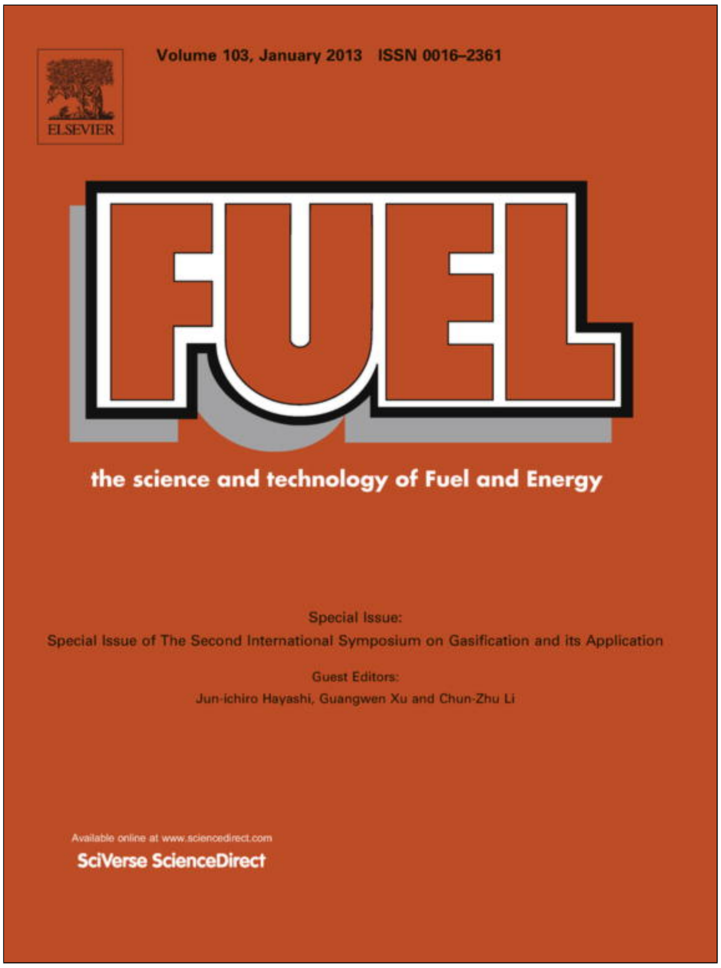

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Synthesis of zeolites X and A from fly ashes for cadmium and zinc removal from aqueous solutions in single and binary ion systems

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HIGHLIGHTS

- ▶ Pure zeolites X and A were selectively synthesised from different fly ashes.
- ▶ Zeolites A and X present high capacities in Cd and Zn adsorption in single or binary systems.
- ▶ Competitive adsorption occurs in binary-ion systems.

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ABSTRACT

Two different Brazilian fly ashes were used to selectively synthesize pure zeolites X and A by a two-step process. The zeolites were characterized in terms of mineralogical composition (XRD), morphological analysis (SEM), specific surface area (BET method), and cation exchange capacity (CEC). XRD and SEM results indicated that pure zeolites X and A were obtained from fly ash samples, possessing high CEC at 3.1–3.9 meq/g. The pure zeolites X and A were used in adsorption of zinc and cadmium in single and binary systems. The adsorption studies showed that zinc is more preferentially adsorbed on pure zeolites than cadmium in both single and binary systems under similar experimental conditions. Zeolite-A presented higher adsorption than zeolite-X. The adsorption isotherms followed the Langmuir model. The adsorption capacities for zinc and cadmium on the pure zeolites ranged 156–220 mg/g and 57–195 mg/g in the single and binary ion systems, respectively. The removal of both ions by zeolites A was less affected by the presence of a competitive ion, different from zeolites X.

1. Introduction

The fast economic development occurring in the world would heavily rely on the use of energy supplies from fossil fuels. In this context, coal as a major source for energy production accounts for 29.6% of global energy consumption and has had the fastest global growth since 2003 [1]. However, coal-fired power plants are producing larger quantities of fly ash annually, resulting in the problem of solid waste disposal. The properties and chemical composition of fly ashes vary depending on coal source and power-plant operation, which make these materials even more versatile [2]. However, major components of alumina and silica in fly ashes can be used for the synthesis of zeolites, one of environmental-benign applications of fly ashes [3–11].

In recent years, several strategies in zeolite synthesis from fly ashes have been proposed in order to obtain a pure zeolite other than a mixture of zeolitic materials. For example, a fusion step prior to a hydrothermal treatment can make alkali extraction of more silicates and aluminates from ashes [7], increasing the yield of pure zeolites [3]. However, the formation of a particular zeolite strongly depends on the ratio of SiO_2/Al_2O_3 in the starting material for hydrothermal reaction [12]. Zeolites A and X usually have high CEC and large pores [13] and synthesis of these zeolites from fly ashes has been reported in some papers [2,3,6,14–20]. An overview of different SiO_2/Al_2O_3 ratios and types of zeolite produced from fly ashes is given in Table 1.

However, some issues in the synthesis of pure zeolites from fly ashes are to be addressed. Previously, only one type of fly ash was utilized in the investigation and it is not clear whether the same methodology was suitable to synthesize a pure zeolite from different fly ashes. In addition, only alkali extracts from fly ash were used to produce a pure zeolite without using solid phase. Moreover, crystal seeds or structure-directing agents were sometimes employed, making the synthesis more expensive.

In Brazil, fly ash disposal is also an issue in solid waste management [11] and conversion of fly ash to pure zeolites will provide an

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Table 1
Overview of SiO_2/Al_2O_3 fly ash ratios and types of zeolite synthesized from different investigations.

Ref.	Fly ash SiO_2/Al_2O_3		Type of zeolite synthesized
	Weight ratio	Molar ratio	
[2]	1.21	2.06	Na-X (FAU) and CAN
[3]	2.19	3.72	Na-X and Na-A
[6]	2.26	3.83	Na-X, Na-A and NaP
[14]	2.26	3.83	Na-X and Na-A
[15]	2.01	3.41	Na-Y, Na-X and Na-A
[16]	1.84	3.12	Na-X
[17]	1.89	3.21	Na A-X (blend)
[18]	1.49	2.53	Na-A
[19]	1.89	3.22	Na-P1, Na-X and Na-A
[20]	2.46	4.18	Na-A and Na-X

economic solution. This study intends to obtain high purity of zeolites (X and A) using the methodologies appropriate to the Brazilian coal fly ash samples. Two different raw fly ashes were used in order to obtain same high purity products. The ashes were used without pre-treatment and no seeds or structure-directing agents were used in the synthesis. In general, zeolites from fly ash present negatively charged surfaces, hence these synthetic materials can be used as sorbents for adsorption of positively charged contaminants such as toxic metal ions from water [21–23]. However, previous investigations using synthetic zeolite mainly focused on single metal ion adsorption. In this work, the synthesized pure zeolites were tested for the removal of zinc and cadmium ions from water in both single- and binary-ion systems.

2. Materials and methods

2.1. Materials

Two coal fly ash samples were collected directly from electrostatic precipitators of different Brazilian coal-fired power plants: Jorge Lacerda Power Plant (JL) located in Santa Catarina State, and Charqueadas Power Plant (CH) located in Rio Grande do Sul State. Both fly ashes were used without any pretreatment and their properties were characterized by various techniques. Both samples have contents of SiO_2 and Al_2O_3 above 70 wt.% and other oxides below 5 wt.%. Quartz and mullite were found as the main phases [11]. Sodium hydroxide (97%) and sodium aluminate (99.99%) obtained from Sigma–Aldrich Pty. Ltd. (Aus) were used in zeolite synthesis.

2.2. Zeolite synthesis from fly ashes

Synthesis of zeolite-X took a two-step process [3]. Typically, 10 g of fly ash were mixed with 12 g of NaOH. The mixture was heated at 823 K for one hour. After cooling at room temperature, sodium aluminate was added to the grinded mixture to control the molar ratio of SiO_2/Al_2O_3 and mixed with water. The mixture was then stirred at room temperature for 16 h and further heated to 373 K in an oven for hydrothermal synthesis for 24 h. After cooling down to room temperature, the suspension was filtered and the solid was repeatedly washed with 1 L of deionized water and dried at 378 K for 16 h. The products obtained were labeled as ZXJL and ZXCH, respectively, based on fly ash sources.

In the synthesis of zeolite-A, a similar process was taken, but the hydrothermal treatment was carried out at 373 K for 7 h. The products obtained were then labeled as ZAJL and ZACH. Due to a faster crystallization of zeolite-A, lower synthesis time was thus used [24]. Fig. 1 shows the detailed synthesis processes of zeolites X and A from fly ashes.

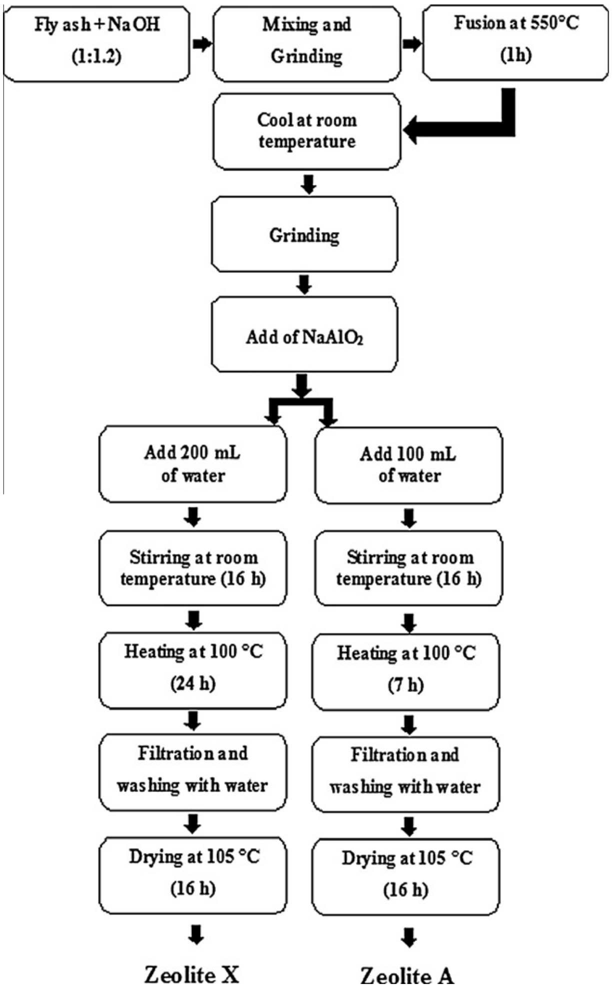

Fig. 1. Syntheses of zeolites X and A by the two-step process.

2.3. Characterization of synthesized zeolites

2.3.1. Mineralogical composition and morphological analysis

The mineralogical compositions of the synthesized samples were determined by X-ray diffraction (Bruker-AXS D8 Advance Powder Diffractometer, USA) using Cu Kα radiation at 40 kV and 40 mA. The scan rate was 0.02°/s in a range of 5–80 (2θ). Phase identification was made by searching the ICDD powder diffraction file database, with the help of Diffrac Plus EVA – Bruker files for inorganic compounds. To verify the morphology, samples were covered with a thin layer of gold to make them conductive and examined using a scanning electron microscope (Zeiss – EVO 40 XVP, Germany).

2.3.2. Specific surface area

The specific surface areas of zeolite samples were determined by a N_2 adsorption analyzer (Micromeritics – Gemini 2360, USA). Prior to determination of the specific surface area, samples were heated at 423 K for 12 h to remove volatiles and moisture in a degasser (Micromeritics – VacPrep 061, USA). The BET surface areas were obtained by applying the BET equation to the nitrogen adsorption data.

2.3.3. Cation exchange capacity (CEC)

In CEC measurements, samples were saturated in sodium acetate solutions (1 M), washed with distilled water (1 L) and then mixed with ammonium acetate solutions (1 M). The sodium ion

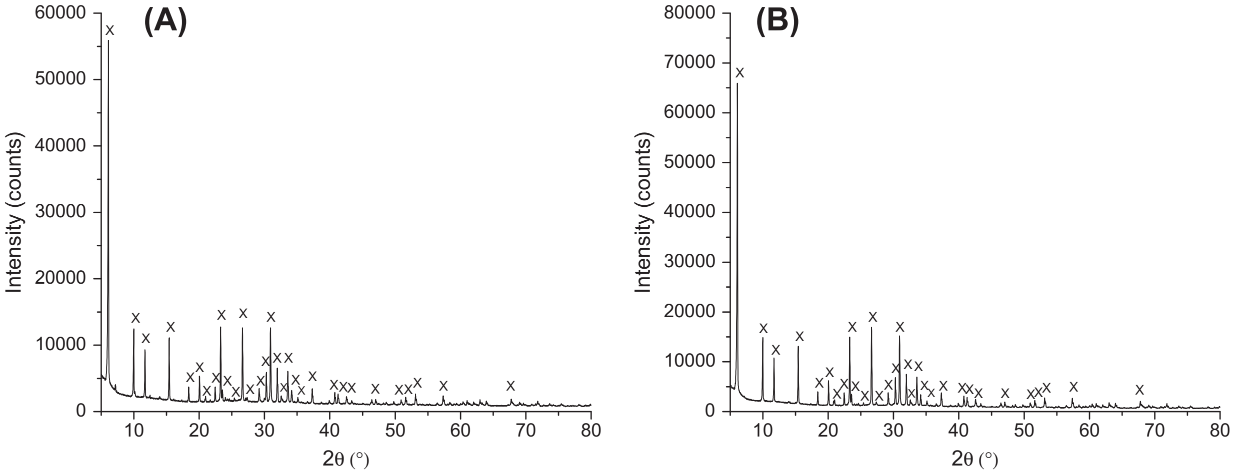

Fig. 2. XRD patterns of zeolite X synthesized by the two-step process (A) ZXJL and (B) ZXCH.

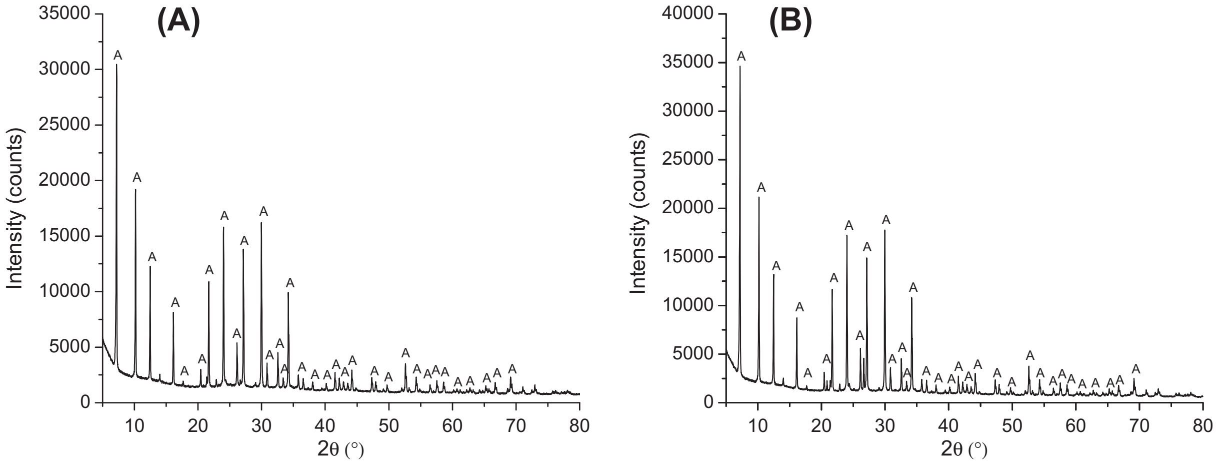

Fig. 3. XRD patterns of zeolite A synthesized by the two-step process (A) ZAJL and (B) ZACH.

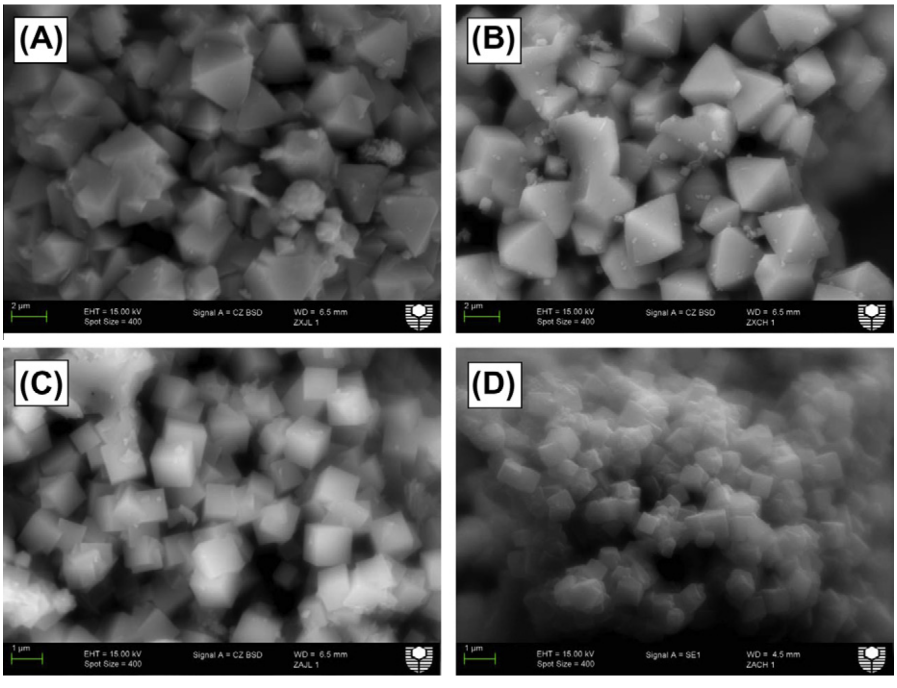

Fig. 4. SEM micrographs of (A) ZXJL; (B) ZXCH; (C) ZAJL and (D) ZACH.

concentration of the resulting solution was determined by atomic absorption spectrophotometry (Varian – Spectraa-50, USA).

2.4. Adsorption studies

Batch processes for metal ion adsorption (Zn^{2+} and Cd^{2+}) were performed in single and binary ion systems by shaking at 120 rpm (Orbital Shaker Incubator – Mod SF-670, Australia), 0.5 g of each zeolite and 50 mL of metal ion solutions with different concentrations. The applied solid/liquid ratio was 10 g/L. The adsorption capacity of the adsorbent per mass unit (q_e) was calculated by Eq. (1). The single metal ion adsorption percentage ($Ad\%$) and the total metal ion adsorption percentage ($Ad_{Tot}\%$) were obtained by Eqs. (2) and (3), respectively.

$$q_e = \frac{C_0 - C_f}{M} V_a \tag{1}$$

$$Ad\% = \frac{C_0 - C_f}{C_0} \times 100 \tag{2}$$

$$Ad_{Tot}\% = \frac{\sum(C_0 - C_f)}{\sum(C_0)} \times 100 \tag{3}$$

where C_0 and C_f are the initial and final metal ion concentrations, respectively, V_a is aqueous phase volume and M is the weight of adsorbent used. The data of isotherms were obtained after an equilibrium time of 24 h. After the equilibrium time, the supernatants were separated from the adsorbent by filtration and the concentrations were determined by atomic absorption spectrophotometry (Varian – Spectraa-50, USA).

For single metal-ion systems, the initial metal concentration ranged from 653.8 to 1961.4 mg/L and from 1124.1 to 3372.3 mg/L for Zn^{2+} and Cd^{2+} ions, respectively. In the binary metal-ion systems, initial concentration of zinc or cadmium was maintained at the lowest concentration to check the influence of competitive ions during the adsorption process under varying concentrations of the second ion. All the tests were carried out duplicate with error within 10% and the average values were reported.

3. Results and discussion

3.1. Mineralogical composition

Several methodologies were tested by using different temperatures, stirring time, quantity of aluminum, etc. to determine the optimal conditions to the synthesis of the pure zeolites (X and A) using the two different Brazilian fly ashes. The crystallization time and the quantity of aluminum were strictly controlled, since both parameters are crucial for avoiding the formation of other zeolitic phases when the relevant zeolite is being formed [6,18].

Figs. 2 and 3 show X-ray patterns of pure zeolites X and A, respectively, obtained from two different types of Brazilian fly ash. According to the diffractograms, the synthetic products presented only one phase of a pure zeolite. Quartz and mullite peaks, normally found in the diffractograms of fly ash, disappeared completely due to the fusion step, which can easily dissolve those components for zeolite formation in the later stage of hydrothermal synthesis.

3.2. Morphological analysis

According to literature, zeolite-X shows an octahedral structure in bipyramidal crystals [2,3,6,7,20] and zeolite-A presents a cubic structure [3,18–20]. Zeolites X and A synthesized from two different Brazilian fly ashes can be clearly seen in Fig. 4. The SEM micrographs confirm the presence of pure zeolites. Zeolites X synthesized from the two different fly ashes presented a similar crystal size whereas the crystal sizes of zeolites A were a bit different. The same type of zeolites can present varying crystal sizes probably due to the different crystal growth rate during the hydrothermal treatment [25].

3.3. Specific surface area

Table 2 shows the specific surface areas (S_{BET}) of all pure zeolites obtained. Zeolites X presented the BET surface area at 249.7 and 397.0 m^2/g for ZXJL and ZXCH, respectively. The specific

Table 2
Characteristics of zeolites X and A from Brazilian fly ashes.

Sample	S_{BET} (m^2/g)	CEC (meq/g)
ZXJL	249.7	3.1
ZXCH	397.0	3.6
ZAJL	15.7	3.9
ZACH	10.9	3.9

Table 3
Comparison of individual and total adsorption percentages by pure zeolites at different Cd^{2+} and Zn^{2+} concentrations after 24 h of contact in single ion systems.

Adsorbent	$C_{o,Cd}$ (mg/L)	$C_{o,Zn}$ (mg/L)	$Ad_{Cd}\%$	$Ad_{Zn}\%$	$Ad_{Tot}\%$
ZXJL (Single)	1124.1	0.0	92.4	–	92.4
	1348.9	0.0	91.5	–	91.5
	1686.2	0.0	74.0	–	74.0
	2248.2	0.0	67.1	–	67.1
	2810.3	0.0	52.1	–	52.1
	3372.3	0.0	49.8	–	49.8
	0.0	653.8	–	98.3	98.3
	0.0	784.6	–	98.4	98.4
	0.0	980.7	–	98.7	98.7
	0.0	1307.6	–	98.4	98.4
	0.0	1634.5	–	95.1	95.1
	0.0	1961.4	–	94.3	94.3
ZXCH (Single)	1124.1	0.0	95.7	–	95.7
	1348.9	0.0	80.2	–	80.2
	1686.2	0.0	71.3	–	71.3
	2248.2	0.0	65.5	–	65.5
	2810.3	0.0	51.4	–	51.4
	3372.3	0.0	49.3	–	49.3
	0.0	653.8	–	98.8	98.8
	0.0	784.6	–	99.0	99.0
	0.0	980.7	–	99.1	99.1
	0.0	1307.6	–	99.0	99.0
	0.0	1634.5	–	96.9	96.9
	0.0	1961.4	–	96.4	96.4
ZAJL (Single)	1124.1	0.0	100.0	–	100.0
	1348.9	0.0	91.8	–	91.8
	1686.2	0.0	74.8	–	74.8
	2248.2	0.0	79.3	–	79.3
	2810.3	0.0	60.0	–	60.0
	3372.3	0.0	59.6	–	59.6
	0.0	653.8	–	100.0	100.0
	0.0	784.6	–	98.7	98.7
	0.0	980.7	–	98.9	98.9
	0.0	1307.6	–	99.1	99.1
	0.0	1634.5	–	97.7	97.7
	0.0	1961.4	–	97.3	97.3
ZACH (Single)	1124.1	0.0	100.0	–	100.0
	1348.9	0.0	92.4	–	92.4
	1686.2	0.0	92.9	–	92.9
	2248.2	0.0	79.8	–	79.8
	2810.3	0.0	60.7	–	60.7
	3372.3	0.0	60.0	–	60.0
	0.0	653.8	–	100.0	100.0
	0.0	784.6	–	99.2	99.2
	0.0	980.7	–	99.3	99.3
	0.0	1307.6	–	99.2	99.2
	0.0	1634.5	–	97.6	97.6
	0.0	1961.4	–	97.2	97.2

surface areas for the pure zeolites are much higher than those of raw fly ashes or the products synthesized by the conventional hydrothermal treatment using the same samples [11]. For zeolites A, the specific surface areas were 15.7 and 10.9 m^2/g for ZAJL and ZACH, respectively. Zeolites X presented higher specific surface than zeolites A, due to the larger pore size of zeolite-X (0.74 nm) as compared to zeolite-A (0.42 nm) [26].

3.4. Cation exchange capacity

According to Table 2, the values of CEC for the pure zeolites ranged from 3.1 to 3.9 meq/g. These values are in accordance with the data found in literature [7,19]. The CEC values presented by the pure zeolites are much higher than those of raw fly ashes or the products synthesized using one-step hydrothermal treatment [11]. Zeolites A presented higher CECs than zeolites X due to the lower Si/Al molar ratio (from 1.0 to 1.2). The smaller Si/Al molar ratio in the zeolite framework produces more charge deficiency. Thus, the framework needs more Na^+ to compensate the excess negative charge and more exchangeable Na^+ ions exist in the zeolitic structure [26,27].

3.5. Adsorption studies

3.5.1. Adsorption of Zn^{2+} and Cd^{2+} in single-ion systems

Initially, the capacity of the pure zeolites to remove Cd^{2+} and Zn^{2+} ions from single aqueous solutions was tested at various concentrations. The adsorption percentages for both ions are shown in Table 3.

According to Table 3, the pure zeolites synthesized from Brazilian fly ashes were found to successfully remove cadmium and zinc ions from single aqueous solution at high concentrations. The metal removal percentages for both ions decreased with increasing ion concentrations due to the adsorbent saturation. In single ion systems, adsorption percentage of zeolites X ranged from 49.3% to 95.7% for Cd^{2+} and from 94.3% to 99.1% for Zn^{2+}, respectively. For zeolites A, the adsorption percentages ranged from 59.6% to 100.0% and from 97.2% to 100.0% for Cd^{2+} and Zn^{2+} ions, respectively. Generally, zeolites A presented higher adsorption percentages for both ions than zeolites X due to higher CEC values. It is known that zeolite-A has a pore size of 0.42 nm, similar to the diameter of Cd^{2+} and Zn^{2+} hydrated ions (Zn^{2+} hydrated ion size = 0.430 nm and Cd^{2+} hydrated ion size = 0.426 nm) [14,26].

It was also found that the amount of adsorbed Zn^{2+} was larger than that of Cd^{2+} on both zeolites. Similar results have been reported in other adsorption studies [28,29]. This preference of Zn^{2+} to pure zeolites may be due to the loss of water molecules of hydration by the ions during the adsorption process. The hydrated ion sizes of Cd^{2+} and Zn^{2+} are much similar, but during the adsorption process, some water molecules were lost, leading to reduced ion size for both metals. The ion size for Zn^{2+} is 0.083 nm, smaller than that of Cd^{2+} (0.103 nm) [30]. Therefore, ions having a smaller radius are easy to fill in the pores in adsorbent surface than those with larger hydrated radius.

The pH values for the supernatant solutions after the adsorption processes in single systems were measured. The average pH values for Cd^{2+} and Zn^{2+} solutions were found to be 6.6 and 6.8, respectively. All pH values were lower than the precipitation pHs for Cd^{2+} (which precipitates at pH around 8.4) and Zn^{2+} (which precipitates at pH of 8.0).

The adsorption equilibrium data in single ion systems using different adsorbents were also obtained and evaluated by the

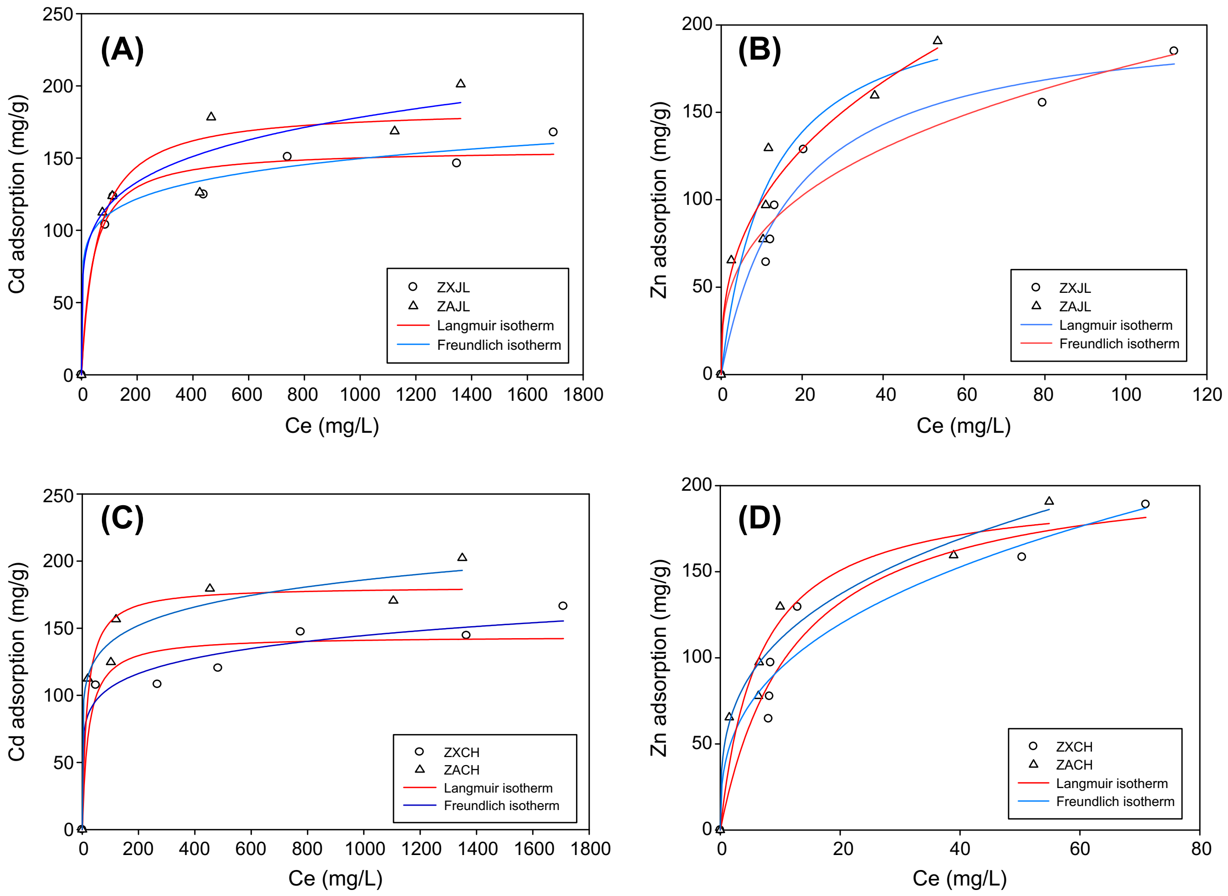

Fig. 5. Adsorption isotherms of Cd^{2+} and Zn^{2+} on synthesized zeolites in single-ion systems. (A) and (C) Cd adsorption; (B) and (D) Zn adsorption.

Langmuir and Freundlich models. These two isotherm equations have been used extensively to evaluate the equilibrium characteristics of adsorption processes. In the Langmuir model, a basic assumption is that the sorption occurs at specific homogeneous sites within the adsorbent, whereas in the Freundlich model, it is considered that the adsorbent surface is heterogeneous and the adsorption process occurs at a non-uniform distribution of heat over the surface [29]. Fig. 5 shows the adsorption isotherms for Cd^{2+} and Zn^{2+} on zeolites X and A with the Langmuir and Freundlich models. The isotherm parameters determined by the Langmuir and Freundlich equations are shown in Table 4.

Table 4
Langmuir and Freundlich parameters calculated from Cd^{2+} and Zn^{2+} isotherms in single-ion systems using pure zeolites synthesized from fly ashes.

Adsorbent	Metal	Langmuir			Freundlich		
		Q_{max} (mg/g)	K_L (L/mg)	R	K_f (mg/g) (L/mg)$^{1/n}$	n	R
ZXJL	Zn^{2+}	205.4	0.0573	0.980	37.2	2.96	0.972
ZAJL	Zn^{2+}	219.6	0.0857	0.957	41.7	2.65	0.974
ZXJL	Cd^{2+}	156.2	0.0247	0.982	61.8	7.81	0.989
ZAJL	Cd^{2+}	185.1	0.0178	0.959	51.4	5.55	0.969
ZXCH	Zn^{2+}	198.8	0.0816	0.975	41.6	2.84	0.969
ZACH	Zn^{2+}	212.7	0.157	0.967	54.9	3.28	0.983
ZXCH	Cd^{2+}	144.2	0.0446	0.953	56.7	7.38	0.982
ZACH	Cd^{2+}	181.2	0.0587	0.967	78.3	7.99	0.982

Table 5
Comparison of individual and total adsorption percentages by pure zeolites found at different Cd^{2+} and Zn^{2+} concentrations after 24 h of contact in binary ion systems.

Adsorbent	$C_{o,Cd}$ (mg/L)	$C_{o,Zn}$ (mg/L)	Ad_{Cd}%	Ad_{Zn}%	Ad_{Tot}%
ZXJL (Binary)	1124.1	653.8	31.0	59.0	41.3
	1348.9	653.8	34.4	59.9	42.8
	1686.2	653.8	24.9	56.7	37.0
	2248.2	653.8	22.7	53.3	29.6
	2810.3	653.8	18.2	51.8	24.5
	3372.3	653.8	15.2	55.0	21.6
	1124.1	784.6	46.9	61.3	52.8
	1124.1	980.7	39.7	52.7	45.7
	1124.1	1307.6	38.2	45.8	42.3
	1124.1	1634.5	22.6	36.9	31.1
	1124.1	1961.4	12.1	30.7	23.9
ZXCH (Binary)	1124.1	653.8	50.0	79.5	60.8
	1348.9	653.8	45.7	78.4	56.4
	1686.2	653.8	39.2	70.5	47.9
	2248.2	653.8	29.8	65.0	37.7
	2810.3	653.8	24.0	62.7	31.3
	3372.3	653.8	20.0	60.2	26.5
	1124.1	784.6	49.9	67.9	57.3
	1124.1	980.7	38.8	54.9	46.3
	1124.1	1307.6	39.3	41.0	40.2
	1124.1	1634.5	31.6	32.9	32.4
	1124.1	1961.4	28.4	32.3	30.9
ZAJL (Binary)	1124.1	653.8	92.4	100.0	95.2
	1348.9	653.8	90.6	100.0	93.7
	1686.2	653.8	74.2	100.0	81.4
	2248.2	653.8	73.5	88.5	76.9
	2810.3	653.8	57.4	73.1	60.4
	3372.3	653.8	54.8	61.9	55.9
	1124.1	784.6	97.2	90.7	94.5
	1124.1	980.7	84.4	88.7	86.4
	1124.1	1307.6	76.9	72.1	74.3
	1124.1	1634.5	67.5	60.0	63.1
	1124.1	1961.4	58.7	46.8	51.1
ZACH (Binary)	1124.1	653.8	93.1	100.0	95.6
	1348.9	653.8	91.4	100.0	94.2
	1686.2	653.8	90.0	100.0	92.8
	2248.2	653.8	77.0	82.3	78.1
	2810.3	653.8	60.2	66.4	61.4
	3372.3	653.8	59.7	57.3	59.3
	1124.1	784.6	100.0	86.9	94.6
	1124.1	980.7	94.5	81.5	88.4
	1124.1	1307.6	81.9	75.3	78.3
	1124.1	1634.5	72.7	61.7	66.2
	1124.1	1961.4	66.7	51.9	57.3

According to the correlation coefficients (R) shown in Table 4, the experimental data for all isotherms complied with the Langmuir and Freundlich models. Adsorption capacities (Q_{max}) for Cd^{2+} and Zn^{2+} on the zeolites from JL fly ash varied from 156 (ZXJL) to 185 mg/g (ZAJL) and from 205 (ZXJL) to 220 mg/g (ZAJL), respectively. For the zeolites from CH, adsorption capacities (Q_{max}) for Cd^{2+} and Zn^{2+} are similar to those on ZXJL and ZAJL. The stronger affinity to zinc than cadmium on all pure zeolites was also demonstrated by adsorption constant, K_L.

3.5.2. Adsorption of Zn^{2+} and Cd^{2+} in binary-ion systems

In binary-ion adsorption studies, the influence of competitive cations was tested by varying the initial concentration of one metal ion while the initial concentration of the other competitor cation was fixed. Table 5 summarizes the adsorption percentages for Cd^{2+} and Zn^{2+} under different initial concentrations of the competitor cation.

According to Table 5, the adsorption percentages in the binary-ion systems were in general lower than those in single-ion systems (Table 3) due to the competition between Cd^{2+} and Zn^{2+} ions to occupy exchangeable places in the zeolites. At a fixed Zn^{2+} concentration, adsorption of Cd^{2+} and Zn^{2+} on zeolites will reduce with increasing Cd^{2+} concentration. Similarly, at a fixed Cd^{2+} concentration, adsorption of Cd^{2+} and Zn^{2+} on zeolites will also reduce with increasing Zn^{2+} concentration. The total metal ion adsorption percentages (Ad_{Tot}%) also show a decreasing trend at higher metal

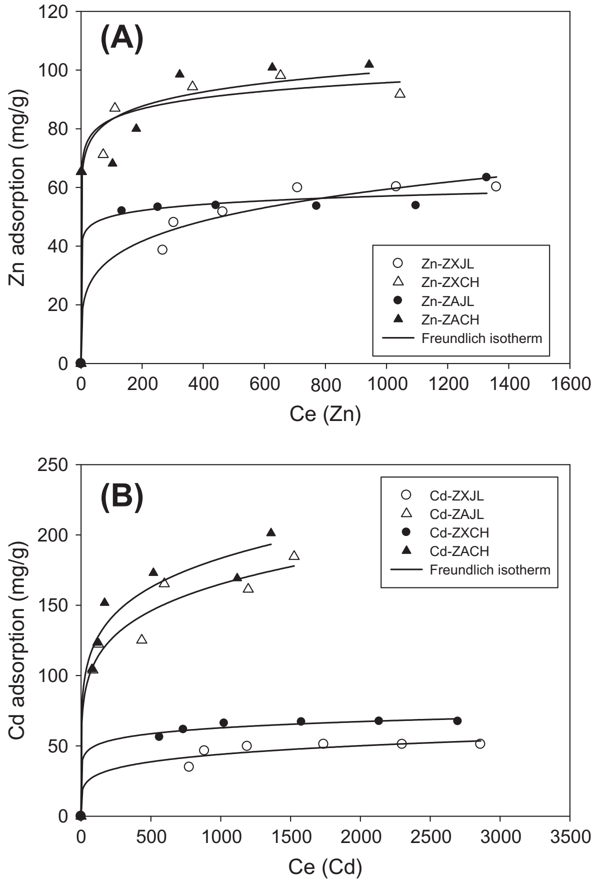

Fig. 6. Adsorption isotherms of Cd^{2+} and Zn^{2+} on synthesized zeolites in binary-ion systems. (A) Zn adsorption (B) Cd adsorption.

Table 6
Langmuir and Freundlich parameters calculated from Cd^{2+} and Zn^{2+} isotherms in binary-ion systems using pure zeolites synthesized from fly ashes.

Adsorbent	Metal	Langmuir			Freundlich		
		Q_{max} (mg/g)	K_L (L/mg)	R	K_f (mg/g) $(L/mg)^{1/n}$	n	R
ZXJL	Zn^{2+}–$Cd^{2+}(f^*)$	70.3	5.83×10^{-3}	0.992	13.0	4.54	0.986
ZAJL	Zn^{2+}–$Cd^{2+}(f^*)$	88.7	2.74	0.969	63.0	16.5	0.987
ZXJL	Cd^{2+}–$Zn^{2+}(f^*)$	59.7	2.82×10^{-3}	0.983	12.1	5.35	0.978
ZAJL	Cd^{2+}–$Zn^{2+}(f^*)$	174.6	0.0160	0.974	48.4	5.64	0.984
ZXCH	Zn^{2+}–$Cd^{2+}(f^*)$	57.5	0.0573	0.988	38.7	17.8	0.991
ZACH	Zn^{2+}–$Cd^{2+}(f^*)$	90.1	2.59	0.940	58.1	12.9	0.972
ZXCH	Cd^{2+}–$Zn^{2+}(f^*)$	72.3	7.28×10^{-3}	0.998	31.7	10.1	0.996
ZACH	Cd^{2+}–$Zn^{2+}(f^*)$	195.3	0.0158	0.989	55.8	5.81	0.982

f^* refers to the ion concentration at a fixed value.

ion concentration. For the two types of zeolite, the total metal ion adsorption percentages ($Ad_{Tot}\%$) for zeolites X and A ranged from 21.6% to 60.8% and from 51.1% to 95.6%, respectively.

By comparing the $Ad_{Tot}\%$ of Cd^{2+} and Zn^{2+} ions between single and binary ion systems, it is clearly indicated that cadmium and zinc adsorption percentages were strongly affected by the presence of competitor ions on zeolites X, while zeolites A still reached high adsorption percentages with the presence of the competitor ions. In general, cadmium removal was more affected by the presence of zinc due to the preference of Zn^{2+} ions by the pure zeolites.

The pHs of all binary ion solutions after the adsorption process were also checked and they were under the precipitation pHs for both ions. The average pH for all solutions was 6.2.

The adsorption equilibrium data for the binary ion studies were presented in Fig. 6 and evaluated by the Langmuir and Freundlich equations for a comparison with the existing data in the mono-component systems. The isotherm parameters determined for Cd^{2+} and Zn^{2+} ions are shown in Table 6.

Based on the correlation coefficients (R) shown in Table 6, the isotherm data for the binary-ion systems complied with the Langmuir and Freundlich models in the concentration range. The adsorption capacities in the binary-ion systems (Q_{max}) for all adsorbents were lower than those values in the single-ion systems (Table 4), due to the competition between Cd^{2+} and Zn^{2+} ions.

The adsorption capacities (Q_{max}) for zeolites X ranged from 57.5 to 70.3 mg/g and from 59.7 to 72.3 mg/g for Zn^{2+} and Cd^{2+} ions, respectively. For zeolites A, the values for the adsorption capacities (Q_{max}) ranged from 88.7 to 90.1 mg/g and from 174 to 195 mg/g for Zn^{2+} and Cd^{2+}ions, respectively. The better performance of zeolites A compared to zeolites X showed in the binary-ion systems corroborates with the results previously shown in the adsorption isotherms for single-ion systems as well as the adsorption percentage studies.

4. Conclusions

1. Pure zeolites X and A were selectively produced from two Brazilian fly ashes. The pure zeolites X and A presented high CEC values ranging from 3.1 to 3.9 meq/g.
2. Pure zeolites X and A demonstrated high potential removal for zinc and cadmium ions from water at high concentrations. Zeolites A presented higher adsorption percentages for Cd^{2+} and Zn^{2+} ions than zeolites X in single and binary ion systems due to the higher cation exchange capacity. The removal of both ions by zeolites A was less affected by the competitor ion in binary systems. Zeolites X and A showed higher affinity to Zn^{2+} than Cd^{2+} for both single and binary ion systems under similar experimental conditions.
3. The adsorption percentages in the binary-ion systems were generally lower than those in single-ion systems. In general, cadmium removal was more affected by the presence of zinc due to the preference for Zn^{2+} ions by the pure zeolites.
4. The experimental data for all isotherms in single and binary ion systems complied with the Langmuir and Freundlich models.

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