Zeolite synthesis from Brazilian coal fly ash for removal of Zn^{2+} and Cd^{2+} from water

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Abstract. A Brazilian fly ash sample (CM1) was used to synthesize zeolites by hydrothermal treatment. Products and raw materials were characterized in terms of real density (Helium Pycnometry), specific surface area (BET method), morphological analysis (SEM), chemical composition (XRF) and mineralogical composition (XRD). The zeolites (ZM1) from fly ash were used for metal ion removal from water. Results indicated that hydroxy-sodalite zeolite could be synthesized from fly ash sample. The zeolite presented higher specific surface area and lower SiO_2/Al_2O_3 ratio than the ash precursor. The adsorption showed that cadmium is more preferentially adsorbed on ZM1 than zinc. The adsorption equilibrium time for both Zn^{2+} and Cd^{2+} was 20 hours in a batch process. The adsorption isotherms were better fitted by the Langmuir model and the highest percentages of removal using ZM1 were obtained at pH 6 and 5 and doses of 15 and 18 g L^{-1} for Zn^{2+} and Cd^{2+}, respectively. Thermodynamic studies indicated that adsorption of Zn^{2+} and Cd^{2+} by ZM1 was a spontaneous, endothermic process and presented an increase of disorder at the interface solid/solution.

Introduction

The use of coal for energy supply is still widely employed around the world and of large importance in the global economy. However, thermal power plants face the problem of coal fly ash disposal. In Brazil, Figueira Power Plant is the only coal-based thermal power plant in the state of Paraná and responsible for supplying energy for aproximately 40,000 residents, moreover, it is the only large industry in the area and responsible for jobs and the state's economy. Nevertheless, the fly ash generated from coal combustion is inappropriately disposed, causing environmental problems. Fly ash generated by power plants can be modified by physical and/or chemical treatment [1]. The treated material has better adsorption capacity than the precursor [2]. Thus, fly ashes have been converted in zeolites and have been used for various applications [3-6].

The present work describes synthesis of zeolites from the fly ash of Figueira Power Plant, Brazil, and characterization of both materials. In addition, adsorption studies using the zeolitic material in removal of Zn^{2+} and Cd^{2+} metal ions will be also reported.

Materials and Methods

Materials. Approximately 1 kg of coal fly ash from bag filters was collected from Figueira Power Plant located in Paraná State (PR), Brazil. The fly ash was used without any pretreatment for the synthesis of zeolite and was labeled as CM1. Sodium hydroxide obtained from Merck was used in the zeolite synthesis. The standard solutions of metal ions, Cd^{2+} and Zn^{2+}, were prepared from their salts. For pH adjustment, 0.01 mol L^{-1} HNO_3 and 0.5 mol L^{-1} NaOH were used.

Zeolite Synthesis. Conventionally hydrothermal treatment [7] was used in the zeolite synthesis: 20 g of coal fly ash were mixed with 160 mL of 3.5 mol L^{-1} NaOH aqueous solution in a Teflon vessel (ash/solution ratio = 0.125 g mL^{-1}). This mixture was heated to 100 °C for 24 h. The suspension was

filtered through a quantitative filter paper and the solid was repeatedly washed with deionized water until the pH of filtrate is at ~ 9. Then the solid was dried at 100 °C for 24 h. The zeolitic product obtained was labeled as ZM1.

Characterization. The real density and the specific surface area of fly ash and zeolite were determined by a helium picnometer (Micromeritics Instrument Corporation - Accupyc 1330) and a BET Surface Area Analyzer (Quantachrome Nova – 1200), respectively. Prior to determination of the specific surface area, samples were heated at 150 °C for 12 h to remove volatiles and moisture in a degasser (Nova 1000 Degasser). The BET surface areas were obtained by applying the BET equation to the nitrogen adsorption data. To verify the morphology, samples were covered with a thin layer of gold to make them conductive and examined using a scanning electron microscope (Philips – XL30). The chemical composition of the samples was determined by X-ray fluorescence (Rigaku Company – RIX 3000 X-ray Fluorescence Spectrometer). The mineralogical composition of the samples was determined by X-ray diffraction (Rigaku - Miniflex II X-ray Diffractometer) using Cu Kα radiation at 30 kV and 15 mA. The scan rate was 0.05 °/s and ranged between 5 - 80 ° (2θ). Phase identification was made by searching the ICDD powder diffraction file database, with the help of Crystallographica Search-Match program and JCPDS (Joint Committee on Powder Diffraction Standards) files for inorganic compounds.

Metal ion removal studies. Batch processes for metal ion adsorption were performed. One gram of zeolite was placed in contact with 100 mL of metal ion solution of known concentration under agitation. The contact time was 2, 4, 6, 8, 12, 15, 20 and 24 hours. The supernatant was separated by centrifugation (10 min at 2000 rpm) and the metal ion concentration was determined by complexometric titration with EDTA. The metal ion removal percentage was obtained by Eq. (1) and the adsorption capacity of the adsorbent per mass unit (q_f) was calculated using Eq. (2):

$$\text{Removal \%} = \frac{C_o - C_f}{C_o} \times 100. \tag{1}$$

$$q_f = \frac{C_o - C_f}{m} \times V. \tag{2}$$

Where: C_o and C_f are the initial and final metal ion concentrations, respectively, V is aqueous phase volume and m is the weight of adsorbent used. A mechanical shaker at 120 rpm (Ética – Mod. 430) and centrifuge were used. The data of isotherms were obtained after an equilibrium time of 24 hours. The concentration of metals ranged from 275 to 922 mg L^{-1}. All experiments were performed in duplicate.

Results and Discussion

Characterization. Physico-chemical properties of CM1 and ZM1 are given in Table 1. Fig. 1 shows X-ray diffraction patterns of the two samples. According to Table 1, Brazilian fly ash is mainly composed of SiO_2 (40.9 wt%), Fe_2O_3 (27.2 wt%) and Al_2O_3 (13.5 wt%). The high contents of silicon and aluminum indicate a good possibility for the synthesis of zeolites. Oxides of potassium, titanium, calcium, zinc, sulfur and others were found in amounts equal to or lower than 5 wt%. For the zeolite synthesized from fly ash, the chemical compositions are mainly silica, alumina, iron oxide and sodium oxide. A significant amount of Na element is incorporated in the final product due to hydrothermal treatment with NaOH solution. The quantities of As, U, Pb, Mg, Sr, Zr and Mn were reduced after hydrothermal treatment, indicating that this process produced a less toxic material to the environment than the raw material, however, this fly ash should be carefully deposited [8]. The SiO_2/Al_2O_3 ratios for fly ash and zeolite were 3.03 and 1.27, respectively. The SiO_2/Al_2O_3 ratio for the zeolite was lower than that of raw fly ash, indicating that the hydrothermal treatment contributed to the increase in the cation exchange capacity of the material. As shown in Table 1, the values of real

density for fly ash (2.38 g cm^{-3}) and zeolite (2.55 g cm^{-3}) were very close. For the specific surface area, CM1 and ZM1 samples presented 12.5 and 66.1 m^2 g^{-1}, respectively. These values agree with the specific surface area values found by other researchers for both fly ash and zeolites from fly ash [9-11]. The increase in the specific surface area of zeolite compared with its ash precursor is due to the formation of zeolitic phases, which will be confirmed by X-ray diffraction analysis. The formation of zeolites after hydrothermal treatment favors the increase of specific surface area because zeolites have high porosity and present channels and cavities, which contribute to their high values. Zeolites with higher surface area will favor the adsorption of metal ions in water. According to Fig.1(a), CM1 is composed mainly of quartz and mullite and presents trace amounts of hematite and magnetite. Hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) are present in this fly ash due to the reactions of pyrite (FeS$_2$) present in a large quantity in the coal, during its burn-off. For ZM1 sample, XRD patterns showed three kinds of hydroxy-sodalite zeolites formed. The differences among the zeolites are the chemical formula and the atoms distance which compose of the unit cell. Quartz and mullite are considered as resistant phases and remained in the zeolite sample after hydrothermal treatment, as shown in Fig.1 (b).

Table 1. Physico-chemical properties of fly ash (CM1) and zeolite from fly ash (ZM1)

Components	Composition (wt %)	
	CM1	ZM1
SiO$_2$	40.9	38.7
Al$_2$O$_3$	13.5	30.5
Fe$_2$O$_3$	27.2	14.6
Na$_2$O	-	6.40
K$_2$O	5.00	0.680
CaO	2.60	2.00
TiO$_2$	2.60	1.70
ZnO	2.20	0.650
SO$_3$	1.40	1.40
P$_2$O$_5$	1.40	1.10
As$_2$O$_3$	1.20	-
U$_3$O$_8$	0.460	0.170
PbO	0.350	0.140
MgO	0.310	1.60
SrO	0.240	-
ZrO$_2$	0.210	-
MnO	0.110	-
SiO$_2$/Al$_2$O$_3$	3.03	1.27
Real density	2.38 g cm^{-3}	2.55 g cm^{-3}
S$_{BET}$	12.47 m^2 g^{-1}	66.12 m^2 g^{-1}
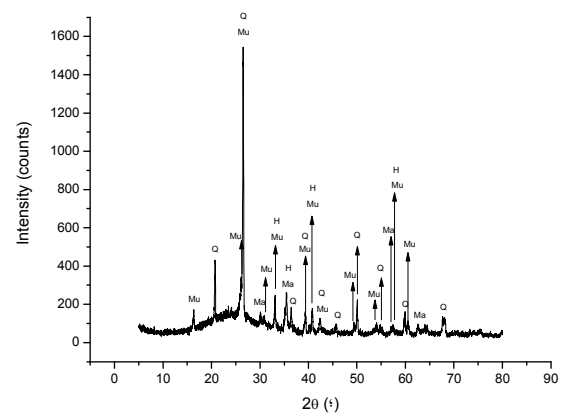
(a)
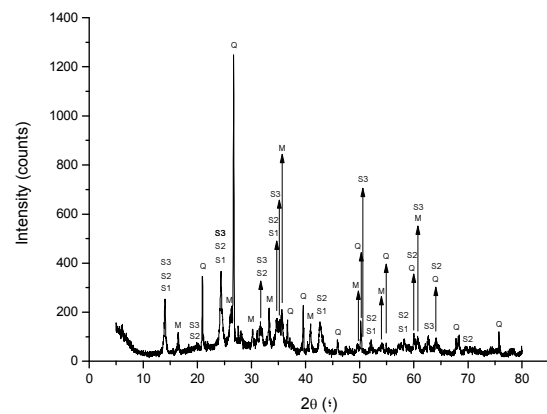
(b)

Fig. 1. XRD Patterns for CM1 and ZM1: Q = SiO$_2$ (Quartz), Mu = Al$_2$(Al$_{2.8}$Si$_{1.2}$)O$_{9.54}$ (Mullite), H = Fe$_2$O$_3$ (Hematite), Ma = Fe$_3$O$_4$ (Magnetite), S1 = Na$_{1.08}$Al$_2$Si$_{1.68}$O$_{7.44}$ · 8H$_2$O, S2 = Na$_6$[AlSiO$_4$]$_6$.4H$_2$O and S3 = Na$_8$Al$_6$Si$_6$O$_{24}$(OH)$_2$(H$_2$O)$_2$ (Hydroxy-sodalite zeolites).

The scanning electron micrographs (SEM) of CM1 and ZM1 are shown in Fig. 2. Coal fly ash particles typically had the predominance of spherical shapes at different sizes and smooth surfaces (Fig. 2a), similar to previous observations from other studies [12-14]. According to Fig. 2 (b), the surface of zeolites is rough, indicating that zeolite crystals were deposited on the surface of fly ash particles during the hydrothermal treatment [13].
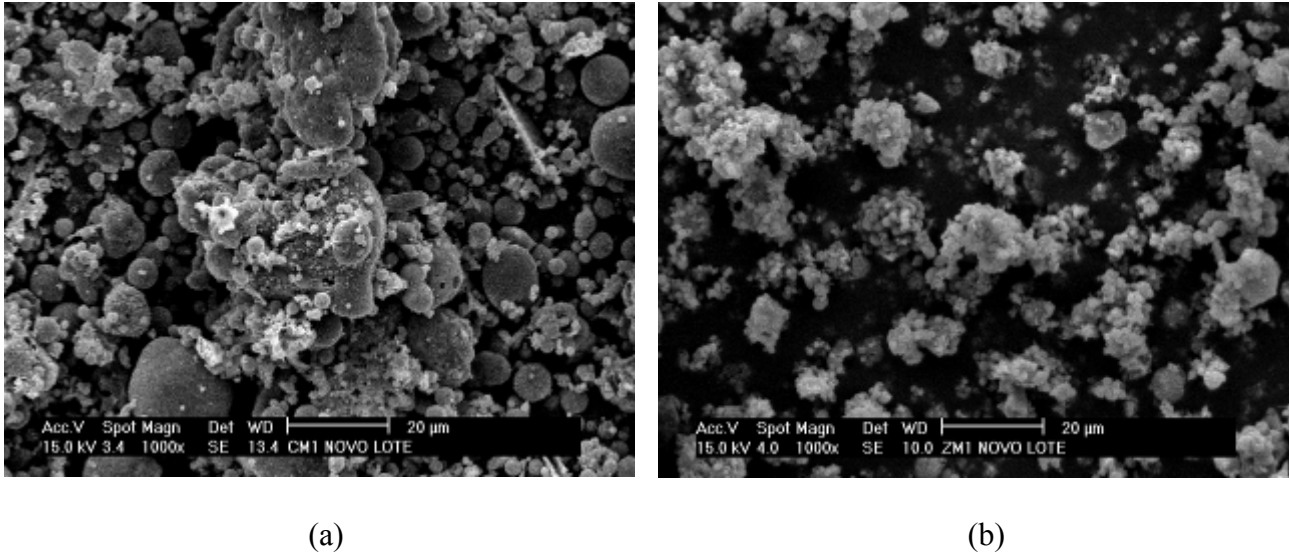

(a)   (b)

Fig. 2. SEM micrographs of a) CM1; b) ZM1.

Metal ion removal studies. In a previous study, CM1 fly ash presented removal percentages under 2.7% for Zn^{2+} and Cd^{2+} ions. On the other hand, ZM1 presented better performance in metal ion removal than its precursor material due to the formation of zeolites after hydrothermal treatment and higher specific surface area. Fig. 3 shows the effect of stirring time in the adsorption of Zn^{2+} and Cd^{2+} under different concentrations using ZM1 as an adsorbent. The stirring time was 2, 4, 6, 8, 12, 15, 20 and 24 hours.
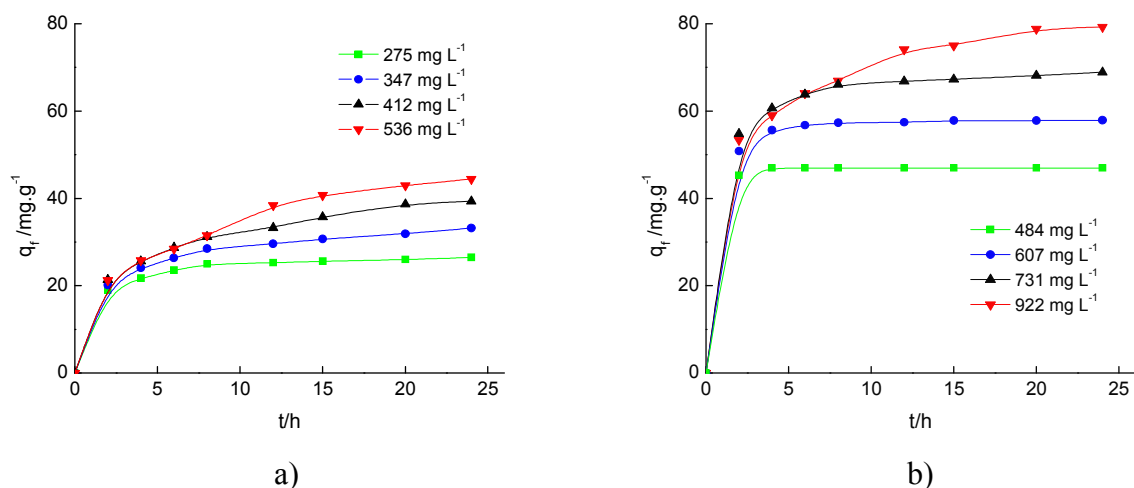

a)   b)

Fig. 3. Effect of stirring time on the adsorption of a) Zn^{2+} and b) Cd^{2+} using ZM1
(weight of adsorbent = 1 g, T = 25 ° C; pH_{in} = 5).

As can be seen from Fig. 3, the equilibrium time achieved by ZM1 for both Zn^{2+} and Cd^{2+} removal was 20 hours. The percentages of adsorption at different concentrations of Zn^{2+} and Cd^{2+} using ZM1 after 24 hours of agitation are shown in Table 3.

Table 3. Zinc and cadmium removal by ZM1 after 24 hours of contact.

Zn^{2+}		Cd^{2+}	
C_o (mg L^{-1})	% Removal	C_o (mg L^{-1})	% Removal
275	96.4	484	97.7
347	96.2	607	95.4
412	95.2	731	94.6
536	82.9	922	86.0

According to Table 3, the removal efficiency ranged from 82.9 to 96.4% for Zn^{2+} and from 86.0 to 97.7% for Cd^{2+}, indicating a higher affinity of Cd^{2+} on ZM1 than Zn^{2+}. A shaking time of 24 hours was used in adsorption isotherm studies to ensure that the process reaches equilibrium. The adsorption isotherms for Zn^{2+} and Cd^{2+} on ZM1 are shown in Fig. 4.
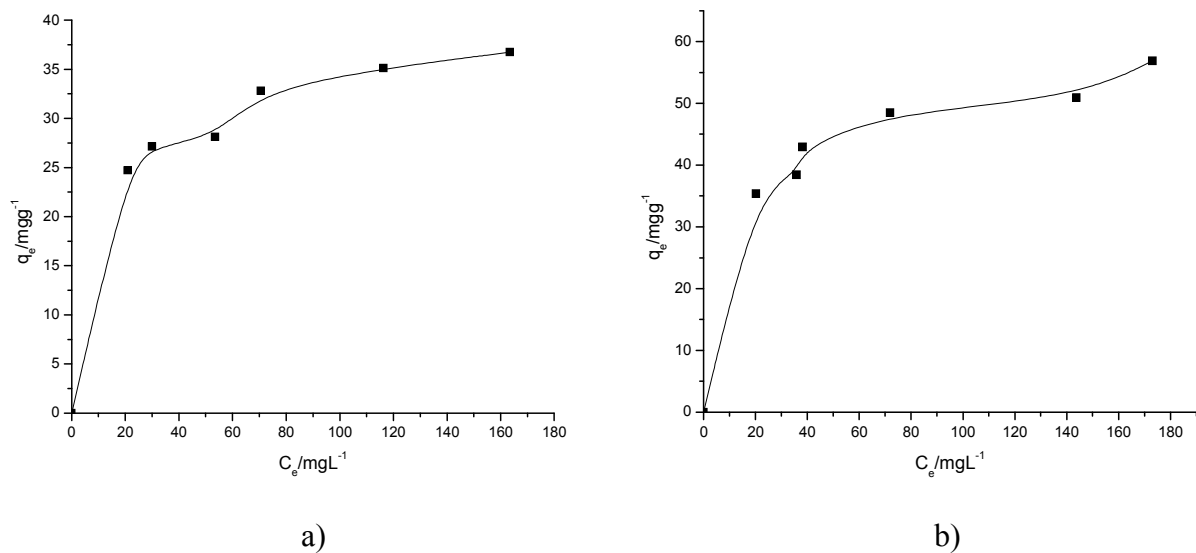

a)   b)

Fig. 4. Adsorption isotherms of a) Zn^{2+} and b) Cd^{2+} on ZM1 (T = 25 °C).

Table 4. Langmuir and Freundlich parameters calculated from Zn^{2+} and Cd^{2+} isotherms using ZM1 adsorbent.

Adsorbent	Adsorbate	Langmuir Parameters		
		Q_o (mg g^{-1})	K_L (L mg^{-1})	R
ZM1	Zn^{2+}	40.1	0.0600	0.998
	Cd^{2+}	60.1	0.0600	0.996
		Freundlich Parameters		
		K_f*	n	R
	Zn^{2+}	13.6	5.10	0.977
	Cd^{2+}	19.3	4.90	0.969

(*)(mg g^{-1}) (L mg^{-1})$^{1/n}$

According to [15], the adsorption isotherms (Fig. 4) showed a general behavior consistent with the types L2 and L3. The L-type isotherms indicate the existence of non-specific interactions between solute molecules and adsorbent interface. For L2 type isotherm, a monolayer is formed and the adsorption affinity increases with increasing concentration of adsorbate until saturation. For L3 type, adsorbate-adsorbate interaction allows the formation of multilayers. The isotherm parameters were determined using the Langmuir and Freundlich equations (Table 4).

According to correlation coefficients (R), the experimental data complied better to the Langmuir model (Table 4). The adsorption capacity (Q_o) was 40.1 mg g^{-1} for Zn^{2+} and 60.1 mg g^{-1} for Cd^{2+}, indicating the following sequence of selectivity: $Cd^{2+} > Zn^{2+}$. This order of selectivity can be resulted from several factors that influence the behavior of ion exchange in zeolites; however, the main factors are the free energy of hydration and the size of hydrated ions [16,17]. Table 5 shows the ionic radius, hydrated radius and hydration energies of the metal ions studied in the present work.

Table 5. Radius and hydration energy for Zn^{2+} and Cd^{2+} [18]

Metal ions	Ionic radius (Å)	Hydrated radius (Å)	Free energy of hydration (Kcal g^{-1}- íon)
Zn^{2+}	0.83	4.30	- 484.6
Cd^{2+}	1.03	4.26	- 430.5

Metals with high free energy of hydration prefer to remain in solution, where its hydration can be satisfied while the metals with low free hydration energies are more easily to be adsorbed. On the other hand, ions having a smaller hydrated radius are better than those with larger hydrated radius to fill in the pores and discontinuities in adsorbent surface [19]. Thus, the higher affinity of ZM1 for Cd^{2+} ion can be ascribed to the lower free energy of hydration and the smaller hydrated radius.

The effect of initial solution pH on Zn^{2+} and Cd^{2+} removal using ZM1 is shown in Fig. 5. The highest removal percentages were 86.4% for Zn^{2+} and 87.1% for Cd^{2+} at pH 5 and 6, respectively. The retention efficiency decreased with decreasing pH value due to competition between protons and metal ions for active sites on adsorbent surface. This study was not performed at pH above 6.0 due to the possibility of metal ion precipitation. Zn^{2+} precipitates at pH values between 7.0 and 8.0 and Cd^{2+} precipitates at pH around 8.4.
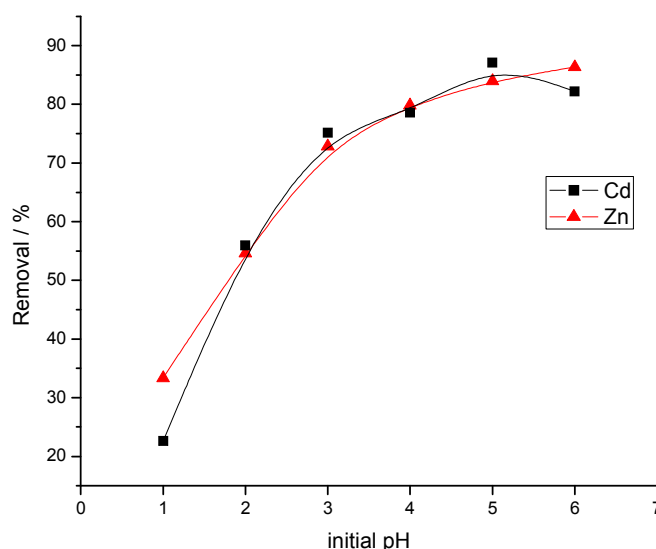

Fig. 5. Effect of initial pH for Zn^{2+} and Cd^{2+} removal by ZM1 (C_o = 337 mg L^{-1} for Zn^{2+} and 607 mg L^{-1} for Cd^{2+}; adsorbent mass = 1 g, T = 25 °C, t stirring = 24 h).

The effect of ZM1 dose on Zn^{2+} and Cd^{2+} removal is shown in Fig. 6. The initial concentrations were 337 mg L^{-1} and 634 mg L^{-1} for Zn^{2+} and Cd^{2+}, respectively. The shaking time of 24 hours and temperature of 25 °C were used in this study.

<p style="text-align:center">a)   b)</p>
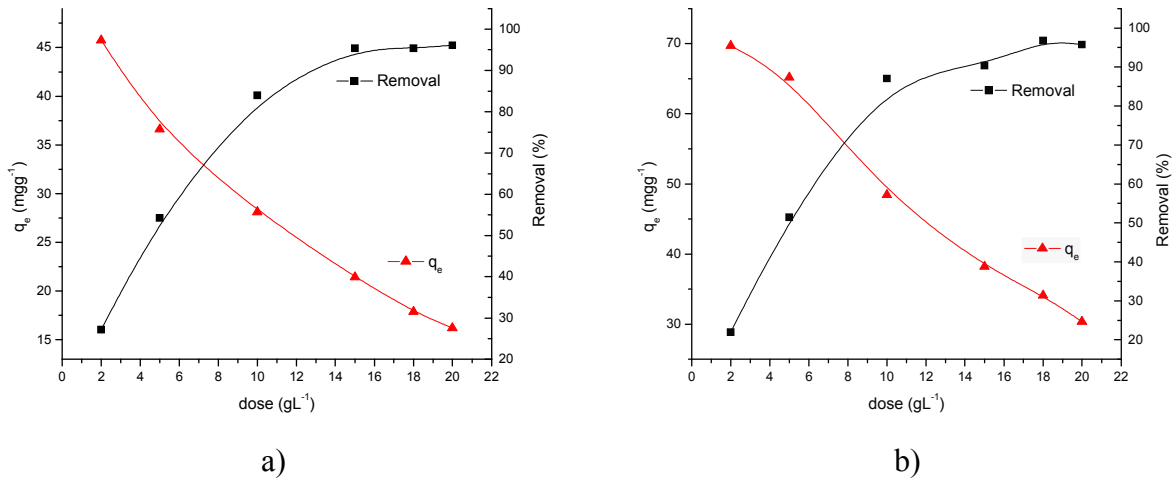
<p style="text-align:center">Fig. 6. Influence of ZM1 dose on removal of a) Zn^{2+} and b) Cd^{2+}.</p>

The removal efficiency of Zn^{2+} and Cd^{2+} increased from 27 to 95% and from 22 to 97%, respectively, with the increase of zeolite dose from 2.0 to 18.0 g L^{-1} and remained approximately constant after reaching 96% of removal under the maximum dose of 20.0 g L^{-1} for both ions. The removal efficiencies of Zn^{2+} and Cd^{2+} increased with increasing of adsorbent dose until reaching an equilibrium level, while the adsorption capacity (q_e - mg g^{-1}) decreased with increasing dose. The increase of adsorption percentage using higher doses occurred due to the increase in specific surface area and the availability of adsorption sites when the amount of adsorbent increases. The adsorption capacity may decrease when the adsorbent dose increases due to the adsorbent aggregation resulted from the high dose of adsorbent. This aggregation could lead to a decrease in the total specific surface area of the adsorbent [20].

In adsorption processes, considerations of energy and entropy should be considered to determine whether the process will occur spontaneously or not. The values of thermodynamic parameters are the indicators for practical application of the adsorption processes. In this study, the characteristics of adsorption in relation to temperature were evaluated in accordance to thermodynamic parameters, such as Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o). These parameters were calculated using Eqs. 5 – 8.

$$K_C = \frac{C_A}{C_s}. \tag{5}$$

$$\Delta G^o = -\,2.303\ RT \log K_C \ (KJ\ mol^{-1}). \tag{6}$$

$$\Delta H^o = 2.303\ R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \log \frac{K_{C_2}}{K_{c_1}} \ (KJ\ mol^{-1}). \tag{7}$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \ (JK^{-1}\ mol^{-1}). \tag{8}$$

Where, K_C is the equilibrium constant, C_A is the adsorbed metal ion concentration at equilibrium, C_s is the concentration of metal ion in the solution at equilibrium, R is the gas constant (8.314 J mol^{-1} K^{-1}). T, T_1 and T_2 are the temperatures in Kelvin and K_C, K_{C1}, K_{C2} are the equilibrium constants at temperatures T, T_1 and T_2, respectively. Table 6 shows the thermodynamic parameters obtained for Zn^{2+} and Cd^{2+} adsorption on ZM1.

Table 6. Thermodynamic parameters obtained for Zn^{2+} and Cd^{2+} adsorption on ZM1.

Metal ion	T / °C	$\Delta G°$ / kJ mol^{-1}	$\Delta H°$ / kJ mol^{-1}	$\Delta S°$ / J K^{-1} mol^{-1}
Zn^{2+}	25.0	-3.62	26.4	101
	30.0	-4.12	24.9	95.9
	40.0	-5.08	-	-
Cd^{2+}	25.0	-5.29	45.5	170
	30.0	-6.14	29.7	118
	40.0	-7.32	-	-

Negative values of $\Delta G°$ at different temperatures indicated that the nature of Zn^{2+} and Cd^{2+} adsorption under the current conditions is spontaneous. The positive values of $\Delta H°$ and $\Delta S°$ confirmed the endothermic nature of adsorption and the increase of disorder at the interface solid/solution during the metal ion adsorption when the zeolite from fly ash was used.

Conclusions

1. Hydroxy-sodalite zeolites could be synthesized from coal fly ash by hydrothermal treatment. ZM1 zeolite presented higher specific surface area, lower SiO_2/Al_2O_3 ratio and better characteristics in Zn^{2+} and Cd^{2+} removal than ash precursor (CM1).
2. Cadmium is more preferentially adsorbed than zinc on ZM1. The adsorption equilibrium time reached by ZM1 for both Zn^{2+} and Cd^{2+} was 20 hours. The highest percentages of removal using ZM1 were obtained at pH 6 and 5 and at doses of 15 and 18 g L^{-1} for Zn^{2+} and Cd^{2+}, respectively.
3. The adsorption isotherms were better fitted by the Langmuir model. Thermodynamic studies indicated that adsorption of Zn^{2+} and Cd^{2+} by ZM1 is spontaneous, endothermic and presents an increase of disorder at the interface solid/solution.

Acknowledgements

References

[1] S. Wang, H. Wu: J. Hazard. Mater Vol. B136 (2006), p. 482.

[2] S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu: Water Res Vol. 39 (2005), p. 129.

[3] X. Querol, N. Moreno, J.C. Umaña, A. Alastuey, E. Hernandez, A. Lopez-Soler, F. Plana: Int. J. Coal Geol Vol. 50 (2002), p. 413.

[4] J. C. Izidoro, D. A. Fungaro: Rev. Bras. Pesq. Des Vol. 9 (2007), p. 101.

[5] T. E. M. Carvalho, D. A. Fungaro, J. C. Izidoro: Quim. Nova Vol. 33 (2010), p. 358.

[6] K-M. Lee, Y-M. Jo: J. Mater. Cycles Waste Manag Vol. 12 (2010), p. 212.

[7] T. Henmi: Soil Science Plant Nutrition Vol. 33 (1987), p. 517.

[8] F. S. Depoi, D. Pozebon, W. D. Kalkreuth: Int. Journal Coal Geol Vol. 76 (2008), p. 227.

[9] C. F. Lin, H. C. Hsi: Environ. Sci. Technol Vol. 29 (1995), p. 1109.

[10] J. Scott, D. Guang, K. Naeramitmarnsuk, M. Thabuot, R. Amal: J. Chem. Technol. Biotechnol Vol. 77 (2001), p. 63.

[11] J. C. Umaña-Peña: PhD Thesis. Universitat Politécnica de Catalunya, Barcelona, Espanha (2002).

[12] I. D. Fernandes, L. Ferret, C. A. Khahl, J. C. T. Endres, A. Maegawa: *Crystaline microstruture modification of brazilian coal ash with alcaline solution* (Proceedings of International Ash Utilization Symposium, University of Kentucky, USA, 1999).

[13] K. Ojha, N. C. Pradhan, A. M. Samanta: Bull. Mater. Sci Vol. 27 (2004), p. 555.

[14] Z. Sarbak, A. Stanczyk, M. Kramer-Wachowiack: Powder Technol Vol. 145 (2004), p. 82.

[15] C. H. Giles, T. H. Macewan, S. N. Nakhua, D. Smith: J. Chem. Soc. London (1960), p. 3973.

[16] H. W. Sherry, in: *Ion Exchange*, edited by Marcel Dekker, The ion exchange properties of zeolites, chapter , 2, New York (1969).

[17] S. K. Ouki, M. Kavannagh: Waste Manage. Res Vol. 15 (1997), p. 383.

[18] M. J. Semmens, M. Seyfarth, In: *Natural zeolites: occurrence, properties, and use*, edited by L. B. Sand and F. A. Mumpton, The selectivity of clinoptilolite for certain heavy metals (1981).

[19] N. Ortiz: PhD Thesis. Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil (2000).

[20] A. Shukla, Y. H. Zhang, P. Dubey, J. L. Margrave, S. S. Shukla: J. Hazard Mater Vol. B95 (2002), p. 137.

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