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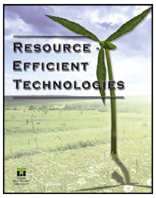

Research paper

Sorption characteristics of economically viable silicate sorbents for sequestration of lead ions from aqueous solutions

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ABSTRACT

The adsorption of Pb^{2+} from aqueous solutions by sorbents based on calcium silicates, obtained in multicomponent systems $CaCl_2–Na_2SiO_3–H_2O$ (sorbent I) and $CaSO_4·2H_2O–SiO_2·nH_2O–KOH–H_2O$ (sorbent II), was studied. Surface area of the two sorbents was found to be 100 and 40 m^2/g respectively. The sorption capacities of the adsorbent materials were found to be 3.6 l/mmol and 8.4 l/mmol respectively. Characterization of the sorbent materials was carried out. The equilibrium data was fitted in Langmuir's isotherm and the adsorption capacity of the adsorbent materials was determined. The distribution coefficients at Pb^{2+} ions for the sorbents were determined at different ratios of solid and liquid phases.

1. Introduction

It is well known that lead and its compounds are highly toxic. Lead is regarded as a poison affecting mainly nervous and vascular systems and directly blood [1,2]. Lead has been reported to be toxic to fauna, flora and human beings. Its adverse effects on living beings through its application in leaded paints, gasoline, and many lead-containing products have been documented [3–5] because of its ill health effects, lead products have been banned in many countries of the world. The application of lead in gasoline was prohibited worldwide but it has been regularly used in aero plane fuels [6–9].

Search for efficient and ecologically safe sorbents for extraction of lead ions, in particular, from aquatic sources is rather urgent.

Scientists have reported adsorption of Pb^{2+} ions with calcium silicates of various compositions and structure. The authors [3] have reported dependence of reactions of natural and synthetic tobermorite $Ca_{10}[Si_{12}O_{31}](OH)_6·8H_2O$, xonotlite $Ca_6[Si_6O_{17}](OH)_2$ and wollastonite $Ca_6Si_6O_{18}$ with salts of heavy metals, including lead nitrate, in the range of ions concentration Pb^{2+} from 100 to 1,000 mg/l with ratio of solid and liquid phases S:L=1:400. It was found that as a result of lead nitrate's reaction with the studied calcium silicates either lead hydroxocarbonate $Pb_3(CO_3)_2(OH)_2$ (hydrocerussite) or lead carbonate $PbCO_3$ (cerussite) is formed. This is acknowledged by X-ray diffraction analysis of samples after they react with lead nitrate: calcite contained in initial samples of wollastonite and tobermorite, tobermorit disappears. As one of possible mechanisms to form lead hydroxocarbonate, the authors suggested hydrolysis and carbonization of hydrolysis products.

The authors [10] studied process of cations exchange between synthetic 1.1 nm tobermorite and solutions containing Pb^{2+} ions in the range of concentrations of Pb^{2+} ions from 100 to 1,800 µg/ml. As a result, it was concluded that reaction of 1.1 nm tobermorite with lead salts, compounds with general empirical formula $Ca_{5\text{-}x}Pb_xSi_6 \ldots nH_2O$ are formed, where x varies from 0.033 to 0.514. It was concluded on prospective use of tobermorite, stable in neutral and alkaline media, for ions exchange processes. The process of extraction of ions Pb^{2+} with wollastonite from water solutions of lead nitrate with ratio of solid and liquid phases S:L=1:50 was studied [11]. The impact of temperature on sorption kinetics at 20, 30 and 40°C was studied at pH=6.4 and initial concentration of Pb^{2+} ions 6 mg/l. It was found that as the temperature

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Table 1
Synthesis conditions, phase structure and BET surface area of sorbents used for sorption of Pb^{2+} ions.

Sorbent	Initial substances and synthesis conditions	Phase structure: Before heat-treatment	Phase structure: After heat-treatment at 900°C	BET surface area, m^2/g
I	Solutions of sodium silicate Na_2SiO_3, CP (silicate module $SiO_2/Na_2O=1$) and calcium chloride ($CaCl_2 \cdot 2H_2O$ content at least 98.3%). Synthesis was made at 20°C.	Amorphous phase, $CaCO_3$	$CaSiO_3$, CaO	100.0
II	Borogypsum (containing basic components, mass %: SiO_2 – 32.2%; CaO – 28.4; SO_3 – 31.3%; Fe_2O_3 – 2.7%) and potassium hydroxide KOH, *pro analysi*. Synthesis was made in autoclave at 1.7 atm. within 2 hours.	Amorphous phase, SiO_2, $CaCO_3$, $CaSO_4 \cdot 2H_2O$	$CaSiO_3$	40.0

increases, removal of Pb decreased from 75.5 to 60.0%, which indicated exothermic nature of sorption. The calculated value of energy of activation of sorption process was 8.730 KJ/mol. The analysis of sorption isotherms by Langmuir equation has shown that the value of maximal sorption capacity falls from 0.308 to 0.234 mg/g (from $1.5 \cdot 10^{-3}$ to $1.13 \cdot 10^{-3}$ mmol/g) as the temperature increases.

The subsequent separation of heavy metals cations [12] from a series of solutions containing Pb^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+} with calcium hydromonosilicate C–S–H, within the range of initial concentrations of Pb^{2+} ions from 0.127 to 2.68 g/l was studied. The following sequence of cations separation was identified: Cu^{2+}, Pb^{2+}, Cd^{2+}. It is reported [13] that the process of Pb^{2+} ions sorption by synthetic xonotlite and wollastonite obtained from two types of anthropogenic waste – phosphogypsum and silica gel provided significant results. The studies were made with aqueous solutions of Pb at pH=5.0, temperature 25°C, ratio of solid and liquid phases S:L=1:250 within 40 minutes. It was shown that sorption capacity of the silicates studied as related to Pb^{2+} ions is 1.3–1.5 mmol/g for xonotlite and 0.9–1.0 mmol/g for wollastonite.

The sorption characteristics of synthetic composite sorbent based on calcium hydrosilicate C–S–H, amorphous silica dioxide and calcium carbonate were studied [14] at initial concentrations 100–600 mg/l, ratio solid/liquid phases S:L=1:200, pH=6.0–6.5 and temperature 17 °C for 60 minutes. The maximal sorption capacity of the sorbent for removal of Pb^{2+} ions is 94.43 mg/g (0.46 mmol/g). Sorption characteristics of nanosize calcium hydromonosilicate C–S–H were studied [15–17]. Its BET surface area was found to be 462.0 m^2/g. Adsorption experiments were made by taking a ratio of solid/liquid phases, S:L=1:100, initial concentrations of Pb^{2+} ions 50 mg/l at room temperature. It was shown that a complete removal of lead was achieved within 6 min which indicates that the process of removal is ‘fast’. Such an effect can be accounted for a large value of BET surface area of calcium hydrosilicates and cations exchange of Ca^{2+} ions with respective metal ions. From the review of scientific literature, it may be concluded that calcium silicates and materials based on them have been attracting attention of researchers for a long time for their application as sorbents to treat aquatic media containing heavy metals ions including Pb^{2+} ions. If the chronology of scientific works is taken into account, it may be seen that the concern for studying sorption characteristics of those compounds has been catching impetus continuously.

This paper focusses on removal of Pb ions from aqueous solutions by sorbents based on calcium silicates (hereinafter referred to as silicate sorbents), obtained in multi-component systems $CaCl_2$–Na_2SiO_3–H_2O (sorbent I) and $CaSO_4 \cdot 2H_2O$–$SiO_2 \cdot nH_2O$–KOH–H_2O (sorbent II), where compounds $CaSO_4 \cdot 2H_2O$ and $SiO_2 \cdot nH_2O$ are components of boric acid production waste (borogypsum). The sorbents are prepared by ‘inexpensive precursors’ and though a detailed ‘cost analysis’ has not been carried out, it is logically understood that the process of removal of Pb on the silicate adsorbents is economically viable.

2. Experimental

2.1. Synthesis of the adsorbents

For synthesis of sorbent 1, solutions of sodium silicate Na_2SiO_3, CP (silicate module $SiO_2/Na_2O=1$) and calcium chloride ($CaCl_2 \cdot 2H_2O$ content at least 98.3 %) were prepared in double distilled water and a temperature of 20 °C was maintained during synthesis. Second sorbent was prepared from Borogypsum (containing basic components, mass %: SiO_2 – 32.2 %; CaO – 28.4; SO_3 – 31.3 %; Fe_2O_3 – 2.7 %) and potassium hydroxide KOH. The synthesis was carried out in an autoclave at 1.7 atm pressure and the reaction was carried out for 2 h. The details regarding phase structure and BET surface area have been given in Table 1.

Synthesis conditions, phase structure and BET surface area of the studied silicate sorbents are listed in Table 1.

2.2. Adsorption experiments

Sorption experiments were carried out in batch adsorption mode with solid/liquid phase ratio 1:1000 and temperature 20 °C. The experiments were carried out with initial lead concentrations in 0.02 to 9.09 mmol/l range. A fixed amount of adsorbent was added to Pb solutions of various concentrations (0.02 to 9.09 mmol/l range) and the solutions were shaken on a thermostatic shaking unit 358 S type (Poland) at shaking frequency 200 rpm for 3 h. As initial concentrations of the solutions were of 10^{-3} order, ionic strength of the solutions was maintained at 0.1 M $NaClO_4$. Besides, simultaneous experiments were run with borogypsum of the said structure being the initial raw material to obtain sorbent II along with the reagents namely calcium carbonate $CaCO_3$, and calcium sulfate $CaSO_4 \cdot 2H_2O$. After 3 h the adsorbents were separated from solutions by filtering through Whatman filter papers. Residual concentrations of Pb and Ca were determined in the aliquot by Atomic Absorption Spectrophotometer (Thermo Electron, the USA).

2.3. Kinetic experiments

To study the dependency of lead distribution factor (K_d) from the ratio of solid/liquid phases (1:40, 1:100, 1:400, 1:1,000) sorption of Pb^{2+} ions with silicate sorbents, different amounts of adsorbent were added to 20 ml solutions of lead of different initial concentrations: 0.21 mmol/l (in experiments with sorbent I) and 0.13 mmol/l (in experiments with sorbent II). As control experiments, sorbent sample weights were put into vessels with distilled water and shaken simultaneously with the studied samples.

The study effect of pH on removal of Pb^{2+} ions, experiments were conducted in pH range from 1.2 to 4.4 with solid/liquid ratio S:L=1:1000 by making a series of solutions. The required value of pH solutions was maintained by adding 0.1N solution NaOH or HCl.

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