

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 ($\sim 2 \text{ g.L}^{-1}$). The AsO_4^{3-} adsorption proceeded selectively only 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 ($\sim 20 \text{ g.L}^{-1}$). 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



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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 undoubted benefits in terms of affordability, easy operation and technical simplicity, and most

importantly, the variability of usable adsorbents from a wide range of natural, synthetic 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 increasing attention in adsorption employing low-cost adsorbents, such as silicates and aluminosilicates, 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 stabilisation, the synthesis of zeolites and now also in wastewater treatment [15–17].

Clays and other silicate minerals, including kaolin, are generally used in various industrial 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 environmental technologies. They have long been considered superior adsorbents due to their wide availability, excellent adsorption properties and environmentally friendly status.

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, antibiotics, aromatics and dyes [20]. Recently, a couple of studies have been focused on the preparation and characterisation of composite adsorbents. Unsurprisingly, aluminosilicates were often incorporated into composite adsorbents thanks to the above declared benefits. Steiger et al. [21] prepared pelletised adsorbent materials from agro-waste biomass, 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 Pb^{2+} , and arsenic (As) as AsO_4^{3-} from model solutions. The adsorption data were fitted by the Langmuir and Freundlich models to verify promising combinations of raw components for the preparation of effective composite adsorbents with extended selectivity towards oppositely 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 Prague, 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+KB-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.

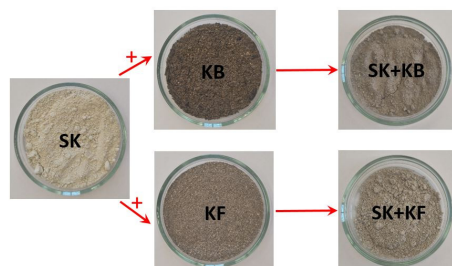


Figure 1. Illustrative photo of composite adsorbents.

2.3. Model Solutions

Model solutions of the tested toxic ions (Pb^{2+} and AsO_4^{3-}) were prepared from analytical-grade inorganic salts ($\text{Pb}(\text{NO}_3)_2$ and KH_2AsO_4 , respectively) in distilled water at a concentration of 0.5 mmol L^{-1} and their natural pH values (≈ 4.5 for Pb^{2+} and ≈ 5.7 for AsO_4^{3-}). This concentration was selected as appropriate for simulating a heavily contaminated water system [26,27].

2.4. Adsorption Experiments

In adsorption experiments, the Pb^{2+} and AsO_4^{3-} 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 (*) ($1\text{--}6 \text{ g L}^{-1}$ for Pb^{2+} adsorption and $20\text{--}30 \text{ g L}^{-1}$ for AsO_4^{3-} 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 $0.45 \mu\text{m}$, 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):

$$q = \frac{Q_t \cdot K_L \cdot c}{1 + K_L \cdot c} \quad (1)$$

$$\frac{1}{q} = \frac{1}{Q_t} + \frac{1}{Q_t \cdot K_L \cdot c} \quad (2)$$

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_t 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 ($\text{mol}\cdot\text{L}^{-1}$), c is the equilibrium concentration of the adsorbate in the solution ($\text{mol}\cdot\text{L}^{-1}$) and m is the mass of the solid phase (g):

$$q = \frac{V_0 \cdot (c_0 - c)}{m} \quad (3)$$

The obvious adsorption parameters of the Langmuir model ($q_{\max}$ —maximum equilibrium adsorption capacity; Q_t —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):

$$q = K_F \cdot c^n \quad (4)$$

$$\log q = \log K_F + n \cdot \log c, \quad (5)$$

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 (ΔG) associated with the adsorption process was calculated from the Langmuir adsorption constant by Equation (6):

$$\Delta G = -RT \cdot \ln K_L, \quad (6)$$

where R is the molar gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), 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 ε is the adsorption yield (%):

$$\varepsilon = 100 - \frac{c \cdot 100}{c_0} \quad (7)$$

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 $\text{CoK}\alpha$ radiation ($\lambda = 0.179026 \text{ nm}$, graphite monochromator and goniometer with Bragg–Brentano geometry) in a 2θ range of $5\text{--}60^\circ$ 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, Ecublens, Switzerland) at a voltage of 20–60 kV and a probe current of 40–80 mA, with an effective area of 490.6 mm^2 . UniQuant v.4 software 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 (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–Kavazoe method and Barret–Joyner–Halenda method (BJH), respectively. In the BJH method, N_2 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 (pH_{ZPC}), 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 pH_{ZPC} 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 pH_{ZPC} 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 $0.5 \mu\text{g L}^{-1}$ and a standard deviation ranging from 5% to 10% of the mean.

The concentration of total As as AsO_4^{3-} 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% NaBH_4 in 0.1 mol L^{-1} NaOH as a reductant. The detection limit was $5 \mu\text{g L}^{-1}$, 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 pH_{ZPC} of source materials.

Material	Chemical Composition (wt%)								S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	pH_{ZPC}
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	K_2O		
SK	53.9	35.7	0.5	0.0	1.6	1.6	0.0	3.2	17.6	2.2
KB	42.1	17.0	5.0	1.5	24.0	2.5	0.7	4.3	48.4	11.1
KF	41.8	28.9	3.9	1.1	11.9	1.2	3.4	2.6	26.1	11.3

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 $\text{KB} \gg \text{KF} > \text{SK}$ [31,32].

The pH_{ZPC} 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.

Material	Mineralogical Composition
SK	kaolinite, muscovite, quartz
KB	muscovite, quartz, calcite, anhydrite, anorthite
KF	muscovite, quartz, calcite, anhydrite

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.

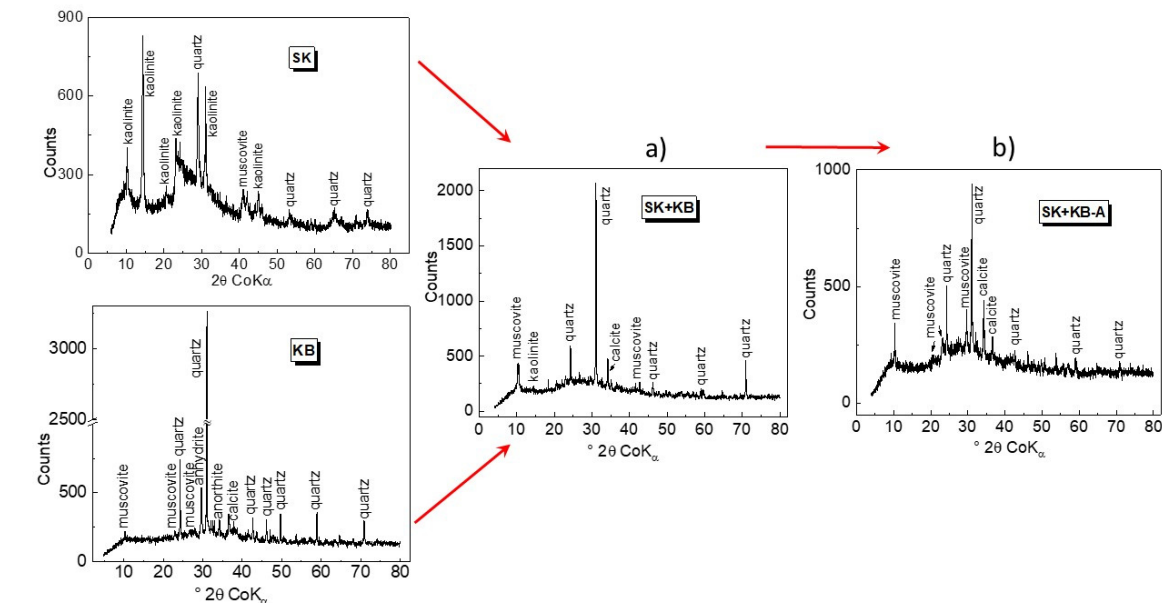


Figure 2. XRD patterns of source materials and SK+KB prepared at different conditions. (a) 20 °C; (b) 110 °C in autoclave (SK+KB-A).

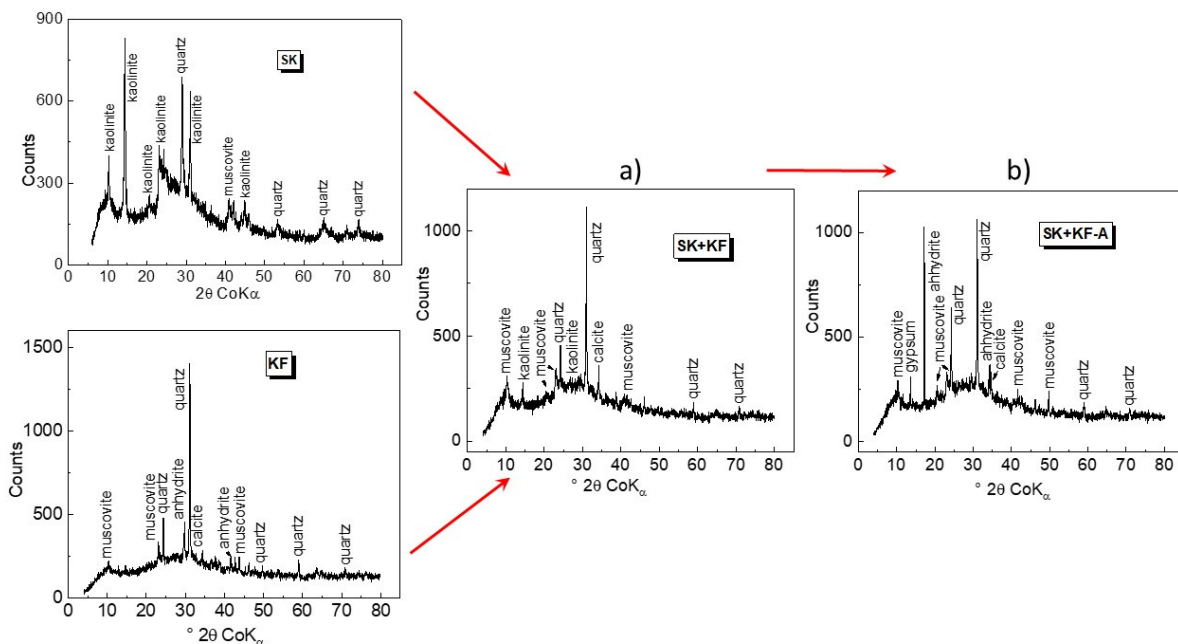


Figure 3. XRD patterns of source materials and SK+KF prepared at different conditions. (a) 20 °C; (b) 110 °C in autoclave (SK+KF-A).

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).

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).

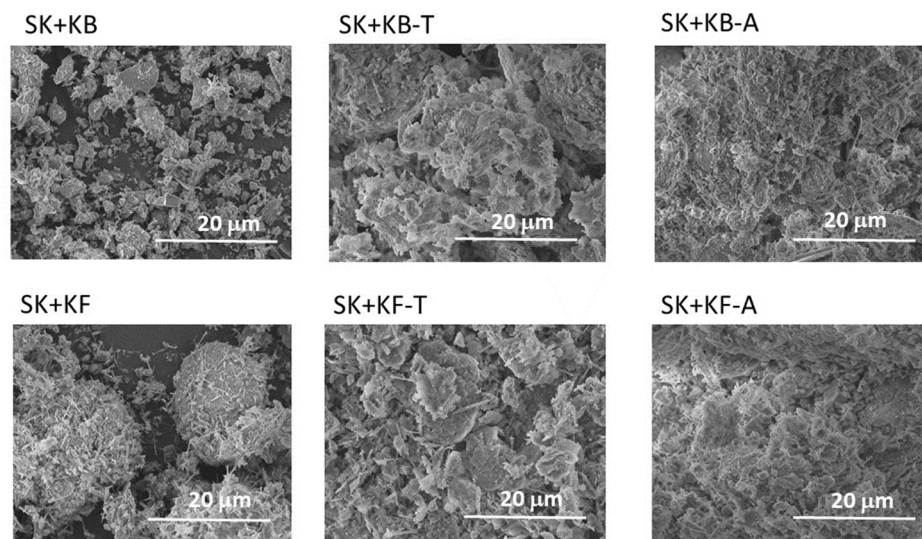


Figure 4. SEM images of composite adsorbents prepared at different conditions; T—preparation temperature of 65 °C; A—preparation temperature of 110 °C in autoclave (magnification of 2500×).

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.

	S_{BET} ($m^2 \cdot g^{-1}$)			pH_{ZPC}		
	20 °C	65 °C-T	110 °C-A	20 °C	65 °C-T	110 °C-A
SK+KB	22.5	20.9	23.8	7.8	6.6	6.6
SK+KF	21.8	23.7	23.1	7.6	7.6	7.2

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

		Total Pore Volume ($cm^3 \cdot g^{-1}$)		
		20 °C	65 °C-T	110 °C-A
Source materials	SK	0.053		
	KB	0.047		
	KF	0.079		
Composites	SK+KB	0.049	0.051	0.049
	SK+KF	0.078	0.081	0.076

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 °C.

3.2. Adsorption of Pb^{2+} on Source Materials and Composite Adsorbents

The parameters of Pb^{2+} 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 Pb^{2+} sorbability on all tested materials except SK. The effective adsorption of Pb^{2+} on various adsorbents, which is well known from many papers, e.g., [2,10,26], is related to a strong pH dependence of Pb^{2+} forms in aqueous environment. At a pH > 7, the hydrolysed Pb^{2+} 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_t , K_L and ΔG , the adsorbents could be ordered by the robustness and energy of adsorption as $\text{SK+KB} > \text{SK+KF} \geq \text{KF} > \text{KB}$. The balanced values of ΔG (Table 5) confirmed a comparable adsorption process for all adsorbents except SK.

Table 5. Parameters of Langmuir and Freundlich models for Pb^{2+} adsorption.

	q_{max} (mmol g ^{−1})	Langmuir Model			q_{max} (mmol g ^{−1})	Freundlich Model			ΔG (kJ.mol ^{−1})
		Q_t (mmol g ^{−1})	K_L (L.mmol ^{−1})	R^2		n	K_F (mmol g ^{−1})	R^2	
SK	0.04	–	–	–	0.04	–	–	–	–
KB	0.42	0.90	76.6	0.986	0.42	0.87	26.92	0.986	−10.7
KF	0.43	0.23	140.6	0.667	0.43	0.66	2.59	0.736	−12.3
SK+KB	0.50	0.58	512.1	0.933	0.50	0.80	50.90	0.980	−15.5
SK+KF	0.47	1.07	213.1	0.938	0.47	0.61	11.91	0.911	−13.3

The efficiency of Pb^{2+} adsorption on all tested adsorbents (Figure 5) supported the above results. Except for SK, all adsorbents showed a high selectivity to Pb^{2+} at a low dosage, which may be associated with the above-discussed formation of insoluble surface precipitates promoting adsorption yield.

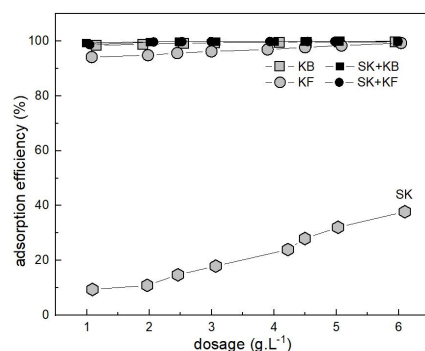


Figure 5. Efficiency of Pb^{2+} adsorption on source materials and composite adsorbents.

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_{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 ΔG , 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.

	$q_{\max}$ (mmol g ⁻¹)	Langmuir Model			Freundlich Model				ΔG (kJ.mol ⁻¹)
		Q_t (mmol g ⁻¹)	K_L (L.mmol ⁻¹)	R^2	$q_{\max}$ (mmol g ⁻¹)	n	K_F (mmol g ⁻¹)	R^2	
SK	0.005	-	-	-	0.005	-	-	-	-
KB	0.02	0.02	331.4	0.819	0.02	0.21	0.05	0.940	-14.4
KF	0.02	0.02	720.8	0.920	0.02	0.14	0.04	0.788	-16.3
SK+KB	0.03	0.04	7.37	0.948	0.02	0.55	0.05	0.957	-5.0
SK+KF	0.01	-	-	-	0.01	-	-	-	-

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].

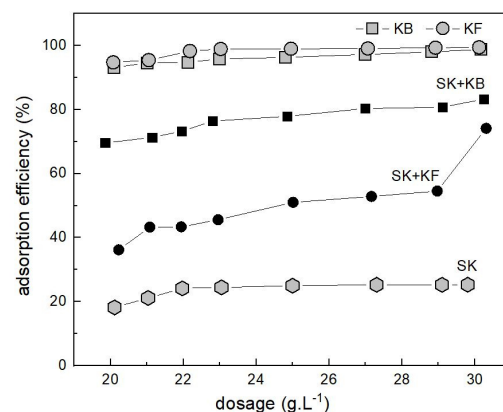


Figure 6. Efficiency of AsO_4^{3-} adsorption on source materials and composite adsorbents.

3.4. Effect of Preparation Temperature on Sorbability of Pb^{2+} and AsO_4^{3-} 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.

In the case of Pb^{2+} , all adsorption systems were fitted by the Langmuir and Freundlich models, at similar values of parameters for different temperatures.

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 ($q_{\max}$) 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) (page 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.

Table 7. Preparation temperature effect on Pb^{2+} adsorption on composite adsorbents.

	Preparation Temperature	Langmuir Model				Freundlich Model				ΔG (kJ.mol ⁻¹)
		$q_{\max}$ (mmol g ⁻¹)	Q_t (mmol g ⁻¹)	K_L (L.mmol ⁻¹)	R^2	$q_{\max}$ (mmol g ⁻¹)	n	K_F (mmol g ⁻¹)	R^2	
SK+KB	20 °C	0.50	0.57	512.1	0.933	0.50	0.80	50.90	0.980	−15.5
	65 °C	0.30	1.23	74.8	0.992	0.30	0.91	71.74	0.985	−11.4
	110 °C	0.48	1.80	68.65	0.824	0.49	0.90	88.55	0.885	−10.5
SK+KF	(autoclave)	0.47	1.07	213.1	0.938	0.47	0.61	11.90	0.911	−13.3
	20 °C	0.30	0.54	202.9	0.902	0.30	0.43	15.92	0.773	−15.4
	110 °C (autoclave)	0.50	0.58	281.7	0.923	0.30	0.71	17.66	0.918	−14.0

Table 8. Preparation temperature effect on AsO_4^{3-} adsorption on composite adsorbents.

	Preparation Temperature	Langmuir Model				Freundlich Model				ΔG (kJ.mol ⁻¹)
		$q_{\max}$ (mmol g ⁻¹)	Q_t (mmol g ⁻¹)	K_L (L.mmol ⁻¹)	R^2	$q_{\max}$ (mmol g ⁻¹)	n	K_F (mmol g ⁻¹)	R^2	
SK+KB	20 °C	0.02	0.04	7.4	0.948	0.02	0.55	0.05	0.957	−5.0
	65 °C	0.02	0.03	9.5	0.790	0.02	0.52	0.06	0.794	−5.6
	110 °C	0.01	-	-	-	0.01	-	-	-	-
SK+KF	(autoclave)	0.01	-	-	-	0.01	-	-	-	-
	20 °C	0.009	-	-	-	0.007	-	-	-	-
	110 °C (autoclave)	0.003	-	-	-	0.003	-	-	0.918	-

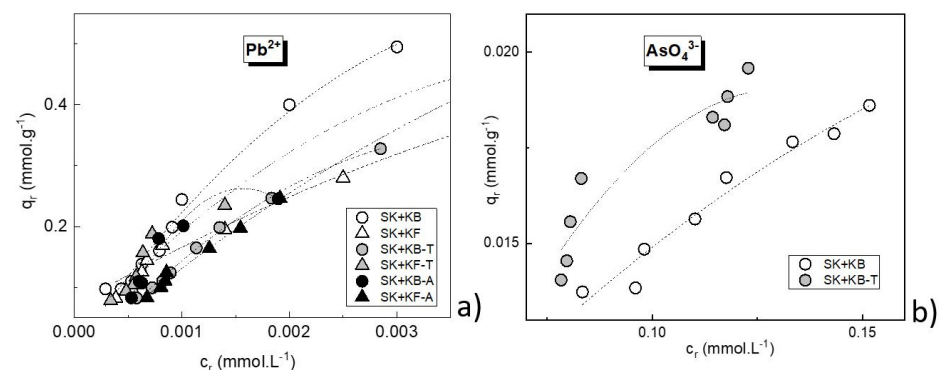


Figure 7. Adsorption isotherms for Pb^{2+} and AsO_4^{3-} adsorption on thermally modified composites calculated from experimental data. (a) Pb^{2+} adsorption; (b) AsO_4^{3-} adsorption.

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.

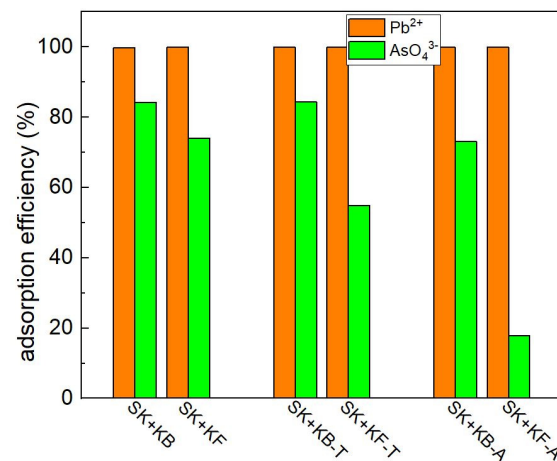


Figure 8. Efficiency of Pb²⁺ and AsO₄³⁻ adsorption on thermally modified composites.

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 Pb²⁺ as a typical cationic pollutant, and AsO₄³⁻ representing a toxic risk anion, from water systems.

Pb²⁺ 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. AsO₄³⁻ adsorption proceeded selectively only on both FAs at an order-of-magnitude lower adsorption capacity compared to Pb²⁺, and an adsorption yield of >97%.

The growing preparation temperature of the composite adsorbents did not affect Pb²⁺ adsorption at all but reduced the efficiency of AsO₄³⁻ 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.

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