



Characterization of Clay Deposits from Egypt and Assessment of their Potential Application for Waste Water Treatment. How Dissolved Organic Matter Determines the Interaction of Heavy Metals and Clay Minerals.

Y.B. Refaey Mohammed

Summary in English

There is an urgent and increasing global need for purification of drinking water and wastewater, given the human and environmental health concerns caused by contaminated by heavy metals (HMs) and organic pollutants. In developing countries, such as Egypt, sophisticated techniques are often not widely available, using natural low-cost local materials as sorbents is therefore an important alternative approach. Pliocene clays from Egypt have a unique physico-chemical properties and these materials may be alternative scavengers for toxic HMs, although their potential application in wastewater treatment technology has not yet assessed because of a lack of information regarding their adsorption/regeneration characteristics.

The aim of the present study was firstly to assess the potential for using Pliocene clay deposits from Egypt in inexpensive purification of industrial wastewater and irrigation water polluted with HMs. Secondly, this thesis also addresses the remediation of the sorbents contaminated with HMs, as this is a crucial step in the regeneration of the sorbents for reuse in multiple cycles of metal adsorption/desorption and/or their clean-up prior to disposal.

The main objectives of the present study are:

- 1) To identify and characterize the different clay mineral types in the context of their application in local wastewater treatment
- 2) To shed light on the paleoclimatic conditions that prevailed during formation of the sediments and their influence on the sediment's composition.
- 3) To assess the influence of OM-coating on sorbent materials on their adsorption of Cu, Ni and Zn.
- 4) To unravel the effect of the timing of the addition of DOM on the competitive adsorption of Cu, Ni and Zn onto different sorbent compositions in static and kinetic systems.
- 5) To quantify the fate and transport of metals in different mineral sorbents as well as gain insights into leaching behavior under actual environmental conditions.

Large reserves of Pliocene clay deposits are distributed along River Nile banks in the Sohag area, Egypt. The suitability of clay materials for potential water clean-up is normally governed by their physico-chemical properties, such as cation exchange capacity (CEC), specific surface area (SSA), micropore volume, and the clay mineral compositions. To this end the Pliocene clay samples were sampled in the Egyptian Sohag region from four different areas (Al-Kwamel, Al-Kola, Al-Ahaywa and Wadi Qasab). The Pliocene clay were characterized by SediGraph analysis, X-ray diffraction analysis through different treatments, ICP-OES analysis and CO₂ gas adsorption (**Chapter 2**). The tested sorbent materials was dominated by fine particles (i.e., mainly silt and clay, 85-98%) and consisted almost exclusively of smectite (59-94%) and kaolinite (4-38%) minerals. In addition, the mineral assemblages in Pliocene deposits suggest an origin from chemical weathering conditions under warm and semi-arid conditions

(Chapter 2). Furthermore, the Pliocene clay showed high values of CEC, SSA and micropore volume. It seems that these physico-chemical properties of these clay materials as well as the type and amount of smectites might be potentially useful in high added-value markets, e.g., as environmentally friendly and inexpensive raw material for waste water treatment. However, to further examine such applications, additional investigations should focus on unraveling the sorption mechanisms between HMs and sorbent components. In addition, as natural dissolved organic matter (NDOM) is often present either in the wastewater itself (e.g., industrial and agricultural effluents) or in the soil (e.g. due to manuring), the presence of DOM can have a significant influence on the removal of HMs from the wastewater. Batch adsorption experiments were performed to determine equilibrium partitioning between the HM ions and the soil adsorption sites (**Chapter 3**). The batch sorption experiments were designed to determine the adsorption of HMs to the materials over a range of HM concentrations. Our results showed that the strong adsorption of the HMs and the sorption isotherms were well described by the initial mass (IM) isotherm model. The large retention of Cu over both Zn and Ni in this research revealed that Cu was mostly bound through inner-sphere complexes on mineral-phase whereas Ni and Zn were found to bind predominantly through electrostatic interactions. This results underline the importance of presence of DOM and its timing of addition on the affinity of Cu, Zn and Ni for the tested sorbent materials. The sequential addition of DOM to sorbent material resulted in reduction in the affinity of tested HMs due to the blocking of binding sites on the surface of sorbents, in particular when hydroxides are part of sorbents. In contrast, concurrent addition resulted in enhancement of all metal adsorption affinity. This chapter concluded that readily available and abundant natural clay materials has important implications for removing a large percentage of Cu, Zn and Ni from wastewater.

Although batch experiments are less time consuming and cheaper than continuous experiments, they do not simulate actual environmental conditions or allow time-dependent monitoring of contaminants leaching from sorbents and waste materials. Therefore, column experiments were performed (**Chapter 4**) which focused on unraveling the mechanisms of such interactions, specifically in quasi-realistic operational settings. Using the column approach, information on the kinetics of adsorption of HMs were determined by quantifying the adsorption capacity for the HMs. Three different scenarios were employed in this research: columns were loaded with Cu, Zn and Ni only (control), first loaded with DOM followed by Cu, Zn and Ni, and DOM, Cu, Zn and Ni simultaneously. The HM mobility was explored in a set of continuous flow column experiments using a well-defined natural sorbent amended with goethite, birnessite and/or smectite. The resulting breakthrough curves were fitted to a modified dose-response model to obtain the adsorption capacity (q_0). Our results revealed moderately enhanced q_0 of Cu (8-25%) compared to the control without DOM, except for the goethite-amended sorbent that exhibited a 10% reduction due to the blocking of binding sites. Meanwhile, for both Zn and Ni sequential addition of DOM reduced q_0 by 1-36% for all tested soils due to preferential binding of Zn and Ni to mineral phases, in a line with our previous findings in chapter 3. In contrast, concurrent addition of DOM and HMs resulted in a strong increase of q_0 for Cu, Zn and Ni and all tested sorbents compared to the control: by 141-299% for Cu, 29-102% for Zn and 32-144% for Ni. Timing of DOM addition with respect to that of HM therefore has to be taken into account when assessing the impact of HM pollution on soils through polluted irrigation- or wastewater in a system where DOM also enters the soil (e.g. agricultural irrigation in combination with manuring). Similarly, both the presence of DOM and timing thereof should be taken into account in design of strategies where soil constituents, e.g. clay minerals, are used to clean-up HM

polluted waste water. The maximum metal adsorption capacity for Cu, Ni and Zn in the column experiments (**Chapter 4**) was higher than that in the batch experiment (**Chapter 3**) indicating that other metal retention mechanisms such as precipitation could be involved in addition to adsorption (**Chapter 4**). Therefore, both column and batch approach are needed for assess the adsorption capacities and removal efficiencies of HMs.

The remediation of the sorbents contaminated with HMs is a crucial step in regeneration of the sorbents and/or their clean-up prior to disposal. Furthermore, it is important to assess the influence of the presence of natural DOM on the regeneration process. To this end, clay mineral-rich column material of varying composition was previously loaded with Cu, Zn and Ni only; first with DOM followed by Cu, Zn and Ni; or DOM, Cu, Zn and Ni simultaneously (**Chapter 4**) and these were used as basis for a set of column desorption experiments (**Chapter 5**). The columns were leached with 0.001 M CaCl₂ in water as a control eluent and 0.001 M CaCl₂ in DOM-containing water as a treatment eluent. The removal efficiency (*E*) of the HMs was calculated from the numerical integration of the regeneration curves. Our results revealed that Ni and Zn that are predominantly bound through outer sphere complexes showed substantial removal of up to 81% (Ni) and 89% (Zn) through simple cation exchange with Ca²⁺. As a result, the removal efficiency of Ni and Zn was reduced when eluted with CaCl₂ dissolved in DOM instead because of binding of exchangeable Ca²⁺ to the DOM. In contrast, removal of predominantly inner-sphere complexed Cu²⁺ was increased by up to 74% when eluted with CaCl₂ dissolved in DOM because of inner sphere complexation of Cu with the DOM. When columns were first loaded with DOM followed by HMs, the highest removal efficiency was achieved using CaCl₂ dissolved in DOM (up to 69% for Zn, 74% for Ni and 78% for Cu). This indicates a partitioning of HMs bound to DOM adsorbed on the solid phase to DOM in solution. However, when columns were loaded by HMs and DOM simultaneously prior to desorption, removal efficiencies were low for all metals (2-25% for Cu; 11-19% for Zn; and 8-17% for Ni depending on clay mineral composition) regardless of whether desorption treatment consisted of CaCl₂ solution in water or in DOM. This indicates that column loading by HMs and DOM when added simultaneously takes place to a large extent through irreversible co-precipitation rather than adsorption. Upon flushing with the control eluent, hydroxide-rich sorbents (soil-birnessite and soil-goethite) showed a low release of tested HMs (**Chapter 5**) and this due to the previously observed large affinity of all tested metals for the birnessite-rich sorbent. In contrast, the soil-smectite sorbent showed a large release for Cu, Zn and Ni which can be explained by the fact that smectite-rich soil is composed of aluminosilicate minerals, which favored cation exchange of metal ions during adsorption. These results have important consequences for the regeneration potential of clay minerals used in wastewater treatment aimed at removal of HMs, as they indicate that such potential will be significantly reduced when the water to be treated is rich in DOM. In contrast, for natural soil systems our results suggest that when HMs enter a soil together with DOM, e.g. as a result of the use of HM-rich manure in agricultural fields, the mobility of the HMs will be lower than expected from interaction dynamics of HMs and clay minerals alone. This confirms that Cu-loaded soils are more susceptible to remobilization of Cu when DOM rich water infiltrates, whereas Ni and Zn-loaded soils are more susceptible to remobilization when cation rich water infiltrates. In circumstances where precipitation plays a role (scenario C) additional measures would be needed, for instance acidification to redissolve precipitates.

The synthesis of the findings of this thesis (**Chapter 6**) discusses the potential application of local Pliocene clay in wastewater clean-up and impact of the insights gained on science and society. Our findings provided new data about low-cost and simple wastewater treatment technologies which can be designed to provide clean water to meet the needs of a growing economy and to protect the environment. Application of Pliocene clays in wastewater treatment can reduce the load of HMs that can pose threat to ground water and soil. As result, large amount of clean water can be provided for irrigation of the new reclamation area in Egypt. Further, this research present a new insights about presence of DOM and its timing of addition in regulating the mobility of HM as this can has an important impact either in treatment technology or protecting groundwater reservoirs from metals pollution.

In general, the data presented in our present study forms a foundation for the potential removal of HM from wastewater using the Pliocene clay material in question. This research work fills some of the existing knowledge gaps on the adsorption mechanisms of Cu, Zn and Ni by clay materials in the presence of DOM and their implications for wastewater treatment technology. The insight in the obtained present work provides new data about the impact of timing of addition of DOM on the wastewater treatment. Nevertheless, further work on the regeneration of exhausted sorbent materials and enhancement of the adsorption capacity of Pliocene clay has to be done to further develop this method.