Bentonites as adsorbents of heavy metals ions from mine waste leachates: Experimental data

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ABSTRACT

Bentonite is a clay raw material with high cation exchange capacity because of their typical layered silicate structure. Experimental studies about the retention of metals (Cu, Co, Ni, and Zn) in Peruvian bentonite have been accomplished for monometallic, bimetallic, trimetallic, and tetrametallic solutions. The influence of parameters such as concentration of metals in solution, and pH, has been considered by means of batch adsorption experiments. Adsorption rates indicate the suitability of these materials to be applied in the environmental industry for retention of heavy metals from mine waste leachates. Then, in addition to its quality as physical barrier to avoid the dispersion through the environment of polluted leachates, bentonite, due to its high cation exchange capacity acts as a chemical barrier too, protecting the quality of surface and groundwater systems. They have in consequence a potential use as screen material, to create security barriers limiting the migration of heavy metals content in mine wastes or tailings stocked in security landfills in surface spaces or in underground cavities.

INTRODUCTION

The increasing problems of dispersion of heavy metals in the environment as the result of mining activities has made that the removal of mine wastes has received considerable attention due to the toxic nature of the potential leachates formed by water circulation. In consequence, the disposal safe of wastes containing heavy metals has become to be a matter of special interest, and adsorption of heavy metals on solid substrates is being studied extensively. Inorganic substrates include oxides and clay minerals; organic substrates include ion exchange resins and biomass.

Clay minerals, because of their low permeability, play an important role, as physical barriers, for the isolation of metal-rich wastes; but chemical barrier too, as consequence of the ability of some types of clay minerals to adsorb heavy metals and to avoid their environmental dispersion.

In this sense, the adsorption of heavy metals by clay minerals is quite well documented in the specialised literature (García Miragaya and Page, 1978; Anderson and Rubin, 1981; Kinniburg and Jackson, 1981; Bourg, 1983; Cavallaro and McBride, 1984; Elliot et al., 1986). From the great variety of clays, bentonite is a raw material essentially composed of montmorillonite and related clay minerals of the smectite group, which have a large surface area per unit weight and a high cation exchange capacity (CEC). Bentonite is known as a good adsorbent for heavy metal ions; and organophilic bentonite has been used too as appropriate adsorbent for organic compounds (Cowan and White, 1962; Cowan, 1963; Tiller et al., 1984).

Smectites have a typical layered silicate structure consisting of an octahedral sheet sandwiched between two tetrahedral sheets. The interlayer space - an essential characteristics of clay minerals from this group- is easily accessible to water and another polar liquids. Smectite group minerals have a good cation exchange capacity due to the presence of hydrated cations as Ca^{2+}, Na^+, K^+, etc., in their interlayer surfaces, and these cations can be easily exchanged by heavy metals compensating the negative charge as follows: 2 Smectite-Na + Me^{2+} → Smectite-Me + 2 Na^+. The cation exchange is a reversible and stequiometric process, which varies with the nature and concentration of metallic ions in solution, pH, and presence of other ions in solution competing with heavy metals for adsorption places. The cationic exchange capacities of calcium and sodium bentonites are 80 and 150 milliequivalents by 100 grams of material, respectively (La Grega et al., 1994).

Experimental data from studies about interaction of monometallic solutions of Cu, Co, Ni and Zn, with Peruvian sodic bentonites of Wyoming type (Vega, 1995; Vega et al., 1995a) can be fitted to a linearized Freundlich equation, and according to Giles classification (Giles et al., 1974), the obtained isotherms are type "L", which correspond to cases where the sorption progress give to a decreasing each time bigger of sorption coefficient. This isotherm type is characteristic of substances that show a great affinity by metallic cations in their superficial adsorption sites. The sorption tends to increase when particulate size decreases, because of the increase of the specific area. The pH conditions the adsorption rate, which increases as the solution is more acidic: in this case the increases of H^+ ions in solution gives to a decreasing of the negative charge of bentonite surfaces and in consequence to an increases of the competence between ions. Furthermore, for very low pH, the bentonite begins to destabilise.

According as there are more metals in solution, there is an increase of the ionic competitivity between metals for superficial sites in bentonite In order to determine the influence of different parameters involved into the process as initial concentration of solution and pH, different experiments have been made with different solutions of Cu, Co, Ni and Zn.

EXPERIMENTAL PROCEDURE.

Two types of Peruvian bentonites, which chemical, mineralogical and physico-chemical characteristics are summarised in tables 1, 2 and figure 1, were selected for the experimental work. According to these characteristics, they can be considered sodic bentonites of Wyoming type (Vega, 1995; Vega et al., 1995)

	Bentonite 1	Bentonite 2
SiO_2	69.07	67.51
Al_2O_3	10.98	12.60
MgO	1.04	2.45
Fe_2O_3	2.08	2.90
MnO	0.01	0.02
K_2O	0.90	0.20
Na_2O	1.92	1.83
CaO	0.90	0.38
P_2O_5	0.16	0.02
TiO_2	0.14	0.17
LOI	12.70	11.87

Table 1. Chemical composition of Peruvian bentonites expressed in weight (%).

	Bentonite 1	Bentonite 2
Specific surface (m^2/g)	43.22	82.59
Zeta Potential (mV)	-53.8	-46.23
Total porosity (%)	53.97	51.31
Grain density (g/cm^3)	2.37	2.47
Organic matter (%)	8.50	8.10
CEC (Meq/100g)	66.8	36.14

Table 2. Physico-chemical properties of Peruvian bentonites.
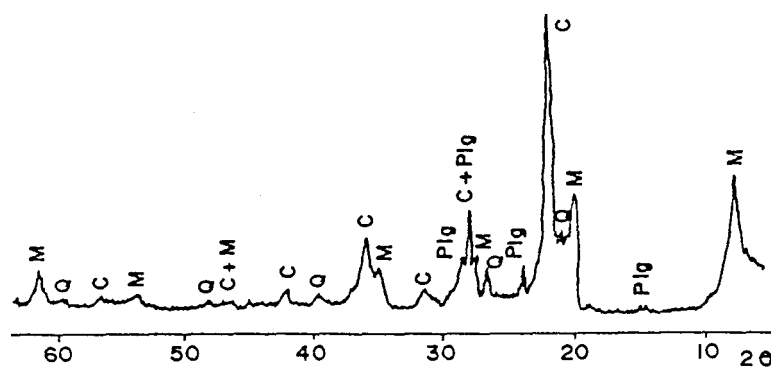
M =Montmorilionite, C =Cristobalite, Q = Quartz, Plq= Plaglioclase,
Figure 1. XRD – Difractogram of Peruvian bentonites.

Samples were ground and sized. Batch adsorption experiments were performed at ambience temperature. For the test series, a bentonite / solution ratio of 2.5 g / 25 ml was used. Monometallic, bimetallic, trimetallic, and tetrametallic solutions of Cu, Co, Ni, and Zn, were prepared stechiometrically at laboratory from commercial sulphates of analytical quality grade and using distilled and deionised water. Mixtures have been made in polyetilene recipients with an agitation system.

Studies have been accomplished for different metal concentrations of solution, and pH. Other experimental conditions as granulometric size of bentonite, mixing time of the system "polluted solution - bentonite", agitation rate and temperature, have been selected according to results of previous experimental studies made with monometallic solutions (Vega, 1995; Vega et al., 1995), and they were as follows. Bentonite was crushed during 1 minute in a rings mill, and only the particle size lower than 71 microns was used for sorption experiments. To keep the sorbent (bentonite) in suspension, the rate of agitation of the system "contaminated solution - bentonite" was regulated at 40 revolutions per minute during the experiments. Five minutes of mixing time is considered enough to achieve equilibrium conditions. This fast sorption of metals by bentonite suggests a mechanism where metals from solution are exchanged with originals ions of the bentonite surface. Finally, the sorbent was separated by centrifugation, and samples of filtered solution have been sent to the analytic laboratory. Heavy metals concentration of solutions has been determined by Flame Atomic Absorption Spectrometry (FAAS).

RESULTS AND DISCUSSION.

Effect of concentration.

Sorption kinetics was studied at 2.5 pH for different initial metallic concentrations. Initial concentrations of 0.005 M, 0.001 M and 0.01 M for each metal have been considered excepted for tetrametallic solutions that only 0.001 M and 0.005 M initial concentrations have been considered.

Studies accomplished with monometallic solutions of Cu, Co, Ni, and Zn, evidence a considerable increase of the adsorption rate when the initial concentration of metal decreases (Table 3).

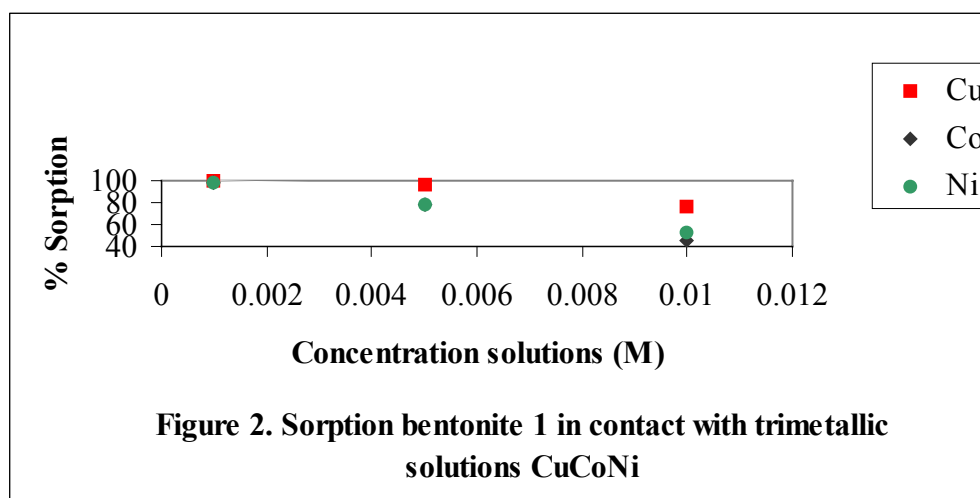|	Initial concentration	0.001 M	0.005 M	0.01 M
Adsorbed	Bentonite 1	99.5	98.5	94.5
Cu (%)	Bentonite 2	98.8	91.5	81.9
Adsorbed	Bentonite 1	99.0	93.4	78.8
Co (%)	Bentonite 2	90.6	82.7	73.8
Adsorbed	Bentonite 1	100.0	96.6	88.2
Ni (%)	Bentonite 2	96.2	77.5	59.3
Adsorbed	Bentonite 1	99.4	97.9	93.2
Zn (%)	Bentonite 2	98.5	77.9	74.3

Table 3. Sorption rate of Peruvian bentonites in contact with monometallic solutions (Initial conditions: 2.5 gr. bentonite in 25 ml solution. pH = 5)

The results of the adsorption tests with both types of bentonite are shown in tables 3 to 5. From experiments of interactions of Cu-Co solutions with crushed bentonite it is observed that adsorption percentages increase according as the initial concentration of Cu and Co decrease (table 4). At the experimental conditions applied, Cu is bigger than Co adsorption, in agreement with other experimental data found in the specialised literature (Wenszt, 1989). The adsorption rates are lower than the corresponding to monometallic solutions, and this fact corroborates that ionic competence between metals exists. According to Phadungchewit (1990), high concentration of metals in solution affects the cationic exchange capacity of bentonite, giving place to low retention rates.

	Initial concentration	0.001 M	0.005 M	0.01 M
Adsorbed	Bentonite 1	96.4	98.7	86.7
Cu (%)	Bentonite 2	95.4	83.9	65.8
Adsorbed	Bentonite 1	96.0	90.7	76.9
Co (%)	Bentonite 2	94.3	82.6	65.3

Table 4. Sorption rate of Peruvian bentonites in contact with bimetallic (Cu-Co) solutions (Initial conditions: 2.5 gr. Bentonite in 25 ml solution. pH = 2.5)

The experimental data from interaction of trimetallic solutions of Cu-Co-Ni with bentonites (Initial conditions: 2.5 gr. bentonite in 25 ml solution. pH = 2.5), show that adsorption rates of the three metals decrease significatively as the initial concentrations increase (figure 2 and 3).

Figure 2. Sorption bentonite 1 in contact with trimetallic solutions CuCoNi
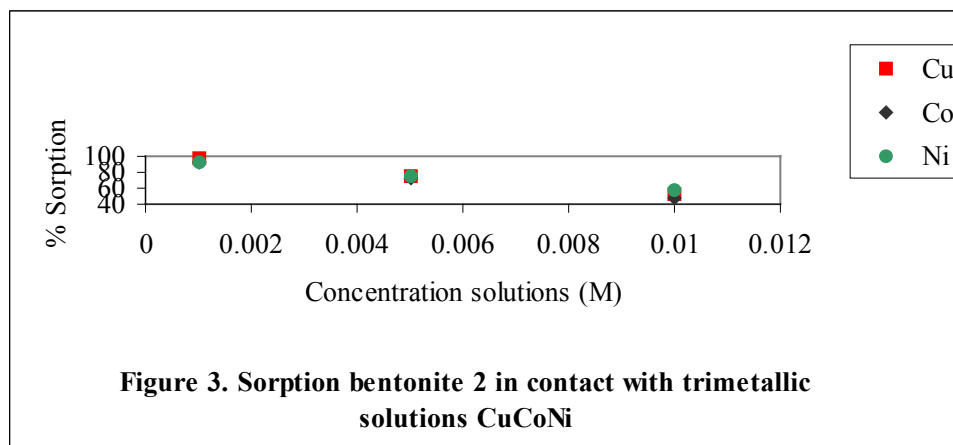
Figure 3. Sorption bentonite 2 in contact with trimetallic solutions CuCoNi

Experimental data from Cu, Co, Ni, Zn solutions show that the adsorption rate of the four metals is high for an initial concentration of 0.001 M, but when the initial concentration of solution increases to 0.005 M the adsorption rate of the four metals decrease significantly (table 5). The tendency is the same for both types of bentonite studied. The comparison of results between experiments with two (Cu-Co), three (Cu-Co-Ni) and four metals (Cu-Co-Ni-Zn) in solution evidences a decreasement of the metals adsorption rate as the number of metals in solution is higher, this is due to the ionic competence for the surface sites of the bentonite. From the different metals studied Cu has the biggest adsorption rate, the second one is the Zn, and the third Co and Ni, which adsorption rate is very similar. These data are in agreement with another studies made with monometallic solutions (Vega et al., 1994; Vega et al., 1995a; Vega et al., 1995b).

	Initial concentration	0.001 M	0.005 M
Adsorbed	Bentonite 1	98.4	90.1
Cu (%)	Bentonite 2	94.8	65.4
Adsorbed	Bentonite 1	97.2	62.7
Co (%)	Bentonite 2	89.6	61.6
Adsorbed	Bentonite 1	96.8	59.8
Ni (%)	Bentonite 2	91.5	60.2
Adsorbed	Bentonite 1	98.3	63.6
Zn (%)	Bentonite 2	91.2	61.0

Table 5. Sorption rate of Peruvian bentonites in contact with tetrametallic (Cu-Co-Ni-Zn) solutions (Initial conditions: 2.5 gr. Bentonite in 25 ml solution. pH = 2.5)

On the effect of initial metallic concentrations can be considered that for each one of the metals a quickly diminution of the adsorption percentage of the different studied metals (Cu, Co, Ni, Zn) when there is an increase of the solution concentration. It can be considered too a diminution of the adsorption percentage for each metal, when other metals such as Fe are present in solution (ionic competence). These effects of ionic competence between metals has a low signification for low concentration of solutions (0.001 M), indicating that the presence of other metals do not impede the obtaining of high adsorption percentages.

It is as well to emphasise that with 0.001 M solutions the competence ionic effect has a low signification and the adsorption percentage of each metal (even in a tetrametallic solution such as Cu-Co-Ni-Zn) hold with values higher than 90% for each one of them. The increments of concentration have lower effects for Cu, which always keeps high grades of adsorption. For other metals (Co, Ni and Zn) the effects of increments of concentration are higher.

Effect of pH.

Although the adsorption grade varies among all metals, a common pH-dependent trend is frequently observed (Shuman, 1975; Kuo and Baker, 1980; Harter, 1983). The pH-dependent behaviour of bentonites interacting with solutions of Cu, Co, Ni and Zn is shown in tables 8, 9 and 10. Experimental data with Peruvian bentonites evidence a remarkable loose of the sorption capacity of this clay material according as the acidic conditions increase.

The adsorption experiments have been made with bimetallic solutions (Cu-Co) of initial concentration 0.001 M for each metal, trimetallic (Cu-Co-Ni) and tetrametallic solutions (Cu-Co-Ni-Zn), both with initial concentrations 0.005 M for each metal. In all cases the pH interval studied has been 1, 2.5 and 5, and data on adsorption rates are presented in tables 6 to 8. From these data can be concluded that the adsorption coefficient for each metal reduces significatively with pH diminution. Ni is the metal experimenting bigger adsorption reductions, whereas copper the lowest.

		pH = 1	pH = 2.5	pH = 5
Adsorbed	Bentonite 1	77.7	96.4	98.2
Cu (%)	Bentonite 2	73.8	95.4	96.2
Adsorbed	Bentonite 1	57.9	96.0	96.2
Co (%)	Bentonite 2	76.2	94.3	94.9

Table 6. Effect of pH in sorption rate of Peruvian bentonites in contact with bimetallic (Cu-Co) solutions (Initial conditions: 2.5 gr. bentonite in 25 ml solution 0.001 M)

		pH = 1	pH = 2.5	pH = 5
Adsorbed	Bentonite 1	47.3	96.4	97.9
Cu (%)	Bentonite 2	50.5	75.8	78.7
Adsorbed	Bentonite 1	35.2	78.6	81.1
Co (%)	Bentonite 2	52.7	72.6	74.8
Adsorbed	Bentonite 1	39.9	77.3	81.0
Ni (%)	Bentonite 2	52.9	74.1	75.9

Table 7. Effect of pH in sorption rate of Peruvian bentonites in contact with trimetallic (Cu-Co-Ni) solutions (Initial conditions: 2.5 gr. bentonite in 25 ml solution 0.005 M)

		pH = 1	pH = 2.5	pH = 5
Adsorbed	Bentonite 1	42.3	90.1	93.8
Cu (%)	Bentonite 2	44.9	65.4	69.9
Adsorbed	Bentonite 1	28.1	62.7	65.1
Co (%)	Bentonite 2	46.2	61.6	63.7
Adsorbed	Bentonite 1	18.3	59.8	62.6
Ni (%)	Bentonite 2	43.8	60.2	62.2
Adsorbed	Bentonite 1	33.2	63.3	68.4
Zn (%)	Bentonite 2	45.3	61.0	63.6

Table 8. Effect of pH in sorption rate of Peruvian bentonites in contact with tetrametallic (Cu-Co-Ni-Zn) solutions (Initial conditions: 2.5 gr. bentonite in 25 ml solution 0.005 M)

There is no general agreement on a simple mechanism responsible for this behaviour, but strong adsorption of metal hydroxide complexes (Forbes et al., 1974), hydrolysis of Al on exchange sites (Cavallaro and McBride, 1980), competition by H^+ for sites (Newton et al., 1976) and acid-catalysed dissolution of reactive oxide sites (Elliot and Huang, 1979) may be involved.

The diminution of the adsorption rate of metals by bentonite with a decreasing of pH of solution is in agreement with the theory that considers that a pH decrease involves a diminution of the cation exchange capacity (CEC) of the sorbent (bentonite), and in consequence a metal removal diminution. This loss of efficiency for metals retention into bentonite, may be explained by the fact that low pH involves high H^+ concentration, which competes with metals for the sorption sites in bentonite. At very low pH (in the order of 1 unit), the bentonite looses in part its crystallographic structure and in consequence its capacity as adsorbent. The different behaviour of both types of bentonite used for the experimental works must be attributed to their differences in mineralogical and chemical characteristics, which correspond too a different cation exchange capacity (CEC) (tables 1,2 and figure 1).

CONCLUSIONS.

The experimental data obtained from interactions of metal solutions with Peruvian bentonites lead to consider this material as a potent adsorbent to retain heavy metals from polluted leachates. According to the experimental data obtained, the heavy metals retention rate is very dependent of the initial concentration of metals in solution and pH. It can be concluded that the sorption coefficient for a metal reduces significatively when concentration increases and pH decreases.

The property of bentonite to retain metals could be used for the isolation of mine wastes with high metallic contents. According to their relatively low hydraulic conductivity (10^{-7} to 10^{-11} cm.s^{-1}), good sorptive characteristics, low solubility and their ability to act in a plastic manner, which makes them self-sealing in certain circumstances, they can be used not only as a physical barrier, but as a chemical barrier too, with the aim to impede the dispersion of metals from pollution sources to the surface and groundwater bodies. In the case of security landfills, where residual leachates are always produced because of the natural humidity of the stocked wastes, bentonites, in combination with artificial liners, has an interesting potential application field in the environmental industry to avoid the dispersion of metals to the environment.

In addition to their very high sorptive capacities for metals they offer real advantages in terms of physical isolation of buried waste materials from circulating groundwater. They act as efficient complement for artificial liners in isolation alternatives for toxic wastes. Bentonite besides to protect physically the artificial liners, minimises the risk of dispersion of contaminants to the environment as it a natural liner acting as a complementary barrier. The storage of leachable heavy metal rich wastes in ponds requires the suitable impermeabilization of pond by use of natural and/or artificial barriers. Because the application of artificial barriers like high density polyethylene and others, has not still a very contrasted long term applicability, as consequence of their short time of experience in the

environmental industry, it will be necessary the monitoring of their conservation state to prevent the soils and water contamination by fugues of contaminated wastes through their and hole of the geotextile, given that the cracked of geotextile is usual after time of operation or use. An hydraulic barrier for pollutants can involve an impermeable layer of bentonite, which has also an important metal adsorption capability due to its internal structure. Having in consideration the abundance and low price of bentonites and their physical and chemical characteristics, they are materials to be in consideration for an efficient application in the environmental industry. These materials could be used too as geochemical barriers for safety deposits designed to impede the leakage of contaminants from toxic residues deposits where acidic leachates rich in heavy metals are formed.

These bentonites which high capacity of heavy metals is proved, come from deposits of great reserves, located in a region of an important metallic mining potential where the ore exploitation will originate metal-rich mine wastes generators of acidic leachates. The interest of these bentonites is not only due to their high potential of cationic exchange, but to their physical properties: very low hydraulic conductivity (10^{-7} to 10^{-11} cm.s^{-1}), and high plasticity that is adequate to be provoke an auto-sealed of fractures, pores, and voids, in general. For all these reasons these bentonites can play a role of chemical barrier for heavy metals, and a physical barrier for the same polluted effluents.

These properties of bentonites are especially suitable for their application as complementary material to the artificial liners type "geotextile". Their role is not only to constitute a second barrier geochemical and physical, located behind or bellow the artificial liners, with capability to act in the case of failures or breaking, given that the bentonite beds can act too as protective material of the liners. Then, in some cases the application of bentonite beds not only minimise the risks of failures or defects of impermeability during the installation of artificial liners, and they assist in the absence of experience in their long-term behaviour as isolation bed, according to relatively recent application in this field.

REFERENCES

Anderson, M., Rubin, A.J. 1981. Adsorption of inorganics at solid-liquid interfaces. Ann. Arbor Science Publishers. Collingwood. England. 17-89.

Bourg, A.C. 1983. Modelisation du comportement des métaux traces à l'interface solide-liquide dans les systémes aquatiques. Documents du B.R.G.M., 62, 1-34.

Cavallaro, N. and McBride, M.B. (1980). Activities of Cu^{2+} and Cd^{2+} in soil solutions as affected by pH. Soil Sci. Soc. Am. J. 44, 729-732.

Cavallaro, N. and McBride, M.B. 1984. Zinc and copper adsorption and fixation by an acid soil clay: Effect on selective dissolutions. Soil Sci. Soc. Am. J. 48, 1050-1054.

Cowan, C. (1963). Adsorption by organo-clays complexes. Part 2. Clay Minerals 10, 226-234.

Cowan, C., White, D. (1962). Adsorption by organo-clays complexes. Clay Minerals 9, 459-467.

Elliott, H. and Huang, C.P. (1979). The adsorption characteristics of Cu (II) in the presence of chelating agents. J. Colloid InterfaceSci. 70, 29-45.

Elliott, H., Liberti, N.R., Huang, C.P. 1986. Competitive adsorption of heavy metals by soils. J. Environ. Qual. 15, 214-219.

Forbes, E.A., Posner, A.M. and Qirk, J.P. (1974). The specific adsorption of inorganic Hg (II) species and Co (III) complex ions on goethite. J. Colloid Interface Sci., 49, 403-409.

García Miragaya, J. and Page, A. (1978). Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition. Water, air and soil pollution, 9, 289-299.

Giles, D., Dsilva, A., Easton, I. 1974. A general treatment and classification of the solute adsorption isotherms. Experimental interpretation. J. Coll. Interface Sci., 47, 766-786.

Harter, R.D. (1983). Effect os soil pH on adsorption of lead, copper, zinc and nickel. Soil Sci. Soc. Am. J., 47, 47-51.

Inskeep W., Baham, J. 1983. Adsorption of Cd (II) and Cu (II) by Na-montmorillonite at low surface coverage. Soil. Sci. Soc. Am. J. 47, 660-665.

Kinniburgh, D.G., Jackson, M.L. 1981. Cation adsorption by hydrous metal oxides and clays. In: Adsorption of inorganics at solid-liquid interfaces. Ann. Arbor Science Publishers, 796-799. USA.

Kuo, S. and Baker, A.S. (1980). Sorption of copper, zinc and cadmium by some acid soils. Soil Sci. Soc. Am. J., 44, 969-974.

La Grega, M.D., Buckingham, P.L., Evans, J.C. 1994. Hazardous waste management. McGraw Hill. 1315p.

Newton, D.W., Ellis, R. Jr. And Paulsen, G.M. (1976). Effect of pH and complex formation on mercury (II) adsorption on bentonite. J. Environ. Qual. 5, 251-255.

Shuman, L.M. (1975). The effect os soil properties on zinc adsorption by soils. Soil Sci. Soc. Am. Proc. 39, 454-458.

Tiller, K., Gerth, J., Brummer, G. (1984). The relative affinities of Cd, Ni, and Zn for different soil fractions and goethite. Geoderma 34, 17-35.

Vega, J.L. (1995). Las bentonitas de la Región Grau (Perú) como adsorbentes de metales pesados. Tesis Doctoral. Universidad de Oviedo. 507 p. Inédito.

Vega, J.L., García Iglesias, J. and Loredo, J. 1995a. Geochemical characteristics of bentonite from Amotape (Grau Region, Peru). In: Exploring the Tropics. Extended Abstracts. K.S. Camuti (Edit.). pp.117-118. Australia.

Vega, J.L., Ayala, J., Loredo, J., García Iglesias, J. 1995. Laboratory experiments about the behaviour of bentonites to removal mercury and cadmium for industrial waste waters. 13th. European Conference Society for Environmental Geochemistry and Health. Aberdeen.

Vega, J.L., Ayala, J., Loredo, J., García Iglesias, J. 1995. Bentonite from Amotape (Grau Region, Peru) as exchange medium for heavy metals in industrial waste waters. In: Exploring the Tropics. Extended Abstracts. K.S. Camuti (Edit.). pp.119-120. Australia.

Vega, J.L., Ayala, J., Verdeja, L.F., Sancho, García Iglesias, J., Loredo, J. y Tamargo, F. (1996). Bentonites as a material for controlling contamination related to zinc hydrometallurgy. En: Iron control and disposal. Dutrizac y Harris (Edits.), p.565-581. Canada.

Wenstz, J. 1989. Hazardous waste management. McGraw Hill Book Co. USA.