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Devonian Clay Modification for the Improvement of Heavy Metal Sorption Properties

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Abstract **– Contamination with heavy metals is an important problem as bioaccumulation effects of those are creating direct and indirect hazards to environment and human health. Contaminated soil remediation can be done by various technologies and the use of soil amendments is one. Clay modification experiments were done to study heavy metal sorption from spiked solutions and leaching from contaminated soils. The aim of this paper is to give an overview of Devonian clay modification possibilities in order to improve heavy metal sorption capacity and immobilization options. Modification was done by using Ca, Na salts, HNO_3 (protonated forms), Fe-oxyhydroxide. Research has shown better sorption due to improved properties of clay through the process of modification. Kinetic experiments have shown good results of Pb removal by using $CaCl_2$ modified clays as the sorption capacity increases comparatively to raw and other types of modified clay. Modified clay as amendments in spiked soils also show negligible improvement of heavy metal immobilization properties comparably to raw Devonian clays. More detailed further research in order to prove batch experimental results should be done in the future.**

Keywords **– remediation, immobilization, contamination, clay, groundwater and soil quality.**

I. Introduction

The quality of soil and groundwater is fundamentally important and different technologies are used for the remediation of diffuse and point sources generated by industrial as well as natural contamination. Development of soil and groundwater remediation technologies is a matter of great importance to eliminate historically and currently contaminated sites as contamination causes loss of land as a resource [1]. Heavy metals are toxic and hazardous for human health and environment; sources are natural processes as volcanoes and erosion of rocks as well as anthropogenic sources as industry, mining, diffuse air pollution precipitation and other [2]. Toxic heavy metal ions are non-biodegradable and tend to accumulate in living organisms, causing severe disorders and diseases [3-5]. Overexposure to heavy metals including lead promotes the development of many occupational illnesses. Occupational Safety and Health Administration (OSHA) introduced a five-year strategic plan in order to diminish the hazardous impact of lead on employees by 15%. As this is a question of concern for threats not only directly to people's health and environment in general, sources of industrial and natural pollution should be analyzed and prevented [6]. There are several physicochemical methods available for heavy metal ion removal from aqueous solution, including chemical precipitation, reverse osmosis, filtration, solvent extraction, electrodeposition, electrodialysis, ion exchange and adsorption, etc. [4; 7; 8-12]. Among these methods, adsorption is considered as an effective method for heavy metal ion removal from aqueous solution due to its cost-effectiveness and high efficiency [3; 11]. Soil amendments often can be used as one of the *in-situ* technologies for the rehabilitation process of contaminated soil. Besides the mining and metal related industries, other sources are metal-laden effluents as leather tanning, batteries, glassware, ceramics, electroplating, paint and photographic industry residuals [13]. Fate of heavy metals including lead is affecting food chains, not only human [14]. Natural zeolites are not as good as synthetic ones, but clay minerals in many cases can be used as good sorbents for heavy metal removal, wastewater can be treated much cheaper with a good efficiency [15]. Zeolite (clay) is a class of alkaline porous alumo-silicate, with a negative charge [16], neutralized by introducing exchanged cations in the structure sites itself [17;18]. Zeolites are being developed, because those are diminishing the solubility and thus the biological availability of metals: salts and complexes, also oxides and metal-carbonate precipitates are formed [19;20]. Research nowadays is concentrated to zeolites as effective treatment agents because of lower costs of them, sorbents as natural and modified clay can be used for groundwater and wastewater treatment from arsenic, tungsten, uranium, selenium, lead and many other elements with toxic impact properties [21]. Comparatively a lot of research has been dedicated to organo-modified clays and surface modified clays, described in review [22]. Acidic treatment can be one of the solutions [23]. Calcium and magnesium is removed, iron and aluminium content of clay minerals are partially removed. Chemical composition through hydrothermal reactions in acidic solutions is changing together with the mineralogical structure of clay minerals. Montmorillonic clays can be more effectively treated compared to kaolinic ones [24]. Sometimes sorption capacity diminishes during acidic treatment [25]. Surface area and pore volume in montmorillonite can diminish when acidic treatment is applied [26]. The mass of clay also decreases by 25–30% through this type of treatment. Devonian clays used in these series of batch tests as soil amendment were studied in [27], where stability constants of ligands were studied considering the contamination of copper in soils. This study was dedicated to clay modification by nitric acid as well as Ca and Na salts in order to prepare surface modified forms and their potential towards nickel [Pb(II)] sorption considering the ion exchange mechanism. Lead was selected as a model pollutant as its salts are used in many industrial applications. Pb(II) is not essential for living organisms and long term exposure to higher Pb(II) concentrations may lead to various health problems of carcinogenic and teratogenic character included. The sorption kinetics on raw and modified clay was examined and the role of functional groups in Pb(II) sorption was discussed based on the data obtained from Fourier transform infrared spectral (FTIR) analysis and other studies.

The aim of this work is to evaluate the use of natural modified zeolites which can be possibly used for remediation of soil and waters contaminated with heavy metals (sewage or groundwater). Improvement of modified clay sorption properties in aquatic phase would show the potential and efficiency of use of innovative materials in remediation industry.

II. Materials and Methods

A. *Soil samples for leaching experiments*

Mineral soil samples were collected in field works from 10 soil profiles of varied soil granulometric composition or soil texture, composition and properties are described in previous studies [28]. Devonian zeolite (clay) amendments are taken from the Lode quarry in the northern part of Latvia, these clays are made of illite with significant content of kaolinite.

B. *Modification of Devonian clay*

Devonian clay was modified by iron oxide-hydroxide. For $Fe(OH)_3$ preparation 250mL of 0.25M and 0.5M $FeCl_3{\cdot}6H_2O$ were amended with 250mL of 3M NaOH for three hours. Washing and decanting was repeated three times and 100g Devonian clay was mixed in $Fe(OH)_3$ dispersion. Mixing, filtration and washing with deionised water is repeated, the drying for 12h is done at room temperature, at the end the drying is fulfilled to the end in Gallenkamp Plus II oven for 4h in temperature 60ºC.

C. *Samples preparation for leaching tests*

Afterwards samples were sieved again and weighted for two different procedures: 10 different samples of soil were taken, 10 were amended with 10% (m/m) of raw Devonian Lode clay, 10% (m/m) Devonian modified clay with 5%FeOOH and 10%FeOOH, respectively. All 40 samples were spiked with lead nitrate in order to apply known contamination of 100 mg kg^{-1} in those.

D. *Leaching tests.*

During the batch leaching test vessels were filled with distilled water till a liquid-to-solid-ratio 10:1 (referred to the dry sample). Under continuous agitation at the rate 130 RPM (Grant OLS200) the batch leaching test was done for samples with agitation time periods of 24 hours. The pH_{H2O} level was measured for all samples after each period using Beckmann pH meter 340. After this time the solution is let to set down for about 10 minutes. For the determination of inorganic compounds the solution was filtered through a 0,45µm filter. The concentration of Pb in the leached eluate was determined by Atomic Absorption Spectrometer (AAS) (GBC 932 Plus, Perkin Elmer) with deuterium background correction and a spectral slit width of 0.5 nm for Pb and wavelength 283.31 nm.

E. *Kinetic experiments*

Modification of Devonian Lode clay was carried out in several ways to compare results of sorption. First type of modification was protonation of the clay – 5g of raw clay was added in 500 mL of 0.2M HNO_3 solution, second type – 5g of sorbent was added in 500mL of 0.5M $CaCl_2$, the third - 5g of sorbent was added in 500mL of 0.5M NaCl. Kinetic experiments were performed with 100 mg l^{-1} lead solution with pH adjusted at 5-5.1. Modified clays were dried in Gallenkamp Plus II at temperature 45°C for 8h (Fig.1).

Fig. 1. Modified Devonian clay - Na modified and Ca modified for sorption kinetics tests at Linnaeus University laboratory

Operating in batch mode at room temperature 0.025g of every type of modified clay sorbent was added to each flask for kinetic experiments. The solution pH was maintained at 5.0 throughout these experiments. Experiments were carried out in 50mL capped Erlenmeyer flasks containing 50 mL Pb (II) solution and 0.025 g raw and modified clays by shaking (130 rpm) (Grant OLS200) at 22°C various time periods of 5,10,15,30,60,120,180,240,300,360,480 and 1440 minutes. After adjusting the pH, no further adjustments were performed and final pH was documented after experiments. After achieving equilibrium, solutions were separated by filtration through cellulose acetate membrane and analyzed for residual lead content by atomic absorption spectrometry (AAS).

III. Results and Discussion

A. *Leaching experiment results.*

Leaching experiment was performed in order to simulate processes in widely distributed soils in Latvia under natural conditions in batch mode without impacts of heavy rains or acid precipitation. One set of experiment is showing leaching from raw soil.

The pH_{H2O} values of all samples were essentially of natural neutral conditions 5.0-6.7 and during the agitation pH_{H2O} was increasing or not significantly changing in all cases, this trend is dictating the behaviour of lead during the leaching experiment. Table I depicts results of leaching from soils of different texture, where there are: no amendments added, raw

Devonian clay added, and two different types of modified clay with FeOOH added. Results show that lead ions are immobilized more when more clay to soil is added thus proving general hypothesis of heavy metal ion immobilization in soils with higher cation exchange capacity. General trends in the table are that soils with higher content of aleiritic and clayey particles with no amendment diminish the leaching of lead under natural pH conditions. If the contents of clayey particles are proportionally increased in the sample, then even less leaching of lead happens. There is little increase of immobilization of lead ions in soil if modified Devonian clay is added with FeOOH. Immobilization efficiency increases by 5-10%, but more advanced experimental work must be applied to prove first pilot results. There is no significant change of immobilization efficiency if more FeOOH is applied in the clay, also the slight differences of results in the experiment with values less than 1 mg L^{-1} can happen under the influence of many circumstances as homogeneity of samples, small scale clay mineral dispersion in various samples, modification irregularities and many more. However, in general leaching of lead from spiked samples with 100 mg kg^{-1} contamination is diminished when Devonian clay is amended and efficiency increases if modified Devonian clay with FeOOH is applied. Benefits of Devonian clay modification with FeOOH for lead immobilization efficiency improvement under natural pH conditions are relatively negligible and disputable, therefore other methods for modification should be found for applied environmental soil remediation projects.

B. Kinetic experiments results

Experimental performance was designed in order to evaluate the sorption of lead from contaminated 100 mg L^{-1} solution by using three types of Devonian modified clays and comparing them with untreated raw clay. Such types of kinetic experiments are a good indicator of sorption properties for materials, which possibly would help the remediation process in aquatic environment, diminishing deleterious impact of toxic heavy metals to environment by migrating further from the source site. Results of sorption kinetics are provided in Figure 2, where the raw clay achieves equilibrium sorption in 6 hours, afterwards the effect is insignificant. Sorption of lead onto raw clay achieves 30-35 mg of lead for g of sorbent under natural conditions. Sodium modified clay achieve higher sorption in the first hour than compared with the raw clay, but the effect is not continuously growing with time.

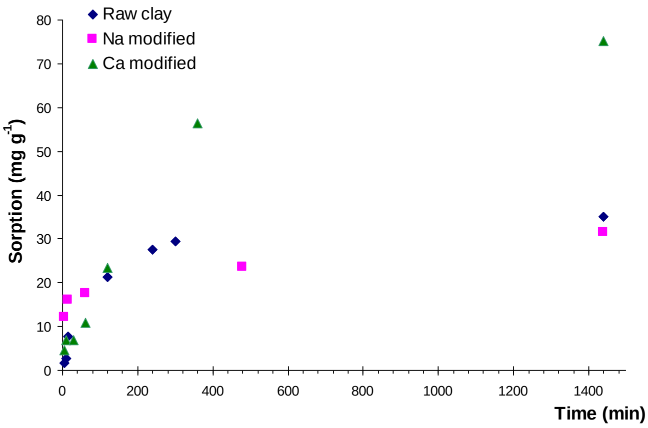

Fig. 2. Lead sorption by Devonian clay raw, Na modified and Ca modified

There is almost no difference for raw and Na modified clay in terms of sorption efficiency in the long term. Protonated forms did not show good results for interpretation thus more detailed analysis should be done in further experimental series; those are not put in a diagram in Fig. 2. It seems that protonation of clay promotes complicated sorption-desorption pair-process and other types of column testing would be a good solution for having more reasonable explanations. The most effective results were yielded from Ca modified clay testing and the effect is significant. Ca modified clay have growing sorption curve and in 24 h it reaches around 75 mg g^{-1}. Calcium modified clays are reasonable for use as the lead sorption agent for wastewater treatment and can be chosen for further analysis of feasibility in different environmental conditions.

TABLE I

LEACHING EXPERIMENT RESULTS FROM SOILS OF DIFFERENT TEXTURE AMENDED WITH RAW AND MODIFIED DEVONIAN CLAY*

Nr.	pH_{KCl} mean value	Soil textural classes	No amendment (mg kg^{-1})	10% Devonian raw clay amended (mg kg^{-1})	10% Devonian 5%FeOOH modified clay amended (mg kg^{-1})	10% Devonian 10%FeOOH modified clay amended (mg kg^{-1})
1	4.97	sandy loam	1.54	0.98	1.05	1.00
2	5.69	sandy loam	1.76	1.14	0.98	0.99
3	4.52	sandy loam	1.22	0.85	0.56	0.61
4	4.88	sandy loam	2.08	1.65	1.45	1.58
5	6.08	Loam	0.45	0.53	0.44	0.48
6	5.10	Loam	1.09	0.67	0.60	0.42
7	6.54	Loam	0.64	0.49	0.47	0.49
8	5.24	silt loam	0.39	0.48	0.31	0.31
9.	5.75	Clay	<0.2	<0.2	<0.2	<0.2
10.	4.23	Sand	2.45	1.67	1.55	1.46

* - leaching mass loss from filtered soil samples which are found in eluates were measured in units mg l^{-1}, but in Table are given recalculated with rate L:S 10:1 and therefore are given for comparison also in mg kg^{-1} by arithmetically multiplying with 10

IV. CONCLUSIONS

Two types of different test series for leaching and kinetics were done in order to test lead immobilization properties for various types of Devonian clays modified with FeOOH, Ca and Na salts, HNO_3. Leaching tests have shown minor effect of FeOOH modified clays contaminated with lead soil treatment. Kinetic test have proven that the most effective results for lead sorption from aqueous spiked solution under natural conditions were achieved by using Ca salts for Devonian clay modification. Sorption reached 70-75 mg of lead per gram of sorbent thus the economic feasibility of local Latvian clay use in heavy metals treatment can be foreseen if experiments are done further in detail.

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