



Research paper

Adsorption capacity of iron oxyhydroxide-coated brick for cationic metals and nature of ion–surface interactions



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ABSTRACT

The adsorption of six metal ions (Cd²⁺, Cu²⁺, Fe²⁺, Ni²⁺, Pb²⁺ and Zn²⁺) from an aqueous solution by a new composite – iron oxyhydroxide (ferrihydrite) deposited onto pre-activated brick grains – was investigated under dynamic experimental conditions. Breakthrough curves were obtained under specified fixed-bed-column conditions, and the determined adsorption capacity (molar basis), Q , followed the order of QPb(II) > QCd(II) ≈ QZn(II) > QFe(II) > QNi(II) > QCu(II). An attempt was made to correlate the ionic characteristics of these cationic metals with adsorption performance, and data revealed how strongly metal cations were attracted to negatively charged brick sites via electrostatic interactions. In addition to electrostatic attractions, a process implicating outer-sphere complexes, $\equiv S^- Na(H_2O)_6^+$ and inner-sphere complexes, $(\equiv S^-)_2 Me^{2+}$ (Me = metal), was suggested. ESEM/EDS analysis showed that cations were preferentially sorbed by ferrihydrite, rather than other hydroxyl groups in brick clays. A correlation also was found between the hydration free energy of Me²⁺ ions and hydrated radius, raising the possibility of water molecules being implicated in this adsorption mechanism. To confirm this hypothesis, ²³Na and ¹H MAS NMR were applied to our samples in order to examine the bonding states of sodium and water molecules and their dynamics at the material surface.

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1. Introduction

Important health-related infrastructure programs were generally launched in larger cities in developing countries by governments and international organizations. Unfortunately, most people in rural areas of developing countries did not enjoy the same access to drinking water and sanitation as the urban population. In part, this lack of access to drinking water had been a steady threat to the development of the rural economy and the living standard therein. This also had been a problem in the Central African Republic and prompted us to investigate the removal of metal contaminants from drinking water and the development of safe water supplies to rural areas at reasonable costs.

Adsorption techniques are now widely employed to remove diverse types of inorganic and organic pollutants from contaminated waters. However, use of commercial adsorbents is often restricted in developing countries because of their high cost, which is especially true in rural regions. Fortunately, there are many low-cost natural adsorbents that

can be used as a replacement for current costly methods (e.g., Ahmaruzzama, 2008; Ali et al., 2012; Bhatnagar and Sillanpaa, 2010; Demirbas, 2008; Kurniawan et al., 2006; Lin and Juang, 2009; Rafatullah et al., 2010). Among them, natural sand impregnated with iron oxide was found to be suitable for the uptake of certain toxic metal ions (Bailey et al., 1992; Lai et al., 2000, 2002; Lee et al., 2012; Mostafa et al., 2011; Xu and Axe, 2005). Similarly, the removal capacity of brick (a common natural material composed mostly of sand, 55–65%, and in part metakaolinite, 20–30%) for trace metals in aqueous solution deserves some attention.

Recent studies have enabled us to demonstrate that brick from the Central African Republic can be used as a low-cost adsorbent for the removal of ferrous ions from groundwater (Allahdin et al., 2013; Dehou et al., 2012a,b,c). Impregnation of brick with iron oxyhydroxide enhanced its removal efficiency, especially if a primary step of acid activation was carried out on the raw brick. Indeed, pre-treating this brick with hydrochloric acid at 90 °C led to an increase in porosity and surface area of the material as well as the elimination of some mineral compounds. In addition, without dramatically modifying the original clay structure upon acid attack (Suraj et al., 1998), the octahedral Al³⁺ ions were preferentially released from amorphous metakaolinite, which was identified as the dominant clay mineral in the brick used in this study at levels up to 30 wt.% (Dehou et al., 2012a). This resulted in the generation of additional Al–OH and Si–OH bonds. Such an acid

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activation was further found to increase and favor deposition of FeOOH via precipitation of Fe^{3+} ions with NaOH up to a pH of approximately 7.

In this report the ability of the composite, ferrihydrite-coated (pre-activated) brick to adsorb divalent metals (namely, Cd^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+}) was investigated under dynamic experimental conditions, i.e., in a fixed-bed column. Data on the physical characteristics of these cations and their hydration free energy were compiled from the peer-reviewed literature and correlated to adsorption capacity in order to assess their relative tendency to be bound to reactive brick sites. Microscopic ESEM/EDS analyses were carried out on modified brick before and after metal adsorption: first to determine the partitioning of the adsorbent on the targeted brick specimens, and second to find binding correlations between the study metal and the major elements constituting the different brick minerals. ^{23}Na and ^1H NMR were also used in this study to better understand how sodium ions and water molecules intervened in the adsorption process. From these investigations, a mechanism for chemical phenomena involved at the brick–water interface is proposed.

2. Materials and methods

The raw brick used in this study was obtained from the Bangui region in the Central African Republic. It was previously characterized by X-ray diffraction and chemical analysis (Dehou et al., 2012a): ~61 wt.% quartz; ~21 wt.% metakaolinite; 3–4 wt.% illite; ≤ 4 wt.% iron oxides/hydroxides; and ≤ 2 wt.% feldspar + mica + biotite. As described before by Dehou et al. (2012a,b), several physical/chemical treatments were carried out on the raw brick. Briefly: (i) it was broken into grains and sieved with sizes ranging from 0.7 to 1.0 mm; (ii) the resulting particles were leached with a 6 M HCl solution at 90 °C for 3 h; and (iii) finally a deposition of FeOOH onto HCl-treated brick was performed by precipitation of iron (III) with a NaOH solution. Previously, it was noticed that HCl concentration, reaction temperature and time had a significant influence on the final meso-structure of the material (Dehou et al., 2012b). Therefore, following the acid leaching procedure described above, the surface area (S.A.) and pore volume (V_{pore}) were found to increase notably from S.A. = $31.2 \text{ m}^2 \text{ g}^{-1}$ and $V_{\text{pore}} = 0.15 \text{ cm}^3 \text{ g}^{-1}$ in the raw brick to S.A. = $75.5 \text{ m}^2 \text{ g}^{-1}$ and $V_{\text{pore}} = 0.21 \text{ cm}^3 \text{ g}^{-1}$ in 6 M HCl-treated solids at 90 °C for 3 h. However, after deposition of ferrihydrite, a slight decrease in the surface area (S.A. = $70 \text{ m}^2 \text{ g}^{-1}$) was observed.

All chemicals used in the study were analytical grades. Sodium hydroxide and hydrochloric acid were supplied by DISLAB (France). The following salts $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ were purchased from Prolabo, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was obtained from Scharlau, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was obtained from Merck and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was obtained from Fluka. Divalent-metal salts were diluted in Milli-Q water to obtain $1.79 \times 10^{-3} \text{ mol/L}$ solutions (in the case of iron, this concentration corresponded to 100 mg per liter). Before column experiments, the stock solutions of cationic metals were diluted ten-fold to obtain an influent concentration of $1.79 \times 10^{-4} \text{ mol/L}$. This influent concentration was chosen in this work because it generally represents a maximum level of soluble iron ($\approx 10 \text{ mg/L}$) found in groundwater from the Bangui region. The influent pH ranged from 5.5 to 6.5. It is worth noting that Fe^{2+} ions initially present in the prepared influent solution ($\approx 10 \text{ mg/L}$) remained at oxidation state II under the physicochemical conditions of this study (pH ≈ 4.4 ; Eh = +347 mV vs. Ag/AgCl/[KCl] = 3 mol/L; $[\text{O}_2] = 5.77 \text{ mg/L}$). The thermodynamic stability of ferrous ions in solution was further confirmed theoretically by examining the $p\text{E}$ –pH diagrams for the iron–water system (Stumm and Morgan, 1996). Spectrophotometric analysis by phenanthroline reagent confirmed experimentally the stability of such a diluted iron(II) solution during the course of our experiments.

Microphotographies of representative brick specimens before and after metal adsorption were recorded by using an environmental scanning electron microscope (ESEM, Quanta 200 FEI). Elemental analysis

was performed using ESEM/EDS (ESEM, model: QUANTA-200-FEI, equipped with an energy dispersive X-ray spectrometer EDS X flash 3001 and monitored by a QUANTA-400 software elaborated by Bruker). EDS measurements were carried out at 20 kV at low vacuum (1.00 Torr) and the maximum pulse throughput was 20 kcps. Surface areas ranging from 0.5 to 3.5 mm^2 were targeted on brick grains and examined by ESEM/EDS. Micro-observations along cross-sections of FeOOH-coated brick samples were also performed by ESEM/EDS. Atomic quantifications and mathematical treatments were undertaken using a QUANTA-400 software in order to determine the averaged elemental composition of the brick surface and to detect chemical changes in response to metal adsorption.

Solid-state magic angle spinning NMR spectra were recorded at 800.13 MHz on a Bruker Avance 800 (18.8 T) multinuclear spectrometer equipped with a Bruker 3.2 mm CP-MAS probe. The spinning rate of the 3.2-mm zirconia rotor was 20 kHz. For ^1H MAS NMR analysis, depth-pulse sequences were applied with a pulse time of 3.25 μs ($\pi/2$ flip angle), 64 scans, and a recycle delay of 5 s. All the ^1H chemical shifts were referenced to TMS. As for ^{23}Na ($I = 3/2$) MAS NMR analysis, the pulse program provided by Bruker was used for data acquisition. Sequences with direct detection were applied to our samples with a pulse time of 1 μs ($\sim\pi/5$ flip angle), 1024 scans, and a recycle delay of 2 s. All the ^{23}Na chemical shifts were referenced to a saturated NaCl solution. Overall, the good resolution of MAS-NMR spectra confirmed that the paramagnetic effects of brick iron are negligible due to low amounts of Fe in our samples ($< 1\%$). Also, when comparing NMR spectra of HCl-activated brick before and after deposition of Fe oxyhydroxide, no spectral modifications (which would appear as NMR signal dispersion/dilution towards rotation bands) were observed.

Continuous flow adsorption experiments were conducted in a fixed-bed glass column with an inner diameter of 12.5 mm, a height of 25 cm, and a medium porosity sintered-Pyrex disk at its bottom in order to prevent any loss of material. A bed depth of 8.5 cm (10.0–10.5 g) was investigated at a constant flow rate of 10 mL/min. Before being used in the experiments, about five bed volumes of Milli-Q water were passed through the column for three reasons: (i) to remove any unbound and thin particles/iron oxides/hydroxides; (ii) to check the absence of soluble iron at the outlet; and (iii) to confirm the stability of the FeOOH coating on brick pellets. The initial metal concentration of the influent was $1.79 \times 10^{-4} \text{ mol per liter}$. The schematic diagram of the fixed-bed column reactor used is shown in Fig. 1. The metallic cation solution was pumped through the column at a desired flow rate by means of a peristaltic pump (Labo Moderne, France, type KD1170) in a down-flow mode. Effluent samples exiting the bottom of the column were collected at different time intervals and analyzed for metal contents using ICP-AES (inductively coupled plasma–atomic emission spectroscopy; model Varian Pro Axial View). Flow to the column continued until the effluent metal concentration at time t (C_t) reached the influent metal concentration (C_0): $C_t/C_0 \approx 0.98$. Performance of the packed bed is described in the present work using the concept of the breakthrough curve.

3. Results and discussion

3.1. Metal-adsorption performances of modified brick

The effectiveness of FeOOH-coated (HCl-activated) brick in the removal of the metals Cd(II), Cu(II), Fe(II), Ni(II), Pb(II), and Zn(II) (each studied individually) was assessed under dynamic conditions using a fixed-bed column (as stated in the experimental section). The divalent-metal content in the column influent was fixed at $1.79 \times 10^{-4} \text{ mol/L}$; this concentration corresponds to 20.1 ppm Cd, 11.4 ppm Cu, 10.0 ppm Fe, 10.5 ppm Ni, 37.1 ppm Pb, and 11.7 ppm Zn. Results are presented graphically in Fig. 2. The breakthrough point was defined as the time, t , when the effluent concentration, C_t , attains $0.05 \times C_0$. The corresponding effluent volume at breakthrough was 389, 350, 300, 301, 407 and 401 mL

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