

Sorption of Pb(II) from aqueous solution by Greek attapulgite clay

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Attapulgite clay mined in Grevena, Greece is a readily available material with proven efficiency in the treatment of heavy metal contaminated soil [1]. Here, we present results of laboratory batch experiments aiming to compare raw and heat treated attapulgite clay for the adsorption of Pb(II) from aqueous solution.

Powdered attapulgite clay was supplied by Geohellas S.A. Samples were heat treated in muffle at temperatures of 130, 330, 500 and 800 °C for 4 hours. P-XRD analysis before and after heating at different temperature revealed that attapulgite crystal lattice gets destructed from 330 °C -a lower intensity of the main peak is observed. The comparative study of Pb adsorption efficiency of heat treated and non-treated material was performed for adsorbent dose of 2 to 15 g/L, initial Pb(II) concentration 50 mg/L, maximum shaking time 2h and pH 4. The effect of ionic strength was studied by varying the concentration of NaNO₃ from 0 to 0.5 mol/L. All experiments were carried out in a chamber set at 22 °C.

At least 90% of the metal was retained with a dose of adsorbent of 5 g/L for all tested materials while an increase in the amount of dose of adsorbent to 10 g/L reached almost 100% retention for all materials. With the exception of attapulgite clay heated at 800 °C, maximum adsorption was achieved within the first 5 minutes of reaction. A decrease in adsorption was observed as the concentration of NaNO₃ was raised probably due to competition between Na⁺ and Pb²⁺ for the adsorption sites.

Complexation and ion exchange are probably the main adsorption mechanisms at the studied pH. Heat treatment induces dehydration (zeolitic H₂O loss) at low temperatures (e.g. <150 °C) and dehydroxylation at higher temperatures (350- 510 °C), while the complete destruction of the clay occurs at temperatures over 550 °C [2]. Our data imply that significant changes in adsorption capacity of the used clay are related to alteration of nanoporosity and reduction of its specific area after calcination in temperatures > 550 °C.

[1] Zotiadis *et al* (2012) *J. Geotech. Geoenviron. Engineering* **138**, 633-637. [2] Galan and Singer (2011) *Developments in Clay Science* **3**, p.15.

Temperature determination from speleothems through fluid inclusion and clumped isotope techniques

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Traditionally carbon and oxygen isotope analyses have been used to unravel the paleoclimate history of speleothems. However, the δ¹⁸O of a carbonate is dependent both on the variations in temperature and the δ¹⁸O of the water. In order to solve for the second unknown, an additional proxy is needed and such proxies include fluid inclusions, and/or clumped isotopes. Here we present results from both fluid inclusion and clumped isotope analysis on speleothems from the Bahamas.

Fluid inclusion isotope analysis is the analysis of water filled cavities in speleothems. These cavities preserve drip water at the time of formation and isotopic analysis provides information on the formation water (δ¹⁸O_w) and temperature can be calculated. Here we present a new technique utilizing cavity-ring down spectroscopy (CRDS) for δ¹⁸O and δD analysis of fluid inclusions and compare the acquired data to that measured on the Amsterdam Device, a crusher system linked with an IRMS developed at the VU University Amsterdam [1]. Our results demonstrate an average standard deviation on fluid inclusion isotopic analysis of 0.5 ‰ δ¹⁸O and 2.0 ‰ for δD, which is comparable to other IRMS fluid inclusion analytical methods [1].

In addition to fluid inclusions, clumped isotope analysis of the calcite has been conducted. Our results support an offset between the δ¹⁸O_w measured on the fluid inclusions and the δ¹⁸O_w calculated using the temperature calculated from Δ47. This is similar to the offset observed in the literature for speleothems [2]. To better elucidate the drivers of the Δ47 offset, cave monitoring has been conducted in the Bahamas, including *in situ* calcite farming. Preliminary results from the cave monitoring support an increasing Δ47 offset along a growth band for samples which are thought to precipitate in equilibrium.

[1] Vonhof *et al* (2006) *Rapid. Comm. Mass Spec.*, **20** 2553-2558. [2] Kluge, T., Affek, H. P (2012) *Quaternary Science Reviews*, **49** 82-94.