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ScienceDirect
Journal of Colloid and Interface Science 313 (2007) 574–578
Journal of
Colloid and
Interface Science
www.elsevier.com/locate/jcis

Chromium removal from water using LTA zeolites: Effect of pH

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Received 16 January 2007; accepted 29 April 2007

Abstract

The effect of pH changes on the ability of the synthetic zeolite NaA to remove Cr^{3+} from water by ion exchange was investigated. The exchange rate was improved by working near neutrality. Despite of the occurrence of simultaneous adsorption, precipitation or cation exchange phenomena, spectroscopic analyses of samples taken at different contact times suggested the presence of an unique chromium environment in the solid phase. The increase in pH observed during the ion exchange favored polymerization–precipitation of chromium species present in solution, which, in turn, improved the metal removal capacity of zeolite NaA above the values expected for a pure cationic exchange reaction.

Keywords: Chromium removal; Zeolite A; Ion exchange; Heavy metal retention

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1. Introduction

Chromium removal from industrial wastewaters is a process of great significance on account of the widespread use of this hazardous metal in many industrial and manufacturing processes and of its serious environmental impact. Leather tanning, steelworks, chromium electroplating are, among others, typical processes responsible for polluting natural waterways. Therefore, removal of this metal from wastewaters is a very relevant process. Knowing that Cr(VI) is the most toxic cationic form [1–3], understanding of the behavior of chromium cations as well as of the relationships between Cr(III) and Cr(VI) in water media is critical.

On the other hand, chromium-based catalysts are also usually employed in various chemical processes, including the selective oxidation of hydrocarbons. Recently, several studies were reported on synthesis and characterization of chromium-catalysts supported by mesoporous molecular sieves and zeolites. In them, cation exchange properties of the supports were found to play a fundamental role [4–6].

As others heavy metal cations, chromium is removed from aqueous media by alkaline precipitation, though ion exchange-based processes using zeolites have been proposed as an alternative method [7–10]. Studies carried out by Pansini et al. [7,8] allowed to foresee possible applications of natural zeolites, such as phillipsite and/or chabazite containing tuffs for chromium removal from wastewater. In fact zeolites possess excellent properties to retain di- and trivalent ions. The main divalent ions that displace Na^+ in zeolite A are, to date, Mg^{2+}, Ni^{2+}, Fe^{2+}, and Cu^{2+} [11]. To remove chromium from water using zeolite materials, the pH of the liquid media is generally neutral or acidic. Low pH values are found in solutions that result from electroplating plants or when a reduction of Cr(VI) to Cr(III) is carried out, stabilizing this cation to pH 3.5–4. Additionally, it was reported that during this exchange reaction, a partial loss of zeolite structure has been observed [7].

In this research, the objectives were to assess the influence of the initial pH of chromium solutions on the exchange capacity of NaA zeolite and the modifications that this process undergoes when the zeolite is previously exchanged with Ca(II). The nature of chromium species present in solid and solution phases after the exchange reaction were analyzed by several spectrometric techniques.

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doi:10.1016/j.jcis.2007.04.066

2. Experimental

2.1. Materials

Pure NaA zeolite was used, which was synthesized in our laboratory and possess a theoretical ion exchange capacity of 7.04 meq/g (unhydrated basis) and of 5.48 meq/l (hydrated basis). NaA crystalline powder was synthesized by hydrothermal method. The ingredients of NaA were NaOH (Carlo Erba, 98%), sodium silicate solution (Mejorsil, Technical grade, 29 wt% SiO_2–9.5 wt% Na_2O–61.5 wt% H_2O), commercial sodium aluminate (36.5 wt% Al_2O_3–29.6 wt% Na_2O, 33.9 wt% H_2O) and distilled water. The chemical composition of precursor gel was 1 Al_2O_3–1.93 SiO_2–3.16 Na_2O–128 H_2O. Sodium aluminate, NaOH, and H_2O were mixed at first, and then the mixture was cooled down to room temperature. Sodium silicate solution was added to the mixture with stirring. The mixed gel was heated at 95 °C in a Teflon container for 3 h. After that, the resulting solid products were filtered, and washed with distilled water until the pH of washing water reached below 10.0. The resulting powder was then dried at 100 °C for one night. In addition, CaA zeolite was obtained from zeolite NaA and also utilized for the exchange runs. The Cr-containing solutions were prepared with $Cr(NO_3)_3 \cdot 9H_2O$ (Carlo Erba, p.a.) using demineralized water as solvent.

2.2. Ion exchange runs

Ion exchange runs were carried out under stirring, by contacting 1 or 3 g of zeolite samples with 1 liter of chromium solutions (42 or 135 ppm of Cr^{3+}). In some runs, the initial pH of the solution was modified by adding drops of aqueous NaOH 0.1 M. Samples of the suspension were collected at predetermined times, and the liquid was separated from the solid by filtration. The solid phases were oven-dried at 110 °C and stabilized at room temperature at 35% relative humidity.

The liquid phases were analyzed by atomic absorption spectrometry (AAS) with an IL 457 model double beam spectrophotometer (Instrumentation Laboratory Inc.) and by UV–visible spectrometry (UV-V) using a Varian Super Scan 3 equipment. On the other hand, the solids were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR) utilizing a Bruker IFS 66 equipment, supporting the sample in BrK pellets. Spectra were measured in the range of 400–1500 cm^{-1}. Solid phases were also analyzed by X-ray diffraction (XRD), whose patterns were obtained by using a Phillips PW-1714 diffractometer with built-in recorder. Additionally, diffuse reflectance spectroscopy (DRS) was used, which allowed solid spectra to be recorded in the range of 200–600 nm. The UV–visible Varian Super Scan 3 equipment was, in this case, fitted with a diffuse reflectance chamber with inner $BaSO_4$ surface. Samples were compacted in a Teflon sample holder to obtain a thickness of 2 mm.

Table 1
Evolution of pH and [Cr^{3+}] adding 1 g and 3 g of zeolite NaA ($pH_{initial}$ 3.4–3.6)

Time (min)	1 g of zeolite NaA		3 g of zeolite NaA	
	pH	[Cr^{3+}] (ppm)	pH	[Cr^{3+}] (ppm)
0	3.53	41.08	3.43	38.83
1	5.82	26.37	6.00	1.98
5	6.37	19.38	6.60	0.57
20	6.12	15.32	6.90	0.13
60	6.15	10.34	7.00	0
120	6.45	7.63	7.08	0
150	6.61	7.80	7.07	0

Table 2
Evolution of pH and [Cr^{3+}] adding 1 g and 3 g of zeolite NaA ($pH_{initial}$ 6.00)

Time (min)	1 g of zeolite NaA		3 g of zeolite NaA	
	pH	[Cr^{3+}] (ppm)	pH	[Cr^{3+}] (ppm)
0	3.55	37.36	3.51	38.12
0	6.00	32.61	6.00	28.51
1	6.92	2.498	8.15	0.700
5	8.90	1.791	9.31	0.654
20	8.81	0.586	9.32	0.409
60	8.30	0.598	9.02	0.211
120	8.06	0.029	8.60	0.102
150	7.94	0.62	8.55	0.103

Table 3
Evolution of pH and [Cr^{3+}] adding 3 g of zeolite NaA ([Cr^{3+}]$_{initial}$ = 135 ppm; $pH_{initial}$ 3.4–3.6)

Time (min)	3 g of zeolite NaA	
	pH	[Cr^{3+}] (ppm)
0	3.48	134.16
1	6.02	50.75
5	6.42	32.00
20	6.57	13.70
60	6.75	2.80
120	6.80	2.60
150	6.79	2.78

3. Results and discussion

3.1. Ion exchange experiments

Tables 1 and 2 show the evolution of pH and chromium concentration when zeolite A is contacted with a solution containing 42 ppm of Cr^{3+} at pH 3.4–3.6. Table 1 shows the results obtained adding 1 g and 3 g of NaA, Table 2 corresponds to the results obtained starting from solutions whose initial pH was modified by adding NaOH up to pH 6. Finally, we used a concentrated solution containing 135 ppm of chromium with addition of 3 g of zeolite (Table 3).

According to the data presented in Table 1, the Cr uptake becomes faster and more effective for larger amounts of zeolite. Moreover, the addition of zeolite produces a fast increase in pH up to values close to 7, regardless of the zeolite weight utilized. Variation in Cr concentration was more marked at very short contact times. In the first minute of reaction, Cr concentration falls to values of 1.98 ppm Cr(III) when using 3 g of NaA and