Adsorption Properties of Waste Building Sludge for Environmental Protection

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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 (CSWFe, TSWFe) was tested as an environmentally friendly and cheap sorbent of selected cations (Cd2+, Pb2+, Cs+) and anions (AsO43−, PO43−, CrO42−) 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 FeII (CSWFe and TSWFe) improved their adsorption selectivity to anions by up to 70%. The adsorption of PO43− and AsO43− ran quantitatively (>98%) on modified CSWFe and TSWFe, and also on initial CSW, while CrO42− was effectively adsorbed (∼80%) on TSWFe 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 AsO43− ≈ PO43− > CrO42− for anions.

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

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 landfill 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 (pHZPC) [6], the WBS with a low pHZPC can be considered as predominantly cationic sorbents. Some recently described and applied methods of the surface modification...
of aluminosilicate matrix with Fe$^{2+}$/Fe$^{3+}$ ions, e.g., [7–9], which are essentially based on the change in surface charge ($\text{pH}_{ZPC}$), 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$^{\text{III}}$ belongs to the essential elements involved in regulating blood glucose levels, Cr$^{\text{VI}}$ 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$^{\text{III}}$, 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$^{\text{VI}}$, P$^{\text{V}}$ and As$^{\text{III/VI}}$ 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$\text{Fe}$ and TSW$\text{Fe}$) 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$^{\text{V}}$ as AsO$_4^{3-}$, P$^{\text{V}}$ as PO$_4^{3-}$ and Cr$^{\text{VI}}$ 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$^{\text{II}}$ ran in the batch manner according to [9,18]. The suspension of CSW/TSW (20 g) in 0.6 M FeSO$_4$$\cdot$7H$_2$O (1 L) was shaken in a sealed polyethylene bottle at laboratory temperature ($20 \degree$C) for 24 h. Then, the solid phase was filtered off, washed with distilled water, dried at 60 $\degree$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.

| Sample  | SiO$_2$ (wt%) | Al$_2$O$_3$ | Fe$_2$O$_3$ | TiO$_2$ | CaO | MgO | S$_{\text{BET}}$ (m$^2$·g$^{-1}$) | V$_{\text{pore}}$ * (cm$^3$·g$^{-1}$) | pH$_{ZPC}$ |
|---------|----------------|----------|-------------|---------|-----|-----|-------------------------------|-------------------------------|---------|
| CSW     | 32.3           | 6.6      | 1.3         | <0.1    | 46.9| 1.8 | 38.2                          | 0.1295                       | 10.3    |
| CSW$\text{Fe}$ | 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$\text{Fe}$ | 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 (Cd(NO\(_3\))\(_2\), PbCl\(_2\), CsCl, KH\(_2\)AsO\(_4\), (NH\(_4\))H\(_2\)PO\(_4\) and (NH\(_4\))\(_2\)CrO\(_4\)) of analytical grade and distilled water at concentrations of 0.1 and 0.5 mmol·L\(^{-1}\) and their 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 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 CSW\(_{Fe}\)/TSW\(_{Fe}\)) 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 CSW\(_{Fe}\)/TSW\(_{Fe}\) 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 CoK\(_{\alpha}\) radiation (\(\lambda = 0.179026\) nm, graphite monochromator, goniometer with Bragg-Brentano geometry) in the 2\(\theta\) range of 5–60° with a step size of 0.05° 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-Kawazoe 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\textsuperscript{®}, 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 µg·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 $\text{PO}_4^{3-}$ 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 $\mu$g 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).](image)

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 pHZPC, 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 cm$^3$ 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\textsubscript{Fe} and TSW\textsubscript{Fe}.

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\textsubscript{BET} of CSW\textsubscript{Fe}/TSW\textsubscript{Fe} (Table 1), probably caused by the new amorphous Fe-phase arising on the CSW/TSW surface [9]. Although the S\textsubscript{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\textsubscript{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\textsubscript{Fe} ranged in tenths of a cm\textsuperscript{3}.g\textsuperscript{−1}, the total porosity of TSW/TSW\textsubscript{Fe} was two orders of magnitude lower (Table 1). Using the t-plot method, no micropores were detected in CSW/CSW\textsubscript{Fe} and TSW/TSW\textsubscript{Fe}. According to the parameters discussed above, TSW proved to be a coarser-grained material with a lower S\textsubscript{BET} and worse sorption assumptions compared to CSW, in both original and Fe-modified forms.

Figure 3. SEM images of CSW and TSW before (left) and after (right) surface modification (magnification of 700×).
3.2. Adsorption of Cations (Cd\textsuperscript{2+}, Pb\textsuperscript{2+}, Cs\textsuperscript{+}) 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 illustrate that the adsorption of cations was not comparatively robust. In the case of Cs\textsuperscript{+}, correlation factors \(R^2<0.9\). All adsorption parameters (Table 2, Figure 4) showed the differences among Pb\textsuperscript{2+}, Cd\textsuperscript{2+} and Cs\textsuperscript{+} 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: Cs >> Cd > Pb.

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

| Cation | Sorbent | \(q_{\text{max}}\) (mmol g\textsuperscript{-1}) | \(Q_{\text{theor}}^*\) (mmol g\textsuperscript{-1}) | \(K_L^*\) (L mmol\textsuperscript{-1}) | \(R^2^*\) | \(q_{\text{max}}\) (mmol g\textsuperscript{-1}) | \(Q_{\text{theor}}^*\) (mmol g\textsuperscript{-1}) | \(K_L^*\) (L mmol\textsuperscript{-1}) | \(R^2^*\) |
|--------|---------|---------------------------------|---------------------------------|---------------------------------|--------|---------------------------------|---------------------------------|---------------------------------|--------|
| Pb\textsuperscript{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\textsuperscript{2+} | CSW     | 0.2                             | 0.3                             | 198.3                           | 0.981 | 0.5                             | 0.3                             | 294.1                           | 0.946 |
|       | TSW     | 0.07 \(7 \times 10^{-3}\)       | 0.05                            | 28.5                            | 0.980 | 0.1                             | 0.1                             | 26.2                            | 0.911 |
| Cs\textsuperscript{+} | CSW     | 0.02                            | 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\textsuperscript{2+}, Cd\textsuperscript{2+} and Cs\textsuperscript{+} adsorption on CSW and TSW at initial concentration \(C_0\) of 0.1 mmol·L\textsuperscript{-1} (a) and 0.5 mmol·L\textsuperscript{-1} (b). Percentages above the bars indicate the maximum adsorption efficiency.

The adsorption of Pb\textsuperscript{2+} was balanced for both sorbents (CSW and TSW) and both initial concentrations (0.1 and 0.5 mmol·L\textsuperscript{-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\textsuperscript{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\textsuperscript{2+} on CSW was comparable to that of Pb\textsuperscript{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\textsuperscript{+}, 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\textsuperscript{2+}/Cd\textsuperscript{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 (AsO₄³⁻, PO₄³⁻, CrO₄²⁻) on CSW/TSW and CSW_Fe/TSW_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 Q₉, correlation factors R² and adsorption constants Kₐ), 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 CrO₄²⁻ and also other anions adsorbed on unmodified adsorbents.

Table 3. Adsorption parameters for PO₄³⁻, AsO₄³⁻ and CrO₄²⁻ adsorption on CSW/CSW_Fe and TSW/TSW_Fe.

| Anion       | Sorbent | q_max (mmol g⁻¹) | Q_lopp * (mmol g⁻¹) | K_L * (L·mmol⁻¹) | R² * | q_max (mmol g⁻¹) | Q_lopp * (mmol g⁻¹) | K_L * (L·mmol⁻¹) | R² * |
|-------------|---------|-----------------|---------------------|------------------|------|-----------------|---------------------|------------------|------|
| PO₄³⁻       | CSW     | 0.1             | 0.05                | 975.1            | 0.902| 0.2             | 37                  | 0.840            |
|             | CSW_Fe  | 0.2             | 0.1                 | 3858.8           | 0.913| 0.4             | 1963.8              | 0.814            |
|             | TSW     | 0.06            | 0.04                | 465.8            | 0.930| 0.3             | 699.7               | 0.622            |
|             | TSW_Fe  | 0.1             | 0.2                 | 3362.8           | 0.987| 0.3             | 412.7               | 0.974            |
| AsO₄³⁻      | CSW     | 0.1             | 0.2                 | 149.7            | 0.974| 0.3             | 3717.4              | 0.958            |
|             | CSW_Fe  | 0.01            | 0.01                | 1050.2           | 0.833| 0.1             | 462.8               | 0.979            |
|             | TSW     | 0.1             | 0.1                 | <1               | 0.966| 0.03            | <1                  | 0.959            |
|             | TSW_Fe  | 0.01            | 0.1                 | 5.8              | 0.925| 0.01            | 3.5                 | 0.726            |
| CrO₄²⁻      | CSW     | 0.08            | 0.1                 | 6.4              | 0.972| 0.07            | 3.2                 | 0.899            |
|             | CSW_Fe  | <0.01           | 0.01                | 1050.2           | 0.833| 0.1             | 462.8               | 0.979            |

*: parameters calculated according to the Langmuir model.

Figure 5. Theoretical adsorption capacities Q₉ of AsO₄³⁻, PO₄³⁻ and CrO₄²⁻ adsorption on original (CSW and TSW) and Fe-modified (CSW_Fe and TSW_Fe) sorbents at initial concentration c₀ 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 CSW_Fe/TSW_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.
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Phosphate ($\text{PO}_4^{3-}$) and arsenate ($\text{AsO}_4^{3-}$) were selectively adsorbed on $\text{CSW}_{\text{Fe}}$ and $\text{TSW}_{\text{Fe}}$ 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., $\text{Pb}^{2+}$, $\text{Cd}^{2+}$, $\text{Cs}^+$) on aluminosilicate-like phases and anions ($\text{AsO}_4^{3-}$, $\text{CrO}_4^{2-}$) in their Fe-modified forms.

The adsorption of chromate ($\text{CrO}_4^{2-}$) was typically worse compared to the other oxyanions [24–26], which can be associated with a lower adsorption energy of $\text{CrO}_4^{2-}$ and its prevailed electrostatic binding via outer-sphere surface complexes [27]. Another reason for the weaker and less efficient adsorption of $\text{CrO}_4^{2-}$ compared to, e.g., $\text{AsO}_4^{3-}$ or $\text{PO}_4^{3-}$ can be related to the different protonation of divalent ($\text{CrO}_4^{2-}$) and trivalent ($\text{AsO}_4^{3-}$) oxyanions, which, as a weaker trihydric acid anions, dispose of a much broader adsorption edge and higher adsorption affinity than stronger dihydric acid anions ($\text{CrO}_4^{2-}$, $\text{SO}_4^{2-}$) [24–27]. As can be seen in Table 3 and Figure 5, the adsorption of all tested oxyanions on original $\text{CSW}$ and $\text{TSW}$ differed markedly. While the adsorption of $\text{AsO}_4^{3-}$ and $\text{PO}_4^{3-}$ on $\text{CSW}$ could be fitted to the Langmuir model and ran very effectively, the original $\text{TSW}$ 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 ($\varepsilon > 80\%$). In that case, the maximum experimental adsorption capacity $q_{\text{max}}$ 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 mmol·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 ($\text{Pb}^{2+}$, $\text{Cd}^{2+}$, $\text{Cs}^+$) adsorption related to the sorbent consumption (Figure 6a) showed more effective adsorption of $\text{Pb}^{2+}$ and $\text{Cd}^{2+}$ compared to $\text{Cs}^+$, and also the higher selectivity of $\text{CSW}$ compared to $\text{TSW}$. The opposite trend in $\text{Cs}^+$ adsorption (much more effective adsorption on $\text{TSW}$ than on $\text{CSW}$) can be explained by the structure and mineralogical composition of $\text{TSW}$ (higher crystallinity, clay fractions), which were found to be crucial for the removal of radionuclides from contaminated waters [28,29].

The adsorption of anions ($\text{AsO}_4^{3-}$, $\text{PO}_4^{3-}$, $\text{CrO}_4^{2-}$) on $\text{CSW}/\text{CSW}_{\text{Fe}}$ (Figure 6b) and $\text{TSW}/\text{TSW}_{\text{Fe}}$ (Figure 6c) illustrated the substantial increase in the affinity of Fe-modified WBS to anionic contaminants. In addition, the quantitative adsorption of $\text{AsO}_4^{3-}$ also on original $\text{CSW}$ (Figure 6b) could almost be related to the high alkalinity of $\text{CSW}$ followed by the formation of insoluble surface precipitate, which participated in the total adsorption yield. The comparison of two Fe-modified sorbents showed that $\text{TSW}_{\text{Fe}}$ was a better anion-active sorbent than $\text{CSW}_{\text{Fe}}$. 
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 mmol·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: Pb$^{2+}$ ≈ Cd$^{2+}$ >> Cs$^+$ for CSW/TSW, and AsO$_4^{3−}$ ≈ PO$_4^{3−}$ > 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.

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