Article

Kaolin–Fly Ash Composite for Pb\(^{2+}\) and AsO\(_4^{3−}\) Adsorption from Aqueous System

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Featured Application: Composite adsorbents can be applied in water treatment and other environmental technologies. Potential benefits include (i) connection of the surface and binding properties of different materials; (ii) an extended range of selectivity; (iii) the consumption of low-grade and/or waste materials; and (iv) favourable prices.

Abstract: The expected benefit of composite adsorbents generally consists in their growing applicability, thanks to the combination of the adsorption properties of individual components. Composite adsorbents were prepared as mixtures of kaolin from a Czech deposit (kaolin Sedlec, SK) and two fly ashes (FAs) from a fluidised bed boiler in Czech operations differing in fuel type. The mixtures of SK with FA in a ratio of 50:50% wt. were prepared at 20 °C, 65 °C, and 110 °C in an autoclave. The source materials and composite adsorbents were tested for the adsorption of lead as Pb\(^{2+}\), and arsenic as AsO\(_4^{3−}\) from model solutions in laboratory conditions. The adsorption of Pb\(^{2+}\) proceeded quantitatively on the source materials except SK, and on both the composites, with an adsorption yield of >97% and a low adsorbent consumption (~2 g L\(^{−1}\)). The AsO\(_4^{3−}\) adsorption proceeded selectively on both FAs, with an adsorption yield of >97% again. The adsorption of AsO\(_4^{3−}\) on the composite adsorbents achieved a worse yield (~80%), with about ten times more adsorbent consumption (~20 g L\(^{−1}\)). An increased preparation temperature did not affect the Pb\(^{2+}\) adsorption at all, but it reduced the efficiency of AsO\(_4^{3−}\) adsorption by up to 30%. The SK–FA composites proved to have promising properties, mostly as cation-active adsorbents.

Keywords: kaolin; fly ash; composite adsorbent; lead; arsenic

1. Introduction

Significant quantities of wastewater are inevitably generated by industrial, agricultural, and domestic activities. Among many inorganic contaminants threatening water quality, such as cadmium, lead, caesium, arsenic, chromium and fluorine, lead (Pb) and arsenic (As) represent typical cationic and oxyanionic pollutants. Arsenic (as AsO\(_4^{3−}\)) is a carcinogenic poison occurring naturally or due to human activities. Its inorganic forms are highly toxic and accumulate in soils and sediments through iron binding [1]. Lead (as Pb\(^{2+}\)) is one such element that has a well known chronic influence on the central nervous system, causing mental retardation, behavioural changes, paralysis and anaemia. Pb is easily accumulated in the body over a lifetime, yet its expulsion is very difficult. Despite the exclusion of tetraethyl lead, other Pb origins, such as battery manufacturers, lead smelters and ammunition industries are significant Pb polluters [2].

Although a number of methods are used in water treatment, such as coagulation, flocculation, precipitation, reverse osmosis, biological processes, gamma radiation and
photocatalysis [3–7], adsorption procedures still take a favoured position due to their un-
doubted benefits in terms of affordability, easy operation and technical simplicity, and
most importantly, the variability of usable adsorbents from a wide range of natural, syn-
thetic and waste materials. Among these approaches, adsorption offers special advantages
due to the possible use of a wide range of natural, synthetic, and waste materials to achieve
pollutants’ removal via chemisorption and/or physisorption [8,9]. There is currently in-
creasing attention in adsorption employing low-cost adsorbents, such as silicates and alu-
minosilicates, iron precipitates, biochar, etc. [10–12].

In this context, fly ash (FA) represents an interesting and promising material mostly
utilised in the concrete industry [13,14]. Furthermore, it finds applications in soil stabi-
lation, the synthesis of zeolites and now also in wastewater treatment [15–17].

Clays and other silicate minerals, including kaolin, are generally used in various indus-
trial processes. Some traditional technologies, mostly the manufacturing of high-quality
 ceramics, paper production, etc., require a high purity and acceptable whiteness of clay
material [18,19]. Therefore, natural clays are also widely used in other industrial and en-
vironmental technologies. They have long been considered superior adsorbents due to
their wide availability, excellent adsorption properties and environmentally friendly sta-

tus.

The coexistence of various contaminants in industrial and household wastewaters
accelerated the development of novel composite adsorbents to overcome some limitations
of commercially used one-component materials, such as a narrow selectivity to a specific
ion and/or a relatively low adsorption ability towards modern contaminants, namely, anti-
biotics, aromatics and dyes [20]. Recently, a couple of studies have been focused on the
preparation and characterisation of composite adsorbents. Unsurprisingly, aluminosili-
cates were often incorporated into composite adsorbents thanks to the above declared
benefits. Steiger et al. [21] prepared pelletised adsorbent materials from agro-waste bio-
mass, kaolinite and chitosan, which showed a comparable adsorption capacity to the more
expensive food waste (spent coffee grounds). Clays such as bentonite, feldspar, kaolinite
and montmorillonite were also mixed with, e.g., waste biomass, particularly with biochar
[22,23], or with FAs [16,24]. It should be emphasised that the mentioned studies were
mainly focused on the characterisation of the prepared composites, while the sorbability
of specific contaminants was tested to a limited extent [25].

The aim of this study was to prepare and characterise composite adsorbents from
kaolin (SK), as a representative of clays, and two FAs from a heating plant differing in the
burned fuel. The mixtures’ adsorption selectivity to cations and anions, compared to their
adsorption of raw components, was tested for the adsorption of lead (Pb) as Pb2+, and
arsenic (As) as AsO4^{3-} from model solutions. The adsorption data were fitted by the Lang-
muir and Freundlich models to verify promising combinations of raw components for the
preparation of effective composite adsorbents with extended selectivity towards oppos-
itely charged toxic ions.

2. Materials and Methods

2.1. Source Materials

The composite adsorbents were prepared from kaolin Sedlec (SK), Czech Republic,
containing mainly kaolinite (~55%), and two fly ashes (FAs) from a heating plant in Pra-
ge, Czech Republic, differing in the spent fuel. Both used fuels (biomass and lignite) were
burned at 780–850 °C in a fluidised bed boiler using the dry method of desulphurisation
and separated with fabric filters. The FAs were marked as KB (from biomass combustion)
and KF (from lignite combustion).

2.2. Preparation of Composite Adsorbents

The composite adsorbents were prepared as dry mixtures of SK with KB or KF in a
ratio of 50:50% wt. This ratio was chosen to verify the properties of the composite with a
balanced amount of both components (SK and FA). Each mixture was suspended in distilled water and then agitated in a batch manner at 20 °C and 65 °C for 24 h, filtered with a membrane cellulose filter 0.45 μm, dried at 60 °C and homogenised mechanically in a mortar [26]. An identical mixture in suspension with distilled water was further aged in an autoclave at 110 °C for 5 days, and then filtered, dried and homogenised with the same regime as before. The prepared mixed adsorbents were labelled as the following: (i) SK+KB (prepared in a weight ratio of 1:1 at 20 °C), (ii) SK+KB-T (prepared in a weight ratio of 1:1 at 65 °C), (iii) SK+KF-A (prepared in a weight ratio of 1:1 in an autoclave at 110 °C); (iv) SK+KF (prepared in a weight ratio of 1:1 at 20 °C), (v) SK+KF-T (prepared in a weight ratio of 1:1 at 65 °C) and, (vi) SK+KF-A (prepared in a weight ratio of 1:1 in an autoclave at 110 °C). An illustrative photograph of selected composite adsorbents is shown in Figure 1.

![Illustrative photo of composite adsorbents.](image)

**Figure 1.** Illustrative photo of composite adsorbents.

### 2.3. Model Solutions

Model solutions of the tested toxic ions (Pb²⁺ and AsO₃³⁻) were prepared from analytical-grade inorganic salts (Pb(NO₃)₂ and KH₂AsO₄, respectively) in distilled water at a concentration of 0.5 mmol L⁻¹ and their natural pH values (~4.5 for Pb²⁺ and ~5.7 for AsO₃³⁻). This concentration was selected as appropriate for simulating a heavily contaminated water system [26,27].

### 2.4. Adsorption Experiments

In adsorption experiments, the Pb²⁺ and AsO₃³⁻ were adsorbed on the source materials (SK, KB and KF, respectively), and on the composites (SK+KB, SK+KB-T, SK+KB-A and SK+KF, SK+KF-T, SK+KF-A).

A suspension of the model solution (50 mL) and a defined adsorbent dose (*) (1–6 g L⁻¹ for Pb²⁺ adsorption and 20–30 g L⁻¹ for AsO₃³⁻ adsorption) was agitated in a batch manner at laboratory temperature (20 °C) for 24 h [11,25,26]. The product was filtered off with a membrane cellulose filter 0.45 μm, and the filtrate was analysed for residual Pb or As content. (*) means the optimal adsorbent dosage determined by preliminary tests.

### 2.5. Data Processing

Adsorption data were fitted to the Langmuir (Equations (1)–(3)) and Freundlich (Equations (4) and (5)) isotherms, as the widely used adsorption models for natural sorbents, including oxides, aluminosilicates and soils [28,29]. The Langmuir isotherm is described by Equation (1) and its linearised form by Equation (2):

\[
q = \frac{q_L K_L c}{1 + K_L c}
\]  

(1)

\[
\frac{1}{q} = \frac{1}{q_L} + \frac{1}{q_L K_L c}
\]  

(2)

where \( q \) is an equilibrium concentration of adsorbed ion (adsorbate) in solid phase (mol g⁻¹), \( c \) is an equilibrium concentration of adsorbate in solution (mol L⁻¹), \( q_L \) indicates the
theoretical adsorption capacity (mol g⁻¹) and $K_L$ is a Langmuir adsorption constant (L mol⁻¹). The equilibrium amount of adsorbate caught in the solid phase ($q$) was calculated using Equation (3), where $V_0$ is the volume of the solution (L), $c_0$ is the initial concentration of the adsorbate in the solution (mol.L⁻¹), $c$ is the equilibrium concentration of the adsorbate in the solution (mol.L⁻¹) and $m$ is the mass of the solid phase (g):

$$q = \frac{V_0(c_0 - c)}{m}$$  \hspace{1cm} (3)

The obvious adsorption parameters of the Langmuir model ($q_{max}$—maximum equilibrium adsorption capacity; $Q_L$—theoretical adsorption capacity; $R^2$—correlation factor; $K_L$—Langmuir adsorption constant) were then used to evaluate the effectiveness of the adsorption systems.

The Freundlich isotherm can be expressed by Equation (4) and its linearised form by logarithmic Equation (5):

$$q = K_F \cdot c^n$$  \hspace{1cm} (4)

$$\log q = \log K_F + n \cdot \log c,$$  \hspace{1cm} (5)

where $q$ is an equilibrium concentration of adsorbed ion (adsorbate) in solid phase (mol g⁻¹), $c$ is an equilibrium concentration of adsorbate in solution (mol L⁻¹), $K_F$ is a distribution coefficient (L g⁻¹) and $n$ is a temperature-dependent constant ($n < 1$).

The Gibbs energy ($\Delta G$) associated with the adsorption process was calculated from the Langmuir adsorption constant by Equation (6):

$$\Delta G = -RT \cdot \ln K_L,$$  \hspace{1cm} (6)

where $R$ is the molar gas constant (J mol⁻¹ K⁻¹), $T$ is temperature (K) and $K_L$ is a Langmuir adsorption constant (L mol⁻¹).

The adsorption efficiency was then calculated using Equation (7), where $\varepsilon$ is the adsorption yield (%):

$$\varepsilon = 100 - \frac{c \cdot 100}{c_0}$$  \hspace{1cm} (7)

The adsorption value was calculated as the average of three identical measurements in which the standard deviation did not exceed 10%.

### 2.6. Analytical Methods

Powder X-ray diffraction (XRD) was performed using a Seifert XRD 3000P diffractometer (Seifert, Ahrensburg, Germany) with CoKα radiation ($\lambda = 0.179026$ nm, graphite monochromator and goniometer with Bragg–Brentano geometry) in a 2θ range of 5–60° with a step size of 0.05°.

X-ray fluorescence analyses (XRFs) of the solid phase were performed using an ARL 9400 XP+ spectrometer (ARL, Ecuiblens, Switzerland) at a voltage of 20–60 kV and a probe current of 40–80 mA, with an effective area of 490.6 mm². UniQuant v.4 software was used to evaluate the data (Thermo ARL, Ecuiblens, Switzerland).

The specific surface area ($S_{ BET}$) was measured on a Micromeretics ASAP 2020 (accelerated surface area and porosimetry) analyser (Micromeritics, Norcross, GA, USA) using gas sorption. The ASAP 2020 device assesses single- and multipoint BET surface areas and the Langmuir surface area, performs Temkin and Freundlich isotherm analyses, and determines pore volume and pore area distributions in the micro- and macropore ranges. Macro- and micropore samples were analysed using the Horvath–Kawazoe method and Barret–Joyner–Halenda method (BJH), respectively. In the BJH method, N₂ was used as the analysis adsorbent, and the analysis bath temperature was -195.8 °C. The samples were degassed at 313 K for 1000 min.
The point of zero charge (pHzPC), which generally allows the estimation of the preferential targeting of adsorption in aqueous systems [30], was determined using zeta potential analyser Stabino, version 2.0 (Particle Metrix GmbH, Meerbusch, Germany) equipped with a cylindrical polytetrafluoroethylene-measuring beaker and piston. The pHzPC was measured using the pH titration method to assess stable pH regions and determine the isoelectric point (IEP) with an extremely high resolution (0.1 pH). Three suspensions of the same solid sample in a KCl solution with an identical solid-to-liquid ratio (1:100) but different ionic strengths of KCl (0.1 M, 0.01 M and 0.001 M) were titrated to the IEP by 0.01 M HCl or NaOH in a dynamic regime. The pHzPC was calculated as the average of three pH values corresponding to the zero potential with a standard deviation range of 0.05-0.7 pH units.

The structure of samples was investigated by scanning electron microscopy (SEM) on a Tescan Vega 3, Czech Republic, and energy dispersion spectrometry on an Inca 350 spectrometer, Oxford Instruments, Abingdon, UK.

The concentrations of Pb in liquid samples were measured by performing atomic absorption spectrometry (AAS) using a SpectrAA-880 VGA 77 unit (Varian, Palo Alto, CA, USA) in flame mode. The accuracy of the AAS analyses was guaranteed by the Laboratory of Atomic Absorption Spectrometry of the University of Chemistry and Technology, Prague, Czech Republic, with a detection limit of 0.5 µg L⁻¹ and a standard deviation ranging from 5% to 10% of the mean.

The concentration of total As as AsO₄³⁻ in the liquid samples was measured by performing hydride generation atomic fluorescence spectrometry (HG-AFS) using a PSA 10.055 Millennium Excalibur system (PS Analytical, Kent, UK). The samples were pretreated with a solution of HCl (36% w/v) and KI (50%) with ascorbic acid (10%). The measurement was performed in milligram per litre and microgram per litre modes using HCl (12%), with a KI + ascorbic acid solution as a reagent blank and 7% NaBH₄ in 0.1 mol L⁻¹ NaOH as a reductant. The detection limit was 5 µg L⁻¹, and the standard deviation was experimentally determined to be 2.5%.

3. Results
3.1. Characterisation of Source Material and Composite Adsorbents

The source components of the composite adsorbents (SK, KB and KF) were analysed for semiquantitative chemical composition, phase composition and surface properties (Table 1).

Table 1. Semiquantitative chemical composition, S BET and pHZPC of source materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>S BET (m²·g⁻¹)</th>
<th>pHZPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK</td>
<td>53.9</td>
<td>35.7</td>
<td>0.5</td>
<td>0.0</td>
<td>1.6</td>
<td>1.6</td>
<td>0.0</td>
<td>3.2</td>
<td>17.6</td>
<td>2.2</td>
</tr>
<tr>
<td>KB</td>
<td>42.1</td>
<td>17.0</td>
<td>5.0</td>
<td>1.5</td>
<td>24.0</td>
<td>2.5</td>
<td>0.7</td>
<td>4.3</td>
<td>48.4</td>
<td>11.1</td>
</tr>
<tr>
<td>KF</td>
<td>41.8</td>
<td>28.9</td>
<td>3.9</td>
<td>1.1</td>
<td>11.9</td>
<td>1.2</td>
<td>3.4</td>
<td>2.6</td>
<td>26.1</td>
<td>11.3</td>
</tr>
</tbody>
</table>

The S BET values (Table 1), indicating the primary adsorption affinity of the source materials, differed markedly for all tested materials. This parameter directed the predicted adsorption efficiency in the order KB >> KF > SK [31,32].

The pHZPC values of the source materials showed typical cation-selective behaviour of SK and anion-selective behaviour of KB and KF in solutions with a pH of ≥5 (Section 2.6).

The principal phase composition of the source materials (Table 2) illustrated a similar composition of both FA and the phase purity of used SK.
Table 2. Phase composition of source materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mineralogical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK</td>
<td>kaolinite, muscovite, quartz</td>
</tr>
<tr>
<td>KB</td>
<td>muscovite, quartz, calcite, anhydrite, anorthite</td>
</tr>
<tr>
<td>KF</td>
<td>muscovite, quartz, calcite, anhydrite</td>
</tr>
</tbody>
</table>

The composite adsorbents were characterised identically to the source material, focusing on the changes related to different preparation temperatures (20 °C, 65 °C and 110 °C in an autoclave, respectively). For the comparison of a possible phase transformation, only the marginal temperatures (20 °C and 110 °C) were selected. The mineralogical composition of composite adsorbents prepared at 20 °C and at 110 °C in an autoclave (Figures 2 and 3) proved only negligible phase changes. The phases originated by the preparation of SK+KB at 20 °C (Figure 2a) corresponded to the composition of the source materials, with a dominance of quartz, muscovite and calcite. During the autoclave treatment at 110 °C (Figure 2b), the kaolinite disappeared, with a noticeable growth in the amorphous portion.

In the case of SK+KF prepared at 20 °C (Figure 3a), the phase composition corresponded to the source materials again, revealing the major phases of muscovite, kaolinite and quartz, with the presence of anhydrite and calcite. Autoclave treatment at 110 °C (Figure 3b) caused the extinction of kaolinite, with the concurrent growth of a new phase of gypsum. This time the crystallinity of the autoclave composite remained the same as for the 20 °C adjustment (compare Figure 3a,b).
Figure 3. XRD patterns of source materials and SK+KF prepared at different conditions. (a) 20 °C; (b) 110 °C in autoclave (SK+KF-A).

The SEM micro-observation of the composite adsorbents prepared under different temperatures (Figure 4) proved structural changes consisting of a higher homogeneity of the material in connection with the higher preparation temperature. In this context, the assumed greater amorphous proportion was confirmed for SK+KB (Figure 2b), while for SK+KF, the crystallinity remained the same (Figure 3a,b).

Figure 4. SEM images of composite adsorbents prepared at different conditions; T—preparation temperature of 65 °C; A—preparation temperature of 110 °C in autoclave (magnification of 2500×).

The effect of increasing temperature on the structural and surface properties of composite adsorbents is summarised in Tables 3 and 4.
Table 3. Preparation temperature effect on surface properties of composite adsorbents.

<table>
<thead>
<tr>
<th></th>
<th>$S_{BET}$ (m².g⁻¹)</th>
<th>pHZPC</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 ºC</td>
<td>65 ºC-T</td>
<td>110 ºC-A</td>
<td>20 ºC</td>
</tr>
<tr>
<td>SK+KB</td>
<td>22.5</td>
<td>20.9</td>
<td>23.8</td>
<td>7.8</td>
</tr>
<tr>
<td>SK+KF</td>
<td>21.8</td>
<td>23.7</td>
<td>23.1</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Table 4. Preparation temperature effect on total pore volume of composite adsorbents.

<table>
<thead>
<tr>
<th>Source materials</th>
<th>Total Pore Volume (cm³.g⁻¹)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 ºC</td>
<td>65 ºC-T</td>
<td>110 ºC-A</td>
</tr>
<tr>
<td>SK</td>
<td>0.053</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KB</td>
<td>0.047</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>0.079</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composites</td>
<td>SK+KB</td>
<td>0.049</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>SK+KF</td>
<td>0.078</td>
<td>0.081</td>
</tr>
</tbody>
</table>

As follows from the above results, an increased preparation temperature did not significantly affect either the phase composition or the surface properties of the composites. Although the porosity of the source materials varied markedly (Table 4), in the case of composites it showed comparable values closed to the value of the appropriate FA (KB or KF) for all preparation temperatures. The composite adsorbents became more homogeneous, with a higher proportion of the amorphous phase, particularly for SK+KB; however, the $S_{BET}$ showed only a slight increase when autoclaved at 110 ºC.

3.2. Adsorption of Pb²⁺ on Source Materials and Composite Adsorbents

The parameters of Pb²⁺ adsorption on source materials (SK, KB and KF) and on the composites (SK+KB and SK+KF), calculated according to the Langmuir and Freundlich models (Table 5), indicated a high Pb²⁺ sorbability on all tested materials except SK. The effective adsorption of Pb²⁺ on various adsorbents, which is well known from many papers, e.g., [2,10,26], is related to a strong pH dependence of Pb²⁺ forms in aqueous environment. At a pH > 7, the hydrolysed Pb²⁺ ions formed stable inner-sphere complexes with the active sites on the sorbent surface, and eventually created poorly soluble polynuclear complexes or surface precipitates [33]. Considering the main adsorption parameters, such as $Q_r$, $K_r$ and $\Delta G$, the adsorbents could be ordered by the robustness and energy of adsorption as SK+KB > SK+KF ≥ KF > KB. The balanced values of $\Delta G$ (Table 5) confirmed a comparable adsorption process for all adsorbents except SK.

The efficiency of Pb²⁺ adsorption on all tested adsorbents (Figure 5) supported the above results. Except for SK, all adsorbents showed a high selectivity to Pb²⁺ at a low dosage, which may be associated with the above-discussed formation of insoluble surface precipitates promoting adsorption yield.

Table 5. Parameters of Langmuir and Freundlich models for Pb²⁺ adsorption.

<table>
<thead>
<tr>
<th></th>
<th>$q_{max}$ (mmol g⁻¹)</th>
<th>$Q_r$ (mmol g⁻¹)</th>
<th>$K_L$ (L.mmol⁻¹)</th>
<th>$R^2$</th>
<th>$q_{max}$ (mmol g⁻¹)</th>
<th>$n$</th>
<th>$K_f$ (mmol g⁻¹)</th>
<th>$R^2$</th>
<th>$\Delta G$ (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KB</td>
<td>0.42</td>
<td>0.90</td>
<td>76.6</td>
<td>0.986</td>
<td>0.42</td>
<td>0.87</td>
<td>26.92</td>
<td>0.986</td>
<td>-10.7</td>
</tr>
<tr>
<td>KF</td>
<td>0.43</td>
<td>0.23</td>
<td>140.6</td>
<td>0.667</td>
<td>0.43</td>
<td>0.66</td>
<td>2.59</td>
<td>0.736</td>
<td>-12.3</td>
</tr>
<tr>
<td>SK+KB</td>
<td>0.50</td>
<td>0.58</td>
<td>512.1</td>
<td>0.933</td>
<td>0.50</td>
<td>0.80</td>
<td>50.90</td>
<td>0.980</td>
<td>-15.5</td>
</tr>
<tr>
<td>SK+KF</td>
<td>0.47</td>
<td>1.07</td>
<td>213.1</td>
<td>0.938</td>
<td>0.47</td>
<td>0.61</td>
<td>11.91</td>
<td>0.911</td>
<td>-13.3</td>
</tr>
</tbody>
</table>
Figure 5. Efficiency of Pb\(^{2+}\) adsorption on source materials and composite adsorbents.

3.3. Adsorption of AsO\(_{4}^{3-}\) on Source Materials and Composite Adsorbents

The parameters of AsO\(_{4}^{3-}\) adsorption on source materials (SK, KB and KF) and on the composites (SK+KB and SK+KF), calculated according to the Langmuir and Freundlich models, are summarised in Table 6. As is evident, the Langmuir and Freundlich fits were applicable just to the adsorption on both FA and SK+KB. Compared to Pb\(^{2+}\), the adsorption capacities (\(q_{\text{max}}\) and \(Q_t\)) reached an order-of-magnitude lower values, which corresponded well to a generally worse adsorption of anions, including AsO\(_{4}^{3-}\), on aluminosilicates and other silicate-rich materials [12,34–36]. Indeed, all the source materials belong to this group. The other parameters, such as \(K_L\) and \(\Delta G\), indicated a balanced AsO\(_{4}^{3-}\) adsorption on KB and KF, and less robust adsorption on SK+KB, most probably thanks to the presence of clay in the adsorption mixture.

Table 6. Parameters of Langmuir and Freundlich models for AsO\(_{4}^{3-}\) adsorption.

<table>
<thead>
<tr>
<th></th>
<th>(q_{\text{max}}) (mmol g(^{-1}))</th>
<th>(Q_t) (mmol g(^{-1}))</th>
<th>(K_L) (L:mmol(^{-1}))</th>
<th>(R^2)</th>
<th>(q_{\text{max}}) (mmol g(^{-1}))</th>
<th>(n)</th>
<th>(K_F) (mmol g(^{-1}))</th>
<th>(R^2)</th>
<th>(\Delta G) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KB</td>
<td>0.02</td>
<td>0.02</td>
<td>331.4</td>
<td>0.819</td>
<td>0.02</td>
<td>0.21</td>
<td>0.05</td>
<td>0.940</td>
<td>-14.4</td>
</tr>
<tr>
<td>KF</td>
<td>0.02</td>
<td>0.02</td>
<td>720.8</td>
<td>0.920</td>
<td>0.02</td>
<td>0.14</td>
<td>0.04</td>
<td>0.788</td>
<td>-16.3</td>
</tr>
<tr>
<td>SK+KB</td>
<td>0.03</td>
<td>0.04</td>
<td>7.37</td>
<td>0.948</td>
<td>0.02</td>
<td>0.55</td>
<td>0.05</td>
<td>0.957</td>
<td>-5.0</td>
</tr>
<tr>
<td>SK+KF</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The efficiency of AsO\(_{4}^{3-}\) adsorption on the tested materials (Figure 6) confirmed the results given by the sorption parameters, i.e., the excellent sorbability of AsO\(_{4}^{3-}\) on KB and KF, and almost sufficient AsO\(_{4}^{3-}\) adsorption on composite adsorbents (SK+KB > SK+KF) at a higher sorbent dosage (25–30 g.L\(^{-1}\)). The selectivity of KB and KF to AsO\(_{4}^{3-}\) can be explained by the high pH\(_{ZPC}\) value (Table 1), which, despite a high silicate portion in the FA composition (Table 1), clearly corresponded to anion-active adsorbents [30,37].
3.4. Effect of Preparation Temperature on Sorbability of Pb²⁺ and AsO₄³⁻ on Composite Adsorbents

A possible temperature effect on the structural and surface properties of the composite adsorbents was discussed in Section 3.1. As was found, a higher preparation temperature (65 °C or 110 °C in an autoclave) did not affect the structural and surface properties of the composites. In terms of adsorption properties resulting from the Langmuir and Freundlich models (Tables 7 and 8), no significant trend was observed in connection with increasing temperature.

Table 7. Preparation temperature effect on Pb²⁺ adsorption on composite adsorbents.

<table>
<thead>
<tr>
<th>Preparation Temperature</th>
<th>$q_{\text{max}}$ (mmol g⁻¹)</th>
<th>$Q_t$ (mmol g⁻¹)</th>
<th>$K_L$ (L.mmol⁻¹)</th>
<th>$R^2$</th>
<th>$q_{\text{max}}$ (mmol g⁻¹)</th>
<th>$n$</th>
<th>$K_F$ (mmol g⁻¹)</th>
<th>$R^2$</th>
<th>$\Delta G$ (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK+KB</td>
<td>0.50</td>
<td>0.57</td>
<td>512.1</td>
<td>0.933</td>
<td>0.50</td>
<td>0.80</td>
<td>50.90</td>
<td>0.980</td>
<td>-15.5</td>
</tr>
<tr>
<td>110°C (autoclave)</td>
<td>0.48</td>
<td>1.80</td>
<td>68.65</td>
<td>0.824</td>
<td>0.49</td>
<td>0.90</td>
<td>88.55</td>
<td>0.885</td>
<td>-10.5</td>
</tr>
<tr>
<td>SK+KF</td>
<td>0.47</td>
<td>1.07</td>
<td>213.1</td>
<td>0.938</td>
<td>0.47</td>
<td>0.61</td>
<td>11.90</td>
<td>0.911</td>
<td>-13.3</td>
</tr>
<tr>
<td>110°C (autoclave)</td>
<td>0.50</td>
<td>0.58</td>
<td>281.7</td>
<td>0.923</td>
<td>0.30</td>
<td>0.71</td>
<td>17.66</td>
<td>0.918</td>
<td>-14.0</td>
</tr>
</tbody>
</table>

In the case of Pb²⁺, all adsorption systems were fitted by the Langmuir and Freundlich models, at similar values of parameters for different temperatures.

Table 8. Preparation temperature effect on AsO₄³⁻ adsorption on composite adsorbents.

<table>
<thead>
<tr>
<th>Preparation Temperature</th>
<th>$q_{\text{max}}$ (mmol g⁻¹)</th>
<th>$Q_t$ (mmol g⁻¹)</th>
<th>$K_L$ (L.mmol⁻¹)</th>
<th>$R^2$</th>
<th>$q_{\text{max}}$ (mmol g⁻¹)</th>
<th>$n$</th>
<th>$K_F$ (mmol g⁻¹)</th>
<th>$R^2$</th>
<th>$\Delta G$ (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK+KB</td>
<td>0.02</td>
<td>0.04</td>
<td>7.4</td>
<td>0.948</td>
<td>0.02</td>
<td>0.55</td>
<td>0.05</td>
<td>0.957</td>
<td>-5.0</td>
</tr>
<tr>
<td>65°C</td>
<td>0.02</td>
<td>0.03</td>
<td>9.5</td>
<td>0.790</td>
<td>0.02</td>
<td>0.52</td>
<td>0.06</td>
<td>0.794</td>
<td>-5.6</td>
</tr>
<tr>
<td>110°C (autoclave)</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SK+KF</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>65°C</td>
<td>0.009</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.007</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>110°C (autoclave)</td>
<td>0.003</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.003</td>
<td>-</td>
<td>-</td>
<td>0.918</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6. Efficiency of AsO₄³⁻ adsorption on source materials and composite adsorbents.
The data of AsO$_4^{3-}$ adsorption on composite adsorbents prepared at different temperatures were not fittable by the adsorption models; however, the experimentally measured maximum adsorption capacities ($q_{\text{max}}$) even showed a decreasing trend with growing preparation temperatures. The presumed loss of anion-active adsorption sites for heat-treated composites was confirmed by a slight decrease in pH$_{zpc}$ during heating (Table 3), which could be induced by chemical changes in the available compounds (e.g., alkali oxides and hydroxides).

The adsorption isotherms (Figure 7) calculated according to Equation (3) supported the above aspects. The data obtained by the Pb$^{2+}$ adsorption on all composite sorbents (Figure 7a) could be fitted by the Langmuir and Freundlich models, and the experimental adsorption capacities were comparable for the adsorbents prepared under different conditions (T, A). On the other hand, only the adsorption of AsO$_4^{3-}$ on SK-KB and SK-KB-T proceeded according to the adsorption models (Figure 7b) with a higher sorbability of AsO$_4^{3-}$ on SK-KB-T. As follows from Tables 7 and 8, the correlation factors $R^2$ of both the Langmuir and Freundlich fits rather indicated the decreasing equilibrium of the adsorption process with an increased preparation temperature.

As evident from the graph in Figure 8, the growing preparation temperature of the composites did not affect the adsorption yield of Pb$^{2+}$, but noticeably inhibited AsO$_4^{3-}$ adsorption. This phenomenon was apparently related to surface changes. Elevated temperatures, and especially exposure to high temperatures in the autoclave, could cause binding changes in the active sites on the adsorbent surface.
4. Conclusions

The composite adsorbents were prepared from kaolin (SK) and two fly ashes (FAs) differing in the spent fuel (biomass and lignite combustion). Mixtures of SK with FA in the ratio of 50:50 wt.% were prepared at 20 °C, 65 °C and 110 °C in an autoclave. The source material and composites were tested as the adsorbents of Pb\(^{2+}\) as a typical cationic pollutant, and AsO\(_4^{3-}\) representing a toxic risk anion, from water systems.

Pb\(^{2+}\) adsorption on the source materials, except SK, and on both the composite adsorbents proceeded at a high adsorption yield (>99%) and a low adsorbent consumption. AsO\(_4^{3-}\) adsorption proceeded selectively only on both FAs at an order-of-magnitude lower adsorption capacity compared to Pb\(^{2+}\) and an adsorption yield of >97%.

The growing preparation temperature of the composite adsorbents did not affect Pb\(^{2+}\) adsorption at all but reduced the efficiency of AsO\(_4^{3-}\) adsorption by up to 30%. In terms of the composite adsorbents, a higher preparation temperature (65 °C, 110 °C in an autoclave) did not significantly affect either the phase composition or the structural and surface properties.

The adsorption potential of kaolin–FA composites was preferably observed in the adsorption of cations from contaminated waters. Although anions demonstrated a higher sorbability on individual FAs, the participation of kaolin in composite adsorbent could definitely bring some benefits, particularly in increasing homogeneity and thus the quality of the composite, compared to an individual FA. Except for a wider range of adsorption sites, which is promising for a decontamination of mixed contaminated systems, its low price can play a key role in technological applications.

**Author Contributions:** Conceptualisation, B.D.; adsorption experiments and analysis, B.D., E.B., M.A. and K.M.; methodology, B.D. and M.L.; **S BET** measurement and evaluation, M.L.; XRD measurement, D.K.; material preparation and characterisation, L.P.; 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.

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