



Research paper

A comparison of single and mixed pillared clays for zinc and chromium cations removal

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ABSTRACT

In order to explore the feasibility of improving zinc and chromium ability of zirconium-aluminium pillared clays (PILC), mixed zirconium-aluminium PILC with different Zr/Al ratio (Zr/Al = 100/0, 90/10, 50/50, 10/90 and 0/100) were prepared and investigated for their ability to remove zinc and chromium from water. Single and mixed PILC were characterized with X-ray diffraction, N₂ adsorption–desorption, FT-IR spectroscopy method, etc. Results indicate that, in the case of single PILC, zirconium PILC exhibited an adsorption capacity higher than aluminium PILC. In the case of mixed PILC, adsorption capacity increased as the ratio of Zr/Al increased. The influence of the pH values and the temperature on adsorption capacity was also investigated.

1. Introduction

Industrial activities generate a wide diversity of wastewaters with contaminants that can harm ecosystems and human beings. The residual waters of tanneries are loaded by many heavy metals notably zinc and chromium. This last one is often used in excess to improve the quality of tanning, and by this fact, the waters of dismissal are concentrated strongly in ion chromium-plates (Arfaoui et al., 2005). Chromium is among the heavy metals that can harm the ecosystems (Yu and Margrave, 2003). Zinc can interrupt the activity in soils and may also increase the acidity of waters (Lim and Chee, 2012).

To minimize the impact of industrial wastewaters, contaminant adsorption has often been used as an important approach for resolving such problems. In this context, in contaminated/wastewater processes, natural minerals are usually used as adsorbents and have attracted much attention for their higher removal efficiency, lower cost and variety of properties (Edzwald et al., 1976; Fox and Malati, 1993; Fontes and Weed, 1996). Bentonite one of the most abundant clay at the earth surface, was also found to be an effective adsorbent for the removal of toxic compounds from soil, water, and air (Murray, 2000). Exchanging the interlayer cations of the layered clay for other inorganic species originates pillared interlayered clays (or pillared clays, PILC). PILC are typically synthesized by exchanging the interlayer cations of clay with large oligomeric polycations such as Al, Zr, Fe, Cr, Al–Cu, Al–La, Al–Si, and various other oligomer (Adams and McCabe, 2006; Bergaya et al., 2006; Vicente et al., 2013) The synthesis and

characterizations of PILC have been carried out by a number of authors. Bergaya et al. (2006) summarized the different pillaring methods and the various pillaring species over the past 30 years.

The chemical surface and structural PILC properties establish the potentiality of applications, such as adsorbent (Bouchenafa-Saïb et al., 2007; Ranbo et al., 2008; Tian et al., 2009; Gil et al., 2011; Jalil et al., 2014; Menglin et al., 2015; Georgescu et al., 2018) or as catalyst (Gil and Luis, 2000; Gil et al., 2008; Menglin et al., 2015; Louloudi and Papayannakos, 2016; Sesegma et al., 2017). The latter process is illustrated in a wide range of reactions, such as: cracking, cyclohexane conversion, toluene in methanol alkylation, propylene oligomerization, etc. All these applications are also commonly employed in the petroleum industry for long-chain hydrocarbon filtering and azeotropic cracking.

In this study, various PILC were prepared and used for the removal of chromium and zinc cations from water. The structure characteristics were investigated through characterization with X-ray diffraction (XRD). The adsorption isotherms, and kinetics chromium and zinc cations adsorption on PILC were examined and compared. The influences of pH and temperature on adsorption of chromium and zinc cations on PILC were determined. Langmuir and Freundlich adsorption isotherm models were applied in order to fit the experimental data. In addition, a kinetic study was performed by considering the experimental data, which were adjusted to the pseudo-first-order Lagergren and pseudo-second-order.

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2. Experimental conditions

2.1. Preparation of Na⁺-bentonite

In order to prepare the pillared materials, the bentonite was purified by conventional sedimentation. To eliminate the calcite (23%, measured by calcimetry), crude bentonite was first treated with 0.3 M HCl. The pretreated sample was then stirred for 12 h at room temperature and at a rate of 100 g l⁻¹ in a molar solution of sodium chloride. The dispersion was then centrifuged at 3000 rev min⁻¹. The ion exchange was repeated five times. After the final centrifugation, the clay exchanged with sodium was washed by centrifugation and then separated from its impurities by sedimentation/decantation. Finally, removal of the excess chloride by dialysis with distilled water gave Na⁺-bentonite (Na⁺-Bent). The chemical composition of the Na exchanged purified fraction, expressed in the oxide form/100 g of the calcined sample, is SiO₂ 61.38, Al₂O₃ 24.80, Fe₂O₃ 8.03, Na₂O 3.06, MgO 1.38, CaO 0.13, K₂O 1.40. The structural formula of Na⁺-Bent was found to be: ^{IV}[Si_{7.43}Al_{0.57}]^{VI}[Al_{2.96}Fe_{0.73}Mg_{0.24}] Na_{0.71}K_{0.21}Ca_{0.01}O₂₂. Its cation exchange capacity (CEC) is 78 meq/100 g and its surface characteristics are: specific surface area (SSA), 107 m² g⁻¹, microporous surface area (S_{µp}) is 39.7 m² g⁻¹, porous volume (V_p) is 0.15 cm³ g⁻¹, and microporous volume (V_{µp}) is 0.02 cm³ g⁻¹.

2.2. Synthesis of PILC with single and mixed oxide pillars

These materials were synthesized by a cationic exchange reaction of sodium clays with hydroxyoligomeric solutions with different cations (Al, Zr and Zr–Al). Zirconium tetrachloride (ZrCl₄) was used as a source of zirconium polycations. The aluminium pillaring solution was prepared using Al (NO₃)₃·9H₂O as the precursor salt. Pillaring solutions of Al, Zr and Zr–Al were prepared by slowly adding a basic solution (NaOH 0.2 M) to the corresponding cationic solution (0.1 M) under constant stirring at room temperature until the desired pH was reached (Table 1). The solution obtained was aged through stirring at room temperature for 24 h. Then the pillaring solution was added drop wise to a 1 wt% Na⁺-Bent dispersion in distilled water with a metal/clay ratio of 10 mmol g⁻¹. This ratio is the most widely used in the literature either for Zr-PILC (Maes et al., 1997; Chae et al., 2001; Ben Chaabene et al., 2004; Mishra and Rao, 2004; Rao and Mishra, 2005; Merat et al., 2007; Guerra et al., 2008) or Al-PILC (Yang et al., 1998; Hutson et al., 1999; Bouchenafa-Saïb et al., 2007; Lin et al., 2007; Ksontini et al., 2008) or mixed Al-Zr-PILC (Mnasri and Frini-Srasra, 2012). The mixture was allowed to react at room temperature for 24 h. After intercalation, the resulting products were centrifuged, washed by dialysis with distilled water, dried at 350 K and finally calcined for 2 h at 823 K. The samples are labelled as a function of the nature of the pillars (Zr, Al or Al–Zr). The subindex values indicate the metal percentage in the initial pillaring solution.

2.3. Physico-chemical characterization

The X-ray diffraction (XRD) study was done in a 'PANalytical X'Pert HighScore Plus' device, which operates with Cu K α radiation.

N₂ adsorption–desorption experiments were carried out at 77 K on a Quantachrome, USA instrument. The N₂ isotherms were used to determine the specific surface areas (SAS) using the BET equation. The micropore volume was determined using the t-plot method and the total pore volume of the samples, V_t, was calculated at P/P₀ = 0.99. Before

Table 1
pH used for the synthesis of PILC with single and mixed oxide pillars.

Samples	Zr-PILC	Al ₁₀ Zr ₉₀ -PILC	Al ₅₀ Zr ₅₀ -PILC	Al ₉₀ Zr ₁₀ -PILC	Al-PILC
pH	2.8	3.8	3.8	3.8	4.1

each measurement the samples were outgassed for 2 h at 403 K.

The chemical analysis of the starting material and modified samples was determined by atomic adsorption, the spectrometer used is of the type AAS Vario.

Cation exchange capacity was determined by Kjeldhal method. Samples of 200 mg were exchanged with the ammonium acetate (1 M) three times and then washed with anhydrous methanol; a final wash was performed with deionized water three times. The amount of ammonium retained was determined using a unit Kjeldhal. The CEC is expressed as milli-equivalent per gram of the calcined sample.

Applying the methods described in literature (Noh and Schwartz, 1989), mass titration experiments were performed followed by the pH drift until a steady value was achieved. Each portion of 0.05 g of a dry clay sample was added to 50 ml of NaCl solution at different ionic strength with the pH between 3 and 10. After each addition, the pH was recorded after an "equilibrium time" of about 15 min. Then a new amount of the sample was introduced to make changes in the pH. This procedure was repeated until no pH change occurred.

Brönsted and Lewis acid centers were determined by FT-IR spectroscopy method on the basis of adsorption of butylamine. With this method 10 ml of prepared butylamine in a cyclohexane solution was added to 0.1 g of catalyst. The mixture was shaken at room temperature. After drying, each sample was calcined at different temperatures. FT-IR spectra were recorded in the region 1800–400 cm⁻¹ on a Perkin-Elmer infrared Fourier transform spectrometer using the KBr pellet technique.

2.4. Adsorption

The batch experiments were carried out in a 100 ml stoppered conical flasks where samples of about 50 mg of the PILC dispersed in 20.0 cm³ of aqueous solution and 50 ml of Cr(III) (prepared from Cr₂(NO₃)₃·9H₂O in distilled water) or Zn(II) (prepared from ZnCl₂) metal solution were added. The initial concentration of Cr(III) or Zn (II) was 50.0 mg dm⁻³. The solution pH in each flask was adjusted to the desired value by adding HCl and NaOH as required. The flasks were subsequently capped and shaken in a temperature controlled shaking water bath at 200 rpm for desired temperature. After contact time, the solutions were filtered and analyzed for the concentration of metal ions remaining in the solution by atomic adsorption method. To study the effect of pH, purified and pillared adsorption samples were evaluated by varying the pH in the 1.0–10 range with addition of 0.10 mol dm⁻³ of nitric acid or 0.10 mol dm⁻³ sodium hydroxide. In order to determine the effect of temperature on adsorption, isotherms were established at 298, 308, 318 and 328 K.

The isotherms of concentration as functions of time, pH and the degree of adsorption were obtained through a batch method. Each isotherm can be obtained through the number of moles adsorbed per gram (Nf), calculated by the difference between the initial (ni) and the number of moles of metal remaining in the supernatant (ns) divided by the mass (m) of the compound used, Nf = (ni – ns)/m. From these isotherms the time for surface saturation was used for all other determinations. In such condition the number of moles of cation adsorbed (Nf) increased with concentration in the supernatant (Cs) as a function of pH and time (t), until the plateau related to total saturation of the acid center in the layered structure was obtained (Airoldi et al., 2006; Guerra et al., 2006).

The most common model to adjust the adsorption is that proposed by Langmuir, originally derived for gas adsorption on planar surfaces such as glass, mica and platinum. The process has successfully been extended to heavy metal ions on porous surfaces. The quantity adsorbed is related to the equilibrium solution concentration of the adsorbate, after adjusting to K_L and b parameters from Eq. (1) and the plateau of the isotherm derived K_L value by measuring the adsorbate on the surface. The value of b is the upper limit and represents the maximum adsorption, determined by the number of reactive surface sites by

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