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Research paper

Influence of thermal and marine water and time of interaction processes on the Cu, Zn, Mn, Pb, Cd and Ni adsorption and mobility of silty-clay peloid

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ABSTRACT

In order to improve the technical properties of raw clays for cosmetic and medical treatments, maturation processes are used for peloid preparation. As for metals, only their total concentrations are usually controlled. However, the dosage of the mobile fractions that could be absorbed by the skin is overlooked. By means of data monitoring, we assessed the risks that adsorbed and mobilized metals pose to humans through natural clay maturation. To do so, the total concentrations and mobile fractions of Pb, Zn, Mn, Ni and Cd were determined using a BCR procedure. Except in the case of Cd, metal concentrations in peloids that had been matured with thermal (TW) and marine water (MW) for 12 months were higher than those present in raw clay. The metal mobility indexes equaled zero were very low in raw clay, but they increased systematically with maturation (except in the case of Ni). The increases in metal concentration and mobility were higher in the case of marine than in the case of thermal water. We concluded that the matured mud can be toxic. Thus, the assessment of mobile metal fractions is highly recommended so as to protect human health.

1. Introduction

Clay minerals are highly demanded in cosmetic and therapeutic applications today. They are used to treat different health problems and also for skin care. However, raw clays are often not directly suitable for this usage because their characteristics are below the properties required, so their technical properties must be improved. Different maturation procedures are suggested for this purpose. These clays are usually rich in fine fractions with high specific surfaces. Due to the important surface areas to volume ratio (Forstner and Salomons, 1980), these phyllosilicates can absorb and/or adsorb important metal quantities during the maturation processes (Windom et al., 1989). Thus, the chosen clay contained a high smectite proportions. During maturation, the used thermal and marine water circulate for a long time with continuous flow through these clays and the total metal quantities brings to these clays can be appreciable. Although the metal concentrations in thermal water are very low, prolonged interaction between clay and water mixture, as well as water temperature and its characteristics, contribute to the adsorption or absorption of significant quantities of toxic elements by the peloids (Summa and Tateo, 1998; Mascolo et al., 1999; Carretero, 2002).

The therapeutic role of mud is partly due to oligo-metals with specific actions. Other elements, such as Pb and Cd, are often toxic. Thus, we believe that it is important to determine the total concentrations of toxic metals in the used peloids (matured mud). However, data regarding total concentrations are not enough to assess the degree of toxicity of said metals, since the dangers of these metals pose are strongly linked to the mobile quantities. Since the metals detected in thermal water are Cu, Zn, Mn, Pb, Cd and Ni, the evolution of the concentrations of these metals and their mobility were followed during the maturation process.

Given the foregoing, the aims of this research were first to determine the metal quantities in the initial material and to clarify the effect of thermal and marine water-smectite interaction processes on the evolution of the concentrations of metals, and second to monitor the impact that interaction processes (smectite clay-water sources) have on the evolution of the mobility of chosen metals.

2. Material and methods

2.1. Field sampling and experiments methods

The sampled clay deposit is located in the Oueslatia region, in central Tunisia, about 200 km S-W of Tunis. The ages of geologic series

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in Oueslatia region ranging from lower Cretaceous (Aptian) to Quaternary (pliocene) (Turki, 1977). The sampled Oueslatia clay (Ou) is Upper Lutetian-Priabonian age (Burollet, 1956; Comte and Dufaure, 1973). This clayey sequence has a few tens of meters. It is limited, by the limestones (Lutetien age) and sandstone series (Oligocene) (Burollet, 1956). This marl or mud series is flaky, sometimes nodular green, gray and yellow with some gypsum quantity and abundant fossils, especially Ostrea and pelagic microfauna. It is also alternated by centimetric to decimetric limestone banks in their lower part (Louhaichi, 1981).

Samples were collected from 10 plots (3 m × 3 m) which were selected taking textures, slopes and colors into account. Five samples were collected from each plot (total samples were 50). For each sample, 10 × 10 × 20 cm volume was taken. Fist, the five sediment samples from each plot were homogenized and an equivalent sample was taken. Second, the 10 equivalent samples were also homogenized to have the Oueslatia sample (Ou). This Ou sample was sieved by 2 mm stainless steel sieve and dried at 40 °C (AFNOR, 1979).

Thermal water (TW) and marine water (MW) were sampled in clean polyethylene bottles from Korbous city, about 68 km S-E of Tunis. For analytical purpose, water samples were kept cool at 4 °C.

For each experience, about 3 kg of Ou sample were stored in cubic plastic containers, partially covered to avoid contamination by atmospheric dust. To can examine the performance and effectiveness of the Oust clay (Ou) in adsorption of metals from the two water origins used in maturation, we must do it at the same conditions since the results studies of adsorption process showed that the temperature had strong influences on the adsorption thermodynamic parameters (e.g. Kubilay et al., 2007). Thus, the first experiment (Ou TW) was done in Korbous thermal center, with thermal water of Echfa spam (meaning healing thermal) where water temperature was about 57 °C. The second experience (Ou MW) was performed with marine water that was placed in a thermostat in order to have always about 57 °C (the same temperature of thermal water). Thermal and marine water flowed continuously at ×LHour^{-1} through these clays which were periodically stirred. Forth two cases, the experience was replicated three times and the maturation period was 12 months. Homogeneous samples were taken after each interaction period of 1, 3, 6 and 12 months. Since the trend evolution for the first 6 months was the same, only the results corresponding to 6 and 12 months of maturation were presented.

2.2. Analytical methods

The water temperature and pH were measured in situ using a HI 8424 microcomputer pH meter. Specific conductance was measured with a HI8633 microcomputer electric conductivity meter. In the laboratory, water samples were filtered with 0.45 μm Millipore cellulose membrane filters and stored at 4 °C to be analyzed. Their contents of nitrate (normes ISO 7890-3), of chlorides (Cl) by Mohr method, of PO$_4^-$ by the formation of the complex phosphomolybdique based on the reaction of the orthophosphates ions with the molybdates ions; this acidic complex was reduced by the ascorbic acid and dosed by spectrophotometer in the length 880 nm (Rodier et al., 2016). The cations K, Mg, Na and Ca were determined by atomic absorption type Perkin Elmer associated to graphite furnace HGA900 type major and trace elements were measured using Atomic Adsorption Spectro-Photometry (AAS 200) Perkin Elmer type.

The mineralogical analysis of total rock (powder) is carried out by X-ray diffraction (XRD) SIEMENS D-5000 type with a scanning speed of 1°/2θ min and Cu-Kα radiation (40 kV, 20 mA) from 0° to 70° of the total fraction (Schultz, 1964; Van der Marel, 1966). The clay fractions (≤ 2 μm) were scanned at the same working condition from 0° to 30°. Three oriented aggregate glass slides are prepared: the first is "normal glass", the second is glass heated at 550 °C during 2 h, and the last one is glass treated with ethylene-glycol.

Granulometric analyses were performed by means of a series (AFNOR, 1957). The < 2 mm fraction was analyzed by wet sieving and the < 63 μm was analyzed by X-ray analyzer "Aggregate Meter Laser" type MAVERN (Delaume et al., 1991). As a lot of particles agglomerations were observed, pre-agitations of the sample in ultrasonic basin were always assured.

Total Cd, Pb, Zn, Mn, Cu and Ni contents were determined as follows: 0.5 g of each sample were attacked by hydrofluoric acid, perchloric acid, nitric acid and mL HCl at 180 °C (sand bath) and dissolved in vials with 100 mL of distilled water (AFNOR, 1979). Total metal concentrations were analyzed with Atomic Adsorption Spectro-Photometry (AAS 200) Perkin Elmer type with graphite furnace and with inductively coupled plasma-mass spectroscopy (ICP-MS) from the Technical Center for Borj Cedria.

In order to extract the mobile metal fractions from 1.0 g of prepared mud powder (sediment, peloid), Community Bureau of Reference (BCR) protocol was used (Ure et al., 1993; Davidson et al., 1998; Rauret et al., 2000). Four steps extractions were obtained: F1 (Exchangeable and carbonate bound Fraction): 0.11 molL^{-1} of AcOH; F2 (Fe and Mn oxide bound Fraction): NH$_2$OH-HCl (0.1 molL^{-1}, pH 2); F3 (Organically and sulfur bound Fraction.): H$_2$O$_2$ (8.8 molL^{-1}, pH 3.2) and AcONH$_4$ (1 molL^{-1}, pH 2) and F4 (Residual Fraction): digestion (HCl–HNO$_3$) + HF (150 °C-2 h). After each extraction, the suspension was centrifuged at 6000 rpm and analyzed by Atomic Adsorption Spectro-Photometry with graphite furnace. To ensure the accuracy and reproducibility of each extraction, a blank sample and BCR-701 (reference material) were used. The result of each analyzed sample was accepted only when the value stood below the detection limit and within 2% of the certified value. The statistical analysis of the data was performed using STATISTICA version 6 software. The statistics reported were the arithmetic mean, maximum, minimum and standard deviation.

3. Results and discussion

3.1. Water and clay characterizations

Echfa thermal water temperature was about 57 °C and its pH and salinity were 6.5 and 15.8 gL^{-1}, respectively (Table 1). The marine water was hypersaline (dry residue = 53.6 gL^{-1}), with a relatively low temperature (25 °C). The in-situ pH was basic (8.3) and had a high electric conductivity (54 mScm^{-1}). Concentrations of Cu, Zn, Mn, Pb, Cd and Ni stood at 0.06, 0.032, 0.022, 0.098, 0.068 and 0.019 mgL^{-1}, respectively, for thermal water, and at 0.91, 5.56, 1.51, 0.34, 0.72 and 0.37 μgL^{-1}, respectively, for marine water (Table 1).

The two water sources differed in their pH, EC, T and trace metal

Table 1
Average values of physicochemical parameters of thermal and marine used water.

Parameters	Thermal water	Marine water
pH	6.5	8.3
T (°C)	57	25
E.C. (mScm^{-1})	16.1	53.6
R.S. (mgL^{-1})	11,970	40,180
NO$_3^-$ (mgL^{-1})	1.95	25.5
PO$_4^-$ (mgL^{-1})	0.021	0.017
Na$^+$ (mgL^{-1})	2650	10,600
K$^+$ (mgL^{-1})	69	400
Ca^{2+} (mgL^{-1})	1282.56	641.281
Mg^{2+} (mgL^{-1})	684.24	15,608.72
Cl$^-$ (mgL^{-1})	5005.5	21,300
Cu (mgL^{-1})	0.006	0.91
Zn (mgL^{-1})	0.032	5.56
Mn (mgL^{-1})	0.022	1.51
Pb (mgL^{-1})	0.098	0.34
Cd (mgL^{-1})	0.068	0.72
Ni (mgL^{-1})	0.019	0.37