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Adsorption and transport of polymaleic acid on Callovo-Oxfordian clay stone: Batch and transport experiments

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ABSTRACT

Dissolved Organic Matter (DOM) can affect the mobility of radionuclides in pore water of clay-rich geological formations, such as those intended to be used for nuclear waste disposal. The present work studies the adsorption and transport properties of a polycarboxylic acid, polymaleic acid (PMA, $M_w = 1.9$ kDa), on Callovo-Oxfordian argillite samples (COx). Even though this molecule is rather different from the natural organic matter found in clay rock, the study of its retention properties on both dispersed and intact samples allows assessing to which extent organic acids may undergo sorption under natural conditions (pH 7) and what could be the impact on their mobility. PMA sorption and desorption were investigated in dispersed systems. The degree of sorption was measured after 1, 8 and 21 days and for a range of PMA initial concentrations from 4.5×10^{-7} to 1.4×10^{-3} mol.L^{-1}. The reversibility of the sorption process was estimated by desorption experiments performed after the sorption experiments. At the sorption steady state, the sorption was described by a two-site Langmuir model. A total sorption capacity of COx for PMA was found to be 1.01×10^{-2} mol.kg^{-1} distributed on two sorption sites, one weak and one strong. The desorption of PMA was incomplete, independently of the duration of the sorption phase. The amount of desorbable PMA even appeared to decrease for sorption phases from 1 to 21 days. To describe the apparent desorption hysteresis, two conceptual models were applied. The two-box diffusion model accounted for intraparticle diffusion and more generally for nonequilibrium processes. The two-box first-order non-reversible model accounted for a first-order non-reversible sorption and more generally for kinetically-controlled irreversible sorption processes. The use of the two models revealed that desorption hysteresis was not the result of nonequilibrium processes but was due to irreversible sorption. Irreversible sorption on the strong site was completed after 1 day and represented 96% of the total sorption on this site. On the weak site the irreversible uptake was slower and completed only after 16 days but it also dominated the sorption. 85% of the PMA sorbed on the weak site was not desorbable after 21 days of sorption.

The migration of PMA was studied by applying a hydraulic gradient to a clay core inserted in a stainless steel cell. Breakthrough of polymaleic acid, simulated with a 1D transport model including the two-box first-order non-reversible model, revealed that the mobility of PMA was limited by the same set of reversible/irreversible interactions as observed in the dispersed system. However, to describe efficiently the transport, the total sorption capacity had to be reduced to 33% of the capacity estimated in batch experiments. The irreversible sorption on the weak site was also slower in the intact sample than in the crushed sample. Geometrical constraints would therefore affect both the accessibility to the sorption sites and the kinetics of the irreversible sorption process.

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1. Introduction

In many countries clay-rich geological formations are considered as potential host rocks for nuclear waste disposal among others because of their high sorption capacity towards many radionuclides (ANDRA, 2005; NAGRA, 2002; ONDRAF/NIRAS, 2001). These clayey geological formations generally contain a substantial level of natural organic matter (NOM) which is mainly hydrophobic, insoluble and strongly bound to the clay (Tissot and Welte, 1984). However, a part of the organic material is also dissolved in pore water and evidence of its impact on transport of trivalent actinides and lanthanides (Maes et al., 2006; Ticknor et al., 1996; Wold and Eriksen, 2007) led to consideration of Dissolved Organic Matter (DOM) as a key element in repository safety assessment. Several studies, dedicated to the sorption of organic matter on either soils or pure minerals, showed that the association DOM-rock depends on both the properties of the mineral phases and the properties of the organic matter. Sorption is positively related to the content of Al or Fe oxide/hydroxide and phyllosilicate clay minerals (Chorover and Amistadi, 2001; Kahle et al., 2004; Kaiser and Guggenberger, 2000; Mikutta et al., 2007) and enhanced for high molecular weight fractions of DOM (Meier et al., 1999; Specht et al., 2000; Wang et al., 1997). For pure clay minerals, sorption is maximum at low pH while due to electrostatic repulsions sorption above pH_{PZC} is generally low (Arnarson and Keil, 2000; Feng et al., 2005; Salman et al., 2007). However, at high pH, sorption may be enhanced by cation-mediated bridging of organic matter (Arnarson and Keil, 2000; Feng et al., 2005; Majzik and Tombácz, 2007; Mikutta et al., 2007). While the sorption of DOM has been extensively studied in dispersed systems, only few works attempted to estimate the influence of compaction on sorption of organic compounds. Moreover, only few authors focused on the reversibility of DOM sorption on soil and clay minerals. These two points might yield valuable information on the role of DOM in contaminant transport in geological formations over large time scales. The migration of DOM was studied in bentonite by Wold and Eriksen (2007) who determined a significantly lower sorption on a compact sample than in a dispersed system. Transport of Boom Clay organic matter on an intact drill core was reported by Maes et al. (2006) and Put et al. (1998) but no attempt was made to quantify the interactions in dispersed samples. In both cases, the reversibility of the sorption of DOM on rock has not been investigated.

The Callovo-Oxfordian clay (COx), host rock under investigation in France, contains 0.6 to 1 wt.% of NOM (ANDRA, 2005; Deniau et al., 2008) of which 0.06–0.14% is hydro-soluble (Courdouan et al., 2007a; Huclier-Markai et al., 2010; Vinsot et al., 2008). This DOM is mainly composed of low molecular weight carboxylic acids, fatty acids, aldehydes and amino acids with also a small fraction of humic compounds (Courdouan et al., 2007a; Huclier-Markai et al., 2010). The present work focuses on the interactions of polymaleic acid (PMA) with COx in compact and dispersed systems. Radiolabelled (^{14}C) polymaleic acid is used to improve quantification limits. In this molecule, the molar ratio ^{14}C/stable C is around 4×10^{-5} and no influence of ^{14}C on the chemical behaviour of PMA molecule is expected. ^{14}CPMA is therefore acting as a tracer for PMA behaviour in retention and transport processes. Polymaleic acid is considered by Hess and Chin (1996) in many aspects analogous to NOM. Even though large structural and compositional differences exist between the transportable DOM observed in the COx formation and polymaleic acid, the use of this artificial organic compound allows investigating three key questions: a) Are there interactions between carboxylic groups of organic molecules and clay rock in conditions close to in situ? b) Are those interactions reversible? c) What is the impact of those interactions on the transport of organic acids in clayey geological formations?

2. Materials and methods

2.1. Rock samples/water chemistry

The Callovo-Oxfordian samples originate from the ANDRA underground research laboratory (Bure, Meuse/Haute Marne, France). The sample EST 26460 comes from the subhorizontal borehole, FOR 1118, drilled at −490 m of depth. It was used as crushed rock in the sorption/desorption batch experiments. The sample EST 27346 comes from the upward borehole PAC1011, drilled at −480 m of depth. It was used in the transport experiment. The samples belong to the same region $R0_B$ and the same lithographic unit C2b1 of the formation and their mineralogical composition is assumed to be similar and close to the average composition obtained by Gaucher et al. (2004) from −489 to −474 m (Table 1). To limit oxidation and dehydration, the rock samples were stored under nitrogen atmosphere during transport and re-packed, under a vacuum of 20 mbar, in a double envelope of heat-sealed plasticised aluminium. The composition of the synthetic solution, denoted as S1 (Table 2), is derived from the calculated in situ pore water composition (Gaucher et al., 2007). The composition was simplified but the ionic strength, the relative anion–cation content and the pH were preserved. Carbonate content in the pore water is considered to be controlled by the dissolution of the calcite present in the clay samples (no addition of chemicals). Bromide was added to

Table 1
Average mineralogical composition of Callovo-Oxfordian clay between −489 and 474 m (C2b unit).

Minerals	C2b1 unit: average composition (wt.%) −489 m < depth < −474 m[a]
Illite group	14
Interstratified illite/smectite	29
Kaolinite	2
Chlorite	2
Quartz	23.5
Calcite	20.5
Dolomite/ankerite	3
Potassic feldspars	1.9
Plagioclases	1.0
Pyrite	0.75
Siderite + ferriferous minerals	1.75
Titanium minerals	0.3
Phosphate minerals	0.25
Specific surface area[b]	31.9 $m^2.g^{-1}$

[a] Gaucher et al. (2004).
[b] Grambow (2007).