Preparation of CPB-modified FAU zeolite for the removal of tannery wastewater contaminants

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Abstract The preparation of organomodified zeolites with different framework structures (FAU, LTA and MOR) using *N*-cetylpyridinium bromide (CPB) as tailoring agent was studied. The sorption properties of CPB-modified zeolites were evaluated in the removal of tannery contaminants from aqueous solution. The CPB-modified FAU-type zeolite presented the highest Cr(VI) retention capacity (37 mmol/kg) due to the higher Cr(VI) retention of its unmodified form (larger pore opening) and its high CPB sorption capacity. CPB-modified FAU zeolite also exhibited high thermal stability as consequence of special interactions between the CPB molecules and the zeolite surface. In addition, the intrinsic Cr(III) exchange capacity of FAU zeolite increased with CPB loading (162–527 mmol/kg), which appear to be due to an additional retention mechanism provided by the sorbed cetylpyridinium surfactant layer. On other hand, CPB-modified FAU zeolite also exhibited high toluene retention capacity (62 mmol/kg) due to of the hydrophobic character of its surfactant-modified surface and toluene adsorption on internal sorption sites of FAU zeolite. Thus, CPB-modified FAU zeolite appears as a promising adsorbent for simultaneous removal of Cr(III), Cr(VI) and toluene contaminants from aqueous solution.

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1 Introduction

Zeolitic materials are well known for their high cation exchange capacity and affinity for toxic heavy metals. In particular, in order to use zeolites for the removal of chromium from industrial tannery wastewater, the Cr(III) exchange process has been studied using several naturally occurring and synthetic zeolites [1–4]. Still, hexavalent chromium species existing in the effluent cannot be removed through cation exchange process. Furthermore, the fact that an alkaline medium, aerobic conditions and higher temperatures may oxidize Cr(III) to more toxic and mobile anionic Cr(VI) forms must be taken to account [5]. Hexavalent chromium is well known by its high toxicity as well as by its mutagenic and carcinogenic properties [6]. The cation exchange properties of zeolites can be exploited to modify their surface chemistries to also retain chromate anions and non-polar organic compounds. When brought into contact with zeolite, the cationic surfactants that posses a permanent positive charge selectively exchange with the inorganic cations on the external surfaces of the zeolite crystals and form a surfactant bilayer with anion exchange properties [7]. Additionally, the sorbed surfactant layer provides a hydrophobic medium in which toxic toluene existing in tannery wastewater could be also adsorbed. Clinoptilolite-type zeolite modified with the surfactant hexadecyltrimetil-amonium (HDTMA) has been tested as sorbent for removal of different environmental contaminants from water [8]. Some applications include controlling chemical groundwater contamination, organic compounds removal from oilfield waters, and pathogens removal from sewage effluent. G.M. Haggerty

et al. [7] studied the removal of inorganic oxyanions from aqueous solution by HDTMA-modified clinoptilolite. The starting clinoptilolite had no affinity for the oxyanions, while the HDTMA-modified clinoptilolite showed significant removal capacity for chromate, selenate, and sulfate from 0.005 mol/dm³ CaCl₂ aqueous solution. The mechanism of anion retention appeared to be the formation of an HDTMA-anion precipitate on the zeolite surface. Z. Li et al. [9] found that the sorption of perchloroethylene by the HDTMA-modified clinoptilolite depends on the bound surfactant molecule configuration as well as on the fractional organic carbon content.

Most of the studies on surfactant-modified zeolites have been done using the natural occurring clinoptilolite and using HDTMA as tailoring agent [10]. The surfactant-modification of zeolites with different framework structure could be also accomplished in order to obtain different adsorption behaviors. It has been found that the highest Cr(III) exchange capacity values are obtained using faujasite type zeolites (FAU) [11]. The chromium (III) ion has the largest hydrated ionic radius of any known heavy metals [12] and its exchange in zeolitic materials require a favorable pore opening. The structure of FAU zeolite (natural faujasite and synthetics analogs X and Y) is one of the most open of all zeolites [13], which are composed by arrangement of truncated octahedral-forming cages with large diameters. The pore opening to these cages are 12-membered rings with approximately 0.74 nm in diameter, which favors the exchange of large chromium ions from solution. On the other hand, the use of the *N*-cetylpyridinium bromide (CPB) surfactant as tailoring agent could be an interesting alternative to obtain a selective hexavalent chromium adsorbent. Cetylpyridinium micelles have demonstrated to have high binding affinity for chromate anions. For example, the use of cetylpirydinium in a micellar-enhaced ultrafiltration process (MEUF) increased chromate removal from 48% to 62%, 82% and 99% as the cetylpyridinium-to-chromate molar ratio in the solution increased from 1 to 2, to 5, and to 10, respectively [14].

In this work, we report the preparation of organomodified zeolites with different framework structures (FAU, LTA and MOR) using *N*-cetylpyridinium bromide as tailoring agent. The sorption proprieties of CPB-modified zeolites are evaluated in the removal of Cr(VI), Cr(III) and toluene from aqueous solution, which are typical contaminants found in tannery wastewater.

2 Experimental

2.1 Preparation of surfactant-modified zeolites

Surfactant modification assays on FAU (zeolite 13X, BDH), LTA (zeolite 4A, Union Carbide) and mordenite-type (MOR) zeolites were performed. MOR zeolite was obtained from natural deposit situated about 50 km south of Santiago, Chile and used after being crushed and sieved to –400 Mesh. Table 1 summarizes chemical and textural properties of the raw zeolites. In the modification, *N*-cetylpyridinium bromide monohydrat (CPB, Merck) was used for surface zeolite tailoring. Samples of 2 g zeolite powder were placed in contact with 80 cm³ of aqueous solutions at different CPB concentrations (0.2–3 mmol/dm³) for 24 h in a thermostatic bath at 30 °C. The samples were separated by filtration, washed with 2,000 cm³ of deionized water to remove CPB excess and then air dried. To determine the amount of CPB adsorbed on the zeolite samples, CPB concentration was measured using a Perkin–Elmer Lambda 40 UV–VIS spectrophotometer at $\lambda = 258$ nm of wavelength in the initial and resulting solutions.

2.2 Characterization

Surfactant-modified faujasite powders were characterized by FTIR transmission spectra obtained from KBr disks (1 wt%) using a Nicolet Magna IR 550 spectrophotometer. TG/DTG curves were also obtained using a Mettler Toledo TG/SDTA851 thermo-gravimetric analyzer at a heating rate of 10 °C/min under inert atmosphere of N₂. Textural

Table 1 Chemical and textural properties of the raw zeolites

Zeolite type	Si/Al[a]	CEC (meqCr³⁺/g)	Pore opening (nm)[a]	S_g (m²/g)	V_o (cm³/g)
FAU	1.5	3.52	0.74	578	0.25
LTA	1.0	3.05	0.40	9.4	<0.01
MOR	9.4	0.21	0.67 × 0.70	277	0.11
			0.46 × 0.39		

S_g: Specific surface area

V_o: Microporous volume

[a] From Ref [13]

characterization of selected samples was carried out by N_2 adsorption at 77 K in a Micromeritics Gemini 2370 sorptometer. Apparent specific surfaces areas (S_g) were calculated applying the BET equation to the experimental data obtained from N_2 isotherms.

## 2.3 Contaminant retention on surfactant-modified zeolites

Batch sorption studies with contaminant solutions were conducted as follows: 0.4 g samples of original and organo-modified zeolite powders were put in contact with 80 cm^3 of Cr(III) (500 mg/dm^3), Cr(VI) (500 mg/dm^3) and toluene (40 mg/dm^3). Aqueous solutions were prepared using the basic salt of chromium sulfate Cr(OH)SO$_4$·Na$_2$SO$_4$ used in tannery processes, K$_2$Cr$_2$O$_7$ and Toluene (Merck). Following previous studies on chromium exchange rate in zeolites [15], duplicated sorption assays were achieved during 24 h at 25 °C. The total chromium concentration in the filtrate was measured using a Perkin–Elmer Analyst 100 atomic absorption spectrophotometer (AAS). Additionally, the effect of pH on Cr(VI) sorption was also studied.. The pH of K$_2$Cr$_2$O$_7$ solutions was fixed in the range 2.5–5.5, adjusting as appropriate with hydrochloric acid or ammonia. In order to increase the solubility of toluene in aqueous media, toluene solutions were prepared by dissolving appropriate amounts of toluene in a mixture of 90% deionized water and 10% ethanol. The toluene concentration was determined by UV–VIS spectrometry at $\lambda = 253$ nm of wavelength. In order to assess the evaporation losses of toluene from aqueous solution, controlled sample was also placed under the same sorption conditions without sorbent. Analysis of control and treated samples suggested no losses due to evaporation.

3 Results and discussion

### 3.1 Cr(VI) retention on organomodified zeolites

Figure 1 presents the Cr(VI) retention capacity of unmodified zeolites and samples treated with different CPB concentration. Although, zeolitic materials are cation exchangers, it can be seen that unmodified FAU and MOR zeolites have some affinity for chromate anions, whereas LTA zeolite do not present chromate retention capacity. The anion retention observed in the unmodified FAU and MOR zeolites could be attributed to physically sorbed chromate anions on internal zeolite surface by Van der Wall forces, which is favored by the relatively high surface area and larger pore apertures of faujasite (0.74 nm) and mordenite (0.67 × 0.70 nm for 'c' direction channels a 0.26 × 0.57 nm for 'b' aperture channels) zeolites (Table 1). On the other hand, the lack of Cr(VI) sorption observed in unmodified LTA zeolite can be explained by the steric hindrance effect produced during the sorption of chromate anions of 0.6 nm in ionic diameter [16] through narrow pore aperture of NaA-type zeolite (0.4 nm). This effect explains also the Cr(III) exchange capacity exhibited by LTA zeolite (Table 1). Although, zeolite A have lower Si/Al ratio (higher number of cation exchange sites) than FAU zeolite, the exchange of the sizably hydrated Cr (III) ions on LTA zeolite is decreased by hindrance effect through its narrower pore aperture [11]. Low Cr(III) exchange capacity presented by MOR zeolite is a consequence of its high Si/Al ratio (lower number of cation exchange sites) and due to the presence of non-zeolitic phases existing in the natural material [17]. When the zeolites were CPB modified, their Cr(VI) retention capacity increased. The highest Cr(VI) retention capacity values were obtained using a CPB concentration in the 0.5–0.9 mmol/dm^3 range. As already proposed by G.M.

Fig. 1 Cr(VI) retention capacity of FAU, LTA and MOR zeolites and CPB-modified samples
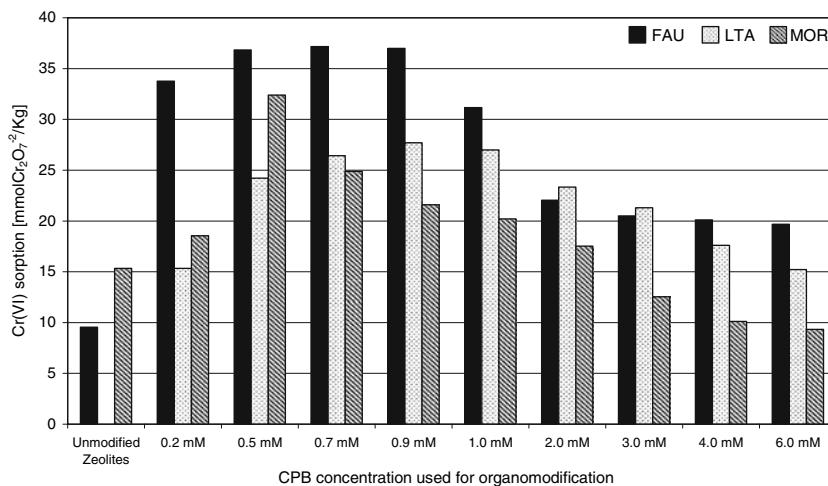
Haggerty et al. [7], the most likely mechanism for Cr(VI) removal on the adsorbed surfactant monolayer (when C < critical micellar concentration, 0.9 mmol/dm^3) appears to be surface precipitation of an surfactant-anion complex. Thus, an organic salt is formed by the electrostatic association of chromium anion with the ''head'' of the CPB surfactant on the zeolite surface. However, when the surfactant bilayer is formed (C ≈ 0.9 mmol/dm^3), the zeolite surface charge is reversed and anion exchange with bromide counterion is the main Cr(VI) removal mechanism. The organomodified FAU-type zeolite presented the highest Cr(VI) retention capacity, with a Cr(VI) sorption maximum of 37 mmol/kg, which is higher than the value found for HDTMA-modified clinoptilolite (HDTMA-HSO$_4^-$, 28 mmol/kg) [18]. This difference appears to be given by the Cr(VI) retention capacity presented by the unmodified FAU zeolite (9.54 mmol/kg) since it have been reported that no sorption of chromate occurs on an unmodified clinoptilolite. When the zeolite samples were treated with CPB concentration beyond 0.9 mmol/dm^3, the Cr(VI) retention tended to decrease. The reduction of the anion retention at the higher surfactant level has been attributed to the release of surfactant excess from adsorbed micelles on the organo-zeolite into the aqueous solution. [7] This may results in CPB competition for the chromates anions in solution and on the zeolite surface. However this surfactant desorption phenomenon can be discarded for zeolite samples modified with low CPB concentrations (<0.9 mmol/dm^3), since the surfactant layers formed under these conditions have shown to have high chemical and thermal stability [19].

Figure 2 shows the amount of CPB adsorbed on FAU zeolite samples treated with different CPB concentrations. It can be seen that CPB sorption increases with the concentration of the CPB solution to form a sorption plateau. The CPB sorption on faujasite can be explained by the general model of adsorption of ionic surfactants on solid
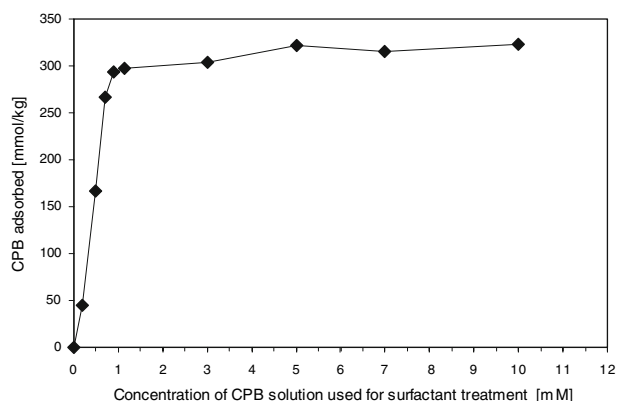
Fig. 2 CPB adsorption on FAU zeolite

surfaces [20]. When the CPB solution concentration is less than its critical micellar concentration (0.9 mmol/dm^3), CPB molecules are adsorbed as a monolayer (hemimicelle) on the negatively charged zeolite surface. The amount of CPB to complete this monolayer is equal to the amount required to complete the zeolite external cation exchange capacity (ECEC). Then, a CPB sorption plateau occurs when the surfactant solution concentration is over its critical micellar concentration. Beyond this concentration, CPB micelles are attached on the zeolite surface (''admicelle'') and can rearrange to forms a more stable surfactant bilayer. The observed maximum CPB sorption on faujasite was of 322 mmol/kg, which is greater than the sorption plateau found for the well-studied sorption of HDTMA-Br on natural clinoptilolite (208 mmol/kg) [7]. This result can be due to the higher purity and theoretical cation exchange capacity of the synthetic FAU zeolite. The presence of the sorbed CPB molecules on the FAU zeolite surface was verified by FTIR analysis. Figure 3a shows the 2,800–3,000 cm^{-1} region, which contain the asymmetric and symmetric –C–H bands of N-cetylpyridinium. In this region, FAU zeolite does not present FTIR signals. When the zeolites are treated with CPB surfactant, the asymmetric and symmetric –C–H bands due to the adsorption of cetylpyridinium can be observed on the spectra. FTIR bands of the sorbed CPB surfactant appear slightly shifted toward higher wavenumbers. This IR shift can be attributed to a crystal-field effect from zeolite framework. It has been found that electrostatic field associated with the zeolite balancing cations can produce significant shift in the IR signals of sorbed molecules [21]. Similar effect has also been found in IR signals of molecules such as methane [22] and pyridine [23] sorbed on zeolite frameworks. In this case IR shift of sorbed CPB could be harnessed due to the high cation population of the FAU-type zeolite framework (low Si/Al ratio, Table 1). On the other hand, the observed FTIR bands in the 1,400–1,500 cm^{-1} region (Fig. 3b) coincide with the characteristics bands observed for pyridine adsorption on zeolitic acid sites [24]. In this case, the presence of adsorbed pyridine bands would indicate some change in the electronic configuration of the adsorbed cetylpyridinium ring. The spectral frequencies observed at 1,535 cm^{-1} and 1,515 cm^{-1} would correspond to CPB adsorption on Brönsted acid sites (surface hydroxyl groups), while the weaker bands in the region 1,435–1,445 cm^{-1} can be attributed at coordinately bonded CPB on Lewis acid sites. On the other hand, the peaks at 1,482–1,492 cm^{-1} could be related with the 1,490 cm^{-1} band found for pyridine adsorption. This band has been assigned to a contribution of both Brönsted and Lewis acid sites [25], although more recently some investigators claim that this peak corresponds to physisorbed pyridine [26]. From these FTIR observations, it can be concluded that

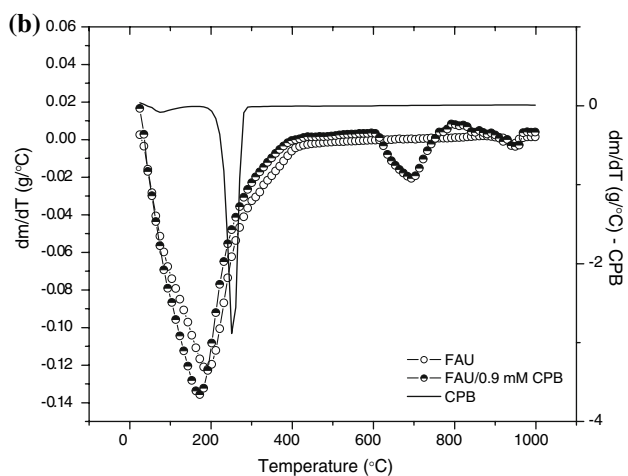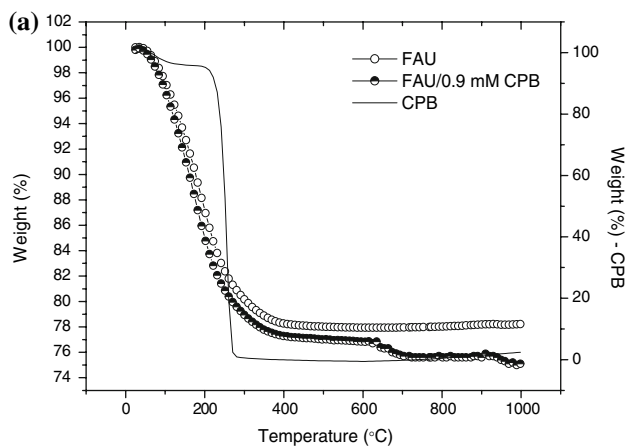**Fig. 3** FTIR spectra of CPB surfactant, FAU zeolite and CPB-modified FAU samples
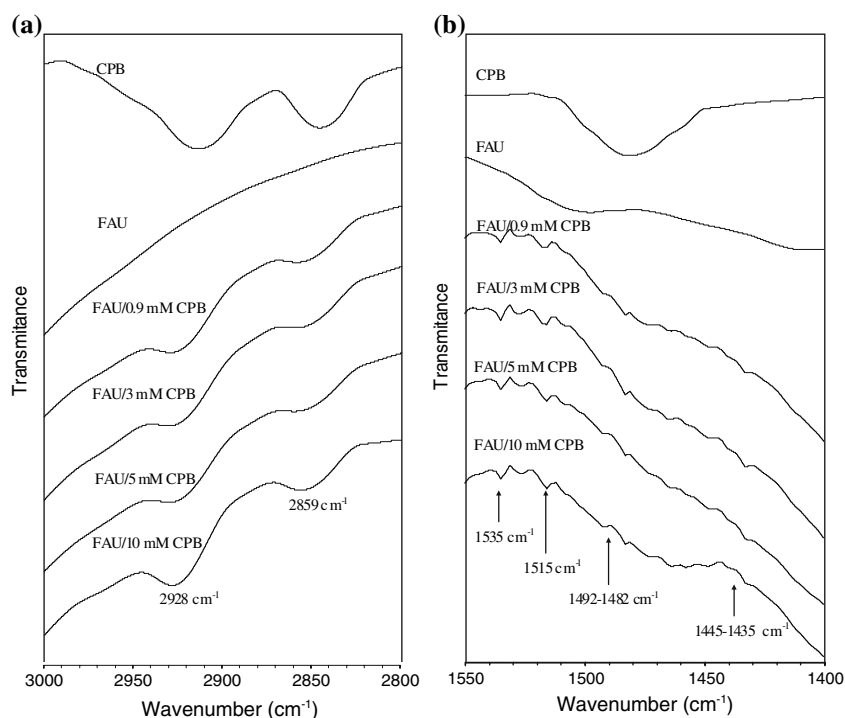
different interactions with the zeolite surface occur in the case of CPB surfactant. As found by Li et al. [18], cation exchange is the main mechanism responsible for retaining the lower surfactant layer on the charged surface. However when the surfactant head group is a pyridinic ring, additional interactions appear to occur as consequence of the adsorption of cetylpyridinium ring on zeolitic acid sites. Thermogravimetric analysis was performed for the CPB surfactant, the raw FAU zeolite, and CPB-modified sample (Fig. 4). The thermal decomposition of pure CPB surfactant can be clearly observed by a weight loss around 250 °C. The FAU zeolite samples present DTG peaks within the 100–300 °C temperature range, which correspond to the characteristic zeolite dehydration step [17]. Additionally, the FAU zeolite modified with a CPB solution of 0.9 mmol/dm^3 presents weight loss at 690 °C due to the decomposition of the adsorbed CPB surfactant. In a comparison with HDTMA-modified clinoptilolite, the adsorbed HDTMA was thermally decomposed at 336 °C [27]. This fact is further evidence of additional interactions between CPB surfactant and the FAU zeolite surface, which provide higher stabilization for the first adsorbed surfactant monolayer.

The effect of pH on Cr(VI) sorption within the pH range 2.5–5.5 was also investigated (Fig. 5). These results shown that for the FAU zeolite modified with a solution 0.7 mmol/dm^3 of CPB (maximum Cr(VI) retention), the highest Cr(VI) retention is obtained at pH 3.5 (39.7 mmol/Kg). According to the chromium speciation diagram [28],

the oxyanion $Cr_2O_7^{2-}$ is the dominant species at pH 3.5. At pH values where the dominant species were $HCr_2O_7^-$ and CrO_4^{2-}, the Cr(VI) retention decreased, indicating that highest affinity between surfactant-modified zeolite surface and hexavalent chromium occurs when the dimer $Cr_2O_7^{2-}$ is the predominant chromium ion.

3.2 Cr(III) and toluene retention on CPB-modified FAU zeolite

In Fig. 6 the Cr(III) and toluene retention capacity of the unmodified FAU zeolite and CPB-modified FAU samples is presented. For comparison, the values of Cr(VI) retention capacity (Fig. 1) are also included. It can be observed that the CPB-modified FAU zeolite exhibited a high Cr(III) retention (146–527 mmol/kg), which indicates that the internal cation exchange sites of faujasite zeolite are still available for metallic cation retention [29]. Additionally, the Cr(III) retention on the organo-zeolites increases with the CPB concentration used during the surfactant treatment, particularly beyond critical micellar concentration. The cation retention on zeolites modified with cationic surfactants has been less studied. In contrast with this work, Li et al. [30] found that an increase in the amount of surfactant loading resulted in a reduction in the uptake of metallic cations by the clinoptilolite zeolite. This fact was ascribed to competition for zeolitic cation sites between exchanged metal cations and cationic HDTMA molecules. In the present study cetylpyridinium surfactant could
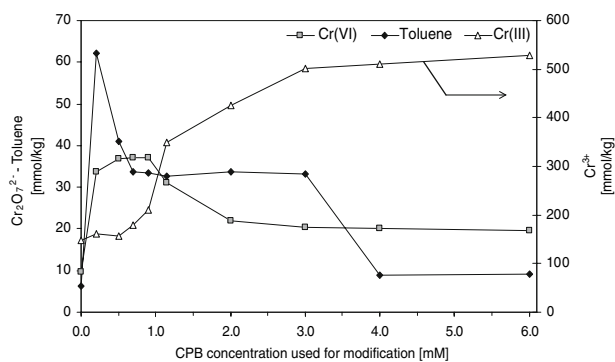
Fig. 6 Adsorption of contaminants on FAU zeolite and CPB-modified FAU samples

more frequently than previously believed [31]. The formation of small multinuclear cationic species by polymerization on solid surface, such as dimers or trimers, may lead to the formation of metal hydroxide. Thus, the presence of cetylpyridinium surfactant on the zeolite surface appears to provide a more favorable surface for chromium precipitation mechanism. Spectroscopic evidence of increased Cr(III) retention on the CPB-modified zeolite can be seen in Fig. 7. Quantitative FTIR spectra were recorded

Fig. 4 Thermogravimetric analysis of CPB surfactant, FAU zeolite and organo-modified FAU samples. (**a**) Weight loss curves (TG), (**b**) Derivative weight loss curves (DTG)
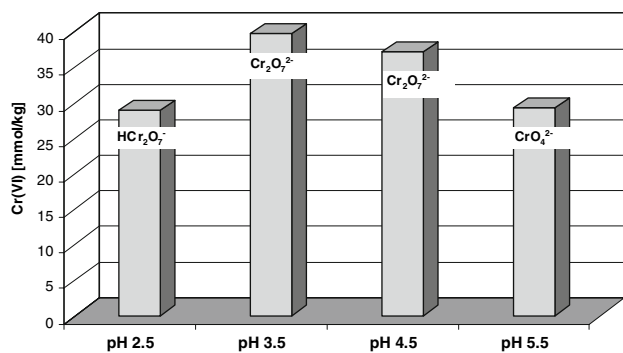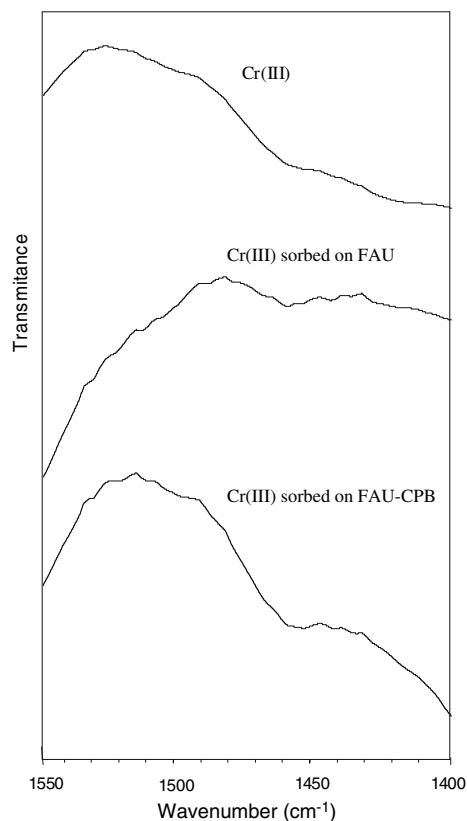

Fig. 5 Effect of pH on Cr(VI) retention in CPB-modified FAU zeolite

provide an additional retention mechanism for the Cr(III) cation. The increase in the Cr(III) retention with the surfactant loading, may be due to a mechanism of surface precipitation. Recent experimental evidence has indicated that surface nucleation of metal hydroxides occurs much

Fig. 7 FTIR analysis of Cr(III) sorption on FAU zeolite and CPB-modified FAU zeolite

for pure Cr(III) salt, FAU zeolite Cr(III) sorbed and CPB-FAU zeolite Cr(III) sorbed. The band around 1,459 cm^{-1} indicates the presence of Cr(III) sorbed on the zeolites. This band is more intense and well shaped for Cr(III) sorbed on the CPB-modified zeolite than found for the unmodified zeolite, confirming a higher Cr(III) retention on the organo-modified FAU zeolite.

In Fig. 6 the removal of toluene from aqueous solution by organo-modified FAU zeolite is also shown. It can be observed that the maximum toluene sorption (62.2 mmol/kg) occurs on the zeolite treated with a CPB concentration of 0.2 mmol/dm^3. The sorption of nonpolar organics compounds (NOCs) by surfactant-modified solids has long been attributed to a partitioning mechanism, the hydrophobic interior of the micelle acts as oil sink into which hydrophobic contaminants can partition. However, NOC sorption also appears to be controlled by bound surfactant molecule configuration. When CPB is present as a monolayer on zeolite surface (0.2 mmol/dm^3), toluene is more efficiently partitioned into CPB. This result is due to the higher hydrophobic character found for monolayer configuration and that the partioning medium of the hydrophobic surface coating changes as the CPB goes from monolayer to bilayer configuration. Above 0.5 mmol/dm^3 CPB concentration, toluene retention decreases to a sorption value 9.4 mmol/kg (almost unmodified zeolite value). These results are consistent with the theory proposed by Li et al. [9] for perchlorethylene sorption on HDTMA-modified zeolite. According to that sorption model, toluene sorption would be limited by a reduced effective volume and an increased density of the hydrophobic core of the sorbed surfactant bilayer, resulting in a decreased toluene sorption. It is important note as well that unmodified faujasite presents a toluene sorption of 6.18 mmol/kg, whereas no NOC sorption from aqueous solution has been reported for other unmodified zeolites. Toluene sorption on

the unmodified FAU zeolite is favored by larger pore opening of FAU-type zeolite, which allows the diffusion of aromatic toluene molecules into internal adsorption sites. Figure 8 presents a schematic representation summarizing the CPB-modified FAU zeolite structure and the sorption mechanisms involved in the retention of the studied contaminants. It can be observed that the tannery contaminants can be selectively sorbed on different sorption sites according to their chemical properties (cation, anion and nonpolar organic compound). Considering that the FAU zeolite modified with CPB concentrations of around 0.5 mmol/dm^3 presented maximum Cr(VI) and toluene retention capacity while maintaining the high Cr(III) exchange capacity of FAU zeolite; CPB-modified FAU zeolite appears as appropriate sorbent for simultaneous removal of Cr(III), Cr(VI) and toluene contaminants from aqueous solution.

4 Conclusion

Zeolites with different framework structures (LTA, MOR and FAU) were modified using *N*-cetylpyridinium as tailoring agent. CBP-modified FAU-type zeolite presented the highest Cr(VI) retention capacity, due to the higher Cr(VI) retention of its unmodified form (larger pore opening) and its high CPB sorption capacity. CPB-modified FAU zeolite also showed high thermal stability due to special interactions between the CPB molecules and the zeolite surface. Additionally, the Cr(III) exchange capacity of FAU zeolite was increased with the CPB loading, which appear to be due to an additional retention mechanism provided by the sorbed cetylpyridinium surfactant. On other hand, CPB-modified FAU zeolite exhibited high toluene retention capacity due to its hydrophobic CPB surface and the toluene retention on

Fig. 8 Schematic representation of CPB-modified FAU zeolite structure and its interaction with the tannery contaminants
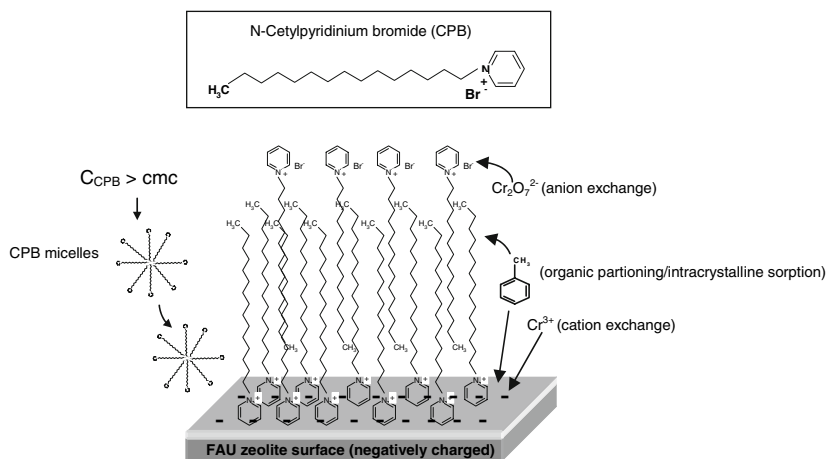
internal sorption sites of faujasite zeolite. Thus, CPB-modified FAU zeolite appears as a promising adsorbent for simultaneous removal of Cr(III), Cr(VI) and toluene contaminants from aqueous solution.

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