

Removal of As(V) and As(III) from aqueous solution using hydrous ceric oxide

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Abstract—Removal of As(V) and As(III) from water using hydrous ceric oxide, $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ (HCO) was investigated under different pH and As loading conditions, using batch equilibrium adsorption and FTIR methods. Adsorption of both As(V) and As(III) anions was virtually independent of pH and up to 100% removal can be achieved in the lower concentration range 0.5 - 5.0 mg L⁻¹ As at sorbent dosage of 1.0 g L⁻¹. As the initial As concentration increased to 50, 100 or 250 mg L⁻¹ for the same sorbent dosage, distinct adsorption maxima of As(V) appeared and shift to lower pH, whereas that of As(III) was found at approximately pH 8. The effect of contact time was dependent on pH but adsorption equilibria were reached after 6 h in all cases for the studied systems. The isotherms fit well in the Langmuir model of adsorption. Both As(V) and As(III) anions were adsorbed on HCO principally by forming inner-sphere complexes as revealed by the FTIR spectra.

Keywords - removal; arsenate; arsenite; hydrous ceric oxide; sorbent; adsorption

I. INTRODUCTION

The presence of naturally occurring high levels of arsenic in the groundwater was proved in many regions of Bangladesh, India, Vietnam, USA and other countries of the world [1-4]. Chronic arsenism poses a serious health problem in China also. About 14.6 million people, mainly distributed in the northwest China including Inner Mongolia, Xinjiang, are exposed to drinking water containing arsenic with a concentration of 0.03 mg L⁻¹ or higher [5]. If Chinese current drinking water standard of As lowers from 0.05 to 0.01 mg L⁻¹, the level adopted by WHO [6] and some developed countries, the population affected will increase significantly. It is important to develop alternative technologies for treating drinking water contaminated with arsenic effectively at a reasonable cost.

Various technologies have been developed for the arsenic removal from aqueous systems. The adsorption technique is regarded as the most promising method or process due to the ease of handling, sludge-free operation, and the successful application in many different systems [7]. Activated alumina [8], natural iron-enriched samples [9], activated red mud [10], and rare-earth based materials [11] have applied to the removal of arsenic from water.

Cerium is one of the cheapest rare-earth elements and is extracted from bastnaesite and monazite. Hydrous ceric oxide, $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ (HCO), has been studied as a promising alternative adsorbent in removing hazardous anions with some

success [11-13]. It is geochemically stable, nontoxic, and therefore environmental friendly [12]. It is of great importance to use HCO based adsorbent for the removal of arsenic in China, as the country is the world largest producer of rare earths. In comparison with other hydrous metal oxides, such as hydrous ferrous oxide or activated hydrous alumina, information of As adsorption on HCO is limited and more testing is necessary. There is a need to study the kinetics and isotherms of the HCO in adsorbing As from water. The objectives of this study were to evaluate the effectiveness of HCO in removing As(V) and As(III) from aqueous solutions using batch equilibrium adsorption and FTIR analyses, under different pH and As loading conditions to better understand how these variables affect the adsorption on As(V) and As(III) on HCO surface.

II. EXPERIMENTAL

A. Materials

All solutions were prepared in HPW (high purity deionized water from Milli-Q apparatus). As(III) and As(V) solutions were prepared by dissolving appropriate amounts of reagent grade sodium (meta)arsenite (NaAsO_2 ; > 99.0%, Fluka) and sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$; > 98.5%, Fluka), respectively, in HPW. Concentrated solutions of NaOH and HNO_3 were used for pH adjustment, and arsenic standard solutions of 1000 mg L⁻¹ (Wako) for Flame Atomic Fluorescence calibrations. All glassware was cleaned by soaking in 5.0% HNO_3 and rinsed three times with HPW.

Hydrous ceric oxide (HCO) was prepared according to the procedure of Nomura et al. [14]. Ammonia reagent was added to a saturated aqueous solution of ammonium nitratocerate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, to effect precipitation of ceric hydroxide. The precipitate was filtered, washed with water, air-dried, and grounded to obtain a fine light-yellow powder and sieved to constrain the grain size less than 0.250 mm.

B. Sorbent characterizations

Specific surface area of the HCO sorbent was determined according to the Brunauer-Emmett-Teller (BET) protocol on a Micromeritics Flow-Sorb III equipment. The point of zero charge (PZC) was evaluated according to the method proposed by Kinniburgh et al. [15] that described as follows: a mass of 1.00 g of finely ground HCO powder was suspended in 100 mL of 0.01 M NaNO_3 for 24 hours to allow partial rehydration

of the surface. Aliquots of the suspensions were then adjusted to various pH values with NaOH or HNO₃. After 60 min for equilibration, the initial pH was measured; then 1.0 g of NaNO₃ was added to each aliquot to bring final electrolyte concentration to about 0.45 M. After an additional 60 min, the final pH was measured. The results, plotted as ΔpH (final pH – initial pH) against final pH, yield the PZC as the pH at which $\Delta\text{pH} = 0$.

C. General adsorption procedure

The adsorption experiments were run at a constant HCO concentration and at adequate pH-ionic strength. Exactly 0.100 g of finely ground HCO powder were added to polyethylene vials and pre-equilibrated for 24 h with 20 mL of HPW at the adequate pH-ionic strength. The pH of the solutions was adjusted using either 1 M HNO₃ or 1 M NaOH. An ionic strength of 0.01 was adjusted with 1 M NaNO₃. Constant shaking was maintained on a reciprocating shaker at $25 \pm 1^\circ\text{C}$. After pre-equilibration, 1 mL of the corresponding pH-ionic strength spike solution was added to their respective sample (final liquid to solid ration 1000:1). The mixture was shaken for 24 h in the above-mentioned conditions. At the end of each adsorption run, the suspensions were filtered immediately through a 0.45 μm membrane filter made of cellulose acetate and the filtrates were selected for the arsenic analyses. A graphite furnace Flame Atomic Fluorescence spectrometer (AFS SK-2002 Rayleigh) equipped with an online hydride generation unit with a determination limit of $0.4 \mu\text{g L}^{-1}$ was used to determine arsenic concentrations in solution. Averages of duplicate adsorption batch experiments are reported, and for all a deviation of less than 10% was found. Sorption of arsenic anions on the vial walls was also checked by running blank experiments and was found to be negligible.

The US-EPA toxicity characteristic leaching procedure (TCLP) [16] was applied to the As-loaded sorbents used in the adsorption experiments to determine the potential mobility of the metals from the HCO adsorbents and, thus, to obtain information about potential hazard of the sorbents before and after arsenic sorption. Samples of sorbents were treated with the standardized extraction fluid (5.7 mL glacial CH₃COOH added to 500 mL of HPW, plus 64.3 mL of 1 mg L^{-1} NaOH and diluted to 1 L, pH 4.9), and agitated on an orbital shaker for 18 h. The solid/ liquid ratio was 1:20. The product was filtered off and the filtrate was analyzed for As content.

D. Effect of pH

The effect of initial pH on As(V) and As(III) sorption onto HCO was studied. For these experiments, the initial pH was varied within the range 4 - 11, temperature was maintained as mentioned above and the agitation time was fixed to 24 h.

E. Sorption kinetic and isotherm of HCO for As(V) and As(III) anions

The Effect of contact time was evaluated by shaking 0.300 g of HCO in a 300 ml of adsorbate solution at the 10 mg L^{-1} As initial concentration of As(V) and As(III) in order to see when equilibration was achieved. The same procedure was used as mentioned above except 20-mL aliquots were removed at

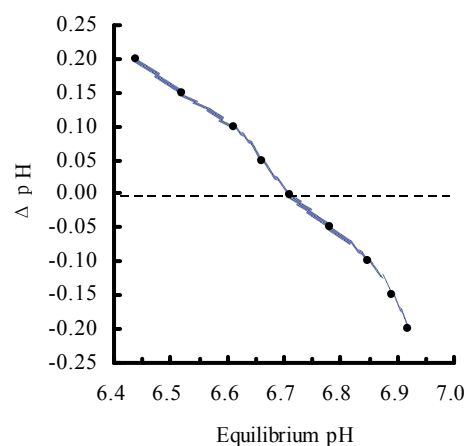


Fig. 1 Point of zero charge determination (PZC: at which $\Delta\text{pH} = 0$) for HCO suspension, with reaction conditions: conc. of HCO, 1.00 g L^{-1} ; initial ionic strength, 0.01 M NaNO_3 ; final ionic strength, 0.45 M NaNO_3 ; the ΔpH is the change in pH during 1 h after increasing the electrolyte concentration.

specified time intervals and analyzed for arsenic. Three experiment sets were run with As(V) and As(III) each involving an initial pH of 4.0, 8.0, and 11.0.

The adsorption isotherms were studied by shaking 0.100 g of HCO in 100 mL of adsorbate solution with varying concentration of anions for 24 h. The initial concentration of As(III) and As(V) in the form of NaAsO₂ and NaH₂AsO₄ ranged from 0.5 to 250 mg L^{-1} As at the selected initial pH 4.0, 8.0, and 11.0.

F. Solid state analysis

Diffuse reflectance FTIR spectra of powdered samples were measured on a Nexus 470 FT-IR (Thermo Electron Corp.). The samples were diluted to a concentration of 2% with IR-grade KBr. Three-two signal-averaged scans were collected at 2 cm^{-1} resolution in the mid-IR region ($4000\text{-}400 \text{ cm}^{-1}$) for pure KBr and for each KBr-mixed sample. Vibrational spectra of each sample were obtained by subtraction of the background spectra (pure KBr) from the spectra of KBr-mixed sample. The ATR-FTIR spectra of aqueous arsenic were examined using the attenuated total reflection Fourier transform infrared spectroscopy.

For all these analysis, arsenic-loaded samples were prepared by contacting 1 g of HCO adsorbent with 200 mL of either As(III) or As(V) 500 mg L^{-1} solution at pH 7.0 for 48 h. Before the corresponding instrumental analysis, samples were washed with HPW in order to eliminate the non-sorbed arsenic and then dried at 60°C until constant weight. Arsenic concentration in solution was analyzed and its concentration in the solid phase was calculated.

III. RESULTS AND DISCUSSION

A. Characterization of HCO

The BET specific surface area of HCO is $80 \text{ m}^2 \text{ g}^{-1}$ with

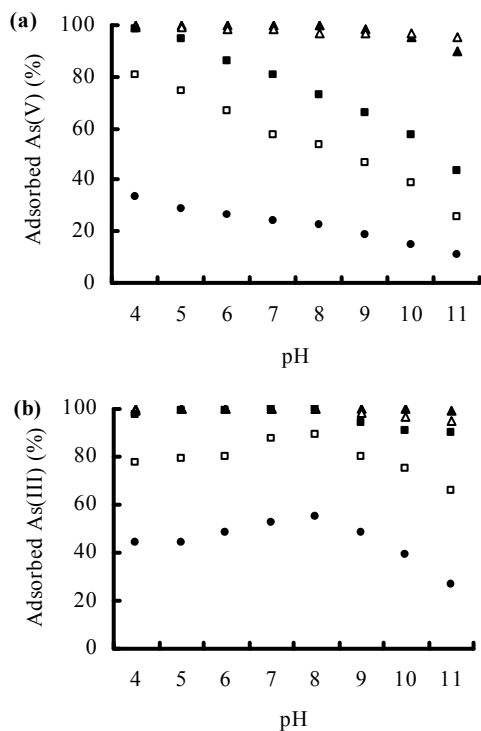


Fig. 2 Effect of pH and initial As concentration on adsorption of (a) As(V) and (b) As(III) on HCO, with reaction conditions: initial As concs. in mg/L; 0.50 (Δ); 5.0 (\blacktriangle); 50 (\blacksquare); 100 (\square); 250 (\bullet); adsorbent dosage, 1.00 g/L; ionic strength, 0.01 M NaNO_3 ; contact time, 24 h.

an average particle size of 612 nm. The PZC of HCO was determined based on the fact that for hydrous oxide, increasing the concentration of an indifferent electrolyte, in this case NaNO_3 , increases the magnitude of the surface charge by causing adsorption or desorption of H^+ or OH^- and only at the PZC is there no change in pH [11]. Fig. 1 indicates that the PZC for HCO fell at approximate pH 6.7, which was in agreement with that reported by Zhang et al. (2005) [13].

B. Effect of pH and initial concentration on arsenic removal

Arsenate speciation is pH dependent and H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-} are the dominant species in the following pH ranges: < 2.3 , 2.3-6.8, 6.8-11.3 and > 11.34 [4], respectively. In addition, the surface charge of HCO is also pH dependent. At pH values below 6.7 (pH_{pzc} 6.7), the surface of HCO particles is positively charged and vice versa, which indicates that surface site speciation changes with pH. Consequently, the adsorption of As(V) species on HCO is expected with pH. The effect of pH on As(V) adsorption on HCO in the pH range of 4-11 at initial As concentrations ranging from 0.5 to 250 mg L^{-1} under 1.0 g L^{-1} sorbent conditions presented in Fig. 2(a). When the initial As(V) concentration was no more than 5 mg L^{-1} , a broad adsorption maximum was observed. The broad adsorption maxima with more than 99% adsorption were observed at pH 4-10 and 4-8 corresponding to the initial As(V) concentrations of 0.5 and 5.0 mg L^{-1} , respectively. Distinct adsorption maxima shifted to

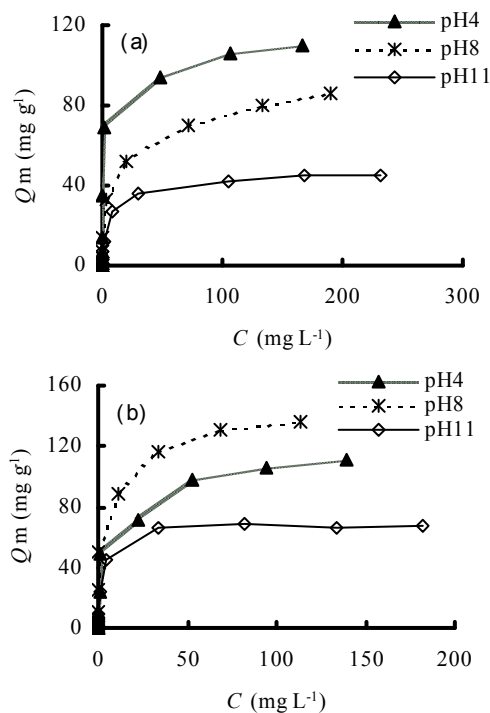


Fig. 3 Langmuir plots for As adsorption from (a) As(V) and (b) As(III) solution on HCO, with reaction conditions: ionic strength, 0.01M NaNO_3 ; adsorbent dosage, 1.00 g L^{-1} ; initial As concs., 0.5-250 mg L^{-1} ; contact time, 24 h.

pH 4 when initial As concentration increased to 50, 100 or 250 mg L^{-1} . Substantially less As(V) was adsorbed at pH values higher than the pH at which the adsorption maxima appeared, which was associated the decrease of HCO surface charge with increasing pH and the variation of As(V) species with pH.

Arsenous acid (H_3AsO_3) is a weak acid with the first pK at 9.23 [4]. Arsenite exists predominantly in the non-protonated H_3AsO_3^0 form at $\text{pH} < 9.2$ and as H_2AsO_3^- at $\text{pH} > 9.2$. H_3AsO_3^0 cannot be adsorbed onto HCO through the electrostatic interaction. The anion, H_2AsO_3^- , is capable of coordinating to the surface metal atom of the adsorbent and adsorption of the anion will occur provided the energy of adsorption is sufficiently large to dissociate the acid. Fig. 2(b) illustrates the adsorption of As(III) under the same reaction conditions. Arsenite were adsorbed up to 100% at the lower initial concentrations of 0.5 to 50 mg L^{-1} As in a wide pH range 4-8. Adsorption reaches a maximum around pH 8, and then decreases as pH increased at the higher initial concentrations. The percentage adsorption of As(III) decreased from 98% to 44% with increase in concentration from 5 to 250 mg L^{-1} As at an optimum pH of 8. The efficiency of As(III) adsorption decreased at pH values lower or higher than the pH at which the adsorption maxima appeared.

C. Adsorption isotherms

The adsorption capacities of the HCO adsorbent for As(V) and As(III) in aqueous solution at pH 4.0, 8.0 and 11.0 were

Table I. Correlation coefficients and isotherm of Langmuir modles (reaction conditions: ionic strength, 0.01M NaNO₃; adsorbent dosage, 1.00 g L⁻¹; initial concs., 0.5-250 mg L⁻¹; contact time, 24 h)

| pH | As(III) | | | As(V) | | |
|----|---------------|--------|-------|---------------|--------|-------|
| | Q_m mg/g | K_L | R^2 | Q_m mg/g | K_L | R^2 |
| 4 | 107 | 0.0681 | 0.986 | 109 | 0.0139 | 0.998 |
| 8 | 150 | 0.0286 | 0.997 | 83 | 0.0562 | 0.979 |
| 11 | 68 | 0.0309 | 0.992 | 44 | 0.0371 | 0.999 |

assessed using the isotherms presented in Fig. 3(a) and 3(b). The Langmuir equation was used to describe the adsorption isotherms in the figures and to determine the adsorption capacities. A conditional maximum adsorption calculated from the Langmuir equation was used as the adsorption capacities. The value of Q_m and K_L obtained from adsorption data at selected pH values was summarized in Table I. As shown in the table, regression coefficients (R^2) from different pH conditions were larger than 0.97, indicating that the Langmuir equation successfully described the adsorption behavior for As(V) and As(III). The HCO adsorbent had similar adsorption capacities for As(III) and As(V) at pH 4. Adsorption capacity Q_m for As(III) was found to be greater than that for As(V) at pH 8 and 11. This may be attributed to the different physicochemical properties of the two arsenic species. One plausible explanation is that the arsenite forms a type of lattice on the HCO particles [17]. In this process, the smaller arsenite is wrapped around the HCO particles whereas the arsenate is less adsorbed.

D. Effect of contact time on arsenic removal

Fig. 4(a) and 4(b) shows the effect of contact time on As(V) and As(III) sorption onto HCO adsorbents, respectively, for an initial As concentration of 10 mg L⁻¹, for the selected initial pH 4.0, 8.0 and 11.0. It was observed that with a fixed amount of HCO, the removal of arsenic increased with time and then attained equilibrium after 6 h. However, the time to reach equilibrium conditions was significantly affected by the initial pH values. At an initial pH of 8, a decrease of As(III) was found from 10 to < 1.0 mg L⁻¹ As in about 1 min and to < 0.01 mg L⁻¹ As in 2 h. This residual As concentration satisfies the drinking water standard level adopted by WHO. The adsorption rate decreased somewhat at an initial pH of 4, whereas a significant decrease in adsorption rate was found at an initial pH of 11. The adsorption rate of As(V) was rapid with 97% completion after ca. 1 min of shaking at an initial pH of 4. In such acidic condition, the residual As concentration of < 1.0 mg L⁻¹ As was attained within 5 min. The As(V) adsorption rates decreases with increasing pH. As(V) concentration decreased from 10 to < 0.1 mg L⁻¹ As at pH values even greater than PZC. Significant amounts of As(V) anions were adsorbed in 20 min at pH 8. At a pH of 11, As(V) concentration decreased to < 0.1 mg L⁻¹ As after 2 h, indicating a formation process of Inner-sphere complexes. However, as maximum adsorption of As(V) anions was

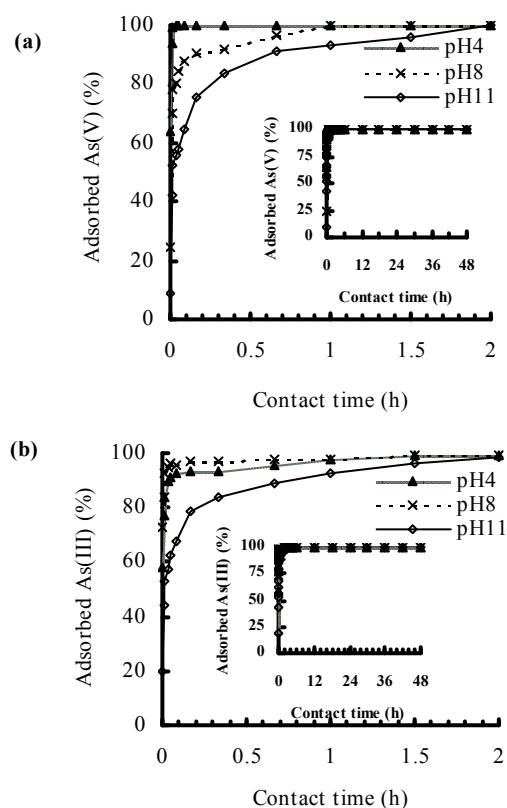


Fig. 4 Effect of contact time on As adsorbent from (a) As(V) and (b) As(III) solution by HCO, with reaction conditions: ionic strength = 0.01 M NaNO₃, adsorbent dosage = 1.00 g/L, initial As concs. = 10 mg/L.

observed to occur at low values of pH, the electrostatic interaction might also be involved when the HCO surface is positively charged.

Removal of As(V) and As(III) by adsorption on HCO was found to be dependent on pH and the initial As concentration. However, at concentration levels of characteristic arsenic contaminated water reportedly in environmental conditions, e.g. 0.05 to 2.30 mg L⁻¹ As [1-5], a minimum dosage of HCO is sufficient to reduce both As(V) and As(III) concentrations to satisfy the drinking water standard within a short time period (< 1 h) in a wide pH range of 4 to 9. In comparison to other arsenic removal methods such as the precipitation and coprecipitation, this method has advantages of small dose, effectiveness in a lower pH range, no increase of salt concentration in treated water and less formation of solid waste. The wide optimum pH range is also advantageous for a practical water treatment because pretreatment of water is not necessary.

E. Solid phase analysis and the adsorption mechanism

The FIRT spectra of untreated HCO and after treatment with both As(V) and As(III) solutions (Fig. 5) exhibited a wide band range 3200 - 3550 cm⁻¹, corresponding to bulk OH stretch and free surface OH groups and another band at 1640 cm⁻¹

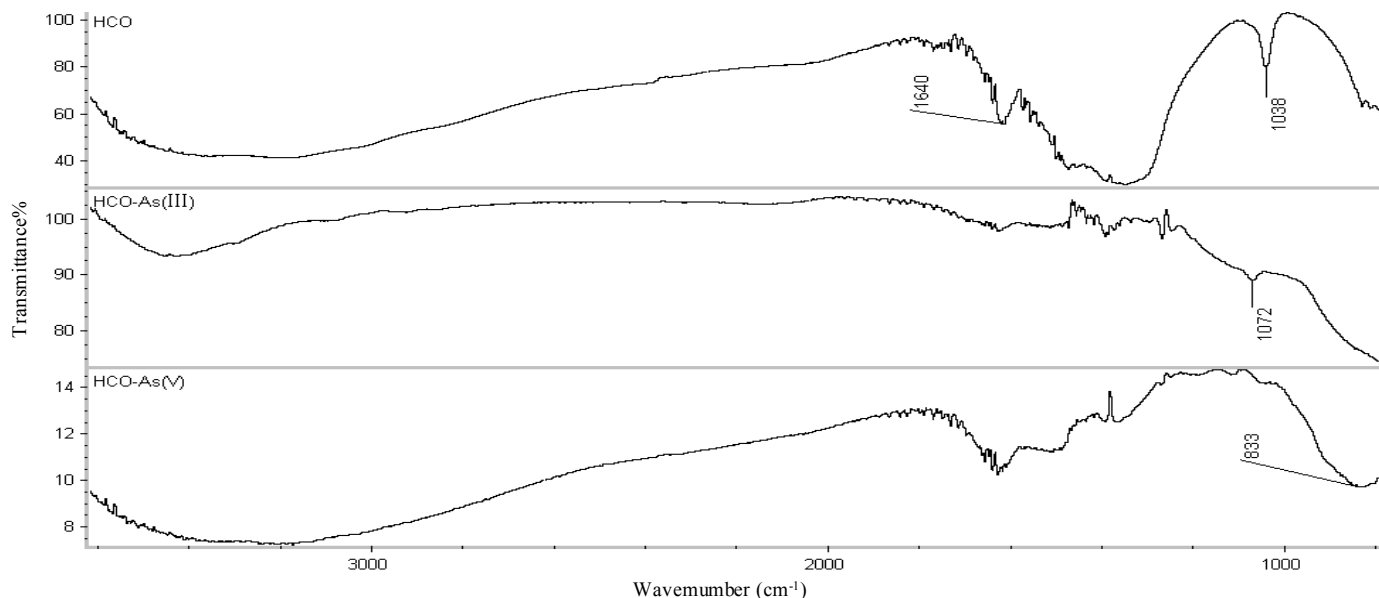


Fig. 5 FTIR-ATR spectra of HCO before and after As(III) or As(V) adsorption.

corresponding to water bending. The band at 1038 cm^{-1} corresponding to Ce-OH bending and the band region $800 \sim 900\text{ cm}^{-1}$, corresponding to the Ce-OH swinging were almost disappeared when loading the sorbent with both As(V) and As(III). This result indicated that interactions of Ce-OH groups with either As(V) and As(III) species would play an important role in the adsorption mechanism [18].

Both As(V) and As(III) anions were found to be adsorbed onto HCO in a wide pH range including neutral and basic conditions, where the pH values is higher than PZC, indicating that a formation process of inner-sphere complexes rather than a purely electrostatic adsorption should be the major driving force in the adsorption of arsenic anions. The results of adsorption isotherms, kinetic studies and FTIR observations give support to this hypothesis.

H_2AsO_4^- is the predominant species at pH 4, and, apparently, the major species being adsorbed. The HCO surface has a net positive charge and adsorption is facilitated by electrostatic interaction, the removal is rapid and adsorption capacity is high because electrostatic interaction can readily take place in conjunction with specific adsorption (Fig. 4(a)).

At a pH of 8, more than 50% of As(V) anions are negative two charges (HAsO_4^{2-}) and less than 50% negative one charges (H_2AsO_4^-). The surface of HCO is already negatively charged. Because all the components have negative charges arsenate adsorption must compete with electrostatic repulsion. The formation of inner-sphere complexes is usually slower than electrostatic interactions since it may be site specific and ligand orientation may be necessary. Therefore, adsorption process of As(V) was slow and adsorption capacity decreased.

Arsenate anions have mostly negative two charges and a few negative three charges at pH 11. The surface of HCO becomes more negatively charged. The negatively charged components would thus repel each other; the adsorption of As(V) must be significantly competed with electrostatic

repulsion. Consequently, As(V) adsorption capacity is suppressed and adsorption rate is significantly decreased.

The formation process of inner-sphere complexes between the no charged H_3AsO_3^0 and HCO surface may also be achieved at pHs > PZC provided the undissociated acid gives a proton to the hydroxyl group on the surface to form H_2O that can be readily displaced by the anion [13]. The facts that rapid adsorption of As(III) occurred in neutral condition and the adsorption maxima fell at pH 8 might be attributed to the difference between the energy release upon adsorption and the energy and the energy required to dissociate the acid is at a maximum. Arsenite adsorption efficiency reduced and the process became slower at a pH > 9. In such alkaline conditions, H_2AsO_3^- is the predominant species and HCO surface becomes negatively charged. Therefore, As(III) adsorption capacity is suppressed and adsorption rate is decreased as all the components have negative charges and thus repel each other as As(III) adsorption must competed with electrostatic repulsion.

During the sorption experiments, the absence of cerium in solution at pHs within the range 4 - 11, where As(III) and As(V) sorption are maximum, indicates that the mechanism the precipitation of an Ce(IV) arsenate or Ce(VI) arsenite is not involved in the removal of both As(V) and As(III). Taking into account (i) the characteristics of HCO material, (ii) the presence of functional groups on the sorbent surface (mainly free hydroxyls) and considering (iii) the nature of arsenic species present in solution at the working pH, the mechanisms for As(V) and As(III) were proposed as follows:

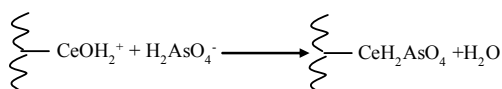
For As(V) removal it is supposed that two different mechanisms can contribute to sorption: (i) non-specific coulombic interactions between As(V) species and the positively charged functional groups on the sorbent surface and (ii) coordination of As(V) species onto metal (hydr)oxides with the formation of coordination compounds of low solubility, according to

Table II. Concentrations in TCLP extracts from HCO sorbents, before and after As sorption; comparison with the MCL (Maximum Contaminant Level) in drinking water and the TCLP limiting values for hazardous waste

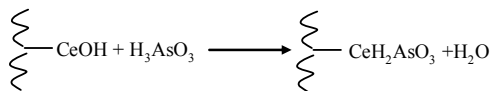
| | As (mg L ⁻¹) |
|----------------|--------------------------|
| HCO | n.d. ^a |
| HCO-As(III) | 0.15 ± 0.02 ^b |
| HCO-As(V) | 0.41 ± 0.03 ^b |
| MCL | 0.01 |
| TCLP=100 x MCL | 1.00 |

a. below determination limit

b. average ± deviation (n=3)



In the case of As(III), the free hydroxyls of the sorbent interact with the species according to



Such a sorption mechanism has been reported in the literature, as responsible for As(III) and As(V) sorption onto an aquifer material of complex mixture mineralogical nature [19].

F. Hazard classification of the spent adsorbent

The EPA Toxicity Characteristics Leaching Procedure (TCLP) was applied to the As-loaded sorbent used in the adsorption experiments to classify this material as inert or hazardous before any disposal [16]. According to the general guidance established by USEPA, if metal concentration in the extract do not exceed 100 times the Maximum Contaminant Level (MCL) in drinking water for that metal, the waste would not be considered hazardous. The final pH of the extracted solution was approximately 5.1. Cerium had not been detected in all extracts during the experiments. Table II shows that the leachate arsenic concentrations for both As(V)- and As(III)-loaded sorbents were below 0.5 mg L⁻¹, much lower than the EPA regulatory level for arsenic (5.0 mg L⁻¹), therefore the spent HCO was not a hazardous material.

IV. CONCLUSION

Adsorption of both As(V) and As(III) anions was virtually independent of pH and up to 100% removal can be achieved in the lower concentration range 0.5 - 5.0 mg L⁻¹ As at a HCO dosage of 1.0 g L⁻¹. As the initial arsenic concentration increased to 50, 100 or 250 mg L⁻¹ for the same sorbent dosage, distinct adsorption maxima of As(V) appeared and shift to lower pH, whereas that of As(III) was found at approximately pH 8. The effect of contact time was dependent on pH but adsorption equilibriums were reached after 6 h in all cases for the studied systems. Adsorption isotherms of both anions fit well in the Langmuir model of adsorption over the As concentration range 0.5 - 250 mg L⁻¹. Both anions were

removed principally by the formation of inner-sphere complexes on the HCO surface as revealed by the FTIR spectra.

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