MAGNETICALLY MODIFIED BENTONITE AND LADLE FURNACE SLAG FOR STRONTIUM SORPTION

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Abstract

The removal of pollutants, especially those with long half-lives, from water remains a current challenge. Commercial bentonite and waste materials - ladle furnace slags - were selected as suitable sorbents for Sr^{2+}. Bentonite and ladle furnace slags were modified with iron oxide (Fe_xO_y) nanoparticles (NPs) with magnetic properties using a microwave-assisted process, which allows easy removal of sorbents, including adsorbed pollutants from aqueous environments with a magnet. The sorption efficiencies of bentonite, ladle furnace slags and their magnetic modifications were compared. The determined sorption capacity of furnace slags and their magnetic modifications was higher than the sorption capacity of bentonite and magnetically modified bentonite. The release of Fe_xO_y NPs from the magnetically modified sorbents during the sorption experiments was monitored as well. The results of the experiments demonstrate the potential of using magnetically modified ladle furnace slags for the removal of Sr^{2+} from aqueous environments.

Keywords: Bentonite, ladle furnace slag, magnetic properties, iron oxide nanoparticles, sorption

1. INTRODUCTION

The presence of different types of metal ions in the environment is related to increasing anthropogenic activities such as the discharge of wastewater, or accidental leaks from storage tanks. Several methods including chemical precipitation [1], extraction [2], membrane separation [3], biological treatment processes [4] or sorption [5] have been investigated for the treatment of liquid solutions containing strontium. Adsorption has several advantages over the above processes, such as ease of operation, high selectivity, rapid removal of contaminants and effectiveness when a suitable adsorbent is selected. The solution of adsorbent separation from the aqueous environment is the modification of the adsorbent surface with iron oxide particles. Iron oxides with paramagnetic properties allow the fast separation of the adsorbent with a magnet.

Composite sorbents containing iron oxides in different polymer matrices [6], cellulose and alginate granules [7], chitosan [8], aluminosilicates [9] have been developed and tested. Especially, inorganic materials of aluminosilicate composition with the content of ion exchange cations Na^+, K^+, Ca^{2+} and Mg^{2+} are characterised by excellent absorption capabilities [10].

Bentonite ($Al_2O_3.4SiO_2.H_2O$) is a clay mineral mainly composed of montmorillonite (85–90%, $(Na, Ca)_{0.33}(Al, Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$), which exhibit a complex porous structure, high ion exchange capacity, large specific surface area, low permeability and no toxicity [10]. A similar chemical composition, particularly in terms of SiO_2 and Al_2O_3 content, is found in ladle furnace slag. Although the ladle furnace slag is a non-metallic waste output of steel production, it has found applications in building materials, soil rejuvenation or CO_2 capture [11]. Metals present in the FS are tightly bound to the matrix due to the high temperature production process, they are not easily leached and, therefore, the FS is considered environmentally safe [12]. The availability of FS, along with its polymineral composition and specific properties that determine its high sorption activity, makes FS an attractive adsorbent [12][15].

The strontium occurs natural in environment and by the anthropogenic activities belongs milling processes, coal burning, fertilizers or nuclear industry [16]. The radioactive isotope ^{90}Sr is one of the main fission products in wastes from nuclear power plant. Due to its long lifetime (half-life of 28 years), it is considered the most dangerous to human health and causes long-term pollution of ecosystems due to its high transferability, high solubility and easy assimilation in living organisms [8]. Sr^{2+} sorption has been tested in silica, iron oxide, aluminium oxides [16] or clays [9]. Therefore, two ladle furnace slags and their magnetically modified form were investigated as sorbents for elimination of Sr^{2+} from aqueous solution. The adsorption data were compared with the adsorption capacity of commercial bentonite and bentonite after magnetic modification. The stability of the prepared magnetically modified composites was also investigated. The release of Fe_xO_y NPs from the composites was monitored as well.

2. MATERIALS AND METHODS

2.1 Materials characterisation

Bentonite (denoted as B) (commercial material, < 40 μm) and two ladle furnace slags (denoted as FSI and FSII, < 100 μm) (they come from a metallurgical complex in the Moravia region of the Czech Republic) were used as substrates for Fe_xO_y NPs with magnetic properties. The chemical composition expressed in weight % was determined using X-ray fluorescence spectroscopy (SPECTRO Analytical Instruments Inc., Germany). The chemical composition of FS depends on the input materials, and is therefore more or less variable (see **Table 1**). CaO, Al_2O_3 and SiO_2 are the main phases of FSI and FSII. Lower contents of Zn, Ti, V, Cr, Sr, Zr oxides are also present and P, Ba, Co, Ni and Rb oxides are less than 0.001 wt.%. FSI and FSII also contain mixtures of iron oxides with magnetic properties: FeO (wüstite), Fe_2O_3 (hematite) and Fe_3O_4 (magnetite).

Table 1 The chemical content of bentonite (B), the main and minority chemical content of ladle furnace slags (FSI and FSII) expressed in weight % (wt.%).

The main oxides content (wt.%)				**The content of the minority oxides (wt.%)**		
	B	**FSI**	**FSII**		**FSI**	**FSII**
SiO_2	71.1	9.26	5.09	TiO_2	0.251	0.419
Al_2O_3	11.9	19.1	7.94	V_2O_5	0.057	<0.01
Fe_2O_3	1.89	3.72	5.11	Cr_2O_3	0.087	0.125
CaO	0.81	50.98	73.9	MnO	2.68	3.99
MgO	1.89	3.52	2.21	ZnO	<0.001	0.022
Na_2O	1.31	0.08	<0.001	SrO	0.046	<0.001
K_2O	0.56	0.02	0.02	ZrO_2	0.016	<0.001
SO_3	0.19	0.89	0.92	Nb_2O_5	0.069	<0.001

2.2 Chemicals

Fe_xO_y NPs were prepared from the precursor $FeSO_4.7H_2O$ (per analyses, MACH CHEMIKÁLIE s.r.o., Ostrava, Czech Republic). NaOH (per analyses, MACH CHEMIKÁLIE s.r.o., Ostrava, Czech Republic) was used to prepare of 1 mol/L solution. $Sr(NO_3)_2$ (per analyses, MACH CHEMIKÁLIE s.r.o., Ostrava, Czech Republic) was used to prepare solutions with various concentration of Sr^{2+} ions.

2.3 Preparation and characterisation of magnetically modified materials

Magnetically modified materials were prepared in two steps based on a verified Fe_xO_y NPs preparation method [16]. In the first step, Fe_xO_y NPs in suspension were precipitated from the iron hydroxide solution and synthesised in a microwave oven. SO_4^{2-} were washed from the suspension by decantation. In a second step, the suspension was mixed with deionised water and dried B (< 40 µm), FSI and FSII (< 100 µm) materials were separately added to the suspensions. The mixtures were filtered the following day. Magnetically modified B, FSI and FSII were denoted as MB, MFSI and MFSII, respectively. The total Fe content in MB, MFSI and MFSII was determined using atomic absorption spectrometer (AAS, UNICAM 969) after their decomposition in acid mixtures. The increase in total Fe content after magnetic modification procedure was as follows: 15.0 wt.% in MB (1.89 wt. % in B), 10.6 wt.% in MFSI (2.60 wt.% in FSI) and 11.0 wt.% in MFSII (3.57 wt.% in FSII).

2.4 Sorption experiment

0.1 g ± 0.01 g of material was mixed with 50 ml of a solution containing Sr^{2+} ions and was shaken in discontinuous rotation container (4.5 rpm) for 1 hour under laboratory conditions. The composite was then removed with a magnet and the concentration of Sr^{2+} in filtered (PRAGOPOR, 0.45 µm) solutions was determined using AAS. The adsorbed amount was calculated according to Equation 1:

$$q_e = \frac{c_0 - c_e}{m} \cdot V \tag{1}$$

where:

q_e – the equilibrium adsorption amount of Sr^{2+} (mg/g)
c_0 - the initial concentration of Sr^{2+} (mg/l)
c_e - the concentration of Sr^{2+} at the equilibrium after sorption experiment (mg/l)
m - the weight of the sample (g)
V - the volume of the sorption solution (l)

The experimental adsorption data were fitted using Freundlich and Langmuir isotherm models [18], [19].

The favourability of the adsorption process provides a separation parameter expressed by Equation 2 [20]:

$$R_L = \frac{1}{1 + b c_0} \tag{2}$$

where:

R_L- the separation factor (-)
b - the Langmuir constant (l/mg)
c_0 - the initial concentration of Sr^{2+} (mg/l)

The concentration of Fe released from composites during the sorption experiments, was also determined in the final extracts using AAS.

3. RESULTS AND DISCUSSION

A comparison of the Sr^{2+} adsorption capacities of B, MB, FS and MFS is shown in **Figures 1 (a-c)**.

The maximum adsorption capacity of Sr^{2+} determined by the Langmuir isotherm model (**Table 2**) was 23.75 mg/g for B and 22.32 mg/g for MB, which is higher compared to the study [5] (19.62 mg/g of Sr^{2+}). Although the Fe_xO_y NPs are participate in the sorption by forming the surface complexes between Sr^{2+} and Fe_3O_4 [21] [22], by ion exchange or complexation which allows Fe-R-OH and Fe-R-COOH groups on the MB surface [23], the Fe_xO_y NPs probably occupied some active sites on the MB surface and, therefore, the adsorption capacity of MB was slightly lower than the sorption capacity of B.

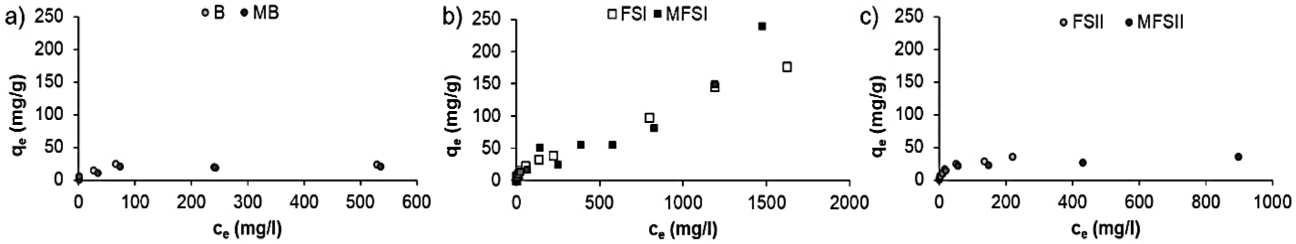

Figure 1 The amount of Sr^{2+} adsorbed on a) B, MB, b) FSI, MFSI, c) FSII, MFSII.

Maximum adsorption capacity was not reached for FSI, FSII, MFSI and MFSII, the amount of Sr^{2+}adsorbed on this sorbent increased with increasing initial Sr^{2+} concentration. The maximum adsorption capacities determined by Langmuir adsorption model were higher than the adsorption capacities on B and MB (see **Table 2)**. **Figure 1 a)** shows, that the magnetic modification of FSI did not affect the adsorption capacity. Similar adsorption amount of Sr^{2+} 175.4 mg/g and 178.6 mg/g were adsorbed on the FSI and MFSI, respectively. The high uptake capacity of FSI and MFSI is a result of the alkalising ability of the FS, the Sr^{2+} probably forms hydrooxocomplexes and is related to the formation of poorly soluble compounds (silicates) on the sorbent surface. The presence of hydroxides allows the pH of the aqueous solution to be increased and catalyses the precipitation of dissolved heavy metal cations [15][24].

The amount of Sr^{2+} adsorbed on the FSII (37.45 mg/g) and MFSII (35.21 mg/g) was lower than the amount of Sr^{2+} adsorbed on the FSI and MFSI. The cause may be either a lower content of SiO_2 and Al_2O_3, a higher CaO content of the FSII and, therefore, the establishment of the chemical equilibria in the solutions during the sorption processes. Therefore, the kinetics of the adsorption process will be studied in detail in the future.

The adsorption capacity for FSI and MFSI, is better than the adsorption properties of FSII, MFSII, B and MB. The Freundlich isotherm constant 1/n was less than 1 and the R_L values were found to be $0 < R_L < 1$, which predicted the favourable adsorption of Sr^{2+} on all the tested sorbents.

Table 2 The Freundlich exponent (*n*), Freundlich isotherm constant (*k*), Langmuir constant (*b*), the maximum adsorption capacity of Sr^{2+} (q_{max}) of B, MB, FSI, MFSI, FSII, MFSII. The equilibrium adsorption amount of Sr^{2+} (q_e), the separation factor (R_L) and correlation coefficient (R^2) are also provided.

		B	**MB**	**FSI**	**MFSI**	**FSII**	**MFSII**
Freundlich	***n* (-)**	1.79	1.88	1.71	1.59	1.65	1.93
	***k* (mg/g)·(l/mg)$^{1/n}$**	1.24	1.20	2.27	1.54	2.03	1.81
	R^2 (-)	0.884	0.934	0.945	0.950	0.866	0.838
Langmuir	***b* (l/mg)**	0.066	0.273	0.004	0.003	0.044	0.026
	q_{max} (mg/g)	23.75	22.32	175.4	178.6	37.45	35.21
	R^2 (-)	0.987	0.993	0.821	0.569	0.975	0.979
	$q_{e.}$ (mg/g)	23.9	20.6	176	240	35.8	26.0
	R_L (-)	0.028	0.027	0.009	0.010	0.065	0.017

The released amount of Fe determined in extracts after sorption experiment were lower than 0.01 mg/l, therefore, the prepared magnetically modified composites are stable. The Fe_xO_y NPs are firmly attached to the MB surface which is in agreement with our previous study [25].

4. CONCLUSION

The present study tested the elimination of strontium ions from aqueous solution using magnetically modified bentonite and two types of ladle furnace slag. Magnetic modification of the adsorbents did not significantly affect the adsorption capacity. The Sr^{2+} adsorption capacity of bentonite and magnetically modified bentonite determined by the Langmuir isotherm model was 23.75 mg/g and 22.32 mg/g, respectively. Ladle furnace slags and their magnetic modification were more efficient in elimination of strontium ions from solution than bentonite and magnetically modified bentonite. The amount of Sr^{2+} adsorbed, determined by the Langmuir isotherm model, reached 175.4 mg/g for FSI and 178.6 mg/g for MFSI. FSII and MFSII adsorbed 37.45 mg/g and 35.21 mg/g of Sr^{2+}. The adsorption amount of Sr^{2+} on the ladle furnace slags increased, therefore, the kinetics of the adsorption process will be a studied in detail the future. Iron oxide nanoparticles were not released during the sorption experiments, so the prepared composites are stable for use in an aqueous environment. In addition, ladle furnace slags and their modification are shown to be inexpensive, effective and viable sorbents for strontium removal.

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