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Use of waste ceramics in adsorption technologies

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ABSTRACT

Waste brick dust (WBD) was tested as a potential sorbent of cationic and anionic contaminants, including radioactive residues. For adsorption experiments, model water solutions of highly toxic and/or ecologically harmful cations (Cd, Pb, Cs) and anions (As, Sb, Cr, U) were selected. The adsorption of Cd^{2+} and Pb^{2+} on WBD was most effective (>95%) at a very low sorbent dosage (up to 6 g L^{-1}). In terms of anionic contaminants, U^{VI} was adsorbed as cationic complex particles $[(UO_2)_n(OH)_{2n-1}]^+$ almost quantitatively (>95%) at a sorbent dosage of 3 g L^{-1}. The effective adsorption of As^V (>90%) occurred at around a dosage of 15 g L^{-1}. The adsorption of Cs^+, Cr^{VI} and As^{III} on WBD was almost ineffective. Except for Cs^+ and Cr^{VI}, all investigated ions were adsorbed according to the Langmuir isotherm model, at the theoretical adsorption capacities $Q_t \approx$ approximately 0.1 mmol g^{-1} for Cd^{2+}, Pb^{2+} and U^{VI}, and approximately. 0.04 for As^V and As^{III}. The leachability of toxic particles from saturated WBD was very low for selectively adsorbed particles (≈0.01–0.08% wt.) and their stability decreased in the order: $Pb^{2+} \approx Cd^{2+} > U^{VI} > As^V > As^{III} \gg Cs^+ \gg Cr^{VI}$. The approximate consumption of WBD per gram of toxic element was found to be about ≈60 g for Pb^{2+} and U^{VI}, ≈100 g for Cd^{2+} and >400 g for As^V.

1. Introduction

Waste ceramics, including brick dust, represent a feasible and challenging material due to several aspects, such as its chemical stability, availability, environmental safety issues, fineness, and silicate properties. The waste ceramic materials can be generally recycled either as aggregates in concrete production (Silva et al., 2014) or, when the waste particles are fine one can take advantage of ceramic composition (high content of active silica and alumina) and apply it as pozzolanic component of cement based materials and thus reduce the Portland cement consumption (Kulovana et al., 2015). In analogy with natural aluminosilicates, these materials may also be applied as cheap but effective sorbents of ionic species in technological or environmental adsorption processes.

Illite is the principal component of many raw materials used for the production of traditional ceramics, including bricks and roof tiles (Dondi et al., 2014); illite improves the plasticity of clayey matter. During the drying and firing process, illite first loses its interlayer water (50–400 °C); illite dihydroxylation then takes place in two steps between 450 and 800 °C. A glass is then formed above 900 °C (Carroll et al., 2005; Ferrari and Gualtieri, 2006) and works as a flux in ceramics. The kinetics of illite dehydroxylation have been described by Ferrari and Gualtieri (2006). Favorable adsorption properties result from a proper chemical composition (Al, Si, Fe content) and surface hydration of the aluminosilicate structure (Lin and Puls, 2000; Zanelli et al., 2015).

The mobility of environmental contaminants can be particularly controlled by their chemistry and phase stability related to the pH/Eh of investigated system (Mc Lean and Bledsoe, 1992). Typical cationic (heavy metals) and anionic (metalloids, non-metals) contaminants generally attract differently charged active sites on a sorbent surface, therefore the pH of zero point of charge, pH_{ZPC} (Fiol and Villaescusa, 2009) can be considered the first indicator of sorbent selectivity. In natural water systems, solids with a low pH_{ZPC} (aluminosilicates, quartz) represent mostly cation active sorbents (Jiang et al., 2009; Padilla-Ortega et al., 2013), while a high pH_{ZPC} is typical for anion active sorbents (Fe/Al oxy(hydroxides), gibbsite) (Cai et al., 2015; Oliviera et al., 2003). The surface of mixed materials (soils, sediments, brick dust) mostly consists of diverse active sites, and the pH_{ZPC} represents more or less the average value of particular components of the solid matrix. Therefore, the sorption selectivity of mixed materials is not unique, and under appropriate conditions they can attract both cationic and anionic particles.

The aim of this work was to verify the sorption properties of waste brick dust in a raw and water-leached state, without any technological pre-treatment. For this purpose, selected toxic heavy metals (Pb^{II}, Cd^{II}), anionic contaminants (As^V/As^{III}, Cr^{VI}) and radioactive wastes (Cs^I, U^{VI}) were investigated in model aqueous systems. Perspectively, a waste brick dust saturated with toxic ions might be incorporated into cement building material.

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2. Materials and methods

2.1. Waste brick dust

The studied sorbent, waste brick dust (WBD), is generated as a waste (grinding dust) during the production of vertically perforated ceramic blocks intended for thin joint masonry. Currently the grinding dust is partially recycled in the production line – it is dosed as non-plastic component of green ceramic mixture. The amount recyclable by this way is obviously limited and thus the surplus ceramic waste is dumped.

The elementary chemical and mineralogical composition of the raw ceramic mixture ("green") used for the production of red-clay ceramics is given in Table 1. The dominant clay mineral was illite (ca. 30%), while the green body further contained chlorite, quartz (ca. 25%), hematite, albite, orthoclase, muscovite, calcite and dolomite. During firing, illite and chlorite were transformed into amorphous matter, and calcite and dolomite decomposed. Akermanite ($Ca_2MgSi_2O_7$) and hedenbergite ($CaFeSi_2O_6$) are the crystalline products of the reactions between illite and carbonates present in the material.

To reduce the high alkalinity and improve the attraction to anions, the raw WBD was washed five times in distilled water at laboratory temperature (20 °C) at a solid-liquid ratio of 1:50. During the procedure, the pH value decreased almost by 3 units, i.e. from 12.5 to 9.8. The washed WBD is referred to as WBD_W.

2.2. Model solutions

Model solutions of Pb^{2+}, Cd^{2+}, Cs^+, $H_2AsO_4^-$, AsO_2^-, $Cr_2O_7^{2-}$ and $U_2O_7^{2-}$ were prepared from inorganic salts ($PbCl_2$, $Cd(NO_3)_2$, CsCl, KH_2AsO_4, $NaAsO_2$, $(NH_4)_2Cr_2O_7$, $(NH_4)_2U_2O_7$) of analytical grade and distilled water, in the concentrations of 0.1 and 0.5 $mmol \cdot L^{-1}$ and the natural pH (i.e. pH ≈ 3.5 for cationic solutions and pH 5–6 for anionic solutions). The concentration range was selected as appropriate for the simulation of a slightly increased amount of the contaminant in a water system to a heavily contaminated solution. The solution of As^{III} as $NaAsO_2$ was prepared under an N_2 atmosphere, at pH ≈ 7.4–8.5 (Doušová et al., 2009, 2011).

2.3. Sorption experiments

During the adsorption experiments the cationic particles (Cd^{2+}, Pb^{2+} and Cs^+, respectively) were adsorbed on the raw WBD, whereas the anions ($As^{III/V}$, Cr^{VI}, U^{VI}) were adsorbed on the water-washed WBD_W.

A suspension of the model solution (50 mL) and defined dosage (0.5–15 g L^{-1}) of WBD (WBD_W) was shaken using a batch procedure at laboratory temperature (20 °C) for 24 h (Doušová et al., 2006). The product was filtered and the filtrate was analyzed for residual cations/anions, while the solid residue (saturated WBD/WBD_W) was kept for leaching tests. WBD saturated with Pb^{2+} and WBD_W saturated with Cr^{VI}, As^{III} and As^V, respectively, were also tested by the solid-state NMR spectroscopy and S_{BET} measurements to verify the structural and/or surface changes caused by adsorption. All sorption data were fitted to the Langmuir equation (Jeong et al., 2007, Misak, 1993), which was verified as a suitable adsorption model for natural oxides, aluminosilicates and soils. The data illustrated the parameters of adsorption (q_{max} – maximum equilibrium sorption capacity; Q_{theor} – theoretical sorption capacity; R^2 – correlation factor; K_L – Langmuir adsorption constant), which were used to compare the adsorption affinities of the investigated ions on brick dust.

2.4. Analytical methods

Powder X-ray diffraction (XRD) was performed with a Seifert XRD 3000P diffractometer with CoK_α radiation (λ = 0.179026 nm, graphite monochromator, goniometer with Bragg-Brentano geometry) in the 2θ range of 5–60° with a step size of 0.05° 2θ.

X-ray fluorescence (XRF) analyses of the solid phase were determined with an ARL 9400 XP+ spectrometer with a voltage of 20–60 kV, probe current of 40–80 mA and effective area of 490.6 mm^2. UniQuant software was used for data evaluation.

The specific surface area (S_{BET}) was measured on a Micromeritics ASAP 2020 (accelerated surface area and porosimetry) analyzer using the gas sorption technique. The ASAP 2020 model assesses single and multipoint BET surface area, Langmuir surface area, Temkin and Freundlich isotherm analysis, pore volume and pore area distributions in the micro- and macro-pore ranges by the BJH method. The micropore option used the Horvath-Kavazoe method, with N_2 as the analysis adsorptive and an analysis bath temperature of −195.8 °C. The samples were degassed at 313 K for 1000 min.

The IR spectra were collected on a Nicolet 6700 FTIR (Thermo Nicolet Instruments Co.) with N_2 purging system. Spectra were acquired using a single reflection ATR SmartOrbit accessory equipped with a single-bounce diamond crystal (angle of incidence: 45°). A total of 64 scans were averaged for each sample and the resolution was 2 cm^{-1}. The spectra were rationed against a single-beam spectrum of the clean ATR crystal and converted into absorbance units by ATR correction. Data were collected in the wavenumber range of 4000–400 cm^{-1}.

Solid-state NMR spectra were measured at 11.7 T using a Bruker AVANCE III HD 500 WB/US NMR spectrometer. The ^{27}Al MAS NMR spectra were acquired at a spinning frequency of 11 kHz, Larmor frequency of 130.287 MHz and recycle delay of 2 s, and the spectra were referenced to the external standard $Al(NO_3)_3$ (0 ppm). The number of scans for the acquisition of a single ^{27}Al MAS NMR spectrum was 512 (total experimental time was ca. 10 min). The ^{29}Si MAS NMR spectra were acquired at a spinning frequency of 11 kHz, Larmor frequency of 99.325 MHz and recycle delay of 10 s. The number of scans for the acquisition of a single ^{29}Si MAS NMR spectrum was 6144 (total experimental time was ca. 17 h). The spectra were referenced to the external standard M_8Q_8 (−109.8 ppm). The NMR experiments were performed at a temperature of 24 °C, and temperature calibration was performed to correct for the frictional heating of the samples.

The concentration of Pb/Cd/Cs in aqueous solutions was determined by atomic absorption spectrometry (AAS) using a SpectrAA-880 VGA 77 unit (Varian) in flame mode.

The concentration of As in aqueous solutions was determined by Hydride Generation Atomic Fluorescence Spectrometry (HG-AFS) using a PSA 10.055 Millennium Excalibur apparatus. The samples were

Table 1
Chemical and mineralogical composition of the green ceramic mixture and waste brick dust (WBD).

Chemical composition (% *wt*)	Green	WBD	Mineralogical composition	Green	WBD
Na_2O/K_2O	1.1/4.2	1.3/4.1		Quartz (25%)	Quartz (22%)
MgO/CaO	3.8/10.6	4.5/11.5		Chlorite	Microcline
Al_2O_3	20.9	20.0		Illite (30%)	Hematite
SiO_2	51.8	51.3		Albite	Albite
P_2O_5	0.9	0.9		Orthoclase	Orthoclase
Fe_2O_3	6.6	5.9		Muscovite	Muscovite
TiO_2	0.9	0.8		Calcite Dolomite	Akermanite Hedenbergite