Li solutions for 48 h at an initial pH 8.0, were washed with 30 mL CH_3COCH_3 90% two times and treated with 25 mL CH_3COONH_4 1N, pH 7.0 twice. They were shaken for 5 min and centrifuged at 6,000 rpm for 5 min. The supernatant liquids were filtered into separate volumetric flasks and Li was determined. In the case of gibbsite, the treatment with 1N CH_3COONH_4, was done once during the desorption process because the adsorption ability of this material is very small.

Results and Discussion

The experimental data fitted well to the Freundlich isotherms ($x = kC^n$), where: x is amounts of Li adsorbed per unit weight of aluminium, (mg/g Al^{3+}), C is equilibrium concentration, (μg/ml), k and n are constants.

In the linear transformation, $\log x = \log k + n\log C$, where k is the amount of Li adsorbed when C=1 which gives units of mL g^{-1} and n is related to the isotherm slope so that it usually increases with increasing slope (Table 1, Fig. 3).

Table 1. Freundlich isotherm constants and R^2 from Li adsorption on $Al(OH)_3$ and gibbsite.

Time	$Al(OH)_3$	pH	8.0	$Al(OH)_3$	pH	6.50		gibbsite	
(h)	k (ml/g)	n	R^2	k (ml/g)	n	R^2	k (ml/g)	n	R^2
½	0.767	1.01	0.7351	0.277	0.910	0.8460	-	-	-
2	1.136	0.937	0.7272	0.139	1.147	0.9850	-	-	-
24	2.532	0.741	0.8602	0.679	0.824	0.9921	0.031	0.667	0.9701
48	3.247	0.676	0.9144	0.609	0.833	0.9934	0.018	0.869	0.9768
72	3.927	0.609	0.8831	0.552	0.851	0.9898	0.020	0.841	0.9877
120	3.936	0.655	0.8805	0.749	0.786	0.9855	0.019	0.849	0.9847

Independently of the initial pH values 6.50 or 8.0, pH ranged at the same values (6.50 – 4.20 or 7.50 – 4.50) in the equilibrium solutions after the adsorption process. These final pH values depended on the equilibrium time and the concentration of Li in the equilibrium solution. Lithium adsorption by amorphous $Al(OH)_3$ was greater at pH 8.0, than at pH 6.5. Generally 1.6 times more Li was adsorbed at pH 8.0 (Fig. 4).
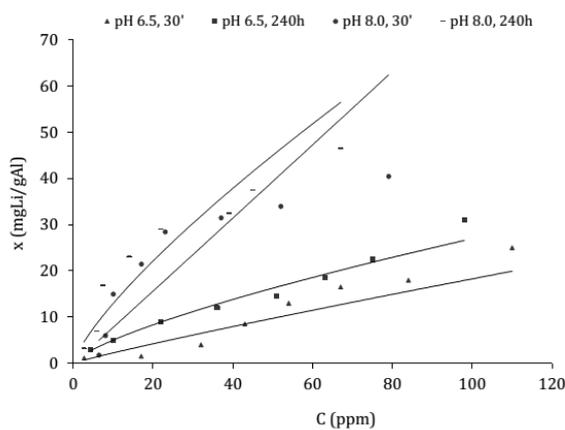
Figure 3. Lithium adsorption data on $Al(OH)_3$ plotted according to Freundlich isotherms
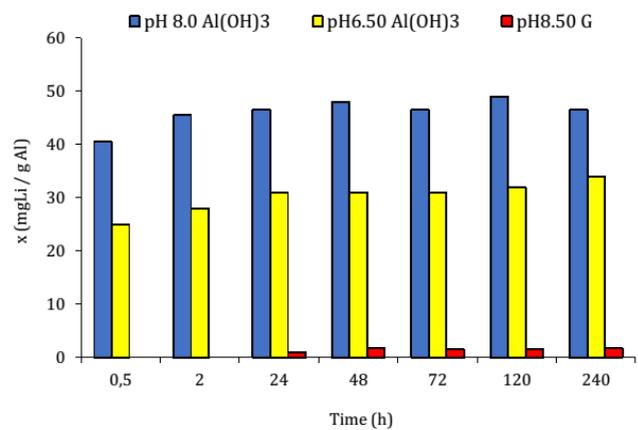
Figure 4. The histograms of Li adsorption with time for concentration of 160 ppm on $Al(OH)_3$ and gibbsite

In the case of pH 6.50, the maximum adsorption of Li occurred at 240 hours, but statistically no significant differences for the equilibrium times used were observed. Also, at pH 8.0 the maximum adsorption occurred at 48 and 120 hours, and in this case, there were no significant differences among the experimental data. However, we have to note that there were observed significant differences among the experimental data of Li adsorption occurred at the two pH values, 6.50 and 8.0. All statistical analyses were accomplished at $P < 0.05$. The results showed that the initial pH value during the adsorption of Li to amorphous $Al(OH)_3$ is important regarding the amounts of Li adsorbed. The adsorption ability of amorphous $Al(OH)_3$ was not reduced with time. The maximum equilibrium time used (10 days) was not efficient to change the crystalline state of this material. Gibbsite adsorbed less quantities of Li, compared with amorphous $Al(OH)_3$. Aluminum hydroxides adsorbed 11.6 to 45.5 times more Li than gibbsite at the two pH values used. The experimental data in the case of gibbsite, fitted well to the Freundlich isotherms (Fig. 5).

Also, the Li adsorption on gibbsite was not influenced by the equilibrium time (Fig. 5). The pH values in the equilibrium solution, were 8.0 to 11.50. These values depended only on Li concentration in the equilibrium solutions. In the desorption process with CH_3COONH_4, greater Li amounts (70.5% mean-values) were extracted during the first treatment compared with the second one (29.5%). During the two treatments with CH_3COONH_4, only 19% of Li was extracted while 81% remained adsorbed on $Al(OH)_3$ (Fig. 6). In the case of gibbsite, 9.6% of Li represents the physical adsorption and 90.4% the chemical one (Fig. 6). Lithium quantities extracted with CH_3COONH_4, were weakly adsorbed on the surface charge and represent the physical adsorption. The retained Li portion was strongly adsorbed by Al-OH groups by diffusion into micropores of material particles and constitutes the chemical adsorption, under these experimental conditions.
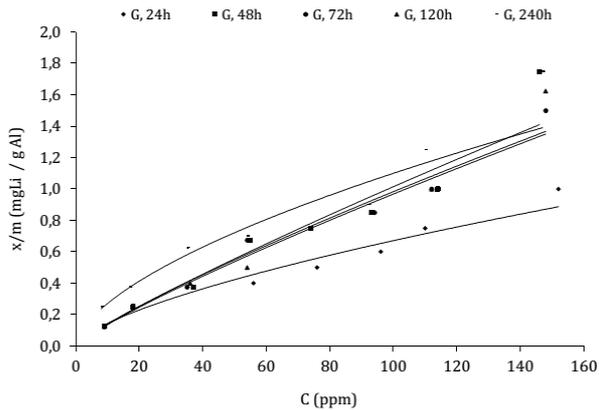
Figure 5. Lithium adsorption data on gibbsite plotted according to Freundlich isotherms
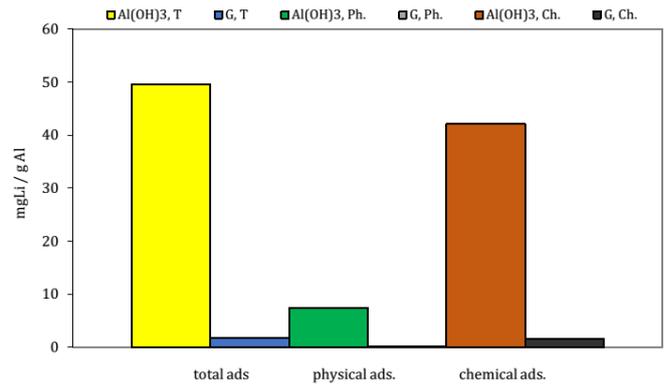

Figure 6. The histograms of Li adsorption, on the two materials, (total, physical and chemical) for concentration 160 ppm

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