

Metal sorption processes by clay minerals in soils and sediments. Effect of the alteration of clay minerals

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Abstract

Sorption of metals in soils and sediments are influenced by the properties of the adsorptive and adsorbate, the properties of the adsorbent and the physical and chemical conditions of the environment. The sorption of a metal cation for clay minerals having a layer charge, such as smectites or vermiculites, can take place on the outer planar crystal surface, and in the interlayer space as hydrated cations. Among clay minerals smectites have large metal ion adsorption. Montmorillonites from bentonites adsorb high amount of metals, considerably higher than illite. Heterogeneous composition of soil clays, and the pedogenic clay mineral transformation processes modify sorption properties. The adsorption capacity of soil smectites and vermiculites is closer to that of almost pure montmorillonite, but still lower. During the clay mineral alteration processes, the formation of intermediate phases, whose properties are between the primary clay mineral and the product affect the sorption properties of soils and sediments.

Resumen

La adsorción de metales en suelos y sedimentos está influida por las propiedades de los metales, las propiedades de las fases adsorbentes y las condiciones físicas y químicas del medio ambiente. La adsorción de un catión metálico en minerales arcillosos con carga de capa, tales como esmectitas o vermiculitas, puede tener lugar en la superficie exterior plana del cristal y en el espacio entre capas como cationes hidratados. Entre los minerales arcillosos, las esmectitas tienen una gran capacidad de adsorción de iones metálicos. Las montmorillonitas de las bentonitas adsorben una gran cantidad de metales, considerablemente más que las illitas. La composición heterogénea de las arcillas del suelo y los procesos de transformación de minerales arcillosos pedogénicos modifican las propiedades de adsorción. La capacidad de adsorción de las esmectitas y vermiculitas del suelo es solo ligeramente inferior a la de la montmorillonita casi pura. Durante los procesos de alteración del mineral arcilloso, la formación de fases intermedias, cuyas propiedades se encuentran entre el mineral arcilloso primario y el producto, afectan a las propiedades de adsorción de suelos y sedimentos

Key-words: Metal; sorption; clays; alteration

1. Introduction

Thanks to the enormous number of studies the main features of the distribution and migration of toxic and bioessential metals in soils and geological formations are sufficiently well known. One of the basic processes is the adsorption of metals by soils, and the most various soil constituents. It is also well known that clay minerals play an important role in these sorption processes due to their unique physical and chemical characteristics. Plenty of data for various adsorbates and adsorbents are available in the literature, providing us the opportunity to predict the sorption properties and processes for almost any material, under any circumstances. Nevertheless, there is not a general rule describing the relationship between soil properties and metal sorption. Additionally, our knowledge about the metal adsorption capacity of individual constituents of soils and sediment is still incomplete. These components are various: minerals and rock fragments (constituted by minerals), organic matter, and even the association of these two, the organo-mineral complexes. As the phase composition of soils are heterogenous, the characterization of their metal sorption is complicated (Strawn, 2021). Moreover, the soil and sediment components are not stable. They have their typical alteration and transformation pathways according to the physico-chemical environment. Consequently, the soil properties – such as the metal sorption capacity – change over time. And finally,

the peculiarities of the Earth planet's surface, the presence of water and life, never should be disregarded. This lecture gives a brief insight through some examples into the change of metal sorption with the alteration of clay minerals in soils and sediments. This review summarizes only a small segment of the mineralogical aspects of metal sorption in soils. Nevertheless, the author hopes for its usefulness for all researchers (geologists, hydrogeologists, soil scientists, chemists, environmental scientist, etc.) working on metal contamination issues related to soils and sediments.

2. Factors influencing the sorption of metals in soils and sediments

Sorption of metals – and thus, their distribution and fate – in soils and sediments are influenced by several factors. These factors can be divided in three groups: factors related to 1. the properties of the adsorptive and adsorbate, 2. the properties of the adsorbent, and 3. the physical and chemical conditions of the environment. An adequate study of the metal sorption requires the characterization each of them. Since sorption of metals in soils and sediments always takes place in aqueous medium, the adsorptive metal and the environment can be considered a solution. Table 1 lists the most important factors for clay minerals (in particular smectites). The factor is considered positive when its rise involves the increase of the sorption. It can be stated that the role of most of them is complex, or variable, depending on other factors. The most important influencing factor from the part of the solution is pH. Chemical species of the adsorbed metal is affected by the pH. In case of ion exchange processes H^+ behaves as a competing cation: adsorption generally increases with pH, because the competition decreases. Moreover, the variable charge of soils is pH dependent, the surface charge becomes more negative with the increasing pH. The sorption sequence of the cations depends on the charge, ionic radius and hydration ability of the cations. The differences in the real sequence series are due to the different and very commonly heterogeneous adsorbents.

Table 1. Effect of sorption influencing factors on the metal sorption of clay mineral adsorbent.

Properties of the adsorbent (clay mineral)	
<i>Factor</i>	<i>Effect on the sorption</i>
permanent charge	positive
origin of permanent charge	variable, cation depending
variable charge	pH dependent, positive with increasing pH
surface area	positive
particle size	positive
swelling capacity	positive
Properties of the solution	
pH	variable, complex
metal ion concentration	positive
chemical form of the metal ion	complex
metal ion	
▪ charge	positive
▪ hydration	negative
ionic strength	negative
temperature	variable
Other factors	
time	positive
solid/fluid ratio	positive

3. General features of the metal sorption by clay minerals

Among clay minerals smectites have large metal ion adsorption capacity therefore they have high environmental and geochemical importance. According to the respected structural models, smectites are phyllosilicates having pyrophyllite like 2:1 basic structure and extremely small crystallite size, some 100 nm lateral dimension and some nanometres thickness. Due to isomorphic substitution in their lattice, they have a permanent negative charge, the

layer charge. This negative charge is responsible for the high cation exchange and adsorption capacity of the smectites. Smectites can integrate water or other polar organic substances into their interlayer space, and thus expanding it. The swelling capacity is an important feature related to the layer charge. The expanding and sorption capacity of smectites is utilised in the isolating layer of landfills.

The sorption of a metal cation can take place on various sites of a clay mineral (Figure 1). On the outer planar crystal surface (A), and in the interlayer space (B) cations are bond by outer-sphere adsorption, which means that these cations are hydrated. These are the most important sorption sites for clay minerals having a layer charge (permanent charge), such as smectites or vermiculites. The mechanism of this type of sorption is cation exchange. The layer charge resulting in 80–120 cmol/kg cation exchange capacity, associated with the huge specific surface area (~800 m²/g) make smectites and vermiculites excellent adsorbents, as demonstrated by some adsorption capacity data in Table 2. On the crystallite edges (C) metals are bond by inner-sphere sorption to the reactive (OH) groups of the octahedral sheet, whose charge is pH dependent (variable charge of the soil). Since clay minerals in soils, particularly smectites and mixed layer clay minerals are very thin in soils (some TOT layers) the ratio of the variable charge is only 10-15% of the total layer charge. Moreover, as the point of zero charge (PZC) of montmorillonite is around pH 6.5 (Tombácz and Szekeres, 2004), this site contributes to the cation uptake at alkaline pH, and they can adsorb anions at acidic conditions. Consequently, 2:1 clay minerals have very restricted adsorption affinity for metals in form of oxyanions (e.g. As, Mo) or for P, the indispensable plant nutrient. Large, generally non-hydrated cations are fixed in the ditrigonal cavities of the silicate tetrahedral sheet (D). This is the typical site of K⁺ (or even NH₄⁺) in illite and high charge vermiculite or smectite, giving a significant role to this site and minerals in plant nutrient issues. Radiocaesium is also preferentially sorbed on this site. Dehydrated cations with smaller than ~0.7 Å ionic radius can migrate upon heating from the interlayer space to the octahedral vacancy (E) of a dioctahedral 2:1 clay mineral and neutralizes the charge originating from the octahedral sheet. This is the well-known Hofmann-Klemen effect, which is used with Li in smectite identification, but it is also known for Cu (He et al., 2001; Németh et al. 2005), and Ni (Németh. 2003).

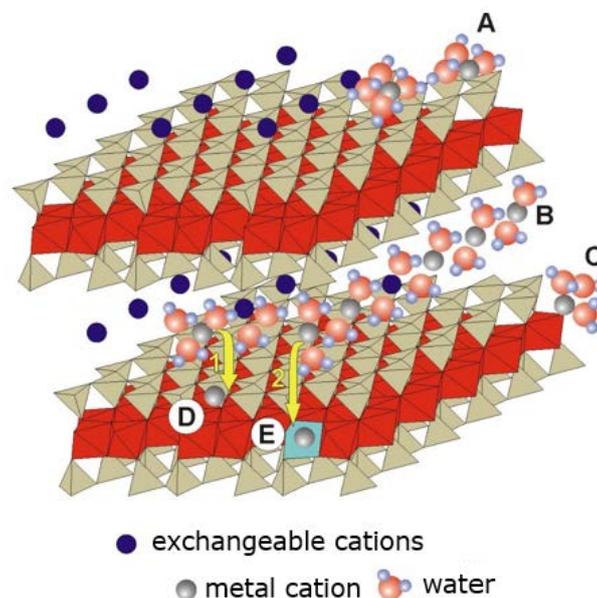


Fig. 1. Possible sorption sites of metal ions in clay minerals (smectites). A: outer planar surface, B: interlayer space, C: edge sites, D: hexagonal/ditrigonal cavity, E: octahedral vacancy.

According to McBride's concept, precipitation is the continuation of the surface adsorption, especially in contaminated medium, where the metal concentration is high (McBride, 2000). The precipitation of cerussite and basic Cu carbonates in calcareous soils is a common way of the immobilization of lead or copper (Sipos et al., 2008; Sipos et al., 2019).

The determination of the adsorption capacity of a sediment or soil can be achieved by batch sorption experiments, but sequential extraction methods also provide a good approach. Table 2 summarizes the maximum adsorption capacity determined from linearized Langmuir isotherms based on batch adsorption experiments (Németh, 2003;

Németh et al. 2005). It can be stated that montmorillonites from bentonites adsorb high amount of metals, considerably higher than illite. However, the adsorption capacity of soil smectites and vermiculites is closer to that of almost pure montmorillonite, but still lower. This is due to the heterogenous composition of soil clays, and the pedogenic clay mineral alteration, transformation processes, which modify the sorption properties.

Table 2. Cu and Zn sorption capacity of various montmorillonites and other clay minerals.

clay mineral	Cu sorption (mg/kg)	Zn sorption (mg/kg)
montmorillonite SWy-2 (Wyoming, USA)	22240	22880
montmorillonite (Istenmezeje, Hungary)	20970	30720
montmorillonite (Oraşu Nou, Romania)	24150	20920
montmorillonite (Valea Chioarului, Romania)	21610	26150
illite (Füzérradvány, Hungary)	3180	
soil smectite (Luvisol, Hungary)	13980	14380
soil vermiculite (Luvisol, Hungary)	13340	14380

4. Clay mineral alteration, transformation and the change of metal sorption

Clay mineral assemblage of brown forest soils of temperate zone, especially Luvisols, shows variability with depth within a soil profile. The typical clay mineral formation, transformation and alteration processes in Luvisols depending on the parent rock are: formation of smectite with heterogenous charge distribution; decrease of the layer charge and illite to smectite transformation, alteration of low charge smectite to high charge vermiculite, vermiculitization of chlorite, hydroxy interlayering of vermiculite (Németh and Sipos, 2006).

Adsorption isotherm curves in Figure 2 show that copper adsorption capacity of the accumulation (B) horizons of a Luvisol profile is 35% higher than the illuviation (E) horizon.

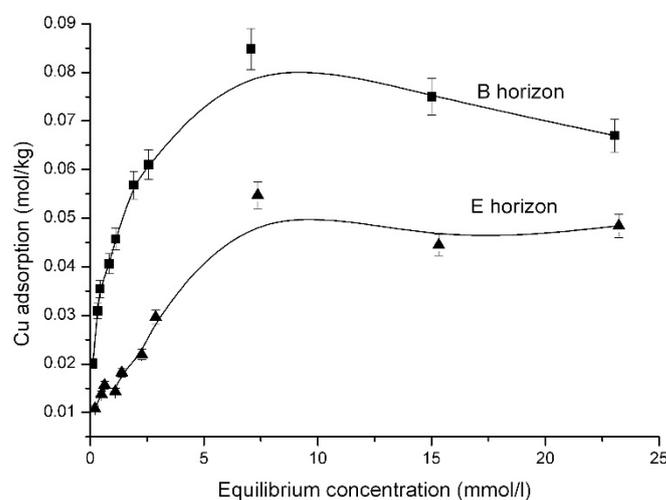


Fig. 2. Copper adsorption isotherms for the E and B horizons of a Luvisol soil profile (Németh et al., 2010).

The difference arises from the different mineral composition of the horizons. Swelling chlorite/vermiculite mixed layer clay mineral and hydrous iron oxides in the accumulation layer enhances the Cu uptake, while hydroxy-interlayering of vermiculite, and absence of iron oxides decrease the sorption of the eluviated horizon.

Adsorption isotherms reflect the adsorption capacity of the bulk soil material. The contribution of the different soil components can be determined by analytical TEM, which is able to measure the chemical composition of individual particles. The cobalt uptake by soil smectite was found to increase as the total layer charge of the smectite increased.

The layer charge of smectite has considerable effect on the sorption properties. Generally, increasing layer charge increases the metal adsorption capacity within the smectite layer charge range. Transformation of chlorite to vermiculite increases the metal uptake capacity due to the hydration of the interlayer space and thus increased specific area. Hydroxy interlayering has an opposite effect due to the formation of Al-Fe-hydroxyde pillars in the interlayer space. The clay mineral loses its expansion capacity, and the surface area is reduced (Németh et al., 2011). Close association of iron-oxides and clay minerals tend to increase the sorption capacity. Illitization of smectite by potassium fixation decreases the uptake of lead.

Clay mineral alteration processes have significant effect on the sorption of metals by soils and sediments. Sorption capacity is a changing property of soils. During the clay mineral alteration processes intermediate phases form, whose properties are between the primary clay mineral and the product.

ACKNOWLEDGMENTS

The author thanks the Organizers of the Workshop for the honourable invitation.

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