

REMOVAL OF HEAVY METALS FROM WASTE WATERS BY NATURAL AND Na-EXCHANGED BENTONITES

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Abstract—Batch sorption studies of Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) were conducted on Ca-bentonite and Na-bentonite to determine their retention capacities for these metal cations commonly present in the waste waters of galvanic industries. The Langmuir model was found to describe the sorption process well, offering maximum sorption capacities of 44.4 mg Cr/g, 6.32 mg Ni/g, 5.75 mg Zn/g, 7.72 mg Cu/g, 7.28 mg Cd/g on Ca-bentonite and 49.8 mg Cr/g, 24.2 mg Ni/g, 23.1 mg Zn/g, 30.0 mg Cu/g, 26.2 mg Cd/g on Na-bentonite. The use of Na-bentonite in the purification of waste waters from Ni, Cr and acid-Zn electroplating processes was an effective treatment in small-scale and in semi-industrial-scale tests. This proves the worth of this method as an alternative to existing methods. In contrast, Na-bentonite was not effective in Zn sorption from cyanide-containing waste waters.

Key Words—Bentonite, Heavy Metals, Purification, Sorption, Waste Waters.

INTRODUCTION

One of the most serious environmental problems concerning heavy metals is the disposal of metal-finishing-industry liquid effluents that have hazardous, but relatively low Cr, Ni, Zn, Cu and Cd concentrations of tens to hundreds of mg/L. The problem is a serious one, due to both the number of enterprises involved in this sector and their geographical dispersion. Current legislation requires metal concentrations down to 0.1–3 mg/L in the liquid effluent disposed and the tendency is towards further restriction. The solutions available at present (precipitation technique, exchange resin columns, etc.) are used infrequently for technical and/or economic reasons. The precipitation technique is, in many cases, incapable of achieving waste-water purification within legal limits because of the presence of organic and inorganic complexing agents as well as high salt concentrations. The complexing agents and salts in the waste water support dissolved metal concentrations greater than that expected based on the metal hydroxide solubility products. Furthermore, this treatment produces a large amount of sludges which are difficult to handle and which are usually characterized as dangerous and toxic wastes. In the case of ion-exchange resins, this treatment, although usually effective, implies relatively high capital investment and operational costs, therefore being a purification system only suitable for the big enterprises of this industrial sector.

An alternative approach to purify these waste waters could be the use of available low-cost sorbent minerals. Sorption is defined as a surface retention process irrespective of mechanism, adsorption or precipitation (Sposito, 1986). Early studies have demonstrated the

capacity of montmorillonites to sorb heavy metals (Menzel and Jackson, 1950; Spencer and Gieseck, 1954; Nelson and Melsted, 1955; Hodgson, 1960; Tiller and Hodgson, 1962). The influence in this process of several factors of the reaction medium such as pH (Bingham *et al.*, 1964; Peigneur *et al.*, 1975; Farrah and Pickering 1976a, 1976b, 1977; Inskeep and Baham, 1983, Zachara *et al.*, 1992), ionic strength (Griffin and Au, 1977; García Miragaya and Page, 1976, 1977; Zachara *et al.*, 1992; Brigatti *et al.*, 1995) and complexing agents (García Miragaya and Page, 1976; Egozy, 1980; Asher and Bar-Yosef 1982; Puls and Bohn, 1988; Hirsch *et al.*, 1989) has also been studied. Their research has shown that cation exchange is the sorption mechanism at low ionic strengths, at low pH and at low concentrations of complexing agent. More recently, studies of montmorillonite with interlayers modified by the introduction of organic ligands and polynuclear Al or Zr compounds (Mercier and Detellier, 1995; Lothenbach *et al.*, 1997; Matthes *et al.*, 1999; Celis *et al.*, 2000) have been performed with the aims of increasing sorption capacity and changing the type of sorption from non-specific to specific. However, in spite of this large amount of work, performed mainly with pure minerals, actual environmental applications have been extremely limited.

The aims of the present work are (1) to study the sorbent behavior of the industrial mineral bentonite, with respect to the metals Cr, Ni, Zn, Cu and Cd in water solution, and (2) to explore the possibility of using this mineral to purify real industrial waste waters of the galvanic industrial sector.

MATERIALS AND METHODS

Sorbent minerals

In this study, a natural Ca-bentonite from the Sierra de Gador deposit, Almeria (Spain) and a Na-exchanged

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DOI: 10.1346/CCMN.2003.0510501

bentonite from the Silver and Baryte Company deposits, Milos (Greece) were used. The Silver and Baryte Company bentonite was transformed from the Ca-form by treatment with Na_2CO_3 . The <0.1 mm particle size-fractions of these bentonites were used.

Chemicals

The metal ions studied were Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II). Synthetic solutions were prepared from standards of 1000 ± 2 mg/L (Panreac) and the pH was adjusted using 0.01, 0.1 and 1 M HNO_3 and NaOH solutions.

Characterization of mineral samples

The mineral samples (Table 1) were characterized by X-ray diffraction (XRD). The semiquantitative analyses were based on diffractometer traces of unoriented powder samples using the methods employed by Schultz (1965) and by Islam and Lotse (1986). The specific surface area (SE) (Table 1) was determined using the single point BET N_2 adsorption method, although only external surface area is determined by this method. The cation exchange capacity (CEC) was determined by the ammonium acetate method (Tan, 1996) (Table 1). The point of zero net proton charge (PZNPC) (Table 1) was determined using a batch titration technique following the method used by Van Raij and Peech (1972).

Batch sorption studies

All sorption studies were carried out in centrifuge tubes by subjecting a given dose of sorbent to a period of shaking with 25 mL of solution on a vertical rotary shaker (50 turns/min) in a chamber set at 22°C. The sorbent was separated using a centrifugation step (4000 rpm) over 10 min. Metal concentrations in the supernatant liquid were determined with a VARIAN SPECTRA AA-2002 Atomic Absorption Spectrophotometer. All assays were carried out in triplicate and only mean values are presented. The studies with synthetic solutions were performed using the following conditions.

Kinetic studies. Sorbent dose: 10 g/L; initial metal concentration: 100 mg/L; pH: 4 for Cr, 5 for Cu and 6 for Ni, Zn and Cd; shaking time: 0.5, 1, 2, 4 and 6 h.

Table 1. Mineralogical composition, specific surface area, cation exchange capacity and PZNPC of bentonites.

	Ca-bentonite	Na-bentonite
Mineralogical composition (%)	Smectite >98 Illite <1 Quartz <1	Smectite 95 Calcite 4 Quartz 1
SE (m^2/g)	57.0	56.0
CEC (meq/100 g)	87.5	104
PZNPC	7.0–7.2	8.8–9.2

Sorption isotherms. Na-bentonite dose: 2.5 g/L and Ca-bentonite dose: 10 g/L for Ni, Zn, Cu and Cd, and 2.5 g/L for Cr; initial metal concentrations range: 10–150 mg/L; pH: 4 for Cr, 5 for Cu and 6 for Ni, Zn and Cd; shaking time: 6 h. The mineral dose used for each metal-mineral system was appropriate to obtain isotherms in the concentration range used. The maximum initial concentration used for each metal, although incorporated in the aforementioned range, was established according to the tendency of sorption isotherms to reach the 'plateau'.

Effect of pH. Na-bentonite dose: 5 g/L for Zn and Ni, and 2.5 g/L for Cu, Cd and Cr; initial metal concentration: 100 mg/L; shaking time: 6 h; pH range: 3–6 for Ni, Zn and Cd, 3–5 for Cu and 3–4 for Cr.

RESULTS AND DISCUSSION

Kinetic studies

The results (Table 2) show that for Ca-bentonite as well as for Na-bentonite, the sorption process occurs very rapidly, being >95% completed in 30 min. In general, the kinetic data do not show a clear tendency for sorption to increase after the first few minutes and this is related to smectite structure. Unlike other clays, the interlayers of smectites expand when wet and this implies cation exchange which occurs almost instantaneously. However, sorption in Na-bentonite undergoes a slight increase with time. This increase has to be related not to the exchange process but to surface precipitation phenomena. These processes require more time to be completed than those of adsorption. The larger partici-

Table 2. Kinetic data of metal sorption on bentonites.

<i>t</i> (h)	Ca-bentonite					Na-bentonite				
	Zn	Cd	Cu	Ni	Cr	Zn	Cd	Cu	Ni	Cr
	Metal sorption (% of equilibrium sorbed amount)									
0.5	97.3	98.5	95.7	100	97.8	95.0	96.4	98.4	95.6	98.5
1	100	100	98.4	100	99.3	96.2	97.6	98.9	97.0	99.0
2	100	100	100	100	99.4	97.5	98.8	99.4	99.2	99.7
4	100	100	100	100	99.8	99.3	99.5	99.9	99.4	99.9
6	100	100	100	100	100	100	100	100	100	100

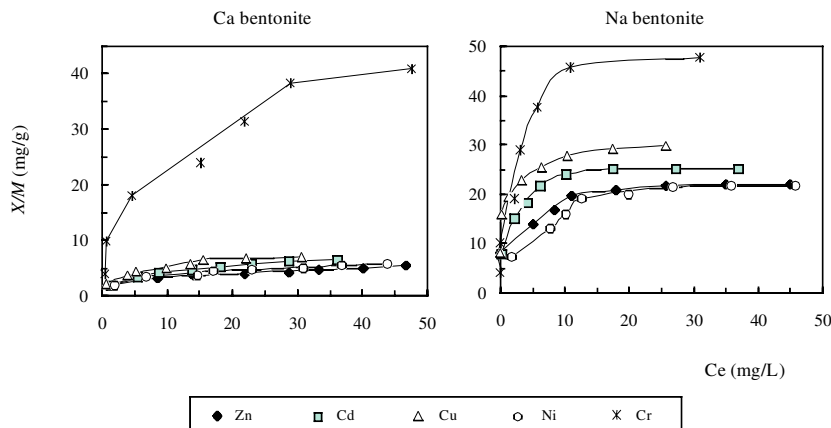


Figure 1. Sorption isotherms of bentonite.

pation of precipitation processes in Na-bentonite must be due to its higher H^+ adsorption capacity and to the presence of calcite (4%) in this sample. Heavy metals can be retained on the surface of calcite by adsorption or precipitation, with adsorption occurring when low concentrations of metals are present in solution and precipitation dominating at high concentrations of metals. The rates of metal sorption by calcite have usually been characterized by fast and slow processes. The fast process (on the order of minutes) is due to adsorption of metal ions on the surface and the slower process (on the order of hours to days) is due to nucleation and growth of a surface precipitate (metal hydroxide, carbonate or hydroxycarbonate) (McBride, 1979, 1980a; Papadopoulos and Rowell, 1988, 1989).

Sorption isotherms

The sorption isotherms are shown in Figure 1. The sorption data were fitted to the Langmuir equation, $X/M = (KbC_e)/(1+KC_e)$, where X/M is the amount of solute retained per unit weight of the sorbent, C_e is the equilibrium concentration of solute remaining in the solution, K is the equilibrium constant (affinity term) and b represents the maximum amount that can be sorbed. The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Table 3.

The Langmuir model effectively describes the sorption data with all R^2 values >0.95 . According to the b parameter (mmol/g), sorption on both bentonites occurs following the sequence: $Cr > Cu > Ni > Zn > Cd$. This decreasing sequence of sorption maxima accurately coincides with the decreasing order of the cation hydration energies, $\Delta G_h(\Delta G_h Cr^{3+} = -4010$ kJ/mol, $\Delta G_h Cu^{2+} = -2010$ kJ/mol, $\Delta G_h Ni^{2+} = -1980$ kJ/mol, $\Delta G_h Zn^{2+} = -1955$ kJ/mol, $\Delta G_h Cd^{2+} = -1755$ kJ/mol; Marcus, 1991). Also, the entropy generated in the system by the exchange process decreases in this order. The most strongly hydrated cations have greater rotational

mobility at the clay surface which implies more disorder (McBride, 1994). Apart from cation exchange, which is the main process responsible for sorption, the metal cations can also be retained by precipitation of the metal hydroxides, which in turn, is favored by the capacity of the bentonites to adsorb H^+ . Metal hydroxide precipitation must take part in Cr retention by both bentonites because Cr sorption surpasses the CECs to such an extent that it cannot be attributed to broken bonds at the edges of the bentonite particles.

The sorption capacity of Ca-bentonite for all the metal cations was lower than Na-bentonite. The lower sorption capacity of Ca-bentonite seems related to its lower H^+ adsorption capacity which implies less metal hydroxide precipitation. The lower CEC and the higher charge of Ca^{2+} may also have decreased retention. The replacement of low-charge by high-charge cations is favored relative to the exchange of same-charge cations. The increase of entropy produced in the system favors this sorption process. The entropy associated with the clay increased because there are more energy-equivalent ways that high-charge cations can occupy the singly-

Table 3. Model parameters and fit of experimental data to the Langmuir equation.

Sample	Metal	b		K L/mg	R^{2*}
		mg/g	mmol/g		
Ca-bentonite	Cr	44.4	0.854	0.156	0.9580
	Ni	6.32	0.108	0.132	0.9799
	Zn	5.75	0.088	0.137	0.9644
	Cu	7.72	0.121	0.265	0.9861
	Cd	7.28	0.065	0.163	0.9876
Na-bentonite	Cr	49.8	0.958	0.676	0.9873
	Ni	24.2	0.412	0.217	0.9947
	Zn	23.1	0.353	0.502	0.9958
	Cu	30.0	0.472	1.67	0.9979
	Cd	26.2	0.233	0.843	0.9989

* All the R^2 values were at $p < 0.001$

Table 4. Characteristics of the waste waters.

Waste water	Without pH conditioning (mg/L)	pH	After pH conditioning (mg/L)	pH
(a) Acid Zn	[Zn] = 138	1.7	[Zn] = 125	6.0
(b) Cyanide Zn	[Zn] = 40.5	12.8		
(c) Cr	[Cr] = 108	1.1	[Cr] = 100	4.0
(d) Ni	[Ni] = 50.0	6.0		

charged sites yielding an increase in what is called configurational entropy (McBride, 1980b). The Na-bentonite sorption capacity for all of the metals was high enough to consider its use in a metal waste-water purification system.

Effect of pH

The effects of pH on the Na-bentonite sorption capacity are illustrated in Figure 2. In general, protons can mainly compete with metal cations for sorption at pH-dependent, variable-charge sites. In contrast, the tendency of protons to react with permanent charge is very limited and only monovalent cations can be substantially subjected to hydrolytic exchange at low electrolyte concentrations (McBride, 1994). Metal sorption by Na-bentonite decreased when pH decreased. This suggests that the sorptive decrease was caused by the competition for exchange sites between H^+ and other metal ions where pH decreases would favor H^+ . A decrease in initial pH decreases the probability of metal hydroxide precipitation because it also decreases the final pH.

Waste-water purification at laboratory scale

The waste waters chosen to carry out the sorption studies come from Cr, Ni and Zn electroplating processes, which are, by far, the most usual galvanic processes. The waste-water samples used were supplied by Industria Galvanica Dalla Torre S.p.a. (Treviso, Italy). Although continuous flow (column study) methods would appear more appropriate, a batch method was used because the swelling and dispersion characteristics of bentonites are not suitable for continuous flow

systems. The swelling phenomena can be avoided by heating the mineral at a temperature great enough to produce dehydroxylation (Grim, 1953), though this treatment would reduce the sorption capacity (De Boodt, 1991) and also increase the cost of the purification system.

Four waste-water samples were used: (a) an acid Zn electroplating process sample, (b) a cyanide Zn electroplating process sample, (c) a typical Cr electroplating process sample after reduction of Cr(VI) to Cr(III) with $Na_2S_2O_5$, and (d) a typical Ni electroplating process (Watts bath) sample.

The metal concentrations and pHs of these samples are presented in Table 4. Prior to the sorption studies, the pH of sample (a) was increased to 6.0 and the pH of (c) was increased to 4.0. The resulting sorption capacities are compared in Figure 3 with values obtained from synthetic solutions with the same pH and metal concentrations (except for cyanide waste-water pH).

The Na-bentonite was able to sorb Zn from the acid electroplating process waste water with only a slight decrease (<10%) in sorption capacity relative to the synthetic solution. This decrease could be due to low concentrations of other metals (Cr, Ni, Cu, etc.) which compete with Zn for sorption sites on the mineral surface. In contrast, Na-bentonite sorbed very little Zn from the cyanide electroplating process sample. This behavior is related to Zn complexation by CN^- . The relatively high stability of the $Zn(CN)_4^{2-}$ complex and the low affinity of the complex for mineral surfaces clearly dominated at the 730 mg CN^-/L waste-water concentration. For Cr and Ni waste waters, Na-bentonite had sorption capacity values practically identical to those in synthetic solutions. These results indicate that Na-bentonite could be used to purify waste waters

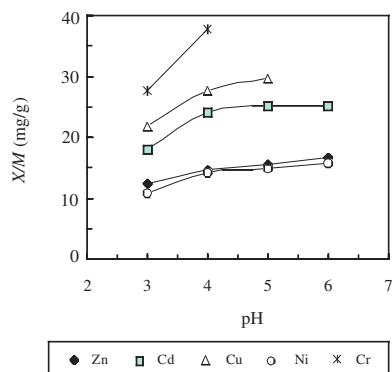


Figure 2. Effect of pH on metal sorption by Na-bentonite.

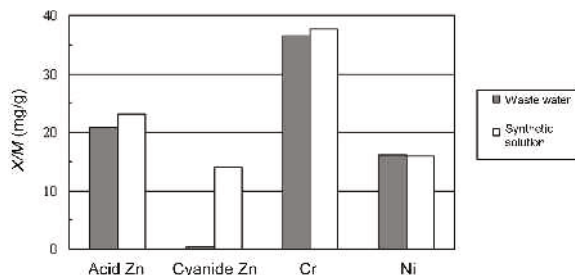


Figure 3. Metal sorption by Na-bentonite from synthetic solutions and real waste waters.

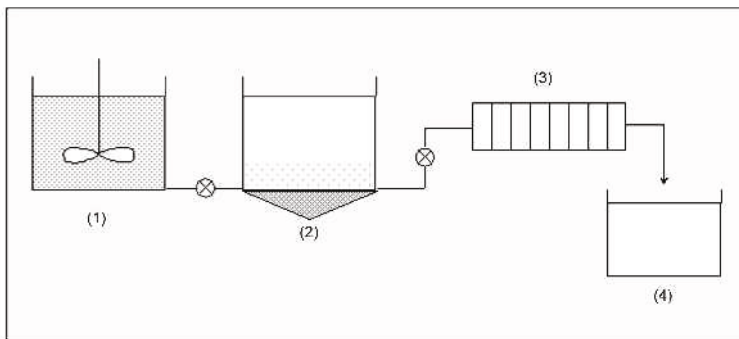


Figure 4. Prototype system of design for waste-water purification. (1) Shaking tank: helicoidal shaker (300 rpm); (2) settling tank; (3) press filter comprising eight plaques made of polyethylene cloth. Each plaque is 3 cm thick and has a filtration area of 0.366 m² per plaque; (4) recovery tank.

generated by Ni, Cr and acid Zn electroplating processes.

Waste-water purification tests at the industrial site

The positive results of the laboratory-scale studies obtained using a shaking system with bentonites need to be validated at a semi-industrial scale to prove its worth as a waste-water purification system. The design of the prototype used in this study is shown in Figure 4. Basically the system consists of a shaking tank where mineral and waste water interact, a settling tank and a press filter used to separate waste water from mineral once its purification has been performed. The waste water chosen to test the system at semi-industrial scale was produced using a typical electroplating process (Watts bath). This waste water can be subjected to a purification process directly without pretreatment (reduction or pH adjustment).

22 kg of Na-bentonite were added to the shaking tank and used to purify 200 L of waste water with an initial pH of 6.5 and a Ni concentration of 100 mg/L. The metal to mineral ratio that was employed was not selected for high metal retention on the clay, but to produce a low metal concentration in the waste water. After a shaking period of 1 h, which was enough to sorb ~100% of the metal cation, the suspended bentonite was settled using a polyelectrolyte. The supernatant water was filtered using a press filter at a flow rate of 50 L/h at a pressure of 3 atm that was increased to 8 atm to finally filter the sludge (50% mineral + 50% water). The concentration of Ni remaining in the filtered water was 0.1 mg/L, far from the most stringent limit of waste established by European environment legislation (2 mg/L) (Real Decreto 849/1986, de 11 de abril). Therefore, this treatment can be considered as an effective waste-water purification system with clear advantages over existing methods: purification of waste to legal limits, low cost, and waste which is easy to handle (in comparison with the waterlogged sludges generated after the physicochemical treatment).

CONCLUSIONS

Heavy metals are retained on Ca-bentonite and on Na-exchanged bentonite according to the following sequence: Cr > Cu > Ni > Zn > Cd. This sequence is consistent with that of the cation hydration energies and with their tendency to form metal hydroxides. Cation exchange processes and precipitation phenomena (mainly for Cr) appear to be the mechanisms involved in metal retention. The sorption capacities of Na-bentonite ($b_{Cr} = 49.8$ mg/g; $b_{Ni} = 24.2$ mg/g; $b_{Zn} = 23.1$ mg/g; $b_{Cu} = 30.0$ mg/g; $b_{Cd} = 26.2$ mg/g) were much greater than those of Ca-bentonite ($b_{Cr} = 44.4$ mg/g; $b_{Ni} = 6.32$ mg/g; $b_{Zn} = 5.75$ mg/g; $b_{Cu} = 7.72$ mg/g; $b_{Cd} = 7.28$ mg/g). This behavior is related to the greater CEC, the lower charge of the exchange cation and the higher H⁺ adsorption capacity of Na-bentonite with respect to Ca-bentonite. The Na-bentonite was able to retain metals from Ni, Cr and acid-Zn electroplating-process waste waters. The positive results obtained from laboratory-scale purification studies were verified at a semi-industrial scale.

ACKNOWLEDGMENTS

This work was carried out under Project BE-97-5093 of Brite Euram III Programme, Directorate General XII, U.E. The authors thank Industria Galvanica Dalla Torre, S.p.a. (Treviso, Italy) for their help in obtaining the waste-water samples.

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(Received 8 October 2002; revised 23 April 2003; Ms. 722; A.E. William F. Jaynes)