

Removal of trivalent chromium from aqueous solution by zeolite synthesized from coal fly ash

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Abstract

The capability of 14 zeolites synthesized from different fly ashes (ZFAs) to sequester Cr(III) from aqueous solutions was investigated in a batch mode. The influence of pH on the sorption of Cr(III) was examined. ZFAs had a much greater ability than fly ash to remove Cr(III), due to the high cation exchange capacity (CEC) and the high acid neutralizing capacity (ANC) of ZFAs. The mechanism of Cr(III) removal by ZFAs involved ion exchange and precipitation. A high-calcium content in both the fly ashes and ZFAs resulted in a high ANC value and, as a result, a high immobilization capacity for Cr(III). The pH strongly influenced Cr(III) removal by ZFAs. Inside the solubility range, removal of chromium increased with increasing pH. Hydroxysodalite made from a high-calcium fly ash had a higher sorptive capacity for Cr(III) than the NaP1 zeolite from medium- and low-calcium fly ashes. On the other hand, at pH values above the solubility range, the efficiency of chromium removal by the ZFAs approached 100% due to the precipitation of Cr(OH)₃ on the sorbent surfaces. It is concluded that ZFAs and high-calcium fly ashes may be promising materials for the purification of Cr(III) from water/wastewater.

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1. Introduction

Chromium is one of the regulated toxic heavy metals in the environment. This element exists in nature mainly in two oxidation states, +3 and +6. Trivalent chromium is extensively used in the leather tanning, paints and pigments, and fungicides industries and in ceramic and glass manufacture. Although trivalent chromium is considerably less toxic than hexavalent chromium, its disposal as a dissolved species in natural waters or as sludge in soils may pose serious health risks because it can be oxidized to hexavalent chromium in the environment [1]. The drinking water guideline recommended by USEPA is 100 µg/L. The legal discharge limit of Cr(III) varies from 0.05 mg/L (in surface waters) to 2.0 mg/L (in sewers) depending on the processing, country, and wastewater treatment methods [2].

Several treatment technologies have been developed to remove chromium from water and wastewater; with chemical

precipitation, especially chromium hydroxide precipitation, the most commonly used method today. The disadvantage of precipitation is the production of high volumes of sludge, which are difficult to deal with. Another shortcoming is that precipitation can only effectively remove chromium from water/wastewater containing relatively high initial chromium concentrations (usually above 100 mg/L) [3]. To overcome these problems, the process of sorption appears to be one of the most promising alternative techniques for trivalent chromium removal. However, use of commercially available sorbents, such as polymeric resins and activated carbons, is not economically appealing. As a result, numerous low cost natural materials, wastes, and products synthesized from wastes have recently been widely investigated as potential replacements for the effective but expensive commercial synthetic sorbents. These novel sorbents include activated carbon produced from organic wastes [4,5], plant-based organic residues such as saltbush [6], coir pith [7], carrot residues [8], *Aspergillus* biomass [9], brown seaweed [10] and cork powder [11]; organic matter-based wastes such as wine processing waste sludge [12] and biogas residual slurry [13]; alginate-based materials such as composite alginate–goethite beads [14] and

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protonated dry alginate beads [15]; fly ashes such as bagasse fly ash [16] and palm oil fuel ash [17]; as well as natural zeolites [18].

Zeolites synthesized from fly ash (ZFA) have a high cation exchange capacity (CEC) [20–28]. Our previous study reported the high potential of ZFAs for removing ammonium from wastewater [24,25]. Several other groups have tested the efficiency of ZFAs for heavy metal removal from wastewater and showed that ZFAs could effectively retain heavy metals, including trivalent chromium [26–29]. However, detailed studies on the retention of trivalent chromium by ZFAs are still lacking. Unlike mono- and divalent metal ions, speciation of trivalent chromium is strongly influenced by the pH in aqueous solution and thus its behavior is more complex. Furthermore, previous studies did not compare the feasibility of ZFAs for heavy metal removal with raw fly ash, which is also a low-cost material [19].

The aims of the present paper were (1) to evaluate the potential of ZFAs as a sorbent for trivalent chromium by comparison with raw fly ashes and other sorbents, (2) to study the mechanism of Cr(III) retention by ZFAs and (3) to provide useful information for the selection of raw fly ashes to synthesize ZFAs that are effective for Cr(III) removal. For these purposes, experiments on Cr(III) removal were performed on 14 ZFAs and their corresponding raw fly ashes. The experiments were also conducted as a function of pH for three representative ZFAs. The relationships of Cr(III) removal to the composition and properties of the different ZFAs are discussed.

2. Materials and methods

2.1. Materials

Coal fly ashes of different coal origins and chemical composition were collected from thermal power plants in China. For ZFA preparation, approximately 25 g of fly ash was placed in a flask and mixed with 150 mL of 2.0 mol/L NaOH solution. The slurry was boiled with reflux for 48 h, with stirring. The solid phase was separated by centrifugation and washed with doubly distilled water five times and with ethanol twice. A high liquid/solid ratio (40 mL/g) was used to wash away the residual NaOH. Finally, the products were dried in an oven at 45 °C, ground to pass through an 80-mesh sieve, and stored in airtight containers for the subsequent experiments. For comparison purposes, the fly ashes were sieved to pass an 80-mesh sieve and used without any other pretreatments.

2.2. Characterization of the materials

Identification of the crystalline phase(s) in the materials was carried out with XRD equipment (D8 ADVANCE) using Ni-filtered Cu K α radiation (40 kv, 40 mA). For the chemical analysis, except for silicon, the fly ashes and ZFAs were digested with hydrogen fluoride in conjunction with perchloric acid and dissolved later by hydrochloric acid. For silicon, the samples were melted with sodium hydroxide. The elemental concentrations were then measured in the digestions by Inductively coupled plasma atomic emission spectrometry (IRIS advantage

1000). The CEC was determined using the ammonium acetate method [30]. About 0.4 g of the samples was first washed five times with a 1.0 mol/L ammonium acetate solution. To remove residual ammonium that was not held by the sample, the solid was further washed with doubly distilled water and ethanol until free from chloride ion (checked with a 1N AgNO $_3$ solution). Finally, the residue was washed five times with a 1.0 mol/L NaCl solution and the released ammonium was determined by the Nessler method [31]. The CECs were thus calculated and expressed as cmol per kilogram of solids.

2.3. Cr(III) sorption tests

The immobilization experiment was done on all fly ashes and ZFAs using an initial Cr(III) concentration of 400 mg/L with a pH value of 3.30 and prepared from doubly distilled water and CrCl $_3$ ·6H $_2$ O of analytical reagent grade. Forty ml of the aqueous solution was added to centrifuge tubes containing 0.4 g of the sample. The tubes were sealed with screw-type lids and then continuously agitated on an orbital shaker at 200 rpm for 4 h at laboratory temperature (ca. 20 °C). A reaction time of 4 h was found to be sufficient for Cr(III) to achieve equilibrium in preexperiments. After 4 h, the pH of the suspensions was measured with a Hach 51910 pH meter and then they were centrifuged. The Cr(III) of the supernatants were determined using a Unico spectrophotometer (model UV-2102PCS). The Cr(III) was first converted into the hexavalent form after oxidation with potassium permanganate at elevated temperature and acidic conditions and then the Cr(VI) concentration was determined at 543 nm following the 1,5-dephenyl-carbazide method [31]. The efficiencies of Cr(III) removal were calculated from the differences between the initial and the final Cr concentrations in solution. The blanks containing no sample were always included in the experiments but no significant retention of Cr(III) by the tube was observed. The experiments were performed in duplicate and the mean data are reported.

The effect of pH on Cr(III) immobilization and the sorption isotherm at a constant pH 4 (± 0.1) were investigated using three representative ZFAs with low, medium and high-calcium contents.

2.4. Acid neutralizing capacity (ANC)

A batch titration procedure was adopted with the three representative ZFAs and their corresponding fly ashes to determine the ANC and to examine the dissolution of the materials at different pH values. A low solid to water ratio (1:100) was employed to avoid the supersaturation of Ca with respect to gypsum [32].

Approximately 0.4 g of each sample was put into centrifuge tubes that were previously acid leached and thoroughly rinsed with doubly distilled water. Forty ml of doubly distilled water and appropriate volumes of 1.0 mol/L HCl were added to the tubes to achieve amounts of H $^+$ ranging from 0 to 8.5 mmol H $^+$ /g of the solid sample. The tubes were immediately sealed with screw-type lids to avoid any contact between the solutions and the atmosphere. The solutions were continuously agitated on

an orbital shaker at 200 rpm for 24 h at laboratory temperature (ca. 20 °C). After being shaken, the solution pH values were determined. The suspensions of the ZFAs with pH values of about 4, 7, and 11 for each ZFA were subsequently centrifuged. The supernatants were determined for concentrations of Na, K, Ca, Mg, Fe, Al by ICP-AES. For each sample, the titration curve of pH versus acid added was drawn to estimate the ANC, which was the amount of acid required to obtain a specific pH value.

2.5. Maximum immobilization capacity

Repeated batch equilibrations were conducted to measure the maximum immobilization capacity of the three representative ZFAs and fly ashes for Cr(III). Forty milliliters of Cr(III) solution with an initial concentration of 200 mg Cr(III)/L and a pH value of 3.36 was put into a pre-weighed centrifuge tube (W1) containing 0.4 g dw of sample (W2). After being shaken for 4 h, the suspension was centrifuged, the supernatant was poured into another container, and the tube with the residue was weighed again (W3). The volume of the residual solution (V) was calculated by assuming the density of the residual solution as 1 g/ml: $V \text{ (ml)} = W3 \text{ (g)} - W1 \text{ (g)} - W2 \text{ (g)}$. The obtained supernatant was analyzed for Cr(III) concentration (C) and the amount of the remaining Cr(III) that was not sorbed by the sample (R), as well as the amount of Cr(III) sorbed by the sample (S), were calculated by the equations: $R \text{ (mg)} = [V \text{ (ml)} C \text{ (mg/L)}]/1000$ and $S \text{ (mg/g)} = [200 - C \text{ (mg/L)} 0.04 \text{ L}]/W2 \text{ g}$. The volume of the residual solution and the amount of the remaining Cr(III) were considered in the calculation of the initial volume and the initial concentration of the subsequent equilibration step. A fresh solution of the same Cr(III) concentration was added and equilibration was repeated until no further uptake by the ZFA was observed. The amount of retained Cr(III) was thus calculated. The experiments were performed in triplicate, and the mean data as well as the calculated standard deviation value are reported.

3. Results and discussion

3.1. Characterization of the materials

The main chemical composition of the ZFAs and their raw fly ashes is given in Table 1, which shows that the SiO₂ content decreased significantly and consistently. No other consistent changes appeared in the chemical composition following the synthesis process. Both the ZFAs and their raw fly ashes were constituted mainly of Si and Al components, followed by Ca and Fe components, while the MgO content was very low. The total content of the above five components decreased by 17.3% on average as a result of the formation of zeolites. This decrease could be ascribed to the increases in the Na₂O and water contents. The negative charge of the ZFAs produced was saturated chiefly by Na⁺ as a result of the use of concentrated NaOH solution in the zeolite conversion process, while the water holding capacity will increase with the formation of zeolite (zeolitic water) [25].

The mineralogical composition and the CEC value of the materials are listed in Table 2. Analysis by the X-ray diffraction method revealed that the major crystalline phases in the fly ashes are quartz, mullite and calcite, together with the amorphous component, which was revealed by the very wide reflection at low 2θ values (~3–18°) on the XRD patterns. The activation of fly ash by an alkaline solution resulted in the great increase in CEC value due to the formation of zeolite, in which a negative charge is constantly generated by an electrical imbalance among the aluminum atom and four oxygen atoms. The monomineral of the NaP1 zeolite (Na₆Al₆Si₁₀O₃₂·12H₂O) was produced following the alkaline activation process for all fly ashes except the Nanshi and Wujin F fly ashes, from which mainly hydroxysodalite (Na_{1.08}Al₂Si_{1.68}O_{7.44}·1.8H₂O), with a small amount of NaP1 as a secondary zeolitic phase, were formed. These two fly ashes typically had high CaO contents compared with the other fly ashes; it thus appears that a high CaO content (>16%) might enable the formation of hydroxysodalite.

Table 1
Main chemical composition of fly ashes and ZFAs studied (wt.%)

No	Material	SiO ₂ (%)		Al ₂ O ₃ (%)		Fe ₂ O ₃ (%)		CaO (%)		MgO (%)	
		Fly ash	ZFA	Fly ash	ZFA	Fly ash	ZFA	Fly ash	ZFA	Fly ash	ZFA
1	Xiamen	46.44	34.20	35.27	32.26	5.55	4.84	5.80	5.31	0.83	0.66
2	Minhang	49.30	34.10	33.01	32.41	4.84	4.96	2.98	3.07	0.95	0.72
3	Shenzhen	47.16	36.14	22.31	29.02	5.78	6.73	3.81	3.65	1.43	0.66
4	Shidongyichang C ^a	49.44	34.96	30.22	20.88	4.96	5.31	3.48	3.65	1.01	1.07
5	Wujin C	47.00	35.62	19.90	15.68	9.91	7.79	13.84	11.03	1.25	1.07
6	Wujin F ^b	42.16	30.74	17.34	14.47	10.62	8.50	16.08	12.10	1.49	1.31
7	Waigaoqiao	45.88	34.46	22.91	18.09	9.91	7.32	10.94	8.54	1.43	1.19
8	Shidongerchang C	51.36	38.06	22.13	18.54	9.70	8.50	6.90	6.13	1.61	1.31
9	Shidongerchang F	52.56	38.04	23.42	20.65	9.23	8.50	6.31	5.72	1.25	1.25
10	Yangpu C	49.80	31.98	38.53	42.36	3.79	4.13	2.16	2.57	0.36	0.36
11	Yangpu F	65.36	39.86	20.24	22.54	4.38	5.19	2.58	3.15	1.61	1.61
12	Datong	50.92	31.46	32.63	34.97	7.81	10.27	2.08	2.49	0.66	0.60
13	Baoshan	51.11	37.60	15.66	18.16	9.41	8.14	8.32	7.30	0.98	0.89
14	Nanshi	34.36	29.30	17.91	14.47	10.40	7.20	20.37	13.26	1.52	1.07

^a C refers to coarse fly ash and zeolite synthesized from coarse fly ash.

^b F refers to fine fly ash and zeolite synthesized from fine fly ash.

Table 2
Mineralogical composition and CEC value of fly ashes and ZFAs investigated

No	Material	CEC (cmol/kg)		Mineralogical composition ^a			
		fly ash	ZFA	Major ^b	Minor ^b	Major ^c	Minor ^c
1	Xiamen	<3	139.0	Am	M, Q	P	M
2	Minhang	<3	159.6	Am	M, Q	P	M
3	Shenzhen	<3	155.7	Am	M, Q	P	M, Q
4	Shidongyichang C ^d	<3	144.4	Am	Q, M	P	M, Q
5	Wujin C	<3	208.9	Am	Q, M	P	M, Ca
6	Wujin F	<3	103.0	Am	Q, M	HS	P, M, Ca
7	Waigaoqiao	<3	201.0	Am	Q, M	P	M, Q
8	Shidongerchang C	<3	187.2	Am	Q, M	P	M, Q
9	Shidongerchang F ^e	<3	168.5	Am	Q, M	P	Q, M
10	Yangpu C	<3	103.3	Am	M, Q	P	M
11	Yangpu F	<3	159.6	Am	Q, M	P	Q, M
12	Datong	<3	88.2	Am	M, Q	P	Q, M
13	Baoshan	<3	213.0	Am	Q, M	P	Q, M, Ca
14	Nanshi	<3	101.0	Am	Ca, Q, M	HS	Ca, M, Q, P

^a Am = amorphous material; Q = quartz; M = mullite; Ca = calcite; P = NaP1 zeolite; HS = hydroxysodalite.

^b Fly ash.

^c ZFA.

^d C refers to coarse fly ash and zeolite synthesized from coarse fly ash.

^e F refers to fine fly ash and zeolite synthesized from fine fly ash.

3.2. Retention of Cr(III) by fly ashes and ZFAs

The efficiency of Cr(III) removal by all the ZFAs and raw fly ashes was investigated as shown in Fig. 1. It is clear that the retention of Cr(III) by the ZFAs was greater than by the fly ashes. Although the high CEC value of the ZFAs, an indicator of the ability to hold cations, apparently contributed to the Cr(III) elimination, the difference in CEC values between the fly ashes and ZFAs was not the only reason accounting for the difference in Cr(III) removal.

Despite the lack of CEC, some fly ashes still had very high (Wujin C, Wujin F, Waigaoqiao and Nanshi) or considerable

(Minhang, Shidongerchang C, Shidongerchang F and Baoshan) purification capabilities for Cr(III) (Fig. 1). These fly ashes had relatively high CaO contents compared with the other fly ashes (Table 1). The Cr(III) removal was negligible for the remaining fly ashes with low CaO contents. Similarly, the ZFAs with high CaO contents showed much greater efficiencies for Cr(III) removal than those with low CaO contents.

The final pH values for the fly ashes and the ZFAs in contact with 400 mg/L of CrCl₃ solution are given in Fig. 2. By taking the K_{sp} value of Cr(OH)₃ as 1×10^{-30} , the pH value at which the precipitation of chromium hydroxide takes place with the initial Cr(III) concentration of 400 mg/L is calculated as 4.71, shown as a dotted line in Fig. 2. From Figs. 1 and 2, It is evident that the fly

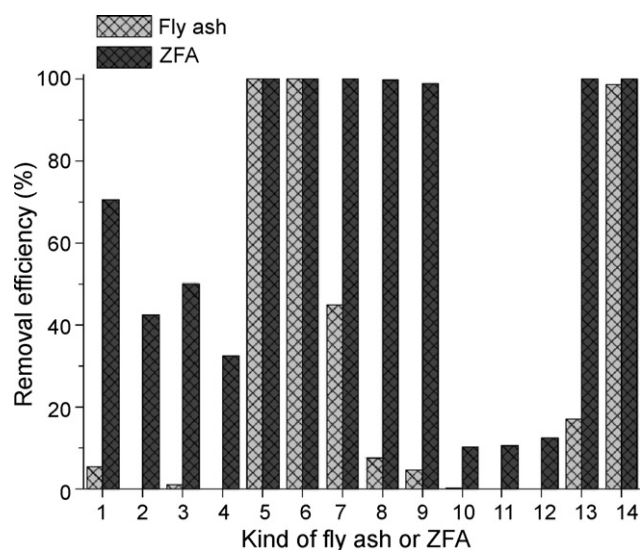


Fig. 1. Efficiency of Cr(III) removal at a concentration of 400 mg/L by fly ashes and ZFAs investigated. 1, Xiamen; 2, Minhang; 3, Shenzhen; 4, Shidongyichang C; 5, Wujin C; 6, Wujin F; 7, Waigaoqiao; 8, Shidongerchang C; 9, Shidongerchang F; 10, Yangpu C; 11, Yangpu F; 12, Datong; 13, Baoshan; 14, Nanshi.

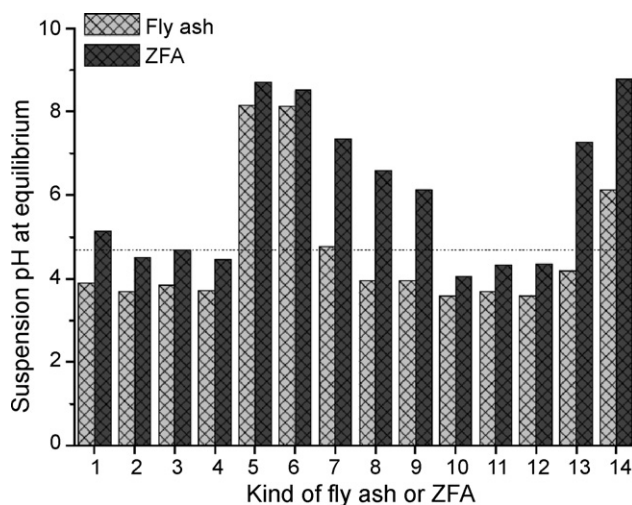


Fig. 2. Equilibrium suspension pH value of fly ashes and ZFAs in contact with 400 mg/L of Cr(III) solution. 1, Xiamen; 2, Minhang; 3, Shenzhen; 4, Shidongyichang C; 5, Wujin C; 6, Wujin F; 7, Waigaoqiao; 8, Shidongerchang C; 9, Shidongerchang F; 10, Yangpu C; 11, Yangpu F; 12, Datong; 13, Baoshan; 14, Nanshi.

ashes and ZFAs with equilibrium pH values exceeding 4.71 had significantly higher efficiencies of Cr(III) removal than those with equilibrium pH values lower than 4.71. It is also obvious from Table 1 and Fig. 2 that a high final pH corresponded well with a high CaO content, and vice versa.

The CrCl₃ solution with a concentration of 400 mg/L is acidic in nature (pH 3.30) (wastewaters resulting from operations employing trivalent chromium are usually similarly acidic) while both the fly ashes and the ZFAs had alkaline pH values within the range from 11.21 to 12.55 when in contact with doubly distilled water (data not shown). As a result, mixing of CrCl₃ with fly ashes or ZFAs raised the pH of the CrCl₃ solution, causing the formation of chromium hydroxide when the final pH exceeded the precipitation limit. Therefore, it appears that precipitation as chromium hydroxide also played an important role in Cr(III) immobilization by the fly ashes and ZFAs. As seen in Fig. 2, the equilibrium pH values for ZFAs are higher than for fly ashes. This indicates that the acid neutralizing capacity of ZFAs was greater than the fly ashes, favoring the efficiency of the decontamination process.

3.3. Acid neutralizing capacity of fly ashes and ZFAs

The titration curves of the three representative ZFAs and raw fly ashes with low, medium and high CaO contents are shown in Fig. 3. Each ZFA exhibits much higher acid buffering capacity than its corresponding fly ash, except for the Wujin F ZFA, which showed a lower buffering capacity at pH values >9 than the Wujin F fly ash. For both the fly ashes and the ZFAs, the ANC increased with increasing CaO content. A titration end point at pH 4.71, which is the precipitation limit for 400 mg/L of CrCl₃ solution, may be considered useful here. Based on the titration curves, the ANC_{4.71} was estimated to be 0.5, 2.3, and 4.0 mmol H⁺/g, respectively, for the fly ashes of Minhang, Shidongerchang C, and Wujin F; whereas for the ZFAs of Minhang, Shidongerchang C, and Wujin F, the ANC_{4.71} was estimated to be 1.2, 3.5, and 7.6 mmol H⁺/g, respectively.

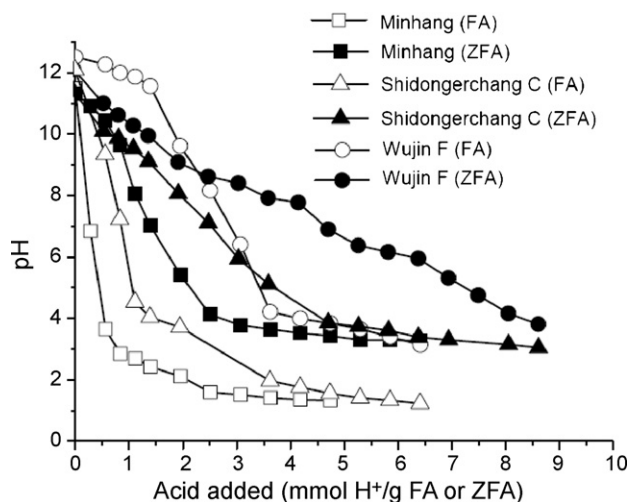


Fig. 3. The titration curves of the representative ZFAs and their corresponding coal fly ashes.

Table 3

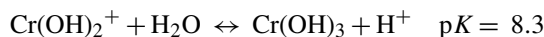
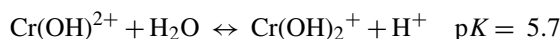
Concentrations of the major cations in extracts of the ZFAs under different pH values (mg/L)

Sample	pH	Al	Fe	Ca	Mg	Na	K
Minhang	4.10	9.8	0.0	123.2	11.5	321.5	4.6
	6.99	1.4	0.0	18.4	2.9	273.4	2.6
	10.90	0.6	0.0	0.6	0.1	204.7	0.1
Shidongerchang C	3.90	37.9	0.1	612.7	27.7	403.2	5.8
	7.15	0.9	0.0	205.1	10.4	358.9	4.4
	10.14	0.4	0.0	5.5	0.2	197.3	2.2
Wujin F	4.08	24.6	0.7	1727.0	32.0	477.1	5.8
	6.82	10.4	0.2	989.2	15.1	365.4	1.5
	10.93	1.3	0.0	5.5	0.4	224.5	1.3

The concentrations of main cations released into solution from the ZFAs by the addition of acid to the end point of alkaline (about 11), neutral (about 7), and acidic (about 4) pH values is given in Table 3. The predominant cations released into solution are Ca and Na ions. Even in the alkaline condition (pH value about 11), the concentration of Na ion was very high. Therefore, the Na concentration in solution was not significantly increased by the addition of acid when compared with the Ca ion. This suggests that the ANC of the ZFAs was dominated by Ca-containing components, especially CaCO₃ and soluble calcium hydroxide/oxide. Johnson et al. [32] reported similar findings for some municipal waste incinerator bottom ashes.

3.4. Influence of pH on Cr(III) immobilization by ZFA

The pH value of the aqueous system is one of the most important parameters affecting the sorption behavior, as it determines the metal ion speciation and, depending on the specific sorbent, the sorbent surface charge as well. The speciation diagram for Cr(III) can be obtained using the following reactions and equilibrium constants:



The solubility limit can be calculated using the following reaction and the K_{sp} value:



Fig. 4 gives the solubility limit of CrCl₃ and shows the distribution of the chromium species (Cr³⁺, Cr(OH)²⁺, and Cr(OH)₂⁺) over the pH range from 1 to 7. Increasing the solution pH hydrolyzes Cr³⁺ to Cr(OH)²⁺ and Cr(OH)₂⁺, and the formation of chromium hydroxide occurs at a relatively low concentration and pH, as shown in Fig. 4.

The removal of chromium by the three representative ZFAs with low, medium, and high CaO contents as a function of pH was investigated over a wide pH range of 2.5–9.0 (Fig. 5). This shows that the sorption of chromium increased with the rise in solution pH from 2.5 to about 6.5 and then stabilized. Unlike

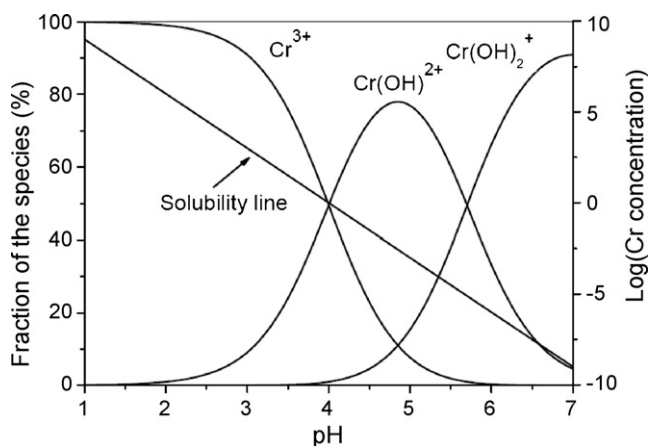


Fig. 4. Solubility limit of CrCl_3 and distribution of the chromium species as a function of solution pH.

other organic compound-based sorbents whose sorptive sites for Cr(III) are functional groups (e.g. carboxyl) with a variable negative charge [3], ZFA has a permanent negative charge that is not influenced by pH. For this study, we consider separately the behaviors observed when the equilibrium pH of the suspensions is lower or higher than the solubility limit of chromium (4.71). Inside the solubility range, the influence of pH on chromium elimination by ZFA may be explained by the fact that (1) as the pH value decreased, the dissolution of metal ions from ZFA was promoted as shown in Table 3 so that, other cations, including hydrogen ions, competed with chromium ion for the negatively charged sites; and (2) the number of chromium sorbed per negative charge varied from 1 (in the case of Cr^{3+}) to 1/3 (in the case of $\text{Cr}(\text{OH})_2^+$) when pH declined, as shown in Fig. 4. At pH values above the solubility limit, however, chromium hydroxide was the main chromium species. This resulted in an almost complete removal of Cr(III) from solution for the three ZFAs via precipitation on the sorbent surfaces. Precipitation of metal hydroxides on the surface of the zeolite or inside the pore walls was also reported for Cu^{2+} and Cr^{3+} on the NaP1 [33] and 4A zeolites [26]. Through electrophoresis measurements, Hertz

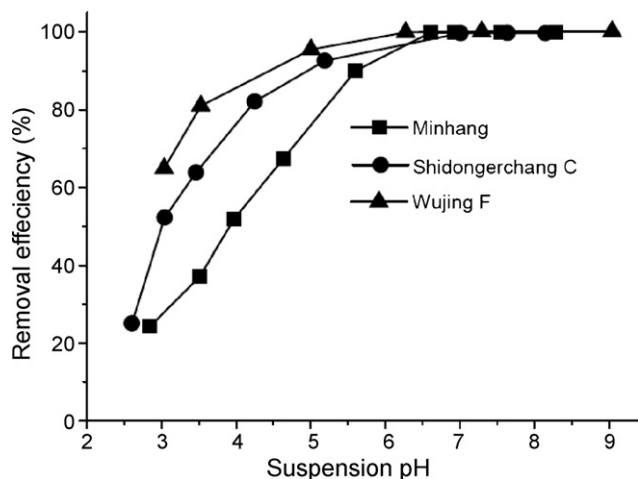


Fig. 5. Efficiency of Cr(III) removal at a concentration of 400 mg/L by ZFAs as a function of pH.

et al. [34] demonstrated that the chromium hydroxide particles maintained residual positive charges even for pH values much higher than the solubility limit, which gave rise to a strong interaction between the negatively charged poly(acrylic acid) gels and the hydroxide particles with a high aggregation number.

Inside the solubility range, the sorptive capacity of Cr(III) by ZFAs was in the order of Wujing F > Shidongerchang C > Minhang. This behavior will be discussed in the next section.

3.5. Sorption isotherm of Cr(III) at pH 4

To evaluate the adsorption of Cr(III) by ZFA, the isotherm studies were performed at the constant equilibrium pH value of 4. This pH value was used since we aimed to exclude the precipitation process and to study the adsorption behavior only. That is, pH 4 is low enough to exclude the possibility of precipitation but high enough to prevent possible deterioration of ZFA structure and to protect Cr(III) adsorption process from strong competition by other cations, including hydrogen ions. A negligible sorption capacity of Cr(III) by fly ashes at pH 4 (± 0.1) was observed. Hence, it is deemed that the electrostatic attraction between the positively charged chromium (Fig. 4) and the negatively charged ZFA results in metal ion sorption at the low pH values.

The isotherms for the chromium removal by the three representative ZFAs at pH 4 (± 0.1) are shown in Fig. 6. The isotherms belong to the high-affinity (H) type in which chromium in dilute solution is greatly sorbed, so that the initial part of the curve is nearly vertical. The almost complete removal of chromium by ZFA in dilute solution yielded a very low residual chromium concentration, which is particularly desirable for removing Cr(III). Consequently, ZFAs may be preferentially utilized for Cr(III) removal from water/wastewater with low concentrations.

Since the analysis of the data of batch sorption studies for Cr(III) at pH 4.0 (± 0.1) revealed that the data were best fitted to a Langmuir equation with r^2 exceeding 0.98, the maximum sorption capacity was calculated based on the equation. The

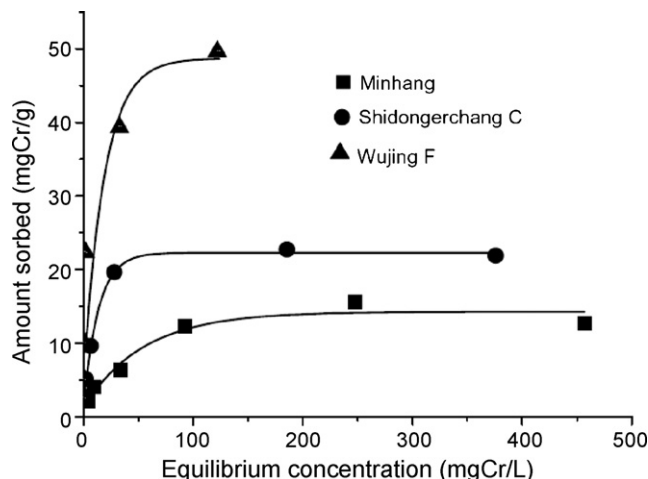


Fig. 6. Sorption isotherm of Cr(III) by the representative ZFAs at a final pH of 4.0 (± 0.1).

Table 4
The Langmuir sorption isotherm parameters of Cr(III) by the ZFAs at pH 4.0 (± 0.1)

Material	Langmuir equation			Q_m (cmol/kg)	CEC (cmol/kg)
	r^2	b (L/mg)	Q_m (mg/g)		
Minhang	0.982	0.068	13.95	67.1	159.6
Shidongerchang C	0.999	0.355	22.08	106.2	187.2
Wujin F	0.996	0.264	50.51	242.8	103.0

Langmuir model can be expressed as

$$\frac{C}{q} = \frac{C}{Q_m} + \frac{1}{bQ_m}$$

where q is the amount of Cr(III) sorbed per unit of sorbent (mg/g), C is the concentration of Cr(III) in solution at equilibrium (mg/L), Q_m is the Langmuir sorption maximum (mg/g), b is a constant related to the binding strength of Cr(III).

The Langmuir parameters calculated for Cr(III) are listed in Table 4. The Langmuir maximum sorptive capacity for Cr(III) at pH 4 (± 0.1) was in the order: Wujin F (50.51 mg/g) > Shidongerchang C (22.08 mg/g) > Minhang (13.95 mg/g). This order was not in agreement with the CEC value (Table 4). To further compare the amount of sorbed Cr(III) with the CEC, the Langmuir maximum sorptive capacity was converted into the unit cmol/kg, which is the same as the unit for CEC. At pH 4.0, approximately 50% of the chromium is in

the form of Cr^{3+} and another 50% is in the form of $\text{Cr}(\text{OH})^{2+}$ (Fig. 4). Therefore, the positive charge carried by one chromium atom at pH 4 can be assumed as 2.5. The converted data are also presented in Table 4. As seen in this table, the maximum sorptive capacity of chromium by the Minhang ZFA and the Shidongerchang C ZFA was well below their CEC values. This can be readily interpreted by the presence of large amounts of competitive cations (Table 3), which reduced the sorption sites available for Cr ions. Surprisingly, the maximum sorptive capacity of chromium by the Wujin F ZFA exceeded its CEC value. This behavior was explained as follows. Firstly, the small pore size of hydroxysodalite (0.23 nm), formed in Wujin F ZFA (Table 2), does not permit the penetration of ammonium ions with an ionic diameter of 0.28 nm (used to determine the CEC). Thus, the real cation exchange capacity for Cr(III) would be higher than the CEC value determined by the ammonium acetate method. The pore size of the NaP1 zeolite is larger than hydroxysodalite. The NaP1 zeolite has two types of pore size, one with a very small diameter of about 0.3 nm and the other with a diameter of 0.46 nm [21]. Secondly, the size of an ion relative to the pore size could be an important factor for metal ion sorption by zeolite. It is presumed that the smaller the ion, the easier it is for the ion to be intercalated into the pores. The Goldschmidt ion diameters are as follows: Cr 0.106; Al 0.09; Fe 0.106; Ca 0.21; Mg 0.156; Na 0.196; K 0.266 (unit: nm). Hence, comparing with the NaP1 zeolite, the small pore size of the hydroxysodalite of the Wujin F ZFA would promote the sorption of chromium by hindering the sorption of relatively large metal ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ ,

Table 5
Comparison of Cr(III) immobilization maxima of tested materials with some literature values

Type	Sorbent	pH	T ($^{\circ}\text{C}$)	MSC ^a (mg/g)	Reference
Coal fly ash	Coal fly ash (low calcium)	3.4	20	1.8 ± 0.6	This study
	Coal fly ash (medium calcium)	3.4	20	9.0 ± 0.7	This study
	Coal fly ash (high calcium)	3.4	20	32.2 ± 1.0	This study
ZFA	ZFA (low calcium)	3.4	20	25.2 ± 0.8	This study
	ZFA (medium calcium)	3.4	20	39.4 ± 0.6	This study
	ZFA (high calcium)	3.4	20	75.5 ± 0.4	This study
Carbon based	Activated carbon from co-mingled organic wastes	3.7	30–45	43.5–46.7	4
	Activated carbon from coconut shell fibers	5.0	10–40	11.0–16.1	5
Plant based	Native saltbush	5.0	–	16.3–27.0	6
	Esterified saltbush	5.0	–	5.5–7.1	6
	Hydrolyzed saltbush	5.0	–	20.8–26.2	6
	Coir pith	3.3	27	11.6	7
	Carrot residues	4.5	25	45.1	8
	<i>Aspergillus</i> biomass	5.0	28	15.6	9
	Brown seaweed (<i>Turbinaria</i> spp.)	3.5	30	31.0	10
Cork powder	4.0	22	6.3	11	
Organic wastes	Wine processing waste sludge	4.0	20–50	10.5–16.4	12
	Biogas residual slurry	2.5	30	7.8	13
Alginate based	Composite alginate–goethite beads	2.0–4.0	20–60	8.9–30.4	14
	Protonated dry alginate beads	3.5, 4.5	25	57.0, 77.0	15
Fly ash	Bagasse fly ash	5.0	30–50	4.2–4.4	16
	Palm oil fuel ash	3.0–6.0	25	6.9–16.4	17
Zeolite	Natural zeolite	3.0	27	6.9	18

^a Maximum sorptive capacity, measured by repeated batch equilibration method (zeolite, coal fly ash, and ZFA) or Langmuir maximum sorptive capacity (other materials).

with Ca^{2+} and Na^{+} the most abundant ions in solution as shown in Table 3).

3.6. Maximum immobilization capacity of ZFAs

The maximum immobilization capacity of the three representative ZFAs and their raw fly ashes, along with the calculated standard deviation values, are presented in Table 5. In this case, the maximum immobilization capacity involved the amount of Cr(III) sorbed via both precipitation and ion exchange, as no pH adjustment was made by adding acid. It is confirmed that, for both fly ashes and ZFAs, the sorption capacity for Cr(III) followed the order of Wujin F (high calcium) > Shidongerchang C (medium calcium) > Minhang (low calcium). It was also observed that the sorption capacity of ZFA for Cr(III) was greater than for fly ash. Furthermore, the increase in Cr(III) removal following the formation of zeolites was more pronounced for a low-calcium fly ash than a high-calcium fly ash. The maximum immobilization capacity increased by 14.0, 4.4, and 2.3 times, respectively, for the ZFAs of Minhang, Shidongerchang C, and Wujin F when compared with their corresponding fly ashes (Table 5).

The maximum immobilization capacity of the ZFAs and coal fly ashes obtained in this study could be compared with other sorbents reported in the literature as summarized in Table 5. It can be seen that the Cr(III) sorption capacity of the Wujin fly ash (high calcium) and the three ZFAs are comparable to those of the available sorbents. In particular, the sorption capacity of the Wujin F ZFA is among the highest, indicating that it is a promising material for Cr(III) removal from water/wastewater.

4. Conclusions

ZFAs (zeolites synthesized from fly ash) are efficient for Cr(III) immobilization from aqueous solution compared with raw fly ashes and other sorbents reported in previous literatures. The mechanism of chromium removal by ZFAs involves ion exchange and precipitation as chromium hydroxide. The greater removal ability of the ZFAs compared with the fly ashes is attributed to the high CEC value and ANC value of the ZFAs. It was observed that a high-calcium content in both the fly ashes and ZFAs resulted in a high ANC value and, as a result, a high immobilization capacity for Cr(III). The pH strongly influenced the Cr(III) removal by the ZFAs. Inside the solubility range, the removal of chromium increased with increasing pH. A low pH caused the release of metals, mainly Na^{+} and Ca^{2+} . The formation of hydroxysodalite, with a smaller pore size than the NaP1 zeolite, from high-calcium fly ash prevented competition from other larger cations (mainly Ca^{2+} and Na^{+}) with chromium for negatively charged sites on the ZFA surface and promoted chromium removal. On the other hand, at pH values above the solubility range, the efficiency of chromium removal by the ZFAs approached 100% due to the precipitation of $\text{Cr}(\text{OH})_3$ on the sorbent surfaces. It was concluded that the ZFAs and high-calcium fly ashes are promising materials for Cr(III) removal from aqueous solution.

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