Development of efficient sorbents by alkali-treatment of high-calcium-content fly ash from the paper industry

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Abstract

Fly ash is a promising waste material for zeolite synthesis, since it is readily available worldwide. However, the high calcium content in fly ash might interrupt zeolite formation. The present study aimed to evaluate the usability of high-calcium-content fly ash from the paper industry for zeolite synthesis. A further aim was to apply zeolites to water treatment according to the concept of waste removal using wastes. The zeolite synthesis was conducted using an unconventional hydrothermal activation, i.e. higher than typical NaOH concentration (14 M) was employed, and the synthesis was performed in an open reactor at mild reaction conditions. The resulting material was identified as containing zeolitic phases, namely sodalite and zeolite Y. The wastewater treatment performance of the produced sorbent was promising in terms of metals (Cu, Co, Zn, Ni, and Cd) and anions (sulfate and phosphate) removal. However, the leaching behavior of sorbent indicated that further cleaning or stabilization measures are needed before application.

Keywords: fly ash, calcium, zeolite, adsorption, wastewater treatment

Introduction

Fly ash, the inorganic residue from the combustion of solid fuels at power plants, is produced in the amount of approx. 500 million tons annually worldwide [1]. The chemical properties of fly ash depend mainly on fuel, combustion temperature, and power plant technology. For instance, lignite combustion produces relatively high-calcium-content fly ash [2]. However, in the paper industry, the fuel frequently consists of paper product residues containing calcite ($CaCO_3$) as a filler material, which results in significantly higher calcium content [3]. High-calcium-content fly ashes are typically characterized by pozzolanic and hydraulic reactions with water, and thus can, for example, be utilized in cement products [1].

Products with higher added value than cement can be obtained if fly ash is used in the preparation of synthetic zeolites [4]. Zeolites (general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot qH_2O$, where n is the valence of the exchangeable cation M) are cation-exchange materials widely studied and used in wastewater treatment [5]. Synthetic zeolites prepared from fly ash represent only approx. 1/100 of the cost of zeolites synthesized from pure aluminosilicate chemicals [5]. On the other hand, landfilling of fly ash is becoming prohibitively expensive in many cases. Fly ash-based zeolites have been used for the removal of various aqueous pollutants, such as metal(loid)s, ammonium, phosphate, and dyes [6]. It has been shown that zeolite synthesis improves the adsorption properties of fly ash severalfold [7]. The application of fly ash-based zeolites for wastewater treatment implements *the concept of waste removal using wastes*.

The most widely studied and used fly ash for the zeolite synthesis comes from coal combustion (for example class F fly ash) [7]. In contrast, high-calcium-fly ashes are less common zeolite raw materials. Calcium can adversely affect zeolite formation due to competition with sodium for the active sites in the zeolite framework structure and the formation of calcium silicate [8]. The high calcium content of fly ash had an unfavorable impact on the ammonium removal capacity of zeolite [9, 10]. However, effective phosphate removal by high-calcium fly ash-based zeolites has been observed [10–12]. In some cases, high-calcium fly ashes required the addition of silica or alumina in order for zeolite synthesis to occur [3, 13]. Another approach was to remove excessive calcium from fly ash by acid leaching before zeolite synthesis [14].

In the present study, high-calcium fly ash from the paper industry was treated with sodium hydroxide solution in an unconventional hydrothermal activation. The conventional hydrothermal activation involves the liquid/solid (L/S) weight ratio of approximately eight and pressure higher than ambient or alternatively an open reflux system [5]. In the present study, the L/S ratio was significantly lower (0.8) and the synthesis was performed in an open reactor. The obtained material was characterized and experimented with for the removal of several harmful metals (Cu, Co, Zn, Ni, and Cd) and anions (sulfate and phosphate) from single-component model solutions. The purpose of the present study was to preliminarily evaluate the suitability of high-calcium-content fly ash for zeolite synthesis using an unconventional hydrothermal activation.

Materials and methods

Sorbent preparation

Fly ash was obtained from a paper industry power plant. The high calcium content of fly ash results from deinking sludge combustion. Fly ash was mixed with a 14 M NaOH solution for 10 min in the L/S ratio of 0.8. The mixture was cast in a silicone mold and allowed to consolidate for 24 h at 22 °C and for an additional 24 h at 105 °C. This treatment was adapted from a study by Al-Zboon et al. [15]. Obtained material was ground to a particle size of 63–125 µm, washed with deionized water, and dried at 105 °C before use.

Sorbent characterization

The chemical composition of the samples was obtained semi-quantitatively using an X-ray fluorescence (XRF) spectrometer (PanAnalytical Minipal 4). Powder X-ray diffraction (XRD) patterns (range 5–80 °2θ and a scan time of 1.25 s per 0.02 °2θ) were measured with a PanAnalytical Xpert Pro diffractometer with Co Kα radiations generated at 40 kV and 40 mA. Specific surface area and pore volumes of samples were determined using N_2 gas sorption-desorption isotherms at the temperature of liquid nitrogen (-196 °C) by using a Micrometrics ASAP 2020 instrument. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) equation. Pore size distributions were calculated from desorption data obtained using the Barrett-Joyner-Halenda (BJH) method. FTIR (Fourier transform infrared) spectra of samples were measured using an Perkin Elmer Spectrum One FTIR device.

Leaching characteristics of fly ash and the prepared sorbent were studied according to a modified standard procedure [16]. Briefly, the dried fly ash sample (4 g) was shaken with deionized water (16 mL) for 6 h. Solids were separated by filtration through a 0.45 µm membrane filter. In the next step, solids and the filter paper were shaken with 40 mL of deionized water for 18 h. Again, a similar filtration procedure was used for the separation of solids. The results are calculated as mg of leached element per kg of material. The leachate samples were analyzed using an optical emission spectrometer (Thermo Electron IRIS Intrepid II XDL Duo) according to a standard procedure [17].

Sorption experiments

The removal of metals (Cu, Co, Zn, Ni, and Cd) and anions (sulfate and phosphate) was studied from single-component model solutions prepared of laboratory grade salts ($Cu(NO_3)_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, $NiSO_4 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, Na_2SO_4, and KH_2PO_4) in deionized water. The removal experiments were done in batch mode. In the metal removal experiments, the studied factors were sorbent dose (range 0.05–5 g/L, metal concentration 50 mg/L, contact time 24 h), contact time (range 1–1440 min, sorbent dose 1–4 g/L, metal concentration 50 mg/L), and metal concentration (range 2 – 75 mg/L, sorbent dose 1 g/L, contact time 24 h). Sulfate removal was studied with a similar set-up, except sorbent doses ranged from 1–10 g/L and sulfate concentrations ranged from 50–5000 mg/L. In phosphate removal experiments, sorbent doses were 0.1–1 g/L and phosphate concentrations 0.05–10 mg/L. The solution pH was adjusted to 2.0 before all experiments in order to avoid the precipitation of metals. Sorbent was separated from solutions by means of centrifuging (3000 rpm, 3 min). The metal concentrations were analyzed using an optical emission spectrometer (Thermo Electron IRIS Intrepid II XDL Duo) [17]. Sulfate and phosphate concentrations were analyzed with a flow injection analysis system (Foss-Tecator Fiastar 5000). The isotherm and kinetics modelling was performed with the Origin software.

Results and Discussion

Sorbent characterization

According to the diffractograms (Fig. 1), gehlenite ($Ca_2Al[AlSiO_7]$) is possibly the phase in fly ash that provides aluminosilicate for zeolite (sodalite, $Na_8(Al_6Si_6O_{24})Cl_2$, and zeolite Y, $(Na_2,Ca,Mg)_{3.5}[Al_7Si_{17}O_{48}]\cdot 32(H_2O)$) formation. According to the Riedveld analysis of the XRD data, sodalite and zeolite Y were formed in the amounts of 13% and 3%, respectively. The FTIR spectra (Fig. 2) shows that the peak at approx. 980 cm^{-1} is intensified, and new peaks appear at 650–730 cm^{-1} as a result of alkali treatment. Regions 950–1500 cm^{-1} and 660–670 cm^{-1} contain asymmetric and symmetric stretching vibrations of Si-O and Al-O bonds, respectively [18]. The semi-quantitative elemental composition, loss on ignition, specific surface area, and pore volumes are shown in Table 1. The raw fly ash material contains a significant amount of CaO (59.28%) but the sum of SiO_2, Al_2O_3, and Fe_2O_3 does not exceed 50%. This indicates that the fly ash cannot be classified as class C fly ash, which would be readily usable in cement products [19]. The alkali treatment of fly ash decreases the concentration of Al and Si due to the alkaline dissolution of reactive aluminosilicates. The high calcium content in fly ash has been reported to form Ca-Al-Si gel and result in microstructural porosity as a result of alkali treatment [20–22]. The increased micro, meso, and macro pore surface areas (Table 1) indicate the increased porosity.

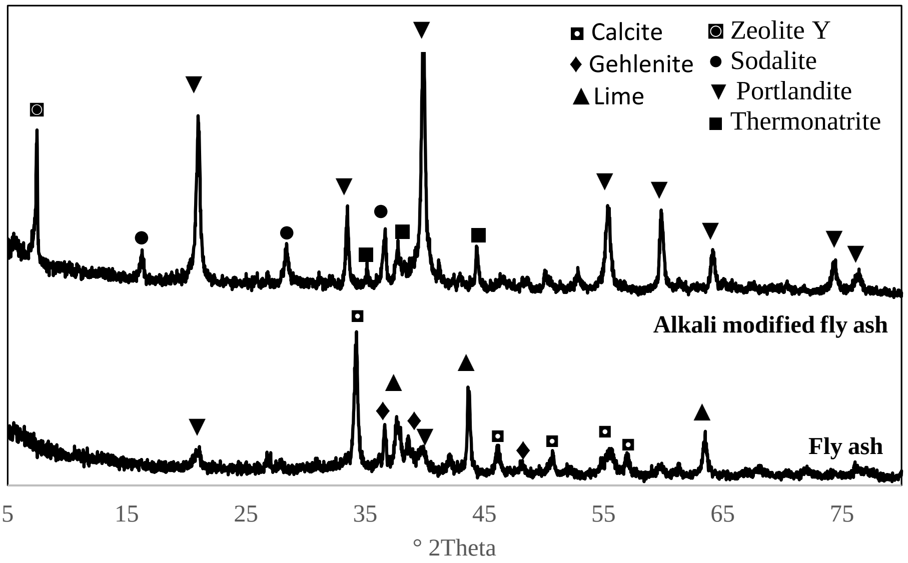

Fig 1. Diffractograms of fly ash and alkali modified fly ash.

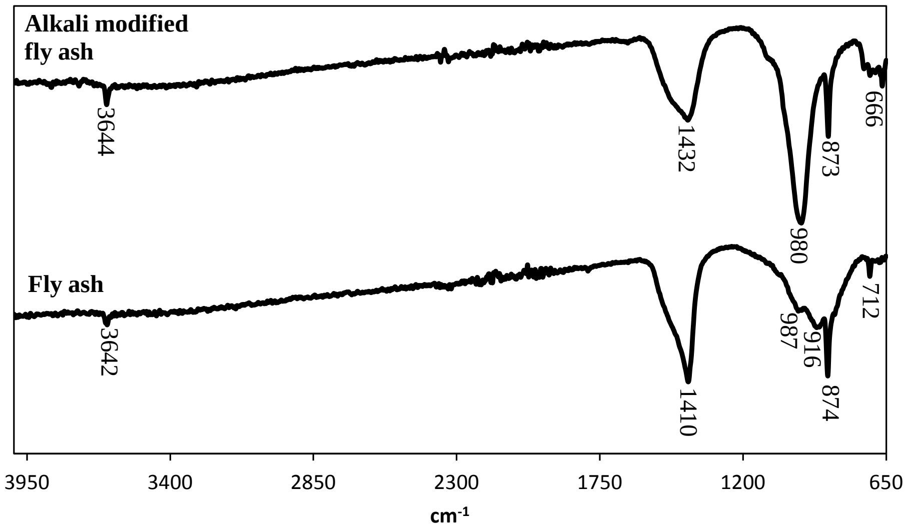

Fig. 2. Infrared spectra of fly ash and alkali modified fly ash.

Table 1. Elemental composition, loss on ignition, surface area, and pore volumes of fly ash and prepared sorbent.

Parameter	Fly ash	Alkali modified fly ash
CaO [%]	59.28	44.18
SiO_2 [%]	13.87	11.04
Na_2O [%]	0.00	15.04
Al_2O_3 [%]	8.91	7.24
Fe_2O_3 [%]	1.37	0.56
SO_3 [%]	0.52	0.32
Cl [%]	0.27	0.18
K_2O [%]	0.42	0.23
Ti [%]	0.24	0.19
Mn [%]	0.03	0.02
Ni [%]	0.00	0.00
Cu [%]	0.04	0.03
Zn [%]	0.03	0.03
Ba [%]	0.04	0.03
Pb [%]	0.02	0.02
P_2O_5 [%]	0.13	0.00
Loss on ignition [%]	14.29	17.31
Specific surface area [m^2/g]	9.80	22.16
Micropore area [m^2/g]	0.29	2.01
Meso and macropore area [m^2/g]	9.51	20.14
Average pore width [nm]	15.45	20.62

The leaching characteristics of raw fly ash and alkali-treated fly ash are shown in Table 2. The alkali treatment of fly ash increased the leaching of several elements (Al, B, Cr, Cu, K, Na, Ni, P, S, and Zn) of which Al and Cr are significant due to the magnitude of their release and toxicity. This might restrict the use of the prepared sorbent in some cases. Consequently, the synthesis method could be altered to produce a chemically more stable end product; alternatively, the raw material could be purified, e.g., by acid-washing fly ash prior zeolite synthesis [14]. Other elements that showed an increase in leaching were less or non-toxic or their concentrations were low. On the other hand, the alkali treatment of fly ash significantly decreased the leaching of Ba and Ca. Several toxic elements (As, Cd, Co, Pb, and Sb) were below the detection limit and the treatment had no impact on their leaching behavior.

Table 2. Leaching properties of fly ash and the prepared sorbent.

[mg/kg]	Fly ash		Alkali modified fly ash	
	1st step (L/S = 4)	2nd step (L/S = 14)	1st step (L/S = 4)	2nd step (L/S = 14)
Al	6.80	7.73	9.74	26.2
As	< 0.03	< 0.17	< 0.03	< 0.17
B	0.07	0.47	0.54	1.89
Ba	17.34	53.86	0.17	2.07
Ca	1396	7535	28.80	555.2
Cd	< 0.004	< 0.022	< 0.004	< 0.022
Co	< 0.006	< 0.033	< 0.006	< 0.033
Cr	< 0.02	< 0.1	0.60	2.04
Cu	0.04	0.06	0.11	0.24
Fe	0.20	0.09	0.09	0.07
K	228	448	312	944
Mg	0.86	0.73	0.26	0.26
Na	80.4	236	9400	28284
Ni	< 0.01	< 0.06	0.01	0.06
P	< 0.10	< 0.50	0.42	0.90
Pb	< 0.03	< 0.17	< 0.03	< 0.17
S	2.36	5.79	120	257
Sb	< 0.030	< 0.166	< 0.030	< 0.166
Zn	0.03	0.01	0.16	0.15

Sorption results

As the initial concentration of metals or anions (Fig. 3) increased, the removal efficiency decreased. This was possibly due to the saturation of the sorbent surface. In the case of zinc and sulfate in particular, there was a drastic drop in the removal percentage. Nickel and cadmium had a low removal efficiency in the concentration range. The cobalt and copper removal decrease as a function of concentration was less pronounced. The sorbent was capable of removing sulfate especially at concentrations below 2000 mg/L, which indicated that the removal mechanism was based on adsorption and not on the gypsum ($CaSO_4 \cdot 2H_2O$) precipitation, which is the widely used sulfate removal method. The gypsum solubility (approx. 2.05 g/L at 20°C) prevents low sulfate concentrations being reached with the gypsum precipitation method [23]. Interestingly, the removal of phosphate increases as a function of initial concentration. This indicates that the removal might be based on the (surface)precipitation of calcium phosphate as it requires certain concentration of phosphate in order to occur.

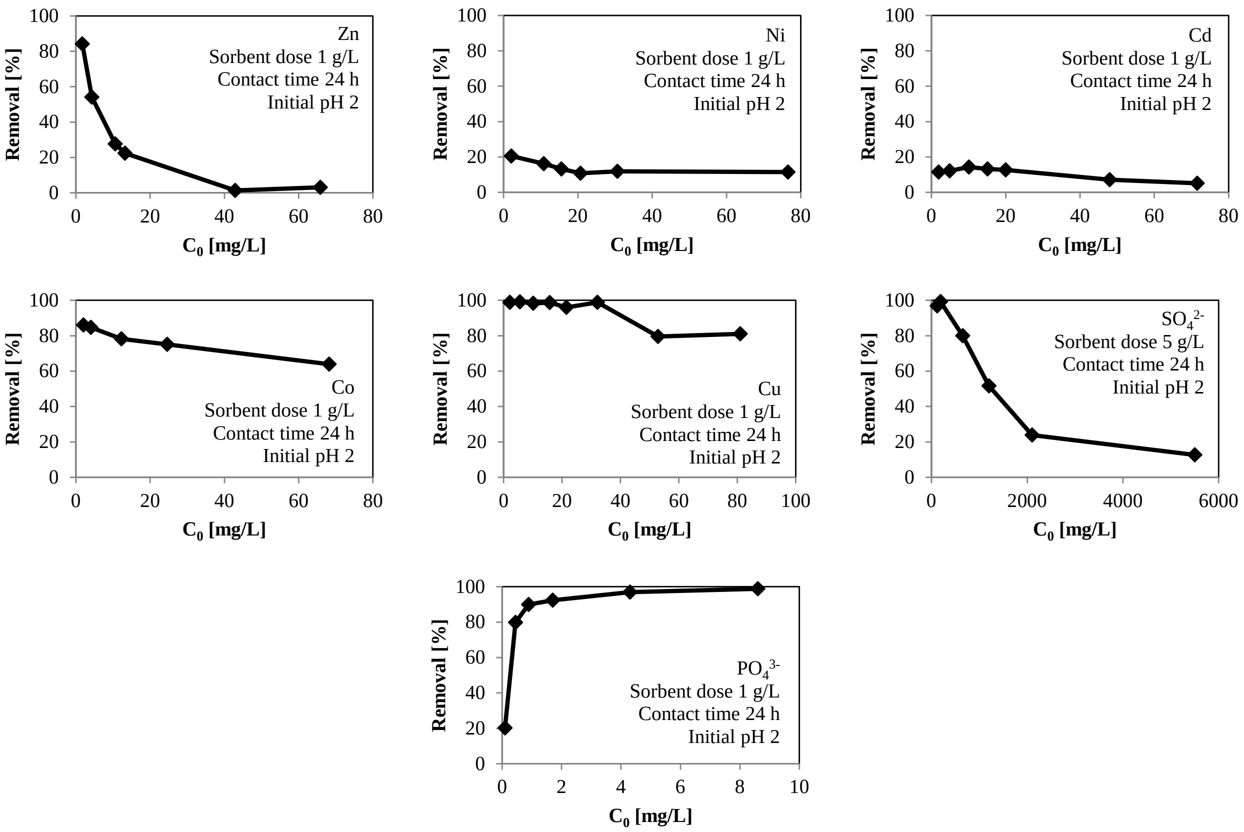

Fig. 3. Effect of initial concentration on the removal of metals and anions.

On the basis of the data presented in Fig. 3, an isotherm fitting was performed. In this case, the isotherm model best describing the sorption was the Sips isotherm (also known as the Langmuir-Freundlich isotherm):

$$q_e = \frac{q_m(KC_e)^n}{1+(KC_e)^n} \tag{1}$$

where q_e (mg/g) is the sorption amount at equilibrium, q_m (mg/g) is the maximum removal capacity of sorbent, K (L/mg) is the sorption coefficient, C_e (mg/L) is the sorbate concentration at equilibrium, and n (dimensionless) is the exponent describing the heterogeneity of the sorbent surface. The obtained parameters are shown in Table 3. The isotherm modelling could performed satisfactorily in the case of Cd, Co, and SO_4^{2-} ($R^2 > 0.9$), whereas the modelling of Zn, Ni and PO_4^{3-} was less successful. The maximum monolayer capacities (q_m) indicate that Ni, Co and especially SO_4^{2-} could be removed reasonably effectively.

Table 3. Isotherm Parameters.

	q_m [mg/g]	K [L/mg]	n	R^2
Zn	2.62	4.17	1.44	0.62
Ni	10.18	0.04	3.57	0.86
Cd	3.99	0.08	1.55	0.99
Co	27.64	0.19	1.19	0.94
SO_4^{2-}	151.62	0.029	0.53	0.97
PO_4^{3-}	0.95	10.84	179.76	0.53

Zinc, nickel, sulfate, and phosphate removal increased linearly as the dose of sorbent increased (Fig. 4). Cadmium, cobalt and copper, on the other hand, underwent an irregular increase in terms of removal at doses higher than 1 g/L. This was probably due to the increase in the pH as the sorbent dose increased. The precipitation of $Cd(OH)_2$, $Co(OH)_2$, and CuO takes place at a pH higher than 8, 8, and 5, respectively. These pH values were exceeded as the doses were over 1 g/L. Consequently, the initial adjustment of solution pH to 2 was not sufficient to prevent the precipitation of metals at higher sorbent doses in all cases.

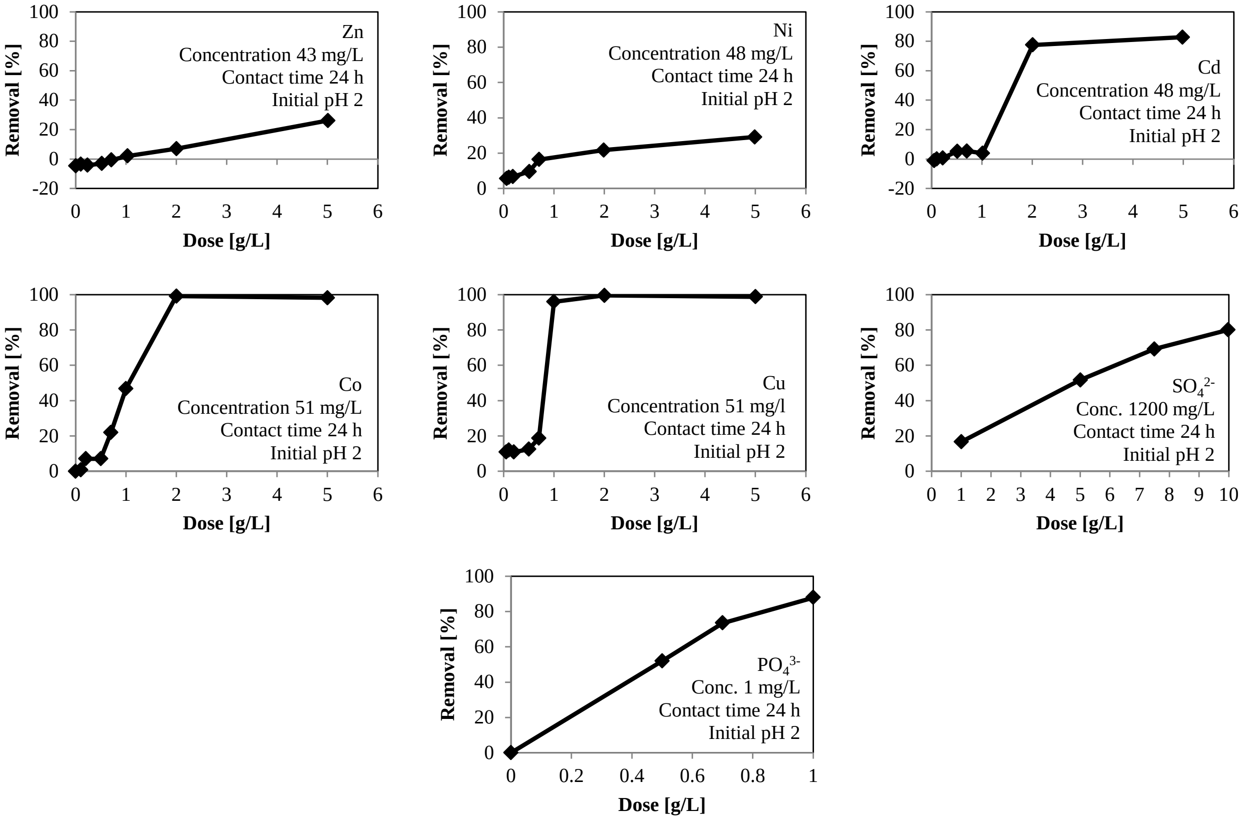

Fig 4. Effect of sorbent dose on the removal of metals and anions.

The effect of contact time is shown in Fig. 5. Most of the removal occurred within the first two minutes in the case of zinc and copper. Cadmium removal was somewhat slower, and the removal percentage increased until the 24 h contact time was reached. Phosphate removal saturated after approx. 280 min. Nickel, on the other hand, was not removed effectively at all. Visa [18] also observed poor nickel removal by fly ash-based zeolite NaP1. Kinetic modelling of the obtained results was performed and the pseudo second order rate equation proved to the best to describe the data. The equation can be presented in an integrated form as follows:

$$\frac{t}{q_t} = \frac{1}{k_{p2} q_e^2} + \frac{t}{q_e} \qquad (2)$$

where q_t is sorption amount at time t (min), and k_{p2} is the pseudo-second-order rate equilibrium constant (g/(mg min)). The results of the kinetics modelling are shown in Table 4.

Table 4. Kinetic modelling parameters.

Metal	C_0 [mg/L]	m (g/L)	Removal [%]	q_e (exp) [mg/g]	q_e (cal) [mg/g]	k_2 [g/(mg min)]	R^2
Zn	50	5	99.8	9.38	9.62	-0.013	0.99
Ni	50	1	5.56	2.69	2.74	0.068	0.99
Cd	50	2	98.4	23.73	24.69	0.00081	0.99
Co	50	2	99.8	24.95	25.13	0.0070	0.99
Cu	50	1	99.8	47.62	47.62	0.34	1
SO_4^{2-}	1500	5	33.3	100	100	0.0003	0.99
PO_4^{3-}	1	1	87.9	0.80	0.81	0.064	0.99

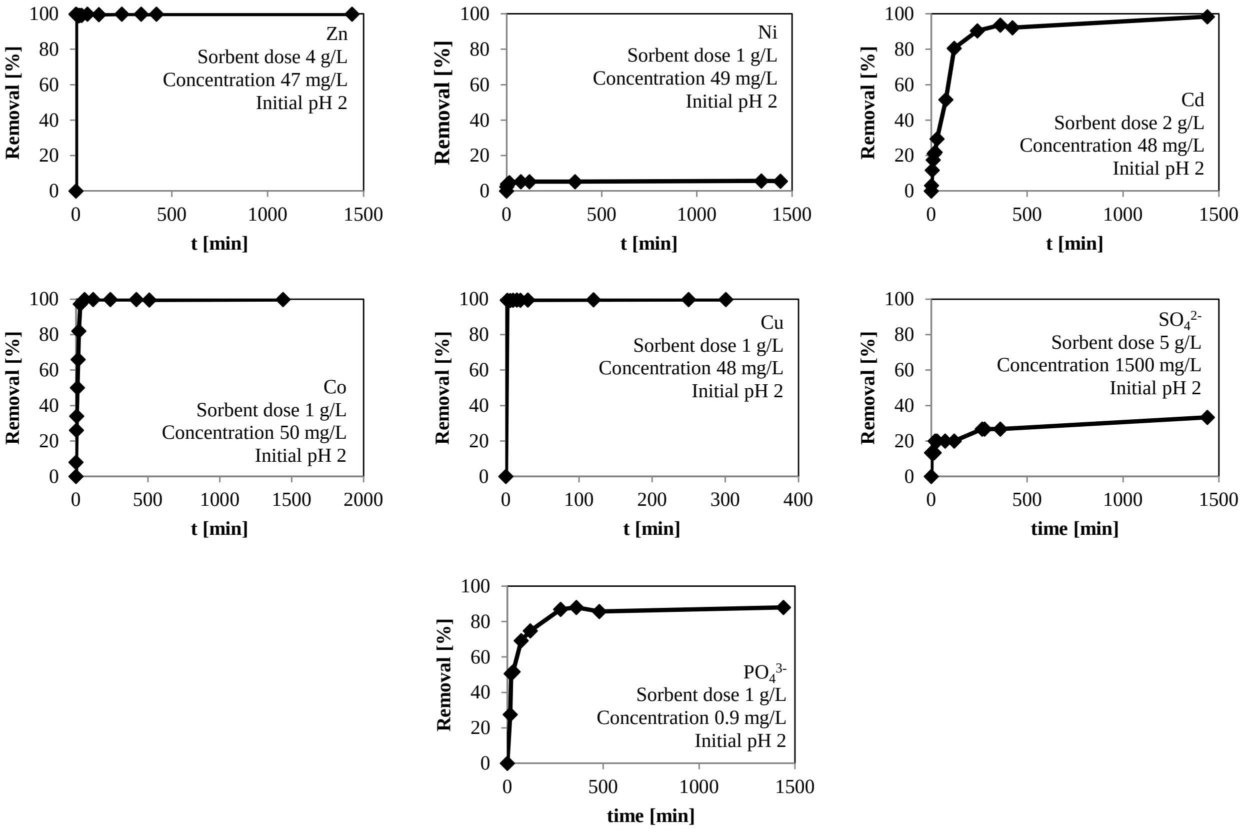

Fig 5. Effect of contact time on the removal of metals and anions.

Conclusions

In the present study, we prepared a sorbent material from high-calcium-content fly ash using an unconventional hydrothermal treatment. The unconventional aspects were a high NaOH concentration (14 M), a low liquid/solid ratio (0.8), and an open reactor in the synthesis. The obtained material contained zeolitic phases, i.e., 13% of sodalite and 3% of zeolite Y. The sorbent was experimented with for the removal of metals (Cu, Co, Zn, Ni, and Cd) and anions (sulfate and phosphate) from single-component model solutions. The performance of the sorbent proved to be promising in terms of observed sorption capacities and kinetics. However, we were able to point out some problems, such as leaching, that can be encountered when processing waste materials into sorbents. The leaching experiments showed an increased release of Cr and Al after hydrothermal treatment. A possible solution could be, for example, acid washing before zeolite synthesis. The following concluding remarks are made:

- High calcium content fly ash from the paper industry proved to be a suitable raw material for zeolite synthesis.
- The removal of Cu, Co, Zn, Cd, sulfate and phosphate proved promising; Ni removal was less efficient.
- The leaching of Cr, Al, and, to a lesser extent, Zn increased as a result of zeolite formation, whereas the leaching of Ba diminished. Leaching needs efficient washing or stabilizing.

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