

REMOVAL OF LEAD (Pb²⁺) AND ZINC (Zn²⁺) FROM AQUEOUS SOLUTIONS BY ADSORPTION ON VERMICULITE FROM ASKOS AREA IN MACEDONIA (NORTHERN GREECE).

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ABSTRACT

The lead and zinc removal from their aqueous solutions by vermiculite samples from Askos area, Northern Greece, was studied using a batch type method. Askos vermiculite is mainly consisted of mixed-layer phyllosilicates. A standard vermiculite sample from Kent, Connecticut was also used for comparison reasons. The concentration of the solutions used varied between 100 and 2000mg/L. The maximum uptake capacity of the Askos vermiculite for lead and zinc was found to reach 95% and 96% from solutions containing 100mg/L, respectively. Much lower uptake capacities: 37% for lead and 76% for zinc were found for the Kent vermiculite. The experimental results showed that the Askos vermiculite exhibited an acceptable high capacity for removing metal ions from aqueous solutions. Thus, this untreated and low-cost mineral can find use in purifying heavy metal wastewaters. The uptake distribution coefficient (K_d) showed that the relative lead and zinc removal is higher for initial concentrations below 1000mg/L. Batch adsorption experiments conducted at room temperature (22±1°C) showed that the adsorption patterns followed the Freundlich isotherm model. The heavy metal (Pb²⁺, Zn²⁺) removal is a rather complicated phenomenon related both to the aqueous chemistry of the elements and the interaction of their cationic species with the used materials. The removal procedure can be attributed to different processes such as ion exchange, adsorption, and precipitation.

1 INTRODUCTION

Nowadays, the development of industrial units very close to big cities has caused several environmental problems.

Heavy metals are a notable source of pollution both in the aquatic and soil environments. Heavy metals are defined as those metals and metalloids generally considered being of sufficient distribution and abundance as to be in some way environmentally or biologically significant as a toxic substance (Lester, 1987). Such are lead (Pb), chromium (Cr), cadmium (Cd), nickel (Ni), and zinc (Zn). High concentrations of them in the environment may constitute long-term health risks to ecosystems and humans.

The presence of heavy metals in an aquatic environment has been known to cause several health problems to animals and human beings (Irving Sax, 1951). The heavy metal levels in waste water, drinking water and water used for agriculture must be decreased at least to the maximum permissible concentration (Mitrakas, 1996). Precipitation, ion exchange, solvent extraction, and sorption on activated carbon and other sorbents are conventional methods for the removal of heavy metal ions from aqueous solutions (Gonzales-Davilla et al., 1990, Huang et al., 1984, Kahashi et al., 1983, Naylor et al., 1975) but due to high maintenance cost, these methods cannot be applied in the developing countries (Viraraghavan et al., 1991). The sorption process is used especially in the water treatment field and investigation has been made to determine the retention capacity of natural materials, which are inexpensive and good sorbents.

Such natural materials are clay rocks and minerals and several investigations have been made to assess their ability to adsorb toxic elements such as radionuclides, rare earth elements and heavy metals or to improve their effectiveness. Besides different mechanisms of sorption on clays (natural or modified) have been proposed (Scheidegger et al., 1996, O' Day et al., 1994). Rozic et al. (2000) investigated the removal of ammoniacal nitrogen from water by treatment with clays and zeolites. Mellah et al. (1997) studied the adsorption of zinc (Zn) by natural bentonite, while Stanton et al. (1997) used montmorillonite and illite samples to adsorb cesium (Cs). Auboiroux et al. (1996) studied the fixation of Zn^{2+} and Pb^{2+} by a Ca-montmorillonite. Chegrouche et al. (1996) studied the ability of bentonite to adsorb lanthanum (La) while Brigatti et al. (1995) used montmorillonite to remove lead (Pb^{2+}) and zinc (Zn^{2+}) cations. Helios-Rybicka et al. (1995) studied the competing sorption of Cd, Cu, Pb, Zn, and Ni cations on clay minerals. Furthermore, Khan et al. (1995) used bentonite samples in order to remove chromium (Cr) and Viraraghavan et al. (1994) study the ability of the same clay rock to remove heavy metals from aqueous solutions. Finally, Griffin et al. (1977) used montmorillonite and kaolinite samples to adsorb mercury (Hg).

Among the clay minerals, expanded vermiculite has the highest CEC (Cation Exchange Capacity) 160meq of cations per 100g. Vermiculite is chemically similar to the trioctahedral micas and smectites and is a hydrous magnesium silicate mineral with various amounts of iron (Fe) and aluminum (Al). Vermiculite presents a positive charge deficiency, which is caused mainly by tetrahedral substitution of Al and Fe(III) for Si, and is generally compensated by the presence of some interlayer cations. The high charge deficiency is responsible for the ability of the vermiculite samples to adsorb elements or organic liquids between their layers. It is formed by hydrothermal activity and/or supergene alteration on precursor micas (Basset, 1963). Expanded vermiculite has several industrial applications. Additionally commercial vermiculite is actually supplied by a few countries worldwide.

Few studies have been made for the ability of vermiculite to adsorb elements. Sikalidis et al. (1991, 1989, and 1988) investigated the mineral in the adsorption of radionuclides such as uranium (U), thorium (Th), and cesium (Cs).

Recently, extensive zones of vermiculite have been found in Askos area at the contacts of serpentinized ultramafic bodies and surrounding two-mica gneisses constituting a significant source of this industrial mineral in Greece (Tsirambides and Michailidis, 1999, Dabitzias and Kougoulis, 1994, Dabitzias and Perdikatsis, 1991).

Serious problems arise due to leaching of lead (Pb) and zinc (Zn) from foundries filter dust which is deposited in many cases in open fields. This dust has high content of Pb and Zn. Leaching experiments of such dust showed concentration of 100 and even above 1000mg/L in the leachates. In the present work Askos vermiculite was investigated as a possible material to be used in the removal of lead and zinc from aqueous leachates.

2 MATERIALS AND METHODS

The material used as an adsorbent for the experimental work was natural vermiculite from the Askos area, Thessaloniki County, Greece. The Askos vermiculite sample was ground in a water suspension with a rotary high-speed stirrer for several hours (Jackson, 1974). The material that passed through a 300-mesh sieve was collected, centrifuged, air dried and used for the removal experiments. Additionally, a vermiculite sample from Kent, Connecticut, U.S.A. supplied by Ward's Natural Science Establishment, Rochester, N.Y., U.S.A. treated in the same way, was used for comparison in the experiments.

Mineral phases were imaged with backscattered electrons and quantitatively analyzed by a JEOL JSM-840 scanning electron microscope equipped with a LINK AN system energy dispersion analyzer (SEM-EDS). Operating conditions were: accelerating voltage at 15kV, beam current <3nA (low enough to permit a reasonable analysis without damaging the minerals), surface electron beam of 1 μ m in diameter, and counting time of 100sec. Corrections were made using the ZAF-4/FLS software provided by LINK. Natural minerals or synthetic equivalents and pure metals were used as standards.

Vermiculite samples were also analyzed for particle size distribution by wet sieving for the sand fraction, and by sedimentation and centrifugation for the silt and clay fractions.

Mineralogical composition of the vermiculite samples was determined by the analysis of the X-ray diffraction (XRD) spectra, which involved the identification and semiquantification of the characteristic peaks of the minerals present. A Philips diffractometer PW1710 with Ni-filtered CuK α radiation was used. Vermiculite samples both randomly and with preferred orientation were scanned over the interval 3-63 $^\circ$ 2 θ at scanning speeds of 1.2 $^\circ$ /sec. The recognition of the mixed layer phases of vermiculite samples was based on the XRD patterns of Moore and Reynolds (1997).

The cation exchange capacity (CEC) was determined by the Alexiades and Jackson (Alexiades et al., 1966) method.

The metal ions studied were lead (Pb $^{2+}$) and zinc (Zn $^{2+}$) since they are common heavy metals in the effluents and/or leachates from factories, foundries or mining activities. Aqueous solutions were prepared by dissolving an appropriate amount of Pb(NO $_3$) $_2$ or Zn(NO $_3$) $_2$ ·6H $_2$ O (Merck, analytical grade) in deionized water. Initial stock solutions of 100, 500, 1000, and 2000mg/L of each element were prepared and their pH-value was measured. The pH-value was measured by means of a Metrohm Herisau pH-meter model E510.

The quantitative determination of Pb $^{2+}$, Zn $^{2+}$, K $^+$, Na $^+$, Ca $^{2+}$, Mg $^{2+}$, Fe $^{3+}$ and Al $^{3+}$ in the solutions was performed by means of Atomic Absorption Spectroscopy (A.A.S.) using a Perkin Elmer, model 901A.

Monoionic forms of vermiculite were prepared by saturation with different cations according to the following procedure: 0.5gr of vermiculite in a 50ml centrifuge tube were washed three times with 0.5N nitrate solutions of the used ions following the procedure of addition, centrifugation and decantation (Alexiades et al., 1966). The samples were then washed three times with deionized water and two times with acetone.

For the removal experiments the following procedure (Sikalidis et al., 1988) was applied: 0.1gr vermiculite sample was placed in a 70ml centrifuge tube. After the addition of 50ml of the appropriate Pb $^{2+}$ or Zn $^{2+}$ solutions the sample was shaken for 45min at room temperature. The 45min contact time was found to be sufficient for the establishment of equilibrium. After equilibrium establishment the mixtures were centrifuged for 5min at 2500rpm and the metal ions lead and zinc were determined in the supernatant solution by means of A.A.S. The solution to solid ratio in the batch experiments was ~500:1. The pH-value of the solutions after the removal experiments was also measured.

The amount of lead and zinc removal was calculated (Eq.1) from the difference between the initial (C $_i$) and determined final (equilibrium) concentration (C $_{EQ}$) in the solution respectively.

$$C_{REMOVAL} = C_i - C_{EQ} \quad (\text{Eq.1})$$

The removal of the studied metal ions by vermiculite was estimated in terms of uptake distribution coefficients K $_d$ and removal percentages (%).

The uptake distribution coefficient K $_d$ (Eq.2) is defined as the concentration of a species adsorbed per gram of the adsorbent divided by its concentration per ml in the liquid phase (Helfferrich, 1962)

$$K_d = (C_i - C_{EQ}) \cdot V / C_{EQ} \cdot m \quad (\text{ml/g}) \quad (\text{Eq.2})$$

where C $_i$ and C $_{EQ}$ are the initial and final (equilibrium) concentration of studied metal ions in their aqueous solutions at the beginning and at the end of removal experiments respectively, V is the volume of the solution in ml and m is the mass of adsorbent in gr.

The removal percentage (Eq.3) was calculated by using the following equation:

$$\text{Removal (\%)} = (C_i - C_{EQ}) \cdot 100 / C_i \quad (\text{Eq.3})$$

where C $_i$ and C $_{EQ}$ are the initial and final (equilibrium) concentration of studied metal ions in their aqueous solutions at the beginning and at the end of removal experiments respectively.

3 RESULTS AND DISCUSSION

3.1 Vermiculite characterization

Grain size distribution, mineralogical composition and chemical analysis of the vermiculite samples used are presented in Table 1.

Table 1. Fractional, mineralogical and chemical composition of vermiculites from Askos, Thessaloniki County, Greece and Kent, Connecticut, U.S.A.

| | ASKOS | | KENT |
|-------------------------------------|-------------|-----------------|-------|
| Grain Size Distribution (%) | | | |
| Sand (>63 μ m) | 70 | | 31.8 |
| Silt (2-63 μ m) | 22 | | 67.4 |
| Clay (<2 μ m) | 2 | | 0.8 |
| Carbonates+Organics+Iron Oxides (%) | | | |
| | 6 | | 0 |
| Mineralogical Compositon (%) | | | |
| Biotite/Vermiculite | >40 | Vermiculite | 54 |
| Chlorite/Vermiculite | 20-40 | Chlorite | 20 |
| Biotite/Smectite | <20 | Mica | 17 |
| Vermiculite/Smectite | <20 | Montmorillonite | 5 |
| Biotite | <5 | Quartz | 3 |
| Electron Microprobe Analysis (%) | | | |
| N*=10 | | | |
| SiO ₂ | 36.72-40.26 | | 46.48 |
| TiO ₂ | 0.65-0.91 | | 0 |
| Al ₂ O ₃ | 12.39-14.79 | | 11.4 |
| Cr ₂ O ₃ | 0.09-0.25 | | 0 |
| Fe ₂ O ₃ | 8.16-10.50 | | 4.95 |
| MnO | 0.02-0.14 | | 0 |
| MgO | 21.19-22.27 | | 28.1 |
| NiO | 0-0.18 | | 0 |
| CaO | 0.17-0.36 | | 0 |
| Na ₂ O | 0 | | 0.07 |
| K ₂ O | 0-5.30 | | 1.9 |
| TOTAL | 83.59-91.09 | | 92.9 |

*N: number of analyses

Askos vermiculite is mainly consisted of mixed-layer phases of phyllosilicates (Fig. 1) such as biotite/vermiculite (with the biotite percentage to dominate in the mixed layer), biotite/smectite, chlorite/vermiculite and traces of discrete biotite and vermiculite. The presence of these mixed layer phases indicate that the reason of the vermiculite formation is the alteration of the meta-ultramafic rocks by both hydrothermal and weathering processes (Tsirambides and Michailidis, 1999). Kent vermiculite is mainly consisted of discrete vermiculite (54%), chlorite, mica, montmorillonite and traces of quartz (Fig. 1).

The cation exchange capacity of vermiculite samples determined was 148meq/100gr for Askos sample and 94meq/100gr for the Kent vermiculite.

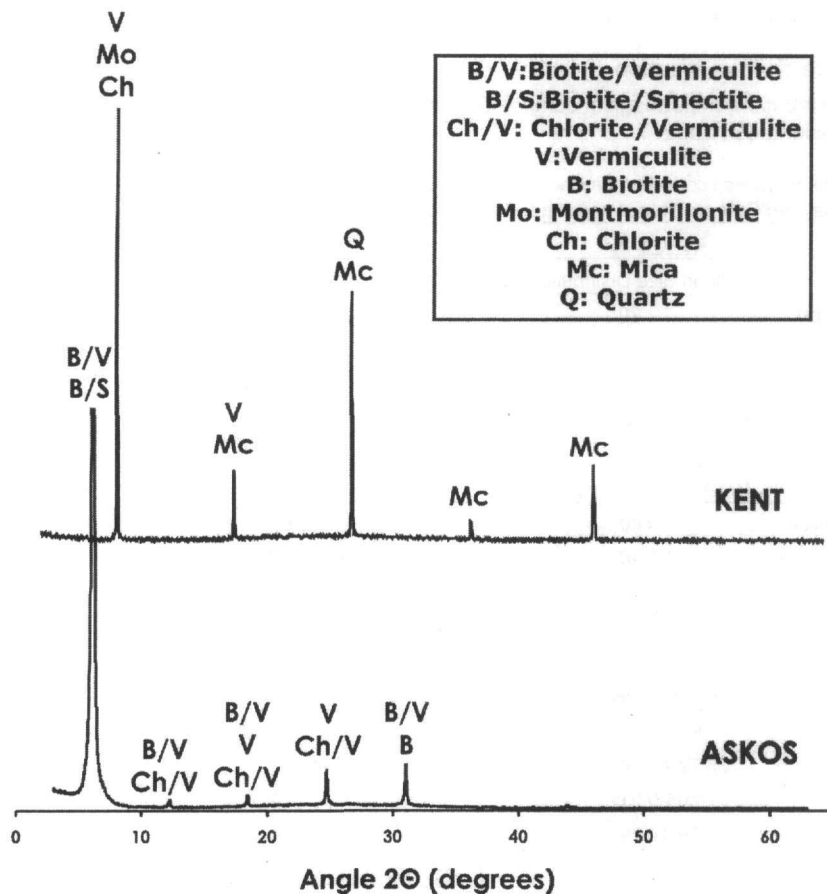


Figure 1. XRD diagrams of oriented vermiculite samples: a) Askos area, Thessaloniki County, Greece, and b) Kent, Connecticut, U.S.A.

3.2 Batch Adsorption Experiments

The removal of metal ions from aqueous solutions with concentration ranging from 100 to 2000mg/L by the vermiculite from Askos, Greece were found to range between 48% and 95% for lead and between 80% and 96% for zinc, respectively (Tab. 2). The removal results for the Kent vermiculite were found 23-37% and 72-76% respectively of the total concentration of the metal ions. According to the experimental results, it seems that vermiculite samples from Askos area are capable to remove higher amounts of the studied metal ions than the Kent vermiculite. Furthermore, taking into account the mineralogy of the vermiculite samples (Tab. 1), it is easy to understand that the Askos vermiculite consisting mainly of mixed layer phases, displays a higher effectiveness for removing heavy metals than the Kent vermiculite in which discrete vermiculite is the major mineral phase.

Additionally, the uptake distribution coefficients (K_d) indicated that the lead and zinc removal was much higher from solutions with initial concentrations below 1000mg/L (Tab. 2, Fig. 2a, 2b). The maximum removal of the studied metal ions (Pb^{2+} , Zn^{2+}) were from solutions with initial concentration 100mg/L which is the closest value of metal concentration to the cation exchange capacity of vermiculite samples. We must, however, denote that the drastic increase in Pb and Zn removal above final pH 6 was probably due to precipitation of metal ions as insoluble hydroxide precipitates and not only due to adsorption (Lehman et al. 1999, Bradl 2004).

Table 2. Removal of (a) lead and (b) zinc from aqueous solutions by the Askos vermiculite samples and comparison to Kent vermiculite.

| (a) | | | | | | | | | |
|--------------|-----------------|-----------------|-------------|--------------|------------------|-----------------|-------------|--------------|------------------|
| ASKOS | | | | | KENT | | | | |
| C_i (mg/L) | pH _i | C_{Eq} (mg/L) | Removal (%) | K_D (ml/g) | pH _{Eq} | C_{Eq} (mg/L) | Removal (%) | K_D (ml/g) | pH _{Eq} |
| 100 | 5.45 | 5.30 | 94.70 | 8933.96 | 7.55 | 63 | 37 | 293.66 | 5.50 |
| 500 | 5.10 | 167 | 66.60 | 997.01 | 5.10 | 376 | 24.60 | 164.90 | 5.15 |
| 1000 | 4.70 | 564 | 43.60 | 386.52 | 4.60 | 766 | 23.40 | 152.74 | 4.80 |
| 2000 | 4.70 | 1039 | 48.05 | 462.46 | 4.50 | 1387 | 30.65 | 220.98 | 4.75 |

| (b) | | | | | | | | | |
|--------------|-----------------|-----------------|-------------|--------------|------------------|-----------------|-------------|--------------|------------------|
| ASKOS | | | | | KENT | | | | |
| C_i (mg/L) | pH _i | C_{Eq} (mg/L) | Removal (%) | K_D (ml/g) | pH _{Eq} | C_{Eq} (mg/L) | Removal (%) | K_D (ml/g) | pH _{Eq} |
| 100 | 6.45 | 4 | 96.00 | 12000.00 | 7.50 | 24 | 76 | 293.60 | 6.70 |
| 500 | 6.10 | 70 | 86.00 | 3071.43 | 6.40 | 130 | 74.00 | 164.90 | 6.20 |
| 1000 | 6.00 | 160 | 84.00 | 2625.00 | 6.20 | 260 | 74.00 | 152.70 | 6.10 |
| 2000 | 5.90 | 400 | 80.00 | 2000.00 | 6.10 | 560 | 72.00 | 220.90 | 6.10 |

C_i : Initial metal ion concentration (mg/L)

C_{Eq} : Final (Equilibrium) metal ion concentration (mg/L)

pH_i: Initial pH value

pH_{Eq}: Final (Equilibrium) pH value

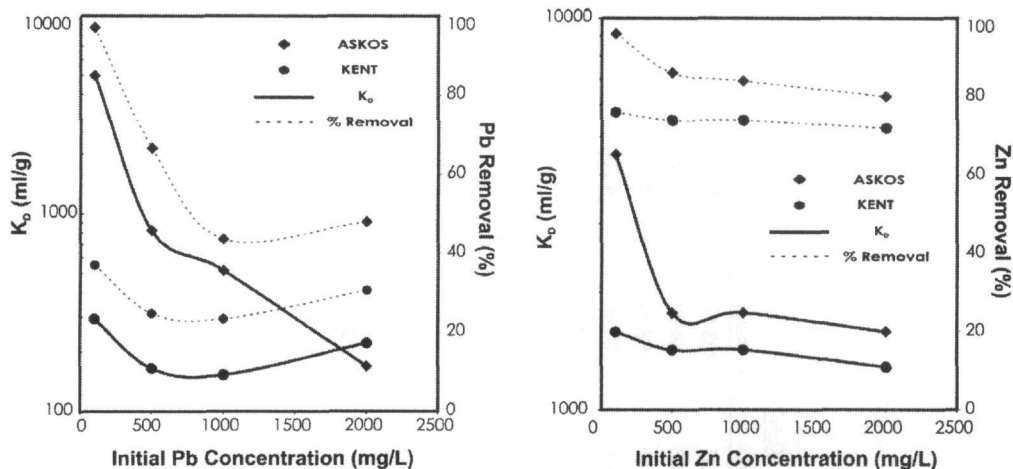


Figure 2. Uptake distribution coefficient (K_D) and removal percentage (%) versus initial metal concentration (a) for lead and (b) for zinc removal.

The initial pH-values of the solutions were significantly increased during the experiments due to the simultaneous hydrogen ion uptake by the vermiculite materials. However, it seems to be conceivably impossible to calculate the absolute hydrogen ion uptake by the materials, based on the pH increase, because hydrogen ions are also involved in hydrolytic reactions of Pb^{2+} and Zn^{2+} ions (Baes et al., 1976).

Table 3. Concentration of K, Mg, and Ca in the equilibrium solutions after the (a) lead and (b) zinc adsorption by the studied vermiculite samples.

| (a) | | ASKOS | | | KENT | | |
|--------------|----------|-----------|-----------|----------|-----------|-----------|--|
| C_i (mg/L) | K (mg/L) | Mg (mg/L) | Ca (mg/L) | K (mg/L) | Mg (mg/L) | Na (mg/L) | |
| 100 | 0.69 | 8.00 | 0.79 | 0.35 | 0.14 | 0.38 | |
| 500 | 0.72 | 23.00 | 1.11 | 0.37 | 0.14 | 0.15 | |
| 1000 | 0.84 | 31.00 | 1.18 | 0.40 | 0.12 | 0.28 | |
| 2000 | 0.85 | 31.00 | 1.34 | 0.44 | 0.14 | 0.34 | |
| (b) | | ASKOS | | | KENT | | |
| C_i (mg/L) | K (mg/L) | Mg (mg/L) | Ca (mg/L) | K (mg/L) | Mg (mg/L) | Na (mg/L) | |
| 100 | 0.63 | 9.00 | 0.91 | 0.37 | 0.14 | 0.26 | |
| 500 | 0.71 | 19.50 | 2.14 | 0.53 | 0.16 | 0.30 | |
| 1000 | 0.72 | 30.00 | 1.91 | 0.43 | 0.18 | 0.20 | |
| 2000 | 0.80 | 31.50 | 2.77 | 0.63 | 0.17 | 0.38 | |

C_i : Initial metal ion concentration (mg/L)

The results of the A.A.S. measurements of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} and Al^{3+} ions in the supernatant solution indicated that the investigated metal ions are exchanged with ions, which are present in the vermiculite structure as exchangeable ions (Tab. 3). In the Askos vermiculite the Pb^{2+} and Zn^{2+} ions are exchanged mainly with Mg^{2+} , which is present in the mineral structure as exchangeable ion.

The up today investigation showed that lead and zinc removal from their aqueous solutions by the Askos vermiculite samples is a rather complicated phenomenon related both to the aqueous chemistry of the elements and the nature of the applied materials. The uptake procedure can be attributed to different removal processes such as absorption by ion exchange, adsorption and surface precipitation (Stumm, 1992, Davis et al., 1990).

3.3 Equilibrium Adsorption Isotherms

The equilibrium adsorption isotherms for lead (Pb^{2+}) and zinc (Zn^{2+}) uptake by vermiculite samples were obtained at various initial concentrations from 100 to 2000mg/L and are presented in Figure 3. The initial slope of the isotherms shows that the affinity of the adsorbent for all the studied ions is extremely high.

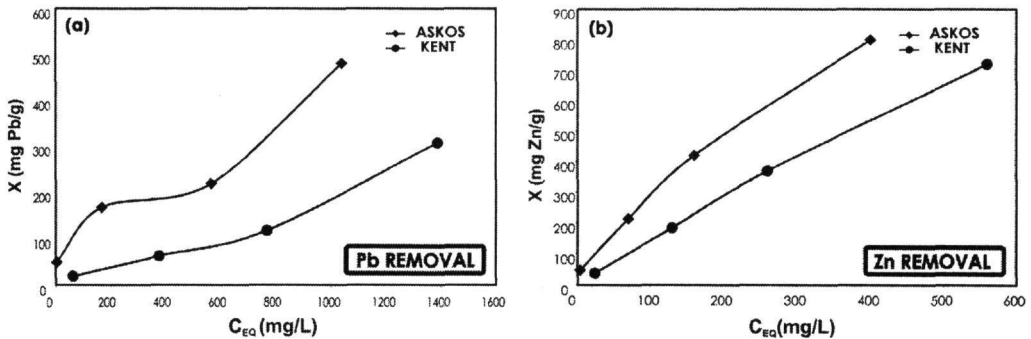


Figure 3. Equilibrium adsorption isotherms of lead (a) and zinc (b) on vermiculite.

The adsorption results were fitted to the Freundlich (Eq.4) and Langmuir (Eq.5) models. The linearized form of Freundlich equation is:

$$\log X = \log K_f + \log C_{EQ}/n \quad (\text{Eq.4})$$

where X is the amount of metal ion adsorbed (adsorbate) per unit weight of adsorbent (mg/g), K_f the equilibrium constant indicative of adsorption capacity, $1/n$ the constant for the system and C_{EQ} the equilibrium metal concentration (mg/L).

The experimental data obtained for the uptake of metal ions in the concentration range from 100 to 2000mg/L fit extremely well to Freundlich isotherm, as seen from Figure 4. A plot of $\log X$ against $\log C_{EQ}$ gives a straight line the slope and intercept of which correspond to $1/n$ and $\log K$ respectively. Linear regression gives a slope of <1 indicating a concentration dependent removal of lead and zinc on vermiculite in the concentration range used.

The linearized form of Langmuir equation is:

$$C_{EQ}/X = 1/K_L \cdot X_m + C_{EQ}/X_m \quad (\text{Eq.5})$$

where X is the amount of metal ion adsorbed (adsorbate) per unit weight of adsorbent (mg/g), C_{EQ} the equilibrium metal concentration (mg/L) and K_L and X_m are constants.

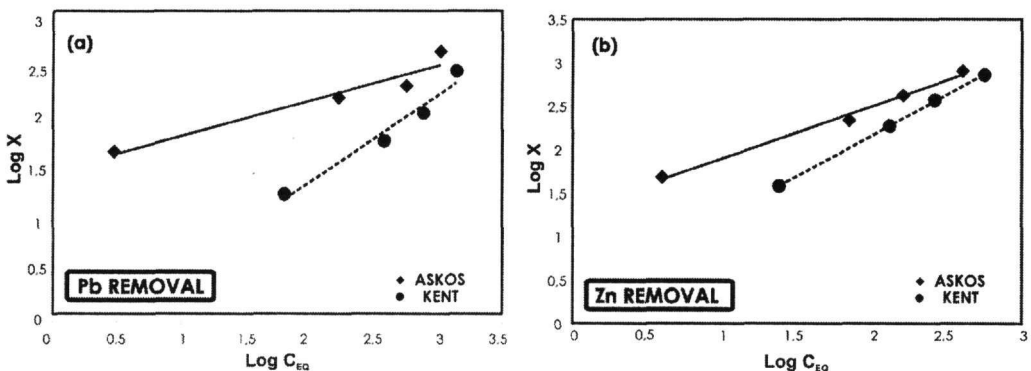


Figure 4. Freundlich plot for (a) lead and (b) zinc removal by vermiculite samples.

The experimental data of the adsorption of lead and zinc did not fit to the Langmuir isotherm.

4 CONCLUSIONS

Vermiculite from Askos area, Northern Greece, shows a considerable ability to remove the heavy metal ions of lead (Pb^{2+}) and zinc (Zn^{2+}) from their aqueous solutions. The absolute lead removal reached the value of 95% and the zinc removal was 96%. Thus, Askos vermiculite, consisting of mixed layer phases of phyllosilicates, can find an application in the detoxification of wastewaters in its natural form. Such a quality of this clay mineral enables its classification into the specialties of industrial minerals. According to the uptake distribution coefficients (K_d), the relative metal uptake for the lead and zinc ions is much higher for solutions with initial concentrations below 1000mg/L. The drastic increase in Pb and Zn removal above final pH 6 was probably due to precipitation of metal ions as insoluble hydroxides and not only due to adsorption. Batch adsorption experiments conducted at room temperature ($22\pm 1^\circ C$) showed that adsorption pattern followed the Freundlich isotherm model. The lead (Pb^{2+}) and zinc (Zn^{2+}) removal by the studied materials is considered as a complicated phenomenon which is attributed to different processes such as absorption by ion exchange, adsorption and surface precipitation.

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