



A comparative study of the removal of trivalent chromium from aqueous solutions by bentonite and expanded perlite

Achraf Chakir^{a,*}, Jacques Bessiere^b, Kacem EL. Kacemi^a,
Bouchaïb Marouf^c

^a *Laboratoire d'Electrochimie and de Chimie Analytique, Département de Chimie, Faculté des Sciences, Université Mohamed V, Avenue Ibn Batouta, Rabat, Morocco*

^b *Laboratoire de Chimie Physique pour l'Environnement, Unité Mixte de Recherche UMR 7564, CNRS—Université H. Poincaré Nancy I, 405 rue de Vandoeuvre, F-54600 villers-les-Nancy, France*

^c *Laboratoire d'Hydrométallurgie and Environnement, Ecole Nationale de l'Industrie Minérale, B.P. 753, Rabat, Morocco*

Received 30 July 2001; received in revised form 21 November 2001; accepted 26 November 2001

Abstract

Local bentonite and expanded perlite (Morocco) have been characterised and used for the removal of trivalent chromium from aqueous solutions. The kinetic study had showed that the uptake of Cr(III) by bentonite is very rapid compared to expanded perlite. To calculate the sorption capacities of the two sorbents, at different pH, the experimental data points have been fitted to the Freundlich and Langmuir models, respectively, for bentonite and expanded perlite. For both sorbents the sorption capacity increases with increasing the pH of the suspensions. The removal efficiency has been calculated for both sorbents resulting that bentonite (96% of Cr(III) was removed) is more effective in removing trivalent chromium from aqueous solution than expanded perlite (40% of Cr(III) was removed). In the absence of Cr(III) ions, both bentonite and expanded perlite samples yield negative zeta potential in the pH range of 2–11. The changes of expanded perlite charge, from negative to positive, observed after contact with trivalent chromium(III) solutions was related to Cr(III) sorption on the surface of the solid. Thus, it was concluded that surface complexation plays an important role in the sorption of Cr(III) species on expanded perlite. In the case of bentonite, cation-exchange is the predominate mechanism for sorption of trivalent chromium ions, wherefore no net changes of

* Corresponding author. Tel.: +212-622-769-29; fax: +212-37-282-596.
E-mail address: acchakir@hotmail.com (A. Chakir).

zeta potential was observed after Cr(III) sorption. X-ray photoelectron spectroscopy measurements, at different pH values, were also made to corroborate the zeta potential results.

© 2002 Published by Elsevier Science B.V.

Keywords: Chromium(III) sorption; Bentonite; Expanded perlite; Zeta potential; X-ray photoelectron spectroscopy

1. Introduction

Chromium is commonly used in acid electroplating, tanning, painting, dye and manufacturing, and petroleum refining [1]. The health and environmental effects of carcinogenic Cr(VI) are well known [2–4]. If Fe(II), HSO₃, or another electron donor such as organic matter is present, Cr(VI) can be reduced to Cr(III), which tends to be attenuated in soil by inorganic phases such as phyllosilicates and hydroxides [5,6].

The oldest and most frequently used method for removal of trivalent chromium from waste water is the precipitation [7–12]. Research on the applicability of various precipitants such as sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, calcium carbonate, basic magnesium carbonate and magnesium oxide, had shown that residual chromium in tanning baths can be converted into denser precipitates when less soluble precipitants are used. Although this process is effective, it has some disadvantages. It produces a large amount of sludge [13] which have a long settling times [14].

For this reason, in recent years, there has been a rapid growth in the use of natural sorbents for controlling the soluble trivalent chromium ion concentration in heterogeneous systems. A number of sorbents have been investigated for their potential for chromium removal from solution. These sorbents have included: clay [15], activated or fibrous carbon [16,17], zeolite [18] and aluminium oxides [19,20].

With the object of investigating the economical upgrading of the local (Morocco) natural resources, we have directed our interest to the feasibility of sorption of chromium(III) onto bentonite and expanded perlite. Those substrates are very abundant materials in Morocco and have a low cost compared to other substrates as activated carbon or zeolite.

Perlite is an inert glassy volcanic rhyolitic rock which will expand when quickly heated to above 870 °C. It expands up to 20 times its original volume [21,22]. Expanded perlite acts as an excellent insulator, both thermal and acoustical, resists fire and is classified as ultra-lightweight material. As most of perlite contains greater than 70% silica, and are adsorptive, they are chemically inert in many environments and, hence, are excellent filter aids and fillers in various processes. Miscellaneous uses of expanded perlite include fillers or extenders in paint, enamels, glazes, plastics, and resins. It is also used as an agent in mixtures for oil-well-cementing [23].

Bentonite, due to its physical and chemical properties, i.e. large specific surface area, cation exchange capacity, and adsorptive affinity for organic and inorganic ions, is considered one of the most promising candidates for use in decontamination and disposal of high level heavy metals wastes [24,25].

2. Materials and methods

2.1. Adsorbents

The bentonite and unexpanded perlite samples were obtained from Nador, Morocco. The perlite was expanded in the Laboratory of the Office of Research and Mineral Participation [21]. Bentonite was used without any heat or chemical treatment for the sorption studies reported here.

2.2. Chemicals

All chemicals used in this study were of reagent analytical grade. The stock Cr(III) solution (10^{-1} M) was prepared by using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck). Chromium(III) solutions were standardised against K_2CrO_4 reference solutions which were prepared by using K_2CrO_4 (Merck). HNO_3 and NaOH used to adjust the pH of the suspensions were purchased from Prolabo. All solutions were prepared with high purity water ($18 \text{ M}\Omega/\text{cm}$) from a Millipore Milli-Q water purification system.

2.3. Instrumentation

The X-ray fluorescence analyses were performed on a dispersion wavelength spectrometer SRS 200. The particle size distribution of both expanded perlite and bentonite was measured using Mastersizer X (Malvern instruments). The specific surface areas were determined by BET Krypton adsorption method. A pH-meter Metrohm 681, with a combined glass electrode, Orion pH Ross 8102, filled with 3 M KCl was used in this study. Quantitative analysis of chromium(III) in solution was made by inductively coupled plasma-atomic emission spectroscopy (ICP–AES, Plasma 2000, Perkin-Elmer). ESCA measurement was performed on a VSW Model HA150 electron spectrometer, employing unmonochromatized Al $\text{K}\alpha$ (1486.6 eV) and Mg $\text{K}\alpha$ (1253.6 eV) sources of photons, the pressure in the analytical chamber being in the low 10^{-7} Pa range. The spectrometer work function was adjusted to give a value of 84.0 ± 0.05 eV for the Au $4f_{7/2}$ level of metallic gold. The survey scans were recorded using a fixed pass energy of 90 eV, while narrow scan spectra of the C 1s, O 1s, Si 2p, Al 2p, K 2p, Na 1s, and Cr 2p levels were recorded using a fixed pass energy of 22 eV. As charge effects were expected in the study of poorly conducting samples, the binding energy of the C 1s level from contamination at 284.6 eV and Si 2p level at 103.00 eV were used as internal reference to calibrate, respectively, every spectrum of expanded perlite and bentonite. Scofield [26] calculated cross-sections and the inelastic mean free path [27] were used for quantification. Spectra processing were performed using standard software. Zeta potential was measured with a Zeta Phoremeter Sephy equipped with a microprocessor unit. The unit calculates the electrophoretic mobility of the particles and converts it to the zeta potential in terms of the Smoluchowski equation.

2.4. Batch mode studies

The sorption of Cr(III) on both bentonite and perlite was studied by the separate batch technique. The general method used for these studies is described below.

Batch sorption experiments were conducted at room temperature of 20 °C using 50 ml screwed cap conical flasks. The reaction mixture consisted of a total volume of 25 ml containing 0.25 g of sorbent and known initial concentration of chromium. The initial Cr(III) concentration used was generally higher for bentonite than for expanded perlite because it was noted, during preliminary experiments, that the sorption of Cr(III) was greater on bentonite. The solution to solid ratio in all these experiments was 100:1. The pH of the suspension was adjusted using either dilute nitric acid or sodium hydroxide to desired values. The solution and the sorbents were maintained in intimate contact over a fixed time period during which samples were agitated using a shaker machine at 120 rpm. Thereafter, the solid and liquid were separated by filtration (0.22 μm , Millipore). The equilibrium concentrations of Cr(III) in the filtrate, were always measured on spectro-flame-ICP apparatus with an inductively coupled plasma excitation source. In some instances X-ray photoelectron spectroscopy (XPS) was used to determine the quantities of chromium adsorbed at the immediate surface of the solids.

3. Results and discussion

3.1. Characteristics of expanded perlite and bentonite

3.1.1. X-ray diffraction analysis

The bentonite sample was first studied by X-ray diffraction. It showed a high mineralogical purity and contained montmorillonite as a major constituent (Fig. 1a). X-ray diffraction

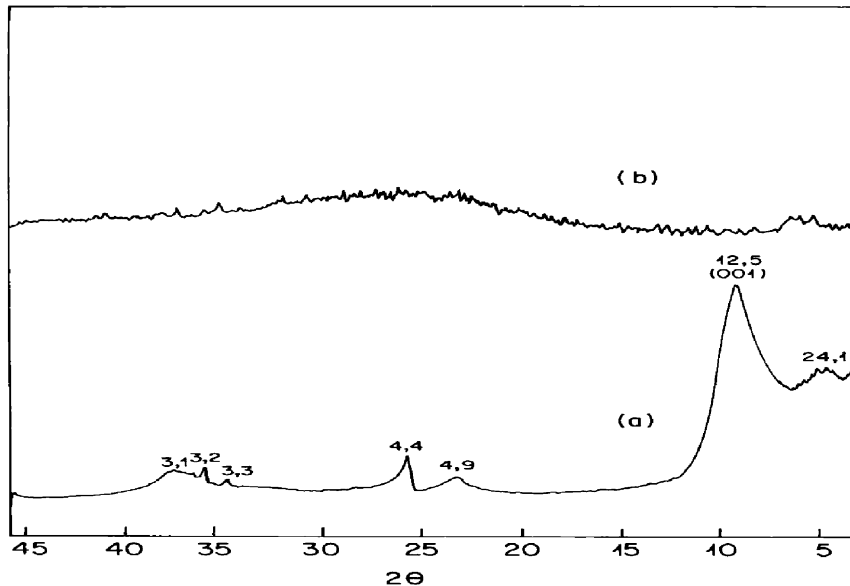


Fig. 1. X-ray diffraction diagram of: (a) bentonite; (b) expanded perlite.

Table 1
Chemical analysis of expanded perlite and bentonite

Constituent	Bentonite (%)	Expanded perlite (%)
SiO ₂	66.04	75.22
Al ₂ O ₃	23.00	13.08
Fe ₂ O ₃	4.33	1.83
P ₂ O ₅	0.08	0.02
TiO ₂	0.16	0.13
CaO	0.72	1.43
MgO	3.10	0.10
MnO	0.01	0.06
K ₂ O	0.64	4.95
Na ₂ O	1.77	3.00

analysis indicated that the expanded perlite was amorphous (Fig. 1b). This result agrees well with literature [22].

3.1.2. X-ray fluorescence analysis

The chemical composition of the expanded perlite and bentonite used in this study is summarised in Table 1. It can be noted that both expanded perlite and bentonite are natural alumino-silicate rich in SiO₂ and Al₂O₃. On the other hand, the SiO₂/Al₂O₃ molar ratio is two times greater for expanded perlite than bentonite.

3.1.3. Surface characterisation by XPS

The only contaminant detected by XPS on the surface of expanded perlite and bentonite was carbon (Fig. 2a and b). For bentonite, which is of high purity, the carbon detected is mainly due to the XPS apparatus. The percentage and binding energy of elements presented at the surface of the two substrates are summarised in Table 2.

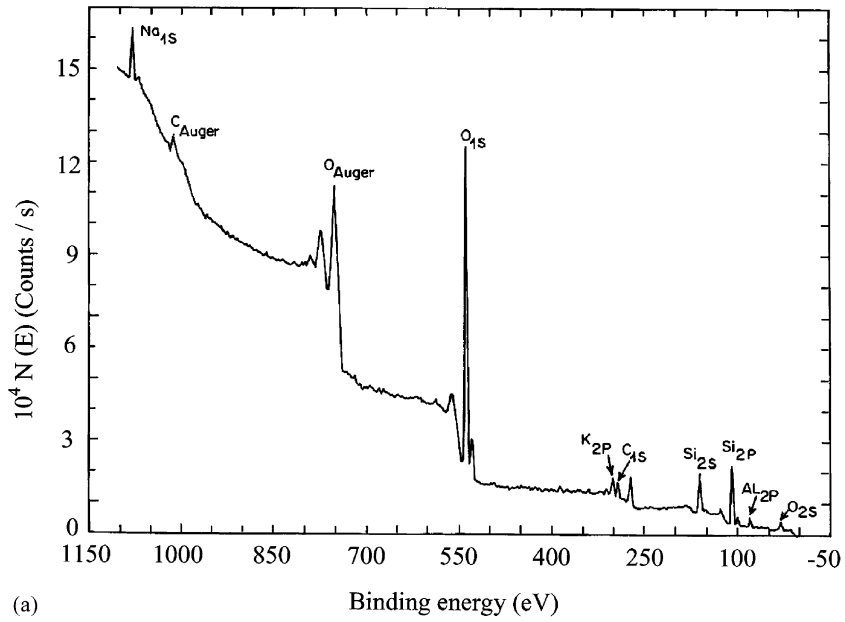
3.1.4. Specific surface area and particle size

The specific surface area of bentonite (33 m²/g) is approximately 19 times larger than that of expanded perlite (1.73 m²/g).

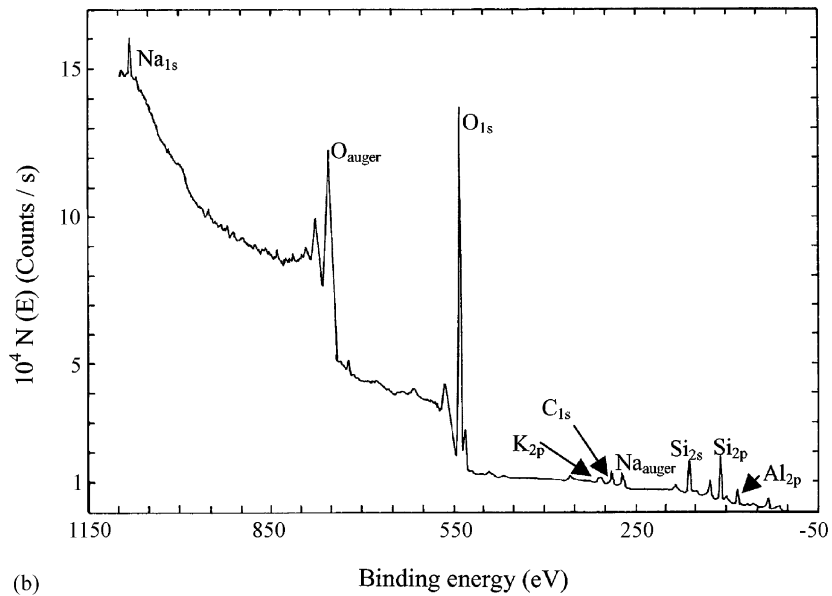
Expanded perlite had an important granulometry compared to bentonite. Thus, particle size of bentonite ranged between 3.4 and 48.4 μm, 50% were 20.3 μm while for expanded perlite it ranged between 7.0 and 65.7 μm, 50% were 30.3 μm.

Table 2
Binding energy and Percentage of element present in the surface of expanded perlite and bentonite

Constituent	Binding energy (eV)		Percentage (%)	
	Expanded perlite	Bentonite	Expanded perlite	Bentonite
Si 2p	102.7	103.0	23.7	20.0
O 1s	532.0	532.2	55.9	59.9
Na 1s	1072.4	1073.4	6.1	4.1
C 1s	284.6	284.5	7.0	7.7
K 2p	293.3	292.5	2.3	0.1
Al 2p	73.9	74.7	5.1	8.0



(a)



(b)

Fig. 2. XPS spectrum of: (a) expanded perlite; (b) bentonite.

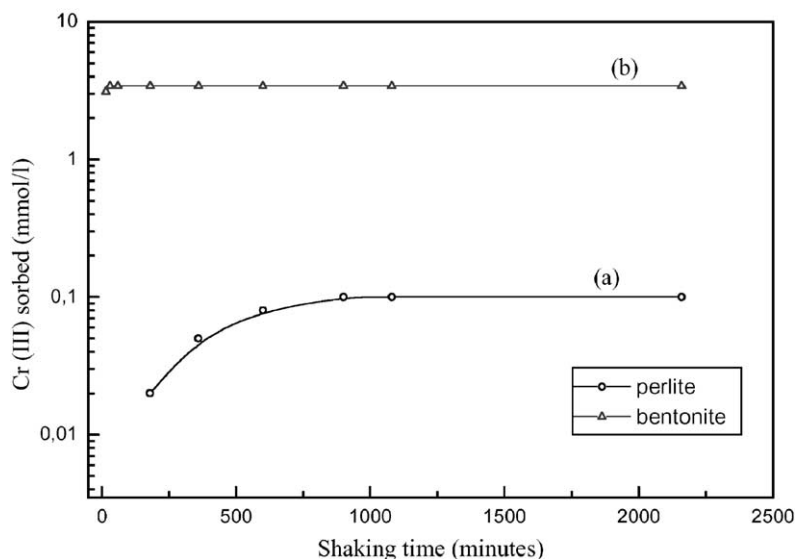


Fig. 3. Effect of shaking time on Cr(III) sorption onto: (a) expanded perlite; (b) bentonite pH = 3, pulp density = 1%.

3.2. Interactions between adsorbat–adsorbents

3.2.1. Effect of shaking time

The sorption of Cr(III) on bentonite and expanded perlite was studied as a function of shaking time.

The kinetic study was performed at pH 3 and an initial Cr(III) concentration of 5×10^{-3} mol/l (bentonite) and 3.8×10^{-4} mol/l (expanded perlite). The results of this study showed that the uptake of Cr(III) by expanded perlite at pH 3 is slow and the equilibrium was reached within 15 h (Fig. 3). However, the uptake of Cr(III) by bentonite is very rapid. The quantity removed from solution reached a maximum value 30 min after mixing and did not change with time (Fig. 3). The rapid equilibrium on bentonite can be attributed to its expanded lattice, which made all exchange sites equally available and permitted exchange readily. Similar results have been reported for the adsorption of cesium on montmorillonite [28].

On the basis of these results a shaking period of 24 h was used for all further studies so that all analysis, for both bentonite and expanded perlite, were made at the same time.

3.2.2. Effect of pH

The effect of pH on the adsorption of trivalent chromium on expanded perlite and bentonite in the pH range 1.5–5.0 is depicted in Figs. 4 and 5. The pH was limited to values less or equal to 5 because of precipitation at higher pH [29].

As can be noted from these figures, the bentonite removes greater quantities of Cr(III) ions compared to expanded perlite. The amounts sorbed by bentonite were approximately

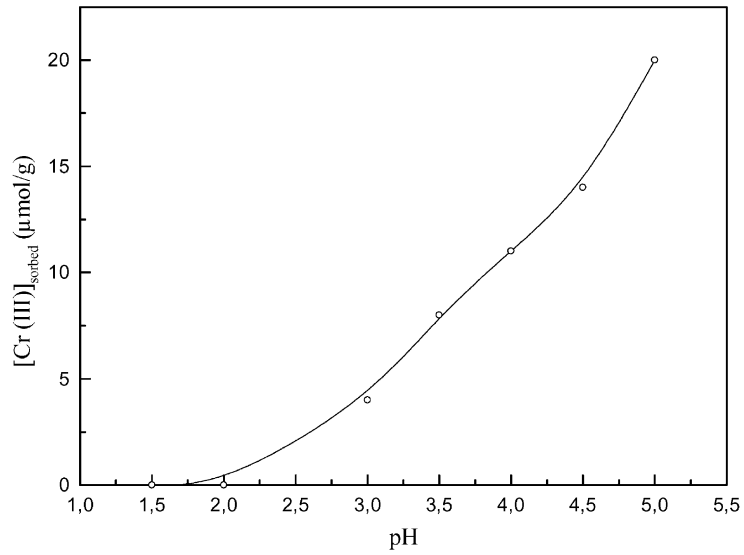


Fig. 4. Effect of pH on Cr(III) sorption onto expanded perlite $[\text{Cr(III)}]_{\text{initial}} = 5 \times 10^{-4}$ mol/l; shaking time = 24 h; pulp density = 1%.

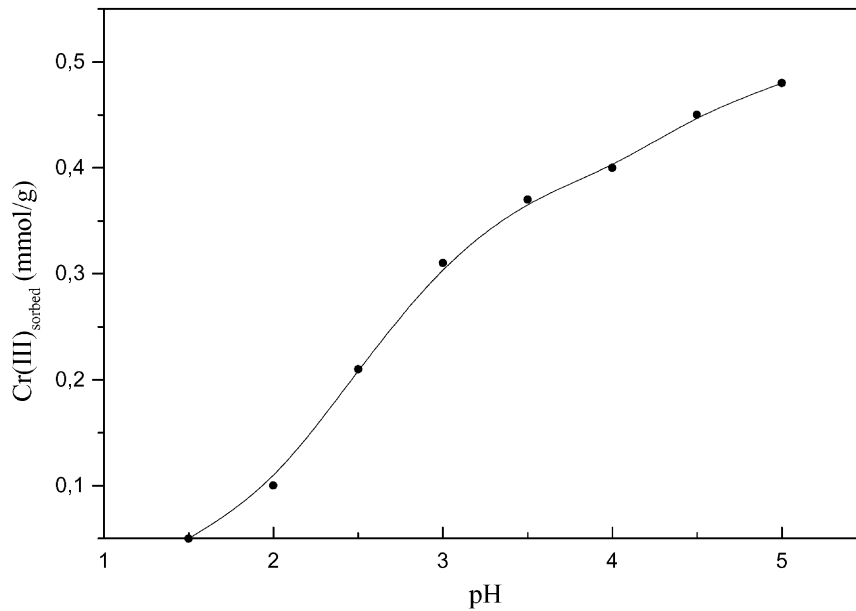


Fig. 5. Effect of pH on Cr(III) sorption onto bentonite $[\text{Cr(III)}]_{\text{initial}} = 5 \times 10^{-3}$ mol/l; shaking time = 24 h; pulp density = 1%.

24–77 times larger than the amounts sorbed by expanded perlite. Although the sorption of Cr(III) ions is much greater onto bentonite than onto expanded perlite, a similar type of pH dependence was observed. In the two cases the adsorption increased with increasing pH. Similar phenomenon has been reported for sorption of Cr(III) on montmorillonite [15], activated carbon [17] and Al_2O_3 [19]. It was generally attributed to the change, with pH, of the properties of both sorbents (charge and potential) and solution composition (metal ion speciation).

3.2.3. Electrokinetic measurements

Since data obtained from electrokinetic measurements on solids systems can in principle be used to carry out a careful investigation of the solid particles and its interactions with the surrounding medium, it was of interest to study the effect of pH on zeta potential of expanded perlite and bentonite before and after Cr(III) sorption.

As shown in Figs. 6a and 7a, the expanded perlite and bentonite samples have no point of zero charge (p.z.c.) and exhibits negative zeta potential value at all pH values. This result agrees with those obtained from electrokinetic measurements of clay minerals [30–32] and Turkish perlite [33]. The origin of this charge is still a controversial issue, but the majority of evidence suggests that this charge arises from isomorphous substitutions, defects in the crystal lattice, broken particle edges, and structural hydroxyl groups [34].

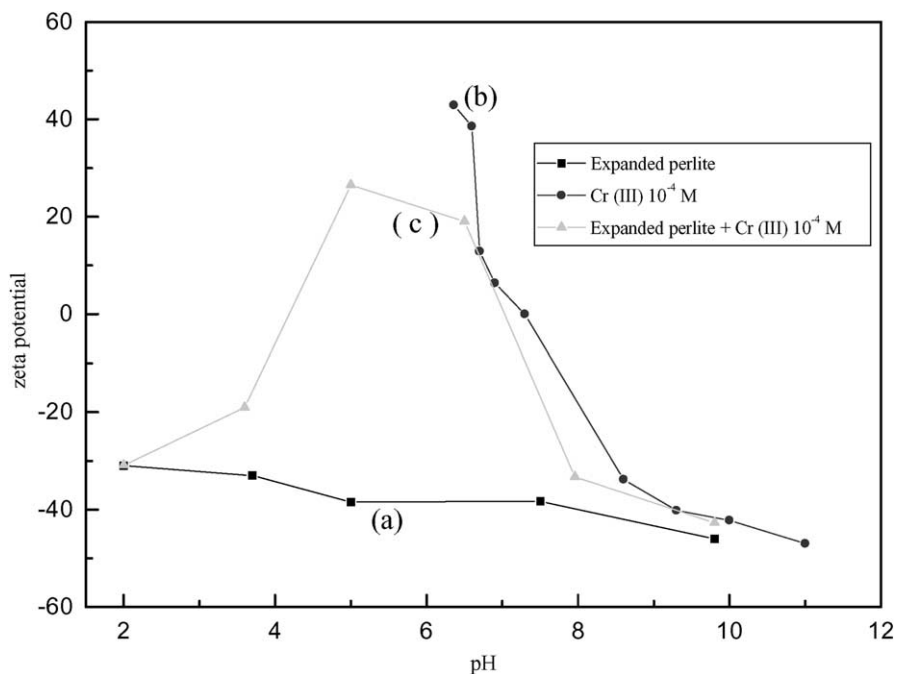


Fig. 6. Effect of pH on zeta potential of: (a) expanded perlite; (b) Cr(III) 10^{-4} M; (c) expanded perlite + Cr(III) 10^{-4} M.

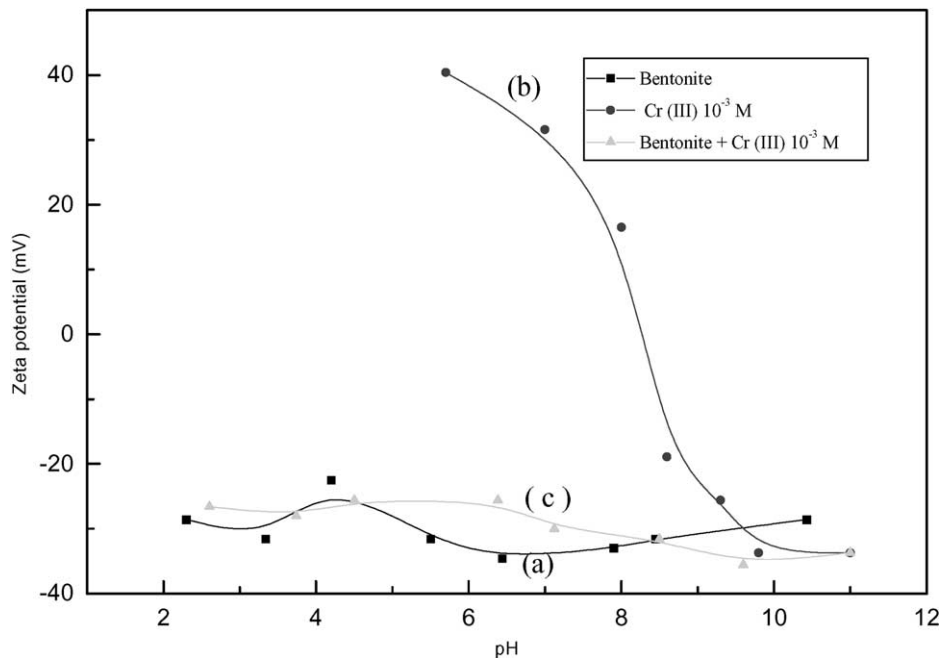


Fig. 7. Effect of pH on zeta potential of: (a) bentonite; (b) Cr(III) 10^{-3} M; (c) bentonite + Cr(III) 10^{-3} M.

The electrical charge at the oxide surface/aqueous phase to protonation/deprotonation of the surface hydroxyl can be ascribed as [35]:



and at p.z.c.,



because there was no p.z.c., the reaction responsible for the surface charge of the solid is mainly the reaction in Eq. (2).

To obtain more information about the nature of Cr(III) adsorption onto expanded perlite and bentonite, it was of interest to investigate the effect of chromium(III), at constant concentration of 10^{-3} M (bentonite) and 10^{-4} M (expanded perlite), on the surface electric properties of the two adsorbents at different pH values.

In the case of expanded perlite, the effect of Cr(III) on the zeta potential (henceforth termed “adsorption zeta potential”) is important and dependent on pH (Fig. 6c). The variation of adsorption zeta potential with pH is quite different to that in the absence of adsorption, in particular, in the pH range 3–7 where the zeta potential is found to be increasing. It exhibits two charge reversals not seen in the absence of chromium. Thus at pH 4.5, the surface charge becomes increasingly positive. Within this pH range, the expanded perlite

has a negative charge (Fig. 6a), while chromium(III) tends to form a cationic species and consequently, has a positive surface charge (Fig. 6b), thus the electrostatic interactions between the surface and Cr(III) complexes are considerable. Therefore, changes to the sign of the zeta potential of expanded perlite in the presence of chromium can be directly related to the specific adsorption of cationic chromium(III) species [33–35]. In a previous paper [36], it was showed that at fixed pH (e. g. pH = 5), the zeta potential of expanded perlite increased with increasing Cr(III) concentration. This fact was attributed (as confirmed by XPS measurement) to the greater amount of Cr(III) sorbed on the surface. On the other hand, based on the literature for the measurement of zeta potentials in the presence of metal ion adsorption [37], the first reversal charge occurs due to the increased positive charge associated with specific adsorption of cationic species. The second charge reversal originates predominantly from the properties of the substrate as modified by the adsorbed metal ion. The influence of the adsorbed metal ion on the second charge reversal depends on the extent of coverage. As illustrated in Fig. 6c, the second charge reversal (pH 7.5) correlate well with the isoelectric point of Cr(III) hydroxide ($[\text{Cr(III)}] = 10^{-4} \text{ M}$) indicating a fully coated substrate and consequently the properties of that coating dominated. However, at $\text{pH} > 7.5$ both the expanded perlite and the chromium hydroxide are negatively charged so that the electrostatic interactions between the surface and Cr(III) are negated.

In the case of bentonite, no net change of the surface was observed in the pH range 2–4 where trivalent chromium ions are sorbed (Fig. 7c). This result indicates that Cr(III) ions are not sorbed at the surface of bentonite. The same behaviour was observed for Pb(II) ions adsorption on zeolite [38]. To explain this finding the particular characteristics and structure of bentonite must be taken into account: bentonite belongs to the family of dioctahedral layer lattice silicates with a 2:1 structure. It is characterised by high negative permanent surface charge partially compensated by hydrated cations positioned in the interlayer spacing of the solid. These cations can be exchanged reversibly with other ions from the surrounding solution [39]. This result is in good agreement with the effect of pH on Cr(III) adsorption observed previously (Fig. 5). Thus, if one accepts that cation exchange is the principal mechanism for cation sorption by bentonite, then chromium(III) is known [40] to be extensively hydrolysed in acid solutions to species such as Cr(OH)^{2+} , Cr(OH)_2 , $\text{Cr}_2(\text{OH})_4$, $\text{Cr}_6(\text{OH})_{12}$, and $\text{Cr}_6(\text{OH})_{15}$. The increased sorption of Cr(III) as pH increased (Fig. 5) could in part, be attributed to exchange—adsorption of hydrolysed Cr(III) species. Competition for exchange sites with hydrogen and aluminium associated with the clay also decreased rapidly as the pH was raised in the range 1.5–5.0 and contributed to the increased sorption.

3.2.4. XPS study

To confirm the electrokinetic results, simultaneous XPS analysis were used.

The surface of bentonite and expanded perlite was characterised by XPS before and after Cr(III) adsorption. XPS examination of substrates after contact with chromium(III) solutions indicates the presence of chromium species at the immediate surface of the substrates. Typical core level spectra obtained for those samples are shown in Figs. 8 and 9, perlite and bentonite, respectively, from batch reactors containing a solution of $5 \times 10^{-4} \text{ M}$ Cr(III) (in the case of expanded perlite) and $5 \times 10^{-3} \text{ M}$ Cr(III) (in the case of bentonite) at different pH values. The Cr 2p binding energies are in reasonable agreement with those available in the literature [41,42] for Cr(III) compounds. The variation in the Cr 2p_{3/2} peak area/Si

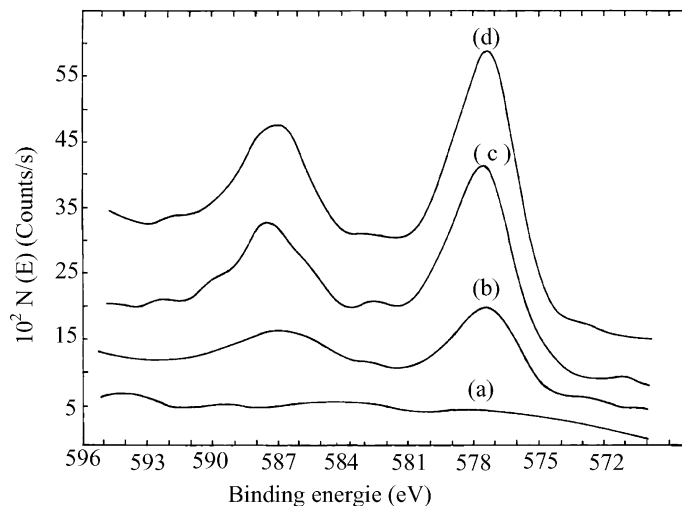


Fig. 8. Cr 2p XPS spectrum of expanded perlite with Cr(III) 5×10^{-4} M at different pH: (a) pH = 2; (b) pH = 3; (c) pH = 4; (d) pH = 5.

2p peak area ratios shown by XPS after adsorption of Cr(III) onto expanded perlite and bentonite at different pH are given in Table 3. It can be noted that at pH 2 or below, no peak, due to chromium was observed. The level of chromium incorporation increases as the pH increases. These results are corroborative of those obtained previously (Figs. 4 and 5).

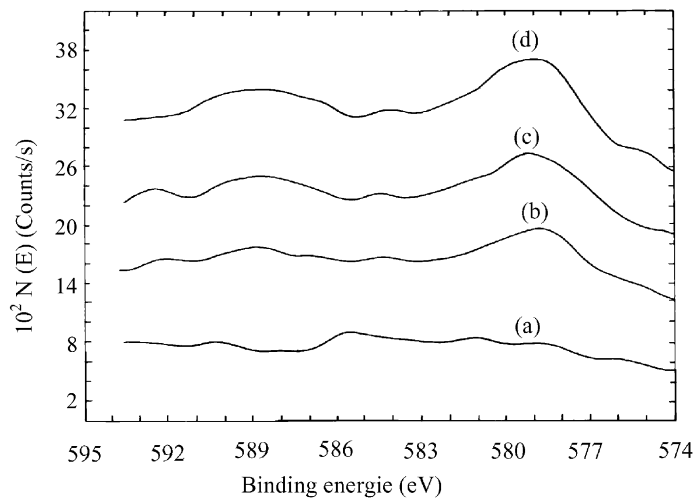


Fig. 9. Cr 2p XPS spectrum of bentonite with Cr(III) 5×10^{-3} M at different pH: (a) pH = 2; (b) pH = 3; (c) pH = 4; (d) pH = 5.

Table 3
Variation of Cr 2p_{3/2} (peak area)/Si 2p (peak area) and removal efficiency with pH^a

pH	Expanded perlite + Cr(III) ([Cr(III)] _{initial} = 5 × 10 ⁻⁴ M)		Bentonite + Cr(III) ([Cr(III)] _{initial} = 5 × 10 ⁻³ M)	
	10 ² (Cr 2p _{3/2} peak area/Si 2p peak area)	Removal efficiency (%)	10 ² (Cr 2p _{3/2} peak area/Si 2p peak area)	Removal efficiency (%)
2	0	0	0	20
3	1.7	8	1.5	62
4	3.5	22	1.8	80
5	7.5	40	2.2	96

^a The removal efficiency, P , is defined as: $(P = C_0 - C_e/C_0) \times 100$, where C_0 is the initial concentration of Cr(III) and C_e is the equilibrium solution concentration.

The amounts of Cr(III) detected at the immediate surface of the expanded perlite were generally greater than those detected on the surface of bentonite. To account for the removal efficiency of both adsorbents determined in Table 3, the lower quantities of Cr(III) detected by XPS at the bentonite surface can be related to the bentonite structure, which favours the sorption of cations on the interior faces. Thus the Cr(III) ions sorbed in the interlayer spacing cannot be observed by XPS which is a surface technique.

However, in the case of expanded perlite, the important quantities detected at the immediate surface (compared to bentonite) could be related to surface complexation phenomenon. XPS characterisation of expanded perlite had shown that the most important constituents of this substrate are silicon and aluminium oxides (Table 2). Therefore, the adsorption of trivalent chromium ions by perlite is assumed to occur with formation of surface complexes between the functional groups of surface oxides and dissolved Cr(III) ions. The same behaviour in the adsorption of Cr(III) ions by Al₂O₃ was reported in the literature. Karthein et al. [43] employed electron spin resonance and electron spin-echo spectroscopy to study the interaction of Cr(III) complexes with hydrous δ -Al₂O₃ and reported that chromium complexation takes place at specific surface sites. The formation of bidentate (SO)₂Cr(H₂O)⁺ surface complex was postulated (where S denoted surface). Chang et al. [19] outlined a study on kinetics of Cr(III) adsorption/desorption at the γ -Al₂O₃/water interface by the pressure-jump technique and concluded that the adsorption of Cr(III) occurred with the formation of both monodentate SOCrOH⁺ and bidentate (SO)₂Cr⁺ inner-sphere complexes at the surface of γ -Al₂O₃.

3.2.5. Adsorption Isotherms at 20 °C

To confirm the results of this study which suggest that surface complexation plays an important role in the adsorption of Cr(III) species on expanded perlite while cation-exchange is the predominate mechanism for sorption of trivalent chromium ions by bentonite, it was of interest to examine the adsorption isotherms.

Adsorption isotherms of trivalent chromium on the two substrates at different pH values are given in Figs. 10 and 11.

All the isotherms indicate a positive adsorption. The removal of chromium by bentonite is much higher in comparison to expanded perlite. The sorption capacity of the two sorbents increases with increasing pH. On the other hand, the adsorption isotherms of bentonite

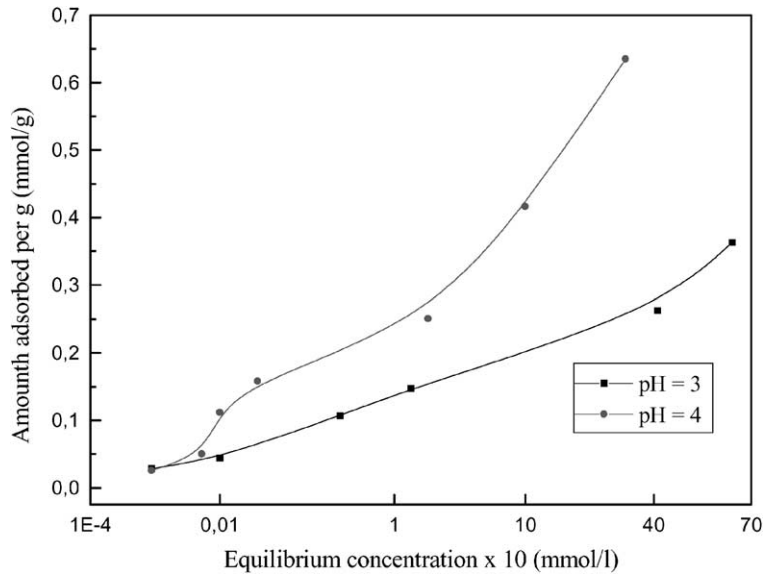


Fig. 10. Adsorption isotherms of Cr(III) sorption on bentonite.

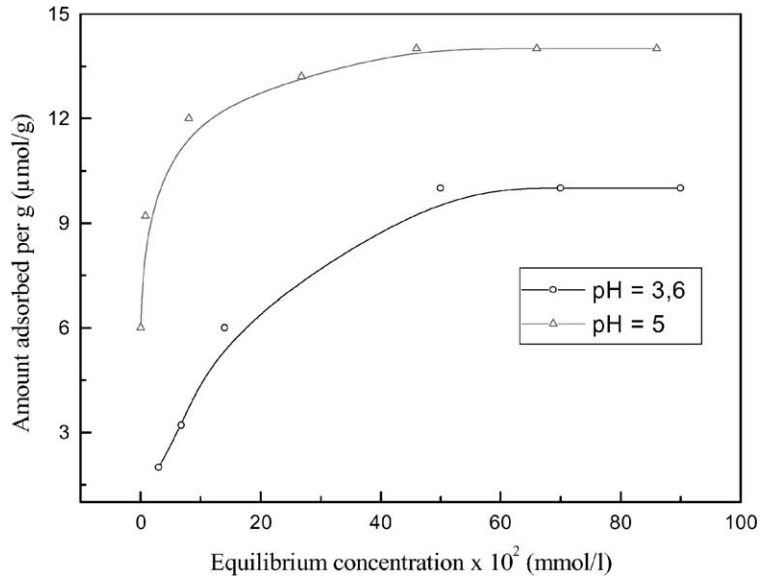


Fig. 11. Adsorption isotherms of Cr(III) sorption on expanded perlite.

have no plateau (Fig. 10), these isotherms could not be defined in a larger concentration range, since, the experimental work was limited by Cr(III) precipitation. Therefore, it seems reasonable to suppose that, in the experimental conditions used, there is no formation of a complete monolayer of trivalent chromium molecules covering the bentonite surface. However, the existence of a plateau for expanded perlite isotherms (Fig. 11) indicated that saturation of the surface has been reached.

In order to discover the adsorption capacities of the two adsorbents, experimental results were analysed in terms of Langmuir and Freundlich isotherms.

The following linearized form of the Langmuir and Freundlich equations were used for this purpose:

$$\frac{C_e}{q_e} = \frac{C_e}{Q^\circ} + \frac{1}{bQ^\circ} \quad (\text{Langmuir})$$

$$\log q_e = \log K_N + \frac{1}{n} \log C_e \quad (\text{Freundlich})$$

where C_e is the measured chromium concentration in solution at equilibrium, q_e the amount of chromium adsorbed per unit weight of adsorbent, Q° the amount of chromium adsorbed per unit weight of adsorbent in forming a complete monolayer coverage on the adsorbent surface, and b is a constant related to the net enthalpy of adsorption. K_N and $1/n$ are empirical constants, being indicative of the extent of adsorption and the degree of non-linearity between solution concentration and adsorption, respectively.

The adsorption isotherms for Cr(III) sorption, in the concentration range 10^{-4} to 10^{-2} mol/l, on bentonite were presented by Freundlich model (Fig. 12). All of the

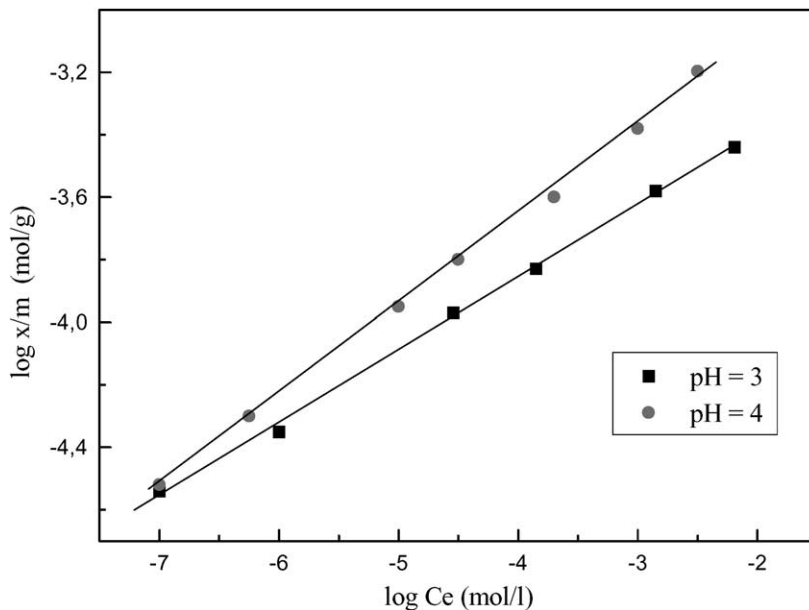


Fig. 12. Freundlich plots for Cr(III) sorption on bentonite.

Table 4
Isotherms characteristics for Cr(III) removal using expanded perlite and bentonite

Sorbent	pH	$Q^{\circ} \times 10^5$ (mol/g)	$1/bQ^{\circ}$	$K_N \times 10^3$	n
Expanded perlite	3.6	1.1	11.96	–	–
	4.5	1.4	0.54	–	–
Bentonite	3.0	–	–	1.18	4.29
	4.0	–	–	3.41	3.35

correlation coefficients R^2 exceeded 0.99 indicating the adequacy of the Freundlich models in describing bentonite isotherm data. Because the sorption data for Cr(III) in the concentration range used did not fit in the Langmuir equation, the results using this model are not presented.

The values of the parameters in the Freundlich isotherms are summarised in Table 4. Over a range of one pH unit, the K_N value was increased by three times. This result confirms the higher reactivity of bentonite for Cr(III) with increasing pH. The slopes of the two Freundlich plots was < 1 , indicating a concentration dependent sorption of trivalent chromium on bentonite in the concentration range used. Similar results were reported for various other adsorption systems where the adsorption is assumed to occur with cation-exchange processes [44–47].

Data obtained for Cr(III) sorption, in the concentration range 5×10^{-5} to 10^{-3} mol/l, on expanded perlite at pH values of 3.6 and 4.5 fits well to the Langmuir model (Fig. 13). All the Langmuir plots gave linear regression values greater than 0.99. Such strong compliance with the Langmuir equation support our hypothesis of adsorption of Cr(III) through

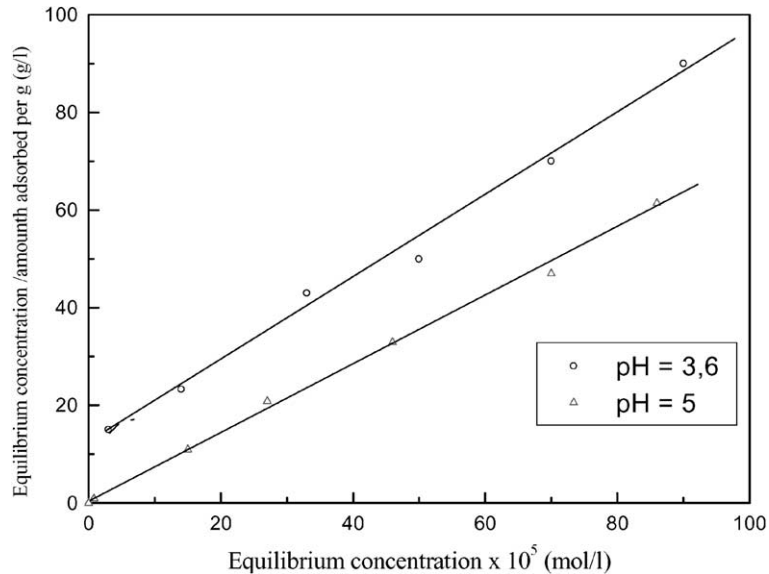


Fig. 13. Langmuir plots for Cr(III) sorption on expanded perlite.

a surface complexation phenomenon. However, it is well documented that the general surface complexation model exhibits Langmuir behaviour at low metal concentration where monolayer adsorptive coverage exists. Farley et al. [48] had shown that at fixed pH the surface complexation model for the sorption of cations on metal oxides in its simplest form is mathematically equivalent to the Langmuir isotherm equation.

From the slopes of the Langmuir plots, adsorption maxima were calculated and are presented in Table 4. The calculated Q_0 values confirm that the increase pH enhanced the adsorption capacity of expanded perlite.

4. Conclusion

Natural bentonite and expanded perlite have been characterised and evaluated for removal of trivalent chromium from aqueous solutions. The following points are the results of this study:

- Electrokinetic measurements associated with XPS study had showed that, in the pH range 2–5.0, surface complexation plays an important role in the sorption of Cr(III) species on expanded perlite while cation-exchange is the predominate mechanism for sorption of trivalent chromium ions by bentonite.
- The adsorption isotherms for Cr(III) sorption, in the concentration range 10^{-4} to 10^{-2} mol/l (bentonite) and 10^{-5} to 10^{-3} mol/l (expanded perlite), were presented, respectively, by Freundlich and Langmuir models.
- For both sorbents, the sorption capacity increases with increasing the pH of the suspensions.
- The removal efficiency has been calculated for both sorbents indicating that bentonite (96% of Cr(III) removed) is more effective for removing trivalent chromium from aqueous solution than expanded perlite (40% of Cr(III) removed).
- The uptake of Cr(III) by bentonite is very rapid compared to expanded perlite.

Acknowledgements

This work was supported by a Cooperation Grant between France and Morocco, A. P. A. P. E., No. 1115.

References

- [1] E. Nieboer, A.A. Jusys, in: J.O. Nriagu, E. Nieboer (Eds.), Chromium in the Natural and Human Environments, Wiley, New York, 1988, p. 25.
- [2] J.A. Davis, J.O. Leckie, J. Colloid Interface Sci. 74 (1980) 32.
- [3] J.M. Zachara, D.C. Girvin, R.L. Schmidt, C.T. Resch, Environ. Sci. Technol. 21 (1987) 589.
- [4] J.M. Zachara, C.E. Ainsworth, C.T. Resch, Soil Sci. Soc. Am. 53 (1989) 418.
- [5] R.L. Barlett, J.M. Kimble, J. Environ. Qual. 5 (1976) 379.
- [6] D.C. Schroeder, G.F. Lee, Water Air Soil Pollut. 4 (1975) 355.
- [7] S. Joseph, A. Langerwerf, J. Soc. Leather Tech. Chemists 69 (1985) 166–174.

- [8] M.S. Maire, J. Am. Leather Chemists Assoc. 72 (1977) 404–418.
- [9] R.P. Daigle, D.J. Benett, J. Am. Leather Chemists Assoc. 81 (1986) 305–311.
- [10] C.M. Santiago Jr., D.B. Isaac, P.G. Anglo, B.M. Garcia, C.M. Silverio, R.L. Esguerra, F.C. Rodillo, M.B. Bigol, *Philippine J. Sci.* 122 (1993) 41–58.
- [11] J.M. Constantin, G.B. Stockmann, *Technicuir* 14 (1980) 49–51.
- [12] D.A. Boast, J. Am. Leather Chemists Assoc. 83 (1988) 17–23.
- [13] G. Macchi, M. Paganot, M. Pettine, M. Santori, G. Tiraventi, *Water Res.* 25 (1991) 1019–1026.
- [14] G. McIntyre, J.J. Rodrigues, E.L. Thackston, D.J. Wilson, *J. Water Pollut. Control Fed.* 55 (1983) 1144–1149.
- [15] R.A. Griffin, A.K. Au, R.R. Frost, *J. Environ. Sci. Health A12* (8) (1977) 431–449.
- [16] A.A. Morozova, *Russian J. Appl. Chem.* 68 (1995) 673–676.
- [17] R. Lyva-ramos, L. Fuentes-Rubio, R.M. Guerrero-coronado, J. Mendoza-Barron, *J. Chem. Tech. Biotechnol.* 62 (1995) 64–67.
- [18] M. Loizidou, K.J. Haralambous, A. Loukatos, D. Dimitrakopoulou, *J. Environ. Sci. Health A27* (7) (1992) 1759–1769.
- [19] K.S. Chang, C.F. Lin, D.Y. Lee, S.L. Lo, T. Yasunaga, *J. Colloid Interface Sci.* 165 (1994) 169–176.
- [20] B. Wehrli, S. Ibric, W. Stumm, *Colloids Surf.* 51 (1990) 77–88.
- [21] M. Salem, R. Jaidi, *Mines Carrières-les tech.* 89 (1989) 95–97.
- [22] W.P. Bolen, *Perlite Am. Ceram. Soc. Bull.* 73 (1994) 117–118.
- [23] C.W. Chesterman, *Industrial Minerals and Rocks*, 4th Edition, AIME, New York, 1975, p. 927.
- [24] M. Takahashi, M. Muroi, A. Ignore, A. Aoki, M. Takizawa, M. Ishigure, N. Fujita, *Nucl. Technol. U.S.A.* 76 (1987) 221.
- [25] W. Zhixiong, Waste repository technology, in: A.H. Hadjian (Ed.), *Proceedings of the Transactions of the 10th International Conference on Structural Mechanics in Reactor Technology*, R. 171, American Association for Structural Mechanics in Reactor Technology, 1989, p. 135.
- [26] J.H. Scofield, *J. Electron. Spectrosc. Relat. Phenom.* 8 (1976) 129.
- [27] M.P. Seah, W.A. Dench, *Surf. Interface Anal.* 1 (1979) 2.
- [28] B.L. Sawhney, *Soil Sci. Soc. Am. Proc.* 30 (1966) 565–569.
- [29] M.J. Avena, C.E. Giacomelli, C.P. De Pauli, *J. Colloid Interface Sci.* 180 (1996) 428–435.
- [30] A. Delago, F. Gonzalez-Caballero, J.M. Bruque, *J. Colloid Interface Sci.* 113 (1986) 203–211.
- [31] Y. Horikawa, R.S. Murray, J.P. Quirk, *Colloids Surf.* 32 (1988) 181–195.
- [32] D.J.A. Williams, K.P. Williams, *J. Colloid Interface Sci.* 65 (1978) 79–87.
- [33] M. Dogan, M. Alkan, Ü. Cakir, *J. Colloid Interface Sci.* 192 (1997) 114–118.
- [34] I. Gülgönül, Master thesis, Istanbul Technical University, Mining Faculty, Istanbul, 1995.
- [35] J.S. Laskowski, *J. Colloid Interface Sci.* 159 (1993) 349–353.
- [36] A. Chakir, J. Bessiere, K. El kacemi, B. Marouf, *Int. J. Environ. Studies*, 2002, in press.
- [37] R.J. Crawford, I.H. Harding, D.E. Mainwaring, *J. Colloid Interface Sci.* 181 (1996) 561–570.
- [38] M.A. Lamdaour, University thesis, Mohamed V University, Science Faculty, Rabat, 2001.
- [39] I. Soundi, J. Biscan, V. Pravdic, *J. Colloid Interface Sci.* 178 (1996) 514–522.
- [40] C.L. Rollinson, in: J.C. Bailar Jr., D.H. Busch (Eds.), *Chemistry of the Coordination Compounds*, Reinhold, NY, 1956 (Chapter 13).
- [41] D. Shuttleworth, *J. Phys. Chem.* 84 (1980) 1629–1634.
- [42] I. Ikemoto, K. Ishii, S. Kinoshita, H. Kuroda, M.A. Alario Franco, J.M. Thomas, *J. Solid State Chem.* 17 (1976) 425–430.
- [43] R. Karthein, H. Motschi, A. Schweiger, S. Ibric, B. Sulzberger, W. Stumm, *Inorg. Chem.* 30 (1991) 1606.
- [44] M.A. Bangash, J. Hanif, M. Ali Khan, *Waste Manage.* 12 (1992) 29.
- [45] S. Ali Khan, R. Rehman, M. Ali Khan, *Waste Manage.* 14 (1994) 629.
- [46] S. Ali Khan, R. Rehman, M. Ali Khan, *J. Radioanal. Nucl. Chem.* 190 (1995) 91.
- [47] S. Aksoyoglu, Cesium sorption on mylonite, *J. Radioanal. Nucl. Chem.* 140 (1990) 301.
- [48] K.J. Farley, D.A. Dzombak, F.M.M. Morel, *J. Colloid Interface Sci.* 106 (1984) 226–242.