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REMOVAL OF CADMIUM AND ZINC FROM AQUEOUS SOLUTIONS USING ZEOLITE SYNTHESIZED FROM COAL FLY ASH AND INDUSTRIAL ALUMINIUM WASTE

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ABSTRACT: Coal fly ash can be used as a source of Silicon and Aluminum for 4A zeolite synthesis. It is necessary to consider the adequate proportion of Si / Al for the synthesis, so the aluminum waste from tertiary industry was used as an alternative and sustainable aluminum source. The synthesis was carried out by alkaline fusion followed by the hydrothermal treatment obtaining sodium aluminosilicate, which was then crystallized in NaOH solution. The samples were characterized by XRF, XRD and cation exchange capacity. The zeolite produced has the capacity to adsorb the Cd (II) and Zn (II) ions from aqueous solutions. The maximum adsorption capacity was 78.0 and 35.8 mg.g^{-1} for the Cd and Zn, respectively. The results showed that the aluminum waste and the fly ash together can be transformed into zeolite A, considered as value-added material and with promising adsorption properties.

KEYWORDS: coal fly ash; non-conventional aluminum source; zeolite A; hazardous waste; adsorption

1. INTRODUCTION

Currently, aluminum is a product with a growing consumption due to its remarkable properties which are suitable in most areas of everyday life as transport, engineering, construction and packaging. The worldwide implementation of aluminum has been successful due to the cost reduction in the manufacture process and the large possibilities of recover.

In Brazil, research on industrial waste recycling started to become popular in the 1970's, with the increase of the steel-making sector. In the early 1990's, with the introduction of aluminum beverage cans in the national Market, aluminum recycling activities started to grow. Since then the sector has continuously grown and today Brazil is one of the world's largest aluminum recyclers, forward of Japan and Europe (Associação Brasileira de Alumínio, 2016).

The aluminum industry (primary and secondary) generates high amounts of slag during the melting process. The primary industry which obtains aluminum from treatment of bauxite (aluminum mineral), this slag may contain up to 80% metallic aluminum (Shinzato and Hypolito, 2001; 2005).

Due to high content of metal, such slags are reused along with aluminum scrap (beverage cans, flakes of industries that use aluminum as raw material and others) by the secondary companies. The secondary industry recovers metal by melting it in rotary kilns fueled by combustible oils, using sodium chloride as a flux. This process generates new slag, less rich in aluminum (amount about 20% of total volume), but with high sodium chloride contents, above metal oxides, carbides and nitrides.

The tertiary industry uses the metal aluminum waste of the secondary industry by the crushing and leaching process. The recovered aluminum returns to the secondary companies, which refund it with the other scraps and sell the recycled metal to transformation industries.

However, there isn't reuse of final waste of the tertiary industry that carries out this recycling. These slags, in general, are a rather complex mixture containing free metals, metal oxides and salts (NaCl) and are discarded at landfills without undergoing any treatment that minimizes their environmental impact. The suggestion is that this solid residue can be reused in some way by remedying the environmental problems caused by this material, especially the contamination of groundwater.

Another area of the industry that produces a large amount of waste is thermoelectrics. The Brazilian thermoelectric power plants produce coal ash (~ 4 million tons / year) during the burning of coal. About 85% fly ashes and 15-35% bottom ashes are produced (Levandowski and Kalkreuth, 2008).

The principal problem of coal ash is related to the disposal of this waste in an inadequate way, that can cause a great environmental impact in the soil and in the groundwater s due to the leaching of toxic elements, mainly As, Cd, Mo, Pb, TI , U, Zn and Hg, present in their composition (Depoi et al., 2008; Quispe et al., 2012). In addition to the environmental impact that this type of disposal causes, siliceous powder from the ash can reach the resident population close to installations by the action of wind on the surface of the sedimentation basins.

Therefore, to synthesize a value-added material, a sustainable alternative is the application of coal fly ash and aluminum slag as a source of silica and aluminum for the synthesis of zeolite. (Izidoro et al., 2012).

Recently, several methods for the synthesis of zeolite from coal ash and aluminum waste have been developed. However, for the formation of different types of zeolite, the ratio SiO_2 / Al_2O_3 and the time of the hydrothermal treatment are the main points that will lead to the formation of zeolite A (Izidoro et al., 2013).

The objective of this study was to synthesize zeolite A from aluminum waste and coal fly ash and to evaluate the use as adsorbent for Zn and Cd removal from aqueous solution.

2. MATERIALS AND METHODS

2.1. Materials

All chemicals used for experimental studies were of analytical grade. Coal fly ash sample (CFA) was collected from electrostatic precipitators of Charqueadas coal-fired power plant, located in Rio Grande do Sul State, Brazil. The residue of aluminum tertiary industry (RA) was provided by the company Latasa Recycling located in São Paulo State, Brazil.

2.2. Zeolite A Synthesis

In the synthesis of zeolite-A, 20g of CFA were mixed with 40g of RA and 72g of NaOH. The RA was added to adjust the molar ratio of SiO_2/Al_2O_3 to 1 and the wastes (CFA + RA): NaOH was fixed at 1:1.2 (wt%). The mixture was heated at 550°C for 1h. The fused sample was allowed to cool to ambient temperature and ground into a fine powder using a mortar and pestle. Then, 600 mL of deionized water were added and the mixture was stirred at room temperature for 16h. The resulting slurry formed was subjected to hydrothermal crystallization at 100°C for 7h. After cooling down to room temperature, the suspension was centrifuged at 2000 rpm for 10 min, the solid was washed with 1L of deionized water and dried overnight at 80°C. The zeolite formed (ZRA) was powdered for further use (Izidoro et al.,2013).

2.3. Characterization of material

The mineralogical compositions were determined by X-ray diffraction analyses (XRD) with an automated Rigaku miniflex 2 diffractometer with Cu anode using Co Kα radiation at 40 kV and 20 mA over the range (2θ) of 5–80°with a scan time of 0.5°/min. The chemical composition was determined by X-ray fluorescence (XRF) in Rigaku RIX- 3000 equipment. Cation exchange capacity (CEC) was determined by a previously described procedure (Izidoro et al., 2013).

2.4. Adsorption Studies

The adsorption was performed using the batch procedure. Equilibrium adsorption experiment was performed using various concentrations of cadmium (438 to 1255 mg L^{-1}) and zinc (152 to 463 mg L^{-1}) solution. A mixture of 0.25 g of ZRA with 25 mL of metal ion solution of various initial concentrations was shaken at 120 rpm for 24 h at 25 °C. The collected samples were then filtrate and the concentration in the filtrate solution was analyzed using inductively coupled plasma optical emission spectrometry (Spectro ARCOS, Spectro Analytical Instruments, Kleve, Germany). All experiments were performed in duplicate.

The adsorption capacity of the adsorbent was calculated using the Eq. (1):

$$q_e = \frac{(C_o - C_e) \times V}{M} \qquad (01)$$

Where *qe* is the amount of metal adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1}), *Co* and *Ce* are the initial and equilibrium concentrations, respectively (mg L^{-1}); *V* the volume of the adsorbate solution added (L) and M the amount of the adsorbent used (g).

The data of the isotherm adsorption equilibrium were fitted using nonlinear equations of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models. The Chi-square (X^2) test for each parameter was used to measure the goodness-of-fit. Apart from X^2, the correlation coefficient (R^2) was also used to determine the best-fitting isotherm to the experimental data (Ncibi, 2008; Alcântara, 2016).

3. RESULTS AND DISCUSSION

3.1. Characterizations of Materials

Physico-chemical properties of coal fly ash has been reported in previous a paper (Izidoro et al., 2013).

The final waste from the tertiary industry consists of metallic aluminum, aluminum oxide and a large amount of salts used as fluxing material. Their chemical composition varies according to the type and quality of the processed scrap, the classification and trapping methods used, etc. (López-Delgado and Tayibi, 2012).

The chemical compositions of RA in the form of oxides are shown in Table 1. The major component was Al_2O_3, Cl and Na_2O along with percentages range between 3.8 and 1.6 wt% of SiO_2, MgO, K_2O and FeO_2.

The high Cl and Na content are attributable to the employ of high amounts of salt (mainly NaCl and KCl) in the melting process to get a higher aluminum recovery (Shinzato and Hypolito, 2005). Others metals may be associated with the different kinds of scrap used in secondary industry.

Table 1. Waste composition (main components) obtained by XRF and expressed as oxides (wt%)

Oxide	**wt%**
Al_2O_3	27.80
Cl	17.40
Na_2O	16.70
SiO_2	3.78
MgO	2.37
K_2O	2.27
Fe_2O_3	1.59
Others	≤ 0.9

The XRD pattern of the residue of aluminum tertiary industry is show in Figure 1. The crystalline phases were mainly composed of corundum (Al_2O_3; ICDD 42-1468), sylvite (KCl; ICDD 0041-1476), spinel ($MgAl_2O_4$; ICDD 002-1084), halite (NaCl; ICDD 001-0994) and fayalite ($2FeO.SiO_2$ ICDD 002-0784). The high background of the XRD profile also indicates the presence of non-well crystallized or amorphous phases in which metallic oxides such as iron oxide, among others, could be included.

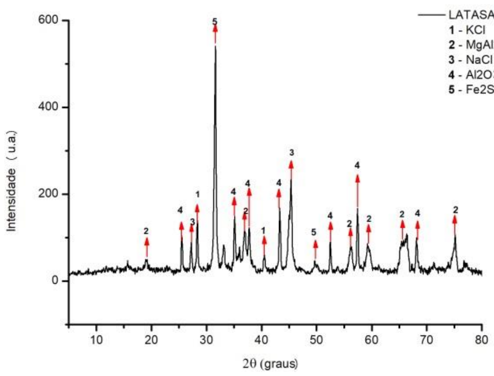

Figure 1. XRD pattern of the aluminum waste sample .

X-ray diffraction analysis was used to determine the morphology of synthesized zeolite from residue of aluminum tertiary industry and fly ash (ZRA). The results indicated that the synthesized zeolite product contain zeolite A as the major constituent phase, whereas hydroxysodalite and quartz were found as minor phases Figure 2. During the reaction some zeolite A was converted into hydroxysodalite and quartz content is due to incomplete dissolution of the Si sources from the wastes.

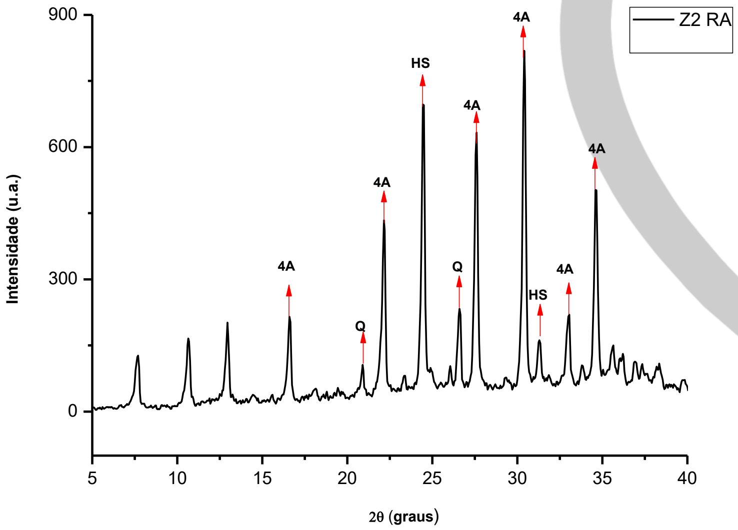

Figure 2. XRD patterns of zeolite synthesized from aluminum waste and coal fly ash.

3.2. Adsorption Isotherms

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R) models were used to describe the equilibrium data. Table 2 shows the values of isotherm parameters, correlation coefficients (R^2) and related standard error (X^2). The modeled isotherms for Cd and Zn are plotted in Figure 3 and 4.

Table 2. Langmuir, Freundlich, Temkin and DR parameters calculated from Cd^{2+} and Zn^{2+} isotherms in single – ion systems using zeolite A.

Parameters	**Cd^{2+}**	**Zn^{2+}**
Langmuir		
Q_o (mg g^{-1})	78.0	35.8
b_L (L mg $^{-1}$)	0.265	0.254
R^2	0.935	0.752
X^2	1.28	6.14
Freundlich		
k_F (mg g^{-1})(L $mg^{-1})^{1/n}$	40.0	13.4
1/n	0.112	0.223
R^2	0.945	0.920
X^2	0.766	1.01
Temkin		
k_T (L g^{-1})	143.0	8.94
B_T	7.13	5.32
b_t (kJ mol^{-1})	0.348	0.466
R^2	0.970	0.899
X^2	0.403	1.48
D-R		
β (mol^2 J^{-2})	1.20×10^{-9}	2.20×10^{-9}
k_{DR} (mol g^{-1})	8.79×10^{-4}	9.95×10^{-4}
E (kJ mol^{-1})	20.4	15.1
R^2	0.973	0.921
X^2	0.376	1.13

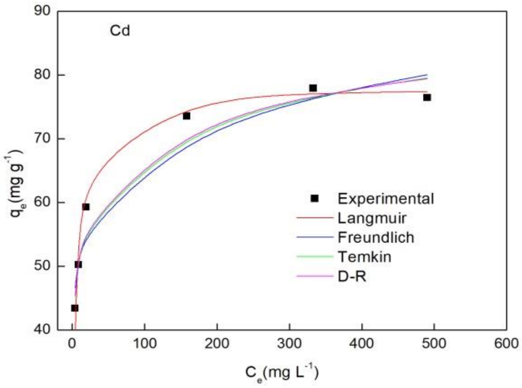

Figure 3. Adsorption isotherms of Cd^{2+} on synthesized zeolite A.

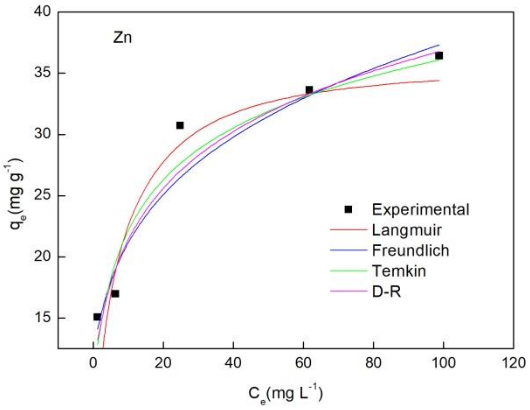

Figure 4. Adsorption isotherms of Zn^{2+} on synthesized zeolite A.

4. CONCLUSIONS

Zeolite was synthesized using a hazardous aluminum waste and coal fly ash as aluminosilicate source via two-step process. The X-ray diffraction analysis demonstrated that NaA was the main zeolitic phase formed after the synthesis. The material synthesized demonstrated high potential removal for zinc and cadmium ions from water at high concentration. The D-R and Freundlich model was the most appropriate for fit of the equilibrium experimental data for Cd and Zn, respectively. It can be concluded that fly ash-and aluminum waste-based zeolite was effective as adsorbent for removal of metals from water.

5. ACKNOWLEDGEMENTS

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