

Article

Adsorption Properties of Waste Building Sludge for Environmental Protection

Barbora Doušová ^{1,*}, Eva Bedrnová ¹, Pavel Reiterman ² , Martin Keppert ² , David Koloušek ¹, Miloslav Lhotka ¹  and Libor Mastný ¹

¹ Faculty of Chemical Technology, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6, Czech Republic; bedrnove@vscht.cz (E.B.); koloused@vscht.cz (D.K.); lhotkam@vscht.cz (M.L.); mastnyl@vscht.cz (L.M.)

² Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 29 Praha 6, Czech Republic; pavel.reiterman@fsv.cvut.cz (P.R.); martin.keppert@fsv.cvut.cz (M.K.)

* Correspondence: dousofab@vscht.cz; Tel.: +42-02-2044-4381

Abstract: Waste building sludge (WBS) originating in the production of concrete prestressed poles (CSW) and technical stone (TSW) used in original and Fe-modified forms (CSW_{Fe}, TSW_{Fe}) was tested as an environmentally friendly and cheap sorbent of selected cations (Cd²⁺, Pb²⁺, Cs⁺) and anions (AsO₄^{3−}, PO₄^{3−}, CrO₄^{2−}) from water. The experiments were performed with 0.1 and 0.5 mmol·L^{−1} model solutions in a batch manner at laboratory temperature. Adsorption data were fitted with the Langmuir model. The adsorption of cations (Pb²⁺ and Cd²⁺) ran almost quantitatively (>97%) on both CSW and TSW. Cesium (Cs⁺) adsorption on TSW reached 80%, while in the case of CSW, it was ineffective. The modification of CSW and TSW with Fe^{II} (CSW_{Fe} and TSW_{Fe}) improved their adsorption selectivity to anions by up to 70%. The adsorption of PO₄^{3−} and AsO₄^{3−} ran quantitatively (>98%) on modified CSW_{Fe} and TSW_{Fe} and also on initial CSW, while CrO₄^{2−} was effectively adsorbed (≈80%) on TSW_{Fe} only. The adsorption affinity of tested ions in terms of adsorption capacity and sorbent consumption declined in order as follows: Pb²⁺ ≈ Cd²⁺ >> Cs⁺ for cations and AsO₄^{3−} ≈ PO₄^{3−} > CrO₄^{2−} for anions.

Keywords: waste building sludge; Fe-modification; adsorption; toxic cations; toxic anions



Citation: Doušová, B.; Bedrnová, E.; Reiterman, P.; Keppert, M.; Koloušek, D.; Lhotka, M.; Mastný, L. Adsorption Properties of Waste Building Sludge for Environmental Protection. *Minerals* **2021**, *11*, 309. <https://doi.org/10.3390/min11030309>

Academic Editors: Binoy Sarkar, Lei Wang and Raj Mukhopadhyay

Received: 29 January 2021

Accepted: 12 March 2021

Published: 17 March 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The rapid progress in materials and technologies of the building industry involves growing production of building waste, whose intensive ecological treatment has increased professional concern. Currently, the separation system applied in concrete production recycles water and coarse aggregates from the concrete waste, while the remaining fine aggregates in the mixture with cement particles (so-called Concrete Slurry Waste, CSW) is landfilled without additional use. In the case of Portland cement as the most widespread building material in the world's production (1–4 wt% of total concrete production), approximately 5 wt% ends up in waste [1]. However, the energy-intensive production of Portland cement [2] initiates the development of new recycling and processing technologies for waste building sludge treatment [3,4]. Many other building wastes, such as powdered waste from the processing of Technical Stone (TSW), whose production is growing in interest, have been completely unused until now.

The promising chemical and surface properties of waste building sludge (WBS)—particularly the aluminosilicate-like chemical composition (Al, Si and Fe content) and structural properties, such as easy hydration and a large specific surface area (S_{BET})—open up the possibility to use it in adsorption technologies as selective and environmentally friendly sorbents [4,5]. Since in adsorption systems, the sorbent selectivity has been primarily controlled by the pH of point of zero charge (pH_{ZPC}) [6], the WBS with a low pH_{ZPC} can be considered as predominantly cationic sorbents. Some recently described and applied methods of the surface modification

of aluminosilicate matrix with $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, e.g., [7–9], which are essentially based on the change in surface charge (pH_{ZPC}), have extended the possible use of these materials to remove anions from contaminated systems.

Lead (Pb) can attack the central nervous system and cause mental retardation, behavioural changes, paralysis and anaemia. It is a neurotoxic and carcinogenic element [10]. Apart from mercury (Hg), cadmium (Cd) is the most toxic element for humans and animals. It is highly carcinogenic, with an extraordinary ability to accumulate in tissues and food chains [11]. As the major radionuclide of spent nuclear fuel, cesium (^{137}Cs) is found in radioactive nuclear waste, which can infiltrate into water resources due to its high solubility [12]. In addition, ^{137}Cs can be easily accumulated in plants and further incorporated into food chains instead of the metabolically similar potassium (K) [13]. The toxicity of chromium (Cr) strongly depends on the oxidation state. While Cr^{III} belongs to the essential elements involved in regulating blood glucose levels, Cr^{VI} represents a typical carcinogen with a mutagenic effect [14]. Arsenic (As) can be considered a historical poison originating in natural and anthropogenic sources, and inorganic As forms, particularly As^{III} , are much more toxic than organic ones. Similarly to the above-mentioned elements, As damages the central nervous system, and in chronic poisoning it attacks the skin, hair and bones (so-called arsenicosis). It is also a strong carcinogen [15]. Although phosphorus (P) in phosphate form is an essential nutrient to all living systems, the increased concentration of several classes of inorganic phosphates can cause acute, subchronic and chronic toxicity, genotoxicity and teratogenicity [16]. Moreover, the co-occurrence of P and As can lead to a competitive adsorption at the water/solid interface [17]. While Pb, Cd and Cs are typical cationic contaminants, Cr^{VI} , P^{V} and $\text{As}^{\text{III/V}}$ in inorganic forms predominantly occur as oxyanions.

The aim of this work is to characterise structural, chemical and surface properties of selected waste building sludge (CSW and TSW) in initial and Fe-modified (CSW_{Fe} and TSW_{Fe}) forms as potential adsorbents of toxic elements from contaminated waters. Adsorption properties were tested on heavy metal cations (Pb^{2+} , Cd^{2+} and Cs^{+}) and toxic oxyanions (As^{V} as AsO_4^{3-} , P^{V} as PO_4^{3-} and Cr^{VI} as CrO_4^{2-}). The study of their chemistry and structure related to the adsorption process allows estimating possible technological applications of these materials, considering economic aspects and environmental protection.

2. Materials and Methods

2.1. Original and Fe-Modified WBS Sorbents

For this study, sedimented CSW, with a high content of cement comprising also mineral additives, fine fillers, admixtures and water, and TSW arising from the production and treatment of technical stone (TechniStone® Company, Hradec Králové, Czech Republic, where the inorganic components are bonded with a polymeric binders, was used. The modification with Fe^{II} ran in the batch manner according to [9,18]. The suspension of CSW/TSW (20 g) in 0.6 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1 L) was shaken in a sealed polyethylene bottle at laboratory temperature (20 °C) for 24 h. Then, the solid phase was filtered off, washed with distilled water, dried at 60 °C, and homogenized. Only a tiny surface layer of available Fe ions in reactive form is sufficient for the adsorption of oxyanions on the active surface sites of bulk oxy(hydroxides). The elementary chemical composition and surface properties are given in Table 1.

Table 1. Chemical and surface properties of CSW/ CSW_{Fe} and TSW/ TSW_{Fe} .

Sample	Chemical Composition (wt%)						S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{pore}^* ($\text{cm}^3 \cdot \text{g}^{-1}$)	pH_{ZPC}
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO			
CSW	32.3	6.6	1.3	<0.1	46.9	1.8	38.2	0.1295	10.3
CSW_{Fe}	26.6	4.3	29.8	0.4	18.7	2.1	118.2	0.1802	7.5
TSW	85.2	35.2	0.01	0.0	3.6	1.8	2.1	0.0049	6.2
TSW_{Fe}	75.6	28.9	5.4	0.06	2.8	1.9	14.9	0.0033	6.7

*: micro- and mesopore volume.

2.2. Model Solutions

Model solutions of cations (Cd^{2+} , Pb^{2+} , Cs^+) and anions (AsO_4^{3-} , PO_4^{3-} , CrO_4^{2-}) were prepared from inorganic salts ($\text{Cd}(\text{NO}_3)_2$, PbCl_2 , CsCl , KH_2AsO_4 , $(\text{NH}_4)\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{CrO}_4$) of analytical grade and distilled water at concentrations of 0.1 and 0.5 $\text{mmol} \cdot \text{L}^{-1}$ and their natural pH (i.e., $\text{pH} \approx 3.5$ for cationic solutions and $\text{pH} = 5\text{--}6$ for anionic solutions). The concentration range was selected as appropriate for the simulation of slightly contaminated to quite heavily polluted water systems.

2.3. Adsorption Process

The suspension of model solution (50 mL) and defined dosage (1–20 g L^{-1} of CSW/TSW or $\text{CSW}_{\text{Fe}}/\text{TSW}_{\text{Fe}}$) was agitated in a batch manner at laboratory temperature (20 °C) for 24 h. The product was filtered off, and the filtrate was analysed for residual concentration of appropriate cation or anion. The cations (Cd^{2+} , Pb^{2+} , Cs^+) were adsorbed on original CSW and TSW, whereas the anions (AsO_4^{3-} , PO_4^{3-} , CrO_4^{2-}) were adsorbed on both CSW/TSW, and $\text{CSW}_{\text{Fe}}/\text{TSW}_{\text{Fe}}$ to verify an increased anion-selectivity of Fe-modified sorbents [9]. Adsorption data were fitted to the Langmuir isotherm [19], which has been proven as a suitable model for powdered sorbents, including aluminosilicates and oxides [4,5,20].

2.4. Analytical Methods

Powder X-ray diffraction (XRD) was measured with a Seifert XRD 3000P diffractometer (Seifert, Ahrensburg, Germany) with $\text{CoK}\alpha$ radiation ($\lambda = 0.179026 \text{ nm}$, graphite monochromator, goniometer with Bragg-Brentano geometry) in the 2θ range of $5\text{--}60^\circ$ with a step size of $0.05^\circ 2\theta$.

X-ray fluorescence (XRF) analyses of the solid phase were carried out using an ARL 9400 XP+ spectrometer (ARL, Ecublens, Switzerland) at a voltage of 20–60 kV, probe current of 40–80 mA and an effective area of 490.6 mm^2 . UniQuant software 4 was used to evaluate the data (Thermo ARL, Ecublens, Switzerland).

The specific surface area (S_{BET}) was measured on a Micromeritics ASAP 2020 (accelerated surface area and porosimetry) analyser using gas sorption. The ASAP 2020 model (Micromeritics, Norcross, GA, USA) 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. The macro-pore and micro-pore samples were analyzed by the Horvath-Kavazoe method (BJH method), respectively. The BJH method used N_2 as the analysis adsorptive and an analysis bath temperature of -195.8°C . Samples were degassed at 313 K for 1000 min. The pH of point of zero charge (pH_{ZPC}) was determined by zeta potential Stabino[®], Version 2.0 (Particle Metrix GmbH, Meerbusch, Germany), equipped with a cylindrical polytetrafluoroethylene (PTFE) measuring beaker and piston. The pH_{ZPC} of the samples was measured using the pH titration method, which allows for the assessment of stable pH regions and the determination of the isoelectric point (IEP) with extremely high resolution (0.1 pH). Three suspensions of the same solid sample in KCl solution, having an identical solid-liquid ratio (1:100) but different ionic strengths of KCl (0.1 M, 0.01 M and 0.001 M), were titrated to IEP by 0.01 M HCl or NaOH in a dynamic regime. The pH_{ZPC} was calculated as the average of three pH values corresponding to the zero potential, with a deviation ranging from 0.05 to 0.7 pH units.

The structure of samples was determined using scanning electron microscopy (SEM) on the Tescan Vega 3 (Brno-Kohoutovice, Czech Republic). Energy dispersion spectrometry (EDS) was conducted on the Inca 350 spectrometer (Oxford Instruments, Abingdon, UK).

The concentrations of Pb, Cd and Cs in aqueous solutions were measured by atomic absorption spectrometry (AAS) using a SpectrAA-880 VGA 77 unit (Varian, Palo Alto, CA, USA) in flame mode. An accuracy of AAS analyses was guaranteed by the Laboratory of Atomic Absorption Spectrometry of UCT Prague, CR, with the detection limit of $0.5 \mu\text{g} \cdot \text{L}^{-1}$, with a standard deviation ranging from 5 to 10% of the mean.

The concentration of As in aqueous solutions was determined by the Hydride Generation Atomic Fluorescence Spectrometry (HG-AFS) using a PSA 10.055 Millennium Excalibur apparatus (PS Analytical, Kent, UK). The declared detection limit was 0.05 ppm, and the standard deviation was experimentally determined as 2.5%.

The concentration of Cr as $\text{Cr}_2\text{O}_7^{2-}$ and P as PO_4^{3-} in aqueous solutions were measured by the UV/VIS spectrophotometry using Evolution 220 (Thermo Fisher Scientific, Waltham, MA, USA) at 350 nm for Cr and 830 nm for P. The verified detection limit was $50 \mu\text{g} \cdot \text{L}^{-1}$, and the experimentally determined standard deviation was less than 5%.

3. Results and Discussion

3.1. Structural and Surface Characterization of Used WBS

The mineralogical composition of CSW and TSW (Figure 1) indicated the differences between both powdered materials. While CSW is dominated by portlandite, calcite and micas, TSW is rich in illite, quartz and feldspars, including high-temperature modifications, which corresponds to the starting material and parameters of CSW/TSW-producing technologies. Due to prevailing amorphous Fe-forms bonded to the surface during the modification, the mineralogical composition of CSW/TSW and Fe-modified CSW_{Fe} / TSW_{Fe} were identical [7,9,18].

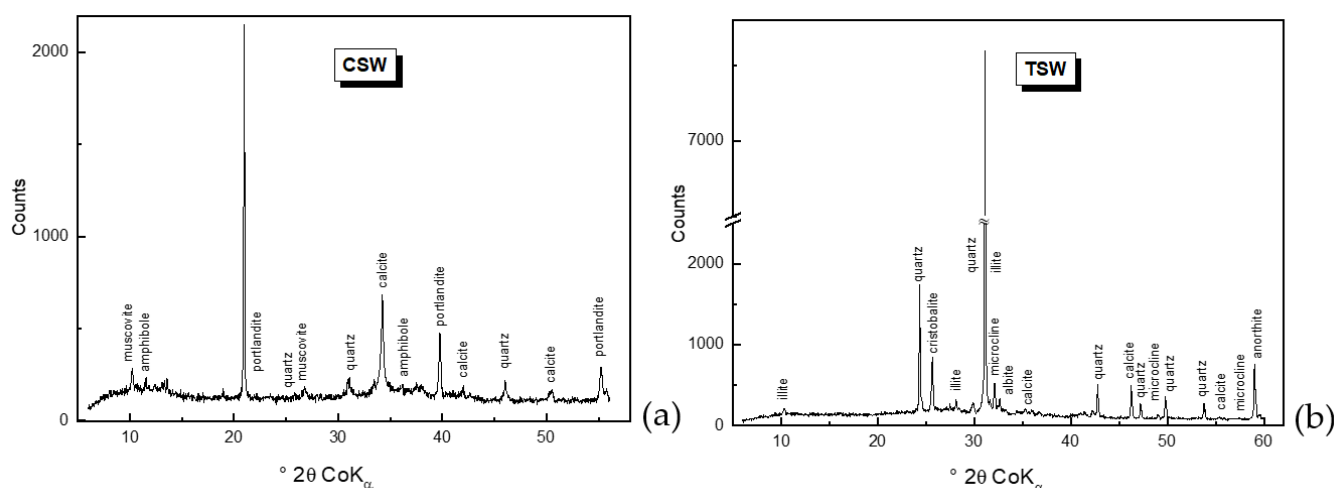


Figure 1. XRD patterns of building wastes. (a) Concrete Slurry Waste, (CSW), (b) Technical Stone Waste (TSW).

During the surface modification, hydrated Fe^{3+} particles in reactive ion-exchangeable form occupied binding positions on the CSW/TSW surface, creating anion-active adsorption sites. The final products (CSW_{Fe} and TSW_{Fe}) represented a brown-coloured homogeneous sorbent with a different pH_{ZPC} , associated with a different adsorption affinity for anionic contaminants (Figure 2).

The SEM micro-observation of initial and Fe-modified CSW and TSW (Figure 3) showed the growth of new phase in both Fe-modified sorbents, which was related to the higher S_{BET} of CSW_{Fe} / TSW_{Fe} (Table 1), probably caused by the new amorphous Fe-phase arising on the CSW/TSW surface [9]. Although the S_{BET} increased in both Fe-modified sorbents, which corresponded to the amorphous character of new Fe-phases, its orders of magnitude higher values for CSW/ CSW_{Fe} indicated a much finer-grained material with smaller particles, where better sorption properties were expected [7,21]. Similarly, the porosity of CSW and TSW differed markedly. While the total pore volume of CSW/ CSW_{Fe} ranged in tenths of a $\text{cm}^3 \cdot \text{g}^{-1}$, the total porosity of TSW/ TSW_{Fe} was two orders of magnitude lower (Table 1). Using the t-plot method, no micropores were detected in CSW/ CSW_{Fe} and TSW/ TSW_{Fe} . According to the parameters discussed above, TSW proved to be a coarser-grained material with a lower S_{BET} and worse sorption assumptions compared to CSW, in both original and Fe-modified forms.



Figure 2. Original (**left**) CSW and TSW and Fe-modified (**right**) CSW_{Fe} and TSW_{Fe} .

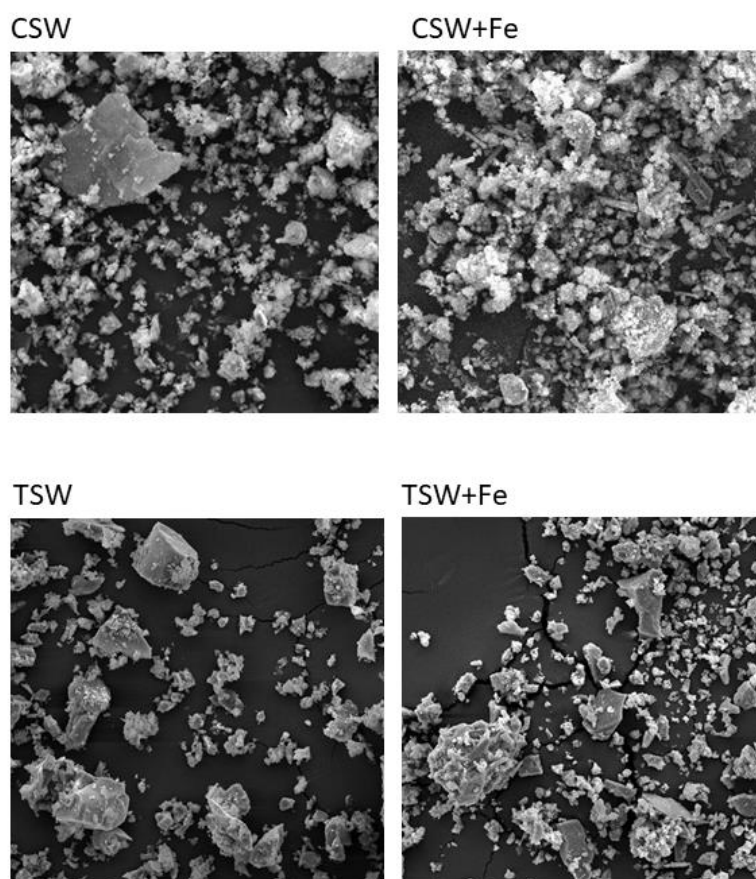


Figure 3. SEM images of CSW and TSW before (**left**) and after (**right**) surface modification (magnification of $700\times$).

3.2. Adsorption of Cations (Cd^{2+} , Pb^{2+} , Cs^+) on CSW and TSW

In the case of mixed sorbents, including CSW and TSW, the participation of both physical and chemical adsorption in the total process can be considered. Whereas all cationic adsorption could be fitted to the Langmuir model, the chemisorption prevailed. The adsorption parameters summarized in Table 2 illustrates that the adsorption of cations was not comparatively robust. In the case of Cs^+ , correlation factors $R^2 < 0.9$. All adsorption parameters (Table 2, Figure 4) showed the differences among Pb^{2+} , Cd^{2+} and Cs^+ adsorption capacities and adsorption constants. According to the K_L and R^2 values, which correspond to the binding energy and stability of the adsorption system, the physisorption coverage decreased in the order: $\text{Cs} \gg \text{Cd} > \text{Pb}$.

Table 2. Adsorption parameters for Pb^{2+} , Cd^{2+} and Cs^+ adsorption on CSW and TSW.

Cation	Sorbent	$C_0 = 0.1 \text{ mM}$				$C_0 = 0.5 \text{ mM}$			
		$q_{\max}$ ($\text{mmol} \cdot \text{g}^{-1}$)	Q_{theor}^* ($\text{mmol} \cdot \text{g}^{-1}$)	K_L^* ($\text{L} \cdot \text{mmol}^{-1}$)	R^2^*	$q_{\max}$ ($\text{mmol} \cdot \text{g}^{-1}$)	Q_{theor}^* ($\text{mmol} \cdot \text{g}^{-1}$)	K_L^* ($\text{L} \cdot \text{mmol}^{-1}$)	R^2^*
Pb^{2+}	CSW	0.2	0.2	218.0	0.984	0.5	0.2	283.6	0.982
	TSW	0.2	0.1	182.4	0.940	0.1	0.1	910.3	0.953
Cd^{2+}	CSW	0.2	0.3	198.3	0.981	0.5	0.3	294.1	0.946
	TSW	0.07	0.05	28.5	0.980	0.1	0.1	26.2	0.911
Cs^+	CSW	7×10^{-3}	0.01	5.3	0.892	0.01	0.02	0.7	0.880
	TSW	0.02	0.02	12.9	0.868	0.03	0.03	7.7	0.901

*: parameters calculated according to the Langmuir model.

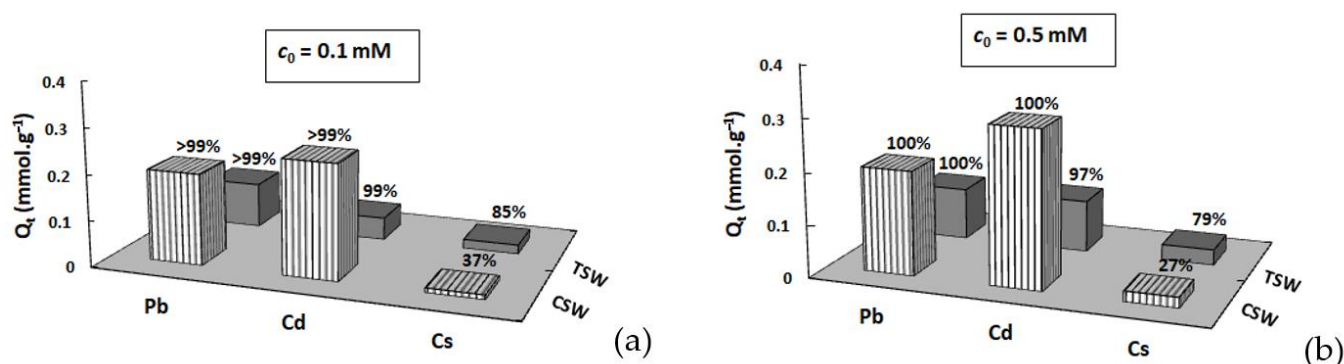


Figure 4. Theoretical adsorption capacities Q_t of Pb^{2+} , Cd^{2+} and Cs^+ adsorption on CSW and TSW at initial concentration c_0 of $0.1 \text{ mmol} \cdot \text{L}^{-1}$ (a) and $0.5 \text{ mmol} \cdot \text{L}^{-1}$ (b). Percentages above the bars indicate the maximum adsorption efficiency.

The adsorption of Pb^{2+} was balanced for both sorbents (CSW and TSW) and both initial concentrations (0.1 and $0.5 \text{ mmol} \cdot \text{L}^{-1}$). The high adsorption constant values (Table 2), together with almost 100% adsorption efficiency (Figure 4), indicated the robust adsorption via inner-sphere surface complexes [4,5]. Moreover, a strongly hydrolysed Pb^{2+} tended to form polynuclear complexes or surface precipitates, especially at a higher pH [5,22]. The insoluble precipitation on the sorbent surface did not affect adsorption parameters but substantially increased the adsorption yield.

The adsorption of Cd^{2+} on CSW was comparable to that of Pb^{2+} , even with a higher Q_t [4,23], while its adsorption on TSW differed markedly. Although the adsorption on TSW at both initial concentrations ran also selectively with almost 100% adsorption efficiency (Figure 4), the theoretical adsorption capacities Q_t and adsorption constants K_L were significantly lower (Table 2), which indicated lower adsorption energy associated with a weaker surface binding and possible other binding mechanisms (partial outer-sphere complexation).

In the case of Cs^+ , the adsorption on CSW and TSW ran at about one or two orders of magnitude lower Q_t values and low sorption effectivity compared to Pb^{2+} / Cd^{2+} adsorp-

tion. Generally worse Cs^+ adsorption corresponded to participating outer-sphere surface complexation. In addition, in the water environment, Cs^+ occurs as small hydrated ion thanks to its low charge and a large crystallographic radius (1.69 Å) [22]. These particles tend to be primarily bound to cation exchange sites by weak electrostatic surface binding (outer-sphere complexation) with minimal pH dependence.

3.3. Adsorption of Anions (AsO_4^{3-} , PO_4^{3-} , CrO_4^{2-}) on CSW/TSW and $\text{CSW}_{\text{Fe}}/\text{TSW}_{\text{Fe}}$

Due to the expected higher adsorption affinity of anions for Fe hydrated particles than for aluminosilicate-like structures, which has been verified in many papers, e.g., [8,9,24,25], anionic contaminants were adsorbed on both initial (CSW and TSW) and Fe-modified (CSW_{Fe} and TSW_{Fe}) adsorbents. The adsorption parameters (theoretical sorption capacities Q_t , correlation factors R^2 and adsorption constants K_L), which were fitted according to the Langmuir model, are summarized in Table 3 and illustrated in Figure 5. Similarly to the cationic adsorption, several anionic adsorptions were difficult to describe by an isothermal model, especially CrO_4^{2-} and also other anions adsorbed on unmodified adsorbents.

Table 3. Adsorption parameters for PO_4^{3-} , AsO_4^{3-} and CrO_4^{2-} adsorption on $\text{CSW}/\text{CSW}_{\text{Fe}}$ and $\text{TSW}/\text{TSW}_{\text{Fe}}$.

Anion	Sorbent	$C_0 = 0.1$ mM				$C_0 = 0.5$ mM			
		q_{max} (mmol·g ⁻¹)	Q_{theor}^* (mmol·g ⁻¹)	K_L^* (L·mmol ⁻¹)	R^2^*	q_{max} (mmol·g ⁻¹)	Q_{theor}^* (mmol·g ⁻¹)	K_L^* (L·mmol ⁻¹)	R^2^*
PO_4^{3-}	CSW	0.1	0.05	975.1	0.902	0.3	0.2	37	0.840
	CSW_{Fe}	0.2	0.1	3858.8	0.913	0.6	0.4	1963.8	0.814
	TSW	0.2	0.03						
AsO_4^{3-}	TSW_{Fe}	0.06	0.04	465.8	0.930	0.3	0.1	699.7	0.622
	CSW	0.1	0.1	149.7	0.974	0.4	0.2	142.7	0.974
	CSW_{Fe}	0.1	0.2	3362.8	0.987	0.3	0.3	3717.4	0.958
CrO_4^{2-}	TSW	0.01				0.01			
	TSW_{Fe}	0.1	0.1	1050.2	0.833	0.1	0.1	462.8	0.979
	CSW	0.01	0.05	<1	0.966	0.03	0.02	<1	0.959
	CSW_{Fe}	0.1	0.1	5.8	0.925	0.01	0.05	3.5	0.726
	TSW	<0.01				0.01			
	TSW_{Fe}	0.08	0.1	6.4	0.972	0.07	0.1	3.2	0.899

*: parameters calculated according to the Langmuir model.

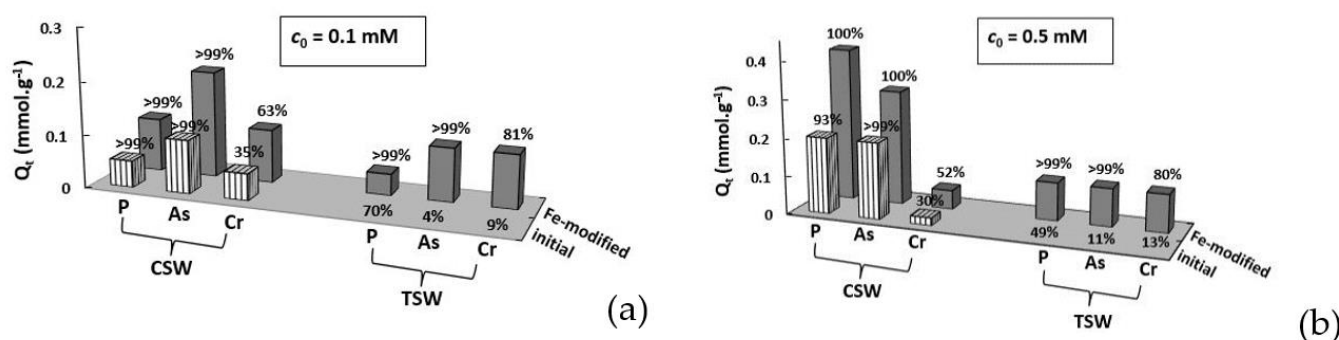


Figure 5. Theoretical adsorption capacities Q_t of AsO_4^{3-} , PO_4^{3-} and CrO_4^{2-} adsorption on original (CSW and TSW) and Fe-modified (CSW_{Fe} and TSW_{Fe}) sorbents at initial concentration c_0 of 0.1 mmol·L⁻¹ (a) and 0.5 mmol·L⁻¹ (b). Percentages above the bars indicate maximum adsorption efficiency.

In all aspects, the adsorption of anions proceeded better and more efficiently to Fe-modified $\text{CSW}_{\text{Fe}}/\text{TSW}_{\text{Fe}}$ compared to original CSW/TSW. The adsorption of all tested oxyanions on the original TSW did not even follow the Langmuir model, indicating the physical character of the adsorption process. Similarly, the anionic adsorption on original CSW was significantly worse compared to Fe-modified sorbents (CSW_{Fe} and TSW_{Fe}) (Table 3) with the most probable participation of weak physical binding.

Phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) were selectively adsorbed on CSW_{Fe} and TSW_{Fe} with almost 100% efficiency at both initial concentrations, which corresponded well to some earlier studies of Doušová et al. [4,9,23] confirming the formation of inner-sphere surface complexes during the adsorption of cations (e.g., Pb^{2+} , Cd^{2+} , Cs^+) on aluminosilicate-like phases and anions (AsO_4^{3-} , CrO_4^{2-}) in their Fe-modified forms.

The adsorption of chromate (CrO_4^{2-}) was typically worse compared to the other oxyanions [24–26], which can be associated with a lower adsorption energy of CrO_4^{2-} and its prevailed electrostatic binding via outer-sphere surface complexes [27]. Another reason for the weaker and less efficient adsorption of CrO_4^{2-} compared to, e.g., AsO_4^{3-} or PO_4^{3-} can be related to the different protonation of divalent (CrO_4^{2-}) and trivalent (AsO_4^{3-}) oxyanions, which, as a weaker trihydric acid anions, dispose of a much broader adsorption edge and higher adsorption affinity than stronger dihydric acid anions (CrO_4^{2-} , SO_4^{2-}) [24–27]. As can be seen in Table 3 and Figure 5, the adsorption of all tested oxyanions on original CSW and TSW differed markedly. While the adsorption of AsO_4^{3-} and PO_4^{3-} on CSW could be fitted to the Langmuir model and ran very effectively, the original TSW was completely ineffective as anion active sorbent.

3.4. Adsorption Efficiency as Indicator of Potential Environmental Application

The adsorption efficiency represents a crucial parameter for assessing a sorbent's selectivity and usability, even if the process cannot be fitted to any thermodynamic model. A number of natural sorbents still demonstrate favorable adsorption properties, such as a high correlation factor ($R^2 > 0.9$), illustrating a balanced adsorption procedure, together with a high efficiency ($\epsilon > 80\%$). In that case, the maximum experimental adsorption capacity q_{max} can be used to estimate the usability and consumption of a given sorbent in environmental and other technologies.

To estimate the technological utilization of tested sorbents, the results from adsorption series with the higher initial concentration ($0.5 \text{ mmol} \cdot \text{L}^{-1}$), simulating a heavily contaminated system, were used. For possible practical use, the sorbent consumption represents an important parameter for the economic and ecological aspects of the adsorption process. The calculated sorbent consumption in the model systems was based on the theoretical or maximum adsorption capacity of sorbent to the particular ion and the adequate sorption efficiency at an appropriate initial concentration. The determination of optimal adsorption conditions resulted from the experimental finding of the optimal sorbent dosage to achieve a sufficient adsorption yield.

The efficiency of cationic (Pb^{2+} , Cd^{2+} , Cs^+) adsorption related to the sorbent consumption (Figure 6a) showed more effective adsorption of Pb^{2+} and Cd^{2+} compared to Cs^+ , and also the higher selectivity of CSW compared to TSW. The opposite trend in Cs^+ adsorption (much more effective adsorption on TSW than on CSW) can be explained by the structure and mineralogical composition of TSW (higher crystallinity, clay fractions), which were found to be crucial for the removal of radionuclides from contaminated waters [28,29].

The adsorption of anions (AsO_4^{3-} , PO_4^{3-} , CrO_4^{2-}) on CSW/ CSW_{Fe} (Figure 6b) and TSW/ TSW_{Fe} (Figure 6c) illustrated the substantial increase in the affinity of Fe-modified WBS to anionic contaminants. In addition, the quantitative adsorption of AsO_4^{3-} also on original CSW (Figure 6b) could almost be related to the high alkalinity of CSW followed by the formation of insoluble surface precipitate, which participated in the total adsorption yield. The comparison of two Fe-modified sorbents showed that TSW_{Fe} was a better anion-active sorbent than CSW_{Fe} .

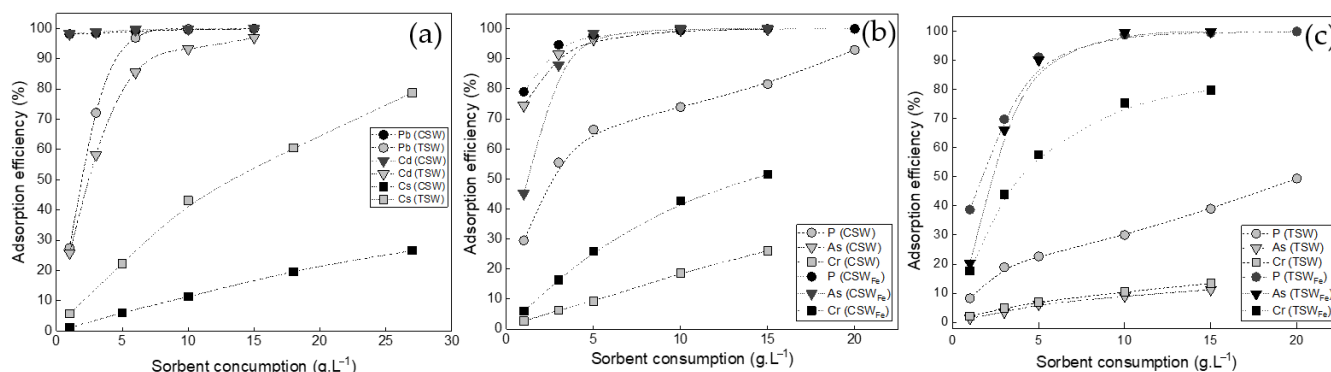


Figure 6. Adsorption efficiency of Pb^{2+} , Cd^{2+} and Cs^{+} adsorption on CSW and TSW (a), AsO_4^{3-} , PO_4^{3-} and CrO_4^{2-} adsorption on CSW and TSW (b) and AsO_4^{3-} , PO_4^{3-} and CrO_4^{2-} adsorption on CSW_{Fe} and TSW_{Fe} (c). Initial concentration $c_0 = 0.5 \text{ mmol} \cdot \text{L}^{-1}$ simulated heavily contaminated waters.

4. Conclusions

Under defined conditions, both tested representatives of waste building sludge (WBS), i.e., CSW and TSW in original and Fe-modified (CSW_{Fe} , TSW_{Fe}) forms, proved to be promising selective sorbents of cationic and anionic contaminants. CSW and TSW differed mostly in mineralogy, crystallinity and alkalinity, which affected their surface and binding properties. A highly alkaline adsorption environment, particularly in CSW systems, supported the formation of surface precipitation followed by possible deviation from the usual adsorption procedure. The adsorption of cations (Pb^{2+} and Cd^{2+}) ran effectively on CSW and TSW (>97%), but preferably on CSW; Cs^{+} was more selectively adsorbed on TSW (80%). The anions were successfully adsorbed onto Fe-modified sorbents with an efficiency of 80–100%. The affinity of tested ions with regard to the adsorption capacities and sorbent consumption declined in the following order: $\text{Pb}^{2+} \approx \text{Cd}^{2+} \gg \text{Cs}^{+}$ for CSW/TSW, and $\text{AsO}_4^{3-} \approx \text{PO}_4^{3-} > \text{CrO}_4^{2-}$ for TSW_{Fe} / CSW_{Fe} . The optimal sorption conditions determined for the model system can be changed due to the specific properties of actual contaminated water (pH, ionic strength, competitive ions, organic complexes). In terms of possible technological applications, CSW was favourable for cationic adsorption, while TSW was more suitable for the surface modification and following adsorption of anions.

Author Contributions: Conceptualization, B.D.; adsorption experiments and analysis, B.D. and E.B.; methodology, B.D., M.K. and P.R.; S_{BET} measurement and evaluation, M.L.; XRD measurement, D.K.; material preparation and characterization, M.K., P.R. and L.M.; writing—original draft preparation, B.D.; writing—review and editing, B.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Czech Science Foundation under the project 1[−]11027S “Concrete slurry-hazardous waste or secondary raw material?”

Data Availability Statement: The data presented in this study is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Xuan, D.; Zhan, B.; Poon, C.S.; Zheng, W. Innovative reuse of concrete slurry waste from readymixed concrete plants in construction products. *J. Hazard. Mater.* **2016**, *321*, 65–72. [[CrossRef](#)] [[PubMed](#)]
- Damtoft, J.S.; Lukasik, J.; Herfort, D.; Sorrentino, D.; Gartner, E.M. Sustainable development and climate change initiatives. *Cem. Concr. Res.* **2008**, *38*, 115–127. [[CrossRef](#)]
- Kubissa, W.; Jaskulski, R.; Reiterman, P. Ecological concrete based on blast-furnace cement with incorporated coarse recycled concrete aggregate and fly ash addition. *J. Renew. Mater.* **2017**, *5*, 53–61. [[CrossRef](#)]
- Dousova, B.; Kolousek, D.; Keppert, M.; Machovic, V.; Lhotka, M.; Urbanova, M.; Brus, J.; Holcova, L. Use of waste ceramics in adsorption technologies. *Appl. Clay Sci.* **2016**, *134*, 145–152. [[CrossRef](#)]

5. Doušová, B.; Koloušek, D.; Lhotka, M.; Keppert, M.; Urbanová, M.; Kobera, L.; Brus, J. Waste Brick Dust as Potential Sorbent of Lead and Cesium from Contaminated Water. *Materials* **2019**, *12*, 1647. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Fiol, N.; Villaescusa, I. Determination of sorbent point zero charge: Usefulness in sorption studies. *Environ. Chem. Lett.* **2009**, *7*, 79–84. [\[CrossRef\]](#)
7. Jiang, M.; Wang, Q.; Jin, X.; Chen, Z. Removal of Pb(II) from aqueous solution using modified and unmodified kaolinite clay. *J. Hazard. Mater.* **2009**, *170*, 332–339. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Sherman, D.M.; Randall, S.R. Surface complexation of arsenic (V) to iron (III) (hydr)oxides: Structural mechanism from ab initio molecular geometries and EXAFS spectroscopy. *Geochim. Cosmochim. Acta* **2003**, *67*, 4223–4230. [\[CrossRef\]](#)
9. Doušová, B.; Grygar, T.; Martaus, A.; Fuitová, L.; Koloušek, D.; Machovič, V. Sorption of As^V on aluminosilicates treated with Fe^{II} nanoparticles. *J. Colloid Interface Sci.* **2006**, *302*, 424–431. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Njati, S.Y.; Maguta, M.M. Lead-based paints and children's PVC toys are potential sources of domestic lead poisoning – A review. *Environ. Pollut.* **2019**, *249*, 1091–1105. [\[CrossRef\]](#)
11. Godt, J.; Scheidig, F.; Grosse-Siestrup, C.; Esche, V.; Brandenburg, P.; Reich, A.; Groneberg, D.A. The toxicity of cadmium and resulting hazards for human health. *J. Occup. Med. Toxicol.* **2006**, *1*, 1–6. [\[CrossRef\]](#)
12. Cornell, R.M. Adsorption of cesium on minerals: A review. *J. Radioanal. Nuclear Chem.* **1993**, *171*, 483–500. [\[CrossRef\]](#)
13. Jalali, R.R.; Ghafourian, H.; Asef, Y.; Dalir, S.T.; Sahafipour, M.H.; Gharanjik, B.M. Biosorption of cesium by native and chemically modified biomass of marine algae: Introduce the new biosorbents for biotechnology applications. *J. Hazard. Mater.* **2004**, *B116*, 125–134. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Wang, Y.; Su, H.; Gu, Y.; Song, X.; Zhao, J. Carcinogenicity of chromium and chemoprevention: A brief update. *OncoTargets and Therapy* **2017**, *10*, 4065–4079. [\[CrossRef\]](#)
15. Roy, P.; Saha, A. Metabolism and toxicity of arsenic: A human carcinogen. *Current Sci.* **2002**, *82*, 38–45.
16. Weiner, M.L.; Salminen, W.F.; Larson, P.R.; Barter, R.A.; Kranetz, J.L.; Simon, G.S. Toxicological review of inorganic phosphates. *Food Chem. Toxicol.* **2001**, *39*, 759–786. [\[CrossRef\]](#)
17. Lambkin, D.C.; Alloway, B.J. Arsenate-induced phosphate release from soils and its effect on plant phosphorus. *Water Air Soil Pollut.* **2003**, *144*, 41–56. [\[CrossRef\]](#)
18. Bonin, D. Method of removing arsenic species from an aqueous medium using modified zeolite minerals. U.S. Patent no. 6,042,731, 28 March 2000.
19. Misak, N.Z. Langmuir isotherm and its application in ion-exchange reactions. *React. Polym.* **1993**, *21*, 53–64. [\[CrossRef\]](#)
20. Han, R.; Lu, Z.; Zou, W.; Daotong, W.; Shi, J.; Jiujun, Y. Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand. II. Equilibrium study and competitive adsorption. *J. Hazard. Mater.* **2006**, *B137*, 480–488. [\[CrossRef\]](#)
21. Tsai, W.T.; Lai, C.W.; Hsien, K.J. Effect of Particle Size of Activated Clay on the Adsorption of Paraquat from Aqueous Solution. *J. Colloid Interface Sci.* **2003**, *263*, 29–34. [\[CrossRef\]](#)
22. Marcus, Y. Thermodynamics of Solvation of Ions. Part 5-Gibbs Free Energy of Hydration at 298.15 K. *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 2995–2999. [\[CrossRef\]](#)
23. Doušová, B.; Riterman, P. Recycling of powdered building wastes in environmental technologies. In Proceedings of the SGEM 2019 (19th International Multidisciplinary Scientific GeoConference), Vienna, Austria, 9–11 December 2019; STEF92 Tehnology Ltd.: Sofia, Bulgaria, 2019; Volume 19, pp. 121–126.
24. Grossl, P.R.; Eick, M.; Sparks, D.L.; Goldberg, S.; Ainworth, C.C. Arsenate and Chromate retention Mechanisms on Goethite. 2. Kinetic Evaluation Using a Pressure-Jump Relaxation Technique. *Environ. Sci. Technol.* **1997**, *31*, 321–326. [\[CrossRef\]](#)
25. Khaothiar, S.; Azizian, M.F.; Osathaphan, K.; Nelson, P.O. Copper, Chromium and Arsenic Adsorption and Equilibrium Modeling in an Iron-oxide-coated sand. Background Electrolyte System. *Water Air Soil Pollut.* **2000**, *119*, 105–120. [\[CrossRef\]](#)
26. Antelo, J.; Fiol, S.; Gondar, D.; Lopez, R.; Arce, F. Comparison of arsenate, chromate and molybdate binding on schwertmannite: Surface adsorption vs anion-exchange. *J. Colloid Interface Sci.* **2012**, *386*, 338–343. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Johnston, C.P.; Chrysochoou, M. Mechanisms of chromate adsorption on boehmite. *J. Hazard. Mater.* **2015**, *281*, 56–63. [\[CrossRef\]](#)
28. Rajec, P.; Macasek, F.; Feder, M.; Misaelides, P.; Samajova, E. Sorption of caesium and strontium on clinoptilolite- and mordenite-containing sedimentary rocks. *J. Radioanal. Nucl. Chem.* **1998**, *229*, 49–56. [\[CrossRef\]](#)
29. Faghihian, H.; Marageh, M.G.; Kazemian, H. The use of clinoptilolite and its sodium form for removal of radioactive cesium and strontium from nuclear wastewater and Pb²⁺, Ni²⁺, Cd²⁺, Ba²⁺ from municipal wastewater. *Appl. Radiat. Isot.* **1999**, *50*, 655–660. [\[CrossRef\]](#)