Synthesis and Characterization of Surface Modified Zeolitic Nanomaterial from Coal Fly Ash

Raquel R. Alcântara*, Juliana C. Izidoro, Denise A. Fungaro

Abstract
Coal fly ash is generated in large amounts in Brazil; therefore, its productive reuse is important. Zeolite was synthesized from coal fly ash obtained from the Presidente Medici Thermal Power Plant by alkaline conventional hydrothermal treatment and then modified using hexadecyltrimethylammonium (HDTMA). Coal fly ash (CFA), non-modified (ZCA) and surfactant-modified (SMZ) nanozeolites products were characterized to obtain chemical and mineralogical composition, surface area, and total and external cation-exchange capacity among other parameters. PXRD patterns revealed that zeolite P1 and hydroxysodalite were the dominant contents of synthesized zeolitic nanomater ials. Due to the zeolitazation, ZCA and SMZ exhibited a greatly enhanced cation exchange capacity and BET area compared to coal fly ash. The SMZ presented negative charge indicating the formation of a partial bilayer of HDTMA on exchangeable active sites on the external surface of unmodified nanozeolite. The characterization results show no changes occurred in ZCA after their surface modification with surfactant.

Keywords
Coal Fly Ash, Surfactant, Surface Modification, Nanozeolite Nanomaterial

1. Introduction
The principal use for the coal mined in Brazil is the combustion for power generation. Approximately 1.5% of the electricity generated in the country is derived from coal-fired power plants, which account for 1.9 GW of total installed capacity.

The largest coal reserves in Brazil, as well as the Presidente Medici coal-fired Power Station (UTPM-446 MW) are located in the region of Candiota, located 380 km from Porto Alegre City in the southwest of state of Rio Grande do Sul. The Candiota coal is a high bituminous class C volatile coal with high ash content [1].

The Brazilian power plants produce approximately 4 Mt tons of ashes every year, which are composed from 65 to 85% of fly ash and 15 to 35% of bottom ash [2]. Only 30% of fly ash is applied as raw material for cement and concrete production.

The remaining solid wastes are disposed in on-site ponds, nearby abandoned or active mine sites, or landfills [3]. The presence of coal ash in the environment is highly detrimental as it pollutes soil, water, and air through the insertion of potentially toxic substances. Thus, it is important to find ways to reuse it.

It has been shown that coal ash which is largely composed of Al and Si can be used as aluminosilicate source in the synthesis of zeolites. Zeolites present ability to act as catalysts, ion exchangers, adsorbents and membrane. There is therefore a wide range of potential applications in the fields of pollution control, radioactive waste management, petrochemical reactions, water purification, purification of gases, agriculture, etc [4].

The removal of heavy metals [5-7] and dyes [8-10] using zeolite synthesized from Brazilian fly ash as adsorbent nanomaterial has been reported in literature.

* Corresponding author
E-mail address: reisa@hotmail.com (R. R. Alcântara)
It is known that zeolitic material modified with quaternary amines can substantially enhance the adsorption of anionic and organic pollutants from aqueous solutions. These quaternary amines are composed of a hydrophilic and positively charged head group and a hydrophobic tail in their molecule structures. One of the most commonly used surfactants for zeolite surface modification is hexadecyltrimethylammonium bromide (HDTMA-Br) because of its availability and low cost [11-13].

Previous studies have reported that surfactant-modified nanozeolites from coal fly ash are effective adsorbents for the removal of anionic azo dyes Reactive Red 198 (RR), Acid Orange 8 (AO8) and Reactive Orange 16 (RO16) from water [14-16]. The maximum adsorption capacity was 5.7, 4.56 and 12.6 mg g\(^{-1}\) for RR, AO8 and RO16, respectively. The adsorption of dyes onto surfactant-modified nanozeolites was attributed to hydrophobic interaction and hydrogen bonding as predominant mechanisms. Hydrophobic interaction involves the hydrophobic tails of HDTMA and the hydrophobic functional groups of dyes molecules, and this mechanism is of London-Van der Waals type. The large number of hydrogen bonds between C or N of HDTMA and alkyl, aromatic and sulphonic groups of dyes is also responsible for the effective adsorption.

In this study, coal fly ash obtained from the Presidente Medici Thermal Power Plant was used to prepare surfactant-modified nanozeolite. The non-modified and modified zeolite and coal fly ash used as raw material were characterized and their properties were compared. The aim of the characterization was evaluated the potential of fly ash sample as a raw material in the production of high value products for increasing the productive chain of coal.

2. Material and Methods

2.1. Materials

All the reagents used for experimental studies were of analytical grade. The sample of coal fly ash (CFA) was collected by electrostatic precipitators of the A phase from the Presidente Medici Thermal Power Plant located in Canidiota City, State of Rio Grande do Sul, Brazil. The quaternary ammonium salt hexadecyltrimethylammonium bromide (HDTMA-Br, Merck), with molar mass 364.46 g mol\(^{-1}\) for RR, AO8 and RO16, respectively. The adsorption of dyes onto surfactant-modified nanozeolites was attributed to hydrophobic interaction and hydrogen bonding as predominant mechanisms. Hydrophobic interaction involves the hydrophobic tails of HDTMA and the hydrophobic functional groups of dyes molecules, and this mechanism is of London-Van der Waals type. The large number of hydrogen bonds between C or N of HDTMA and alkyl, aromatic and sulphonic groups of dyes is also responsible for the effective adsorption.

In this study, coal fly ash obtained from the Presidente Medici Thermal Power Plant was used to prepare surfactant-modified nanozeolite. The non-modified and modified zeolite and coal fly ash used as raw material were characterized and their properties were compared. The aim of the characterization was evaluated the potential of fly ash sample as a raw material in the production of high value products for increasing the productive chain of coal.

2.2. Synthesis of Zeolites from Fly Ash

Coal fly ash (20 g) was mixed with 160 mL of 3.5 mol L\(^{-1}\) NaOH aqueous solution in a 200 mL Teflon vessel. This mixture was heated to 100°C in oven for 24 h. After finishing of the process, the suspension was filtered with 4A quantitative filter paper. The zeolite from fly ash (ZCA) was repeatedly washed with deionized water until the pH of washing water reach ~ 11 and dried at 80°C for 12 h [17]. The modified zeolite (SMZ) was prepared by mixing 10 g of ZCA with 200 mL of HDTMA-Br 1.8 mmol L\(^{-1}\). The mixture was stirred for 7 h at 120 rpm at and 25°C. The suspension was filtered and the solid was dried in oven at 50°C for 12 h [18].

2.3. Characterization of Materials

The mineralogical compositions were determined by X-ray diffraction analyses (XRD) with an automated Rigaku multiflex 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. Scanning Electron micrograph/energy dispersive X-ray (SEM/EDS) was obtained by using XL-30 Philips scanning electron microscope. The particle size of the materials was measured using a laser based particle size analyzer, namely a Malvern MSS Mastersizer 2000 Ver. 5.54.

The bulk density and the specific surface area was determined by a helium picnometer (Micromeritics Instrument Corporation — Accupyc 1330) and by a BET Surface Area Analyser (Quantachrome Nova — 1200), respectively. Prior to determination of the specific surface area, samples were heated at 423.15 K 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. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on Nexus 670 Thermo Nicolet using KBr pellet method.

The cation exchange capacity (CEC) and external cation exchange capacity (ECCE) were determined according to the literature [19, 20].

The pH and the conductivity were measured as follows: samples (0.25 g) were placed in 25 mL of deionized water and the mixture was stirred for 24 h in a shaker at 120 rpm (Etica — Mod 430). After filtration, the pH of the solutions was measured with a pH meter (MSTecnopon — Mod MPA 210) and the conductivity was measured with a conductivimeter (BEL Engineering - Mod W12D).

To determine the point of zero charge (pH PZC) of the ZCA and SMZ, 0.1 g of sample were placed in 50 mL of sodium nitrate (0.1 mol L\(^{-1}\)) and the mixtures were shaken for 24 h on the mechanical shaker (Quimis - MOD Q • 225M) at 120 rpm. The solutions were adjusted to initial pH values of 2, 4, 10, 11, 12 and 13 by adding 0.1, and 1 mol L\(^{-1}\) HCl, or 3 mol L\(^{-1}\) NaOH solutions. The difference values between the initial and final pH (pH ∆) were placed in a graph in function of the initial pH. The point x where the curve intersects the y = 0 is the pH PZC.
3. Results and Discussion

3.1. Chemical Composition

The chemical compositions in form of oxides of the CFA, ZCA and SMZ obtained from XRF technique are shown in Table 1. The main components of CFA are silica (SiO$_2$), alumina (Al$_2$O$_3$) and ferric oxide (Fe$_2$O$_3$). Oxides of potassium, calcium, sulfur and others were found in amounts equal to or lower than 3 wt%.

For the zeolites nanomaterials ZCA and SMZ, the chemical compositions are mainly silica, alumina, iron oxide and sodium oxide. The significant amount of Na incorporated in the final products is the result of alkaline treatment with NaOH [21].

The resulting Al/Si ratio of the modified zeolite is 0.767 which is fairly close to that of the untreated form (0.786). This indicates that the Al atoms were not lost into the aqueous media during surface modification with surfactant. The content of bromide present in SMZ confirms the binding of HDTMA-Br on the surface of the zeolite by electrostatic attraction [18].

<table>
<thead>
<tr>
<th>Compounds</th>
<th>CFA (%)</th>
<th>ZCA (%)</th>
<th>SMZ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>52.4</td>
<td>42</td>
<td>43</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>22.9</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>4.9</td>
<td>6.6</td>
<td>7.2</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>3.0</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>CaO</td>
<td>2.4</td>
<td>3.4</td>
<td>3.7</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.3</td>
<td>11.1</td>
<td>8.6</td>
</tr>
<tr>
<td>MgO</td>
<td>1.1</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.1</td>
<td>1.4</td>
<td>1.6</td>
</tr>
<tr>
<td>S$_2$O</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Br</td>
<td>-</td>
<td>&lt;0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Others</td>
<td>0.011</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
</tbody>
</table>

Previous studies with analysis of coal, fly ash and bottom ash from Presidente Médice Power Plant were reported [1]. The fly and bottom ashes were characterized by relatively high contents of SiO$_2$ (56–59%) and Al$_2$O$_3$ (36–38%) and low contents of alkaline oxides. Elements were classified into three groups based on the analysis of trace element concentrations in fly and bottom ashes, and enrichments or depletions of these concentrations in relation to the coal: Group I (volatile elements with subsequent condensation): As, B, Bi, Cd, Ga, Ge, Mo, Pb, S, Sb, Sn, Ti and Zn; Group II (no volatile elements enriched in bottom ash vs. fly ash): Ca, Fe, Mn, P, Ti and Zr; Group III (low volatile elements with no partitioning between fly and bottom ashes): Al, Ba, Be, Co, Cr, Cs, Hf, K, Li, Mg, Na, Ni, Rb, Sr, Th, U, W, Y and most of heavy rare earth elements.

3.2. Physicochemical Properties

The physicochemical properties of the materials used in this investigation are presented in Table 2. The specific surface area value of the zeolitic materials (average value of 64.4 m$^2$ g$^{-1}$) was ~38 times greater than those of fly ash. The increase in the specific surface area of fly ash after hydrothermal treatment confirmed the formation of zeolitic phases. Zeolites have high porosity and present channels and cavities, which contribute to their high values of specific surface area [5].

Also, the CEC values of the zeolitic materials were ~10 times higher than the value of CFA because the SiO$_2$/Al$_2$O$_3$ ratio, which is associated to the cation exchange capacity, change after the hydrothermal treatment. The CEC of zeolitic material was not affected by the presence of the surfactant on the surface because the sites occupied by the surfactant molecules are not considered in the determination. The external cation exchange capacity (ECEC) of SMZ accounts for 11% of CEC.

The bulk density value of CFA corresponds to material containing particles with high glass phase of quartz and mullite [22, 23]. The bulk density value of zeolites is also generally between 2–2.4 g cm$^{-3}$ and can correlate with its porosity and cation exchange capacity [24].

The pH value of CFA (7.9) indicates that coal ash was moderately alkaline in nature due the presence of alkali and alkaline earth cations combined with carbonates, oxides or hydroxides [25, 26]. The high pH of zeolitic materials is attributed to entrapment of sodium ions to neutralize the negative charge on aluminosilicate gel during the hydrothermal treatment.

The pH$_{pzc}$ value is an important indicator of the net surface charge and the preference for the ionic species for an adsorbent. The results of the determination of the pH$_{pzc}$ were 7.1 and 5.7 for ZFA and SMZ, respectively. For both materials, the pH in water is higher than pH$_{pzc}$ indicating that their surfaces have negative charge in aqueous solution. SMZ has negative charge probably due to the formation of a patchy mono-layer and/or bi-layers form on the number of exchangeable active sites on the external zeolite surface [18].

The conductivity values are related to some compounds present in coal ash and in zeolitic products that can undergo dissolution. Conductivity values of the zeolites were higher than the fly ash samples due to the presence of exchangeable cations in their structures formed by the hydrothermal treatment. The results are in agreement with other studies that reported the values of conductivity for different Brazilian fly ashes and their respective zeolites [27].
3.3. Particle Size Distribution

Particle size distribution (PSD) is a physical characteristic of coal fly ash that strongly affects its reactivity and is an important criterion in ascertaining their utilization potential [28].

PSD of fly ash can vary from time to time depending on the coal combustion conditions in the power station [29-31]. In addition, particle characterization of fly ash is also important in understanding the enrichment of trace elements, which might affect the quality of the synthesized zeolite product [32]. So, such variability in PSD of fly ash could influence the conversion of fly ash into zeolites.

Fig. 1 and 2 report the differential and cumulative particle size distributions for fly ash (CFA) and surfactant-modified nanozeolite (SMZ), respectively. The differential size distribution of the materials presented the expected normal bell-shaped distribution curve. The particle size distributions of materials are given in Table 3. These distributions specify that the majority of particles (90%) lie below 112.477 µm in case of CFA, while in SMZ majority of particles (90%) lie below 102.239 µm. The particle size of the modified zeolite is as a function of the amount and the molecular size of surfactant added. In the present study, the CFA and SMZ exhibited similar PSD patterns, ranging between 0.5 to 355 µm.

Table 2. Physicochemical properties of coal fly ash and zeolitic products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g)</th>
<th>Bulk density (g cm⁻³)</th>
<th>CEC (meq g⁻¹)</th>
<th>pH in water</th>
<th>pHₑₒ₉⁻</th>
<th>Conductivity (µS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFA</td>
<td>1.71</td>
<td>2.12</td>
<td>0.202</td>
<td>7.9</td>
<td>-</td>
<td>140.9</td>
</tr>
<tr>
<td>ZFA</td>
<td>65.8</td>
<td>2.45</td>
<td>2.11</td>
<td>9.6</td>
<td>0.232</td>
<td>632</td>
</tr>
<tr>
<td>SMZ</td>
<td>63.0</td>
<td>2.43</td>
<td>2.02</td>
<td>9.6</td>
<td>7.1</td>
<td>460</td>
</tr>
</tbody>
</table>

(a) cation exchange capacity; (b) external cation exchange capacity; (c) point of zero charge

Previous studies show the grain size distribution of fly ash samples from Presidente Medici Power Plant. The continuous interval of particle sizes was between 0.5 and 600 µm, and the average diameter was 49.30 µm. Ninety percent of the particles had diameters smaller than 232 µm, while the finest particles (< 5 µm) correspond to ~ 1% of the total mass of the sample [1]. In another study, 90% of the particles presented diameters smaller than 70.00 µm and the average diameter was 32.70 µm [26]. These results showed the variability in PSD of fly ashes of the same coal-fired power plant.

3.4. FTIR Spectroscopy

FTIR spectra of the CFA, ZCA and the SMZ are shown in Fig. 3. The broad bands at approximately 3450 cm⁻¹ and the peaks at about 1650 cm⁻¹ are for O–H stretching and O–H bending, respectively. For ZFA and SMZ, these bands can also be related to the water molecules located inside the channels of zeolites and/or associated with exchangeable cations [33].

For CFA, the peak at 1082 cm⁻¹ is attributed to the Si–O–Si and Si–O–Al asymmetric stretching, and the peak at 461 cm⁻¹ is linked to the Si–O and Al–O in-plane flexural vibration modes. The peak at 796 cm⁻¹ is due to symmetric stretching vibrations of SiO₄ [34, 35].

The IR pattern of ZCA and SMZ shows the characteristic peaks at wavenumbers 3452-3456, 1647-1651, 1005-999, 563-565, and 453-457 cm⁻¹ reported for zeolite-P and hydroxysodalite [36]. Besides, the peaks at 2920 and 2845 cm⁻¹ in SMZ can be assigned to HDTMA-Br adsorbed on the zeolite surface as the corresponding peaks are also observed in the IR pattern of HDTMA-Br only. These peaks are indicative of stretching vibrations of the -CH₃ and -CH₂ groups of HDTMA [37].

The presence of characteristic peaks of zeolite-P and
hydroxysodalite for SMZ confirms the structural stability of zeolite after surfactant modification.

3.5. Scanning Electron Microscopic Analysis

The morphology of the starting material and zeolitic materials were observed by scanning electron microscopy. SEM typical images for unmodified zeolite from fly ash (ZFA) have already been presented [27]. Fig. 4(a) and (b) show the scanning electron microscopy images of CFA and SMZ, respectively. The original CFA particles typically had spherical shapes at different sizes, with a smooth surface made of an aluminosilicate glass phase (Fig. 4a). After hydrothermal treatment, the surface became rough due the deposition of zeolite crystals on the fly ash particles (Fig. 4b).

According to the literature, the modification of the zeolite with HDTMA causes no significant difference in their SEM image. The reason is ascribed to HDTMA only bonds on the surface of the zeolite without to cause changes in the morphology [38].

3.6. Energy Dispersive Spectroscopy Analysis (EDS)

EDS analysis can provide the elemental analysis (e.g. Al, Si, O, Na, etc) on the selected spots located on the external surface of a crystal. EDS allows one to identify what those particular elements are and their relative proportions in the sample.

The semiquantitative elemental analysis provided by EDS detected the mainly elements in CFA involved in creating the structure of zeolite which are Si and Al, as shown in Fig. 5. EDS spectra of the studied both samples CFA and SMZ show also strong elemental signal of oxygen, carbon and potassium. The carbon, of course, is not strictly ash, but rather the product of incomplete combustion of coal.

It can be seen that both CFA and SMZ materials has impurities existing as calcium, titanium, magnesium and iron elements. For SMZ, sodium is the main exchange cation in the structure balancing the charge of the aluminosilicate lattice. Table 4 represents the weight percentages of occurrence elements in fly ash raw material and organozeolite powder. The weight percentage of sodium increased and the ratio Si/Al decreased after hydrothermal treatment as it was expected.
Table 4. Weight percentages of occurrence elements in coal fly ash before and after alkaline conventional hydrothermal treatment.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Wt (%)</th>
<th>CFA</th>
<th>SMZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>62.83</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>18.78</td>
<td>27.05</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>6.68</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>8.46</td>
<td>8.45</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>4.06</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>3.61</td>
<td>4.49</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>2.23</td>
<td>3.61</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.04</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>Si/Al</td>
<td>3.35</td>
<td>1.70</td>
<td></td>
</tr>
</tbody>
</table>

3.7. Mineralogical Compositions

Fig. 6 shows the XRD patterns of the coal fly ash (CFA), unmodified zeolite (ZCA) and surfactant-modified zeolite from fly ash (SMZ). The majority crystalline phases in the CFA were quartz (SiO$_2$, ICDD/JCPDS 001-0649), mullite (Al$_2$O ICDD/JCPDS 002-043), Na-P1 (Na$_6$Si$_{10}$Al$_6$O$_{32}$.2H$_2$O, ICDD/JCPDS39-0219) and Hydroxysodalite (JCPDS 31-1271) were the main zeolitic products obtained after conventional alkaline hydrothermal activation of CFA. In addition to the presence of peaks characteristic of zeolites, residual quartz and mullite are also observed.
The structural parameters of the surfactant-modified zeolite are very close to that of corresponding parent zeolite, which indicate that the crystalline nature of the zeolite remained intact after chemical treatment with HDTMA-Br molecules. The surfactant conditioning has no effects on the structure of the zeolitic material from fly ash [18].

Fig. 6. The X-ray diffraction patterns of CFA, ZCA and SMZ (M = Mullite; Q = Quartz; H = Hydroxysodalite; P= NaP1).

4. Conclusion

The properties of coal fly ash are strongly dependent on the geological origin and the combustion process of the coal. So, it is important to characterize coal ashes generated in Brazilian power plant to ascertain its potential uses as raw material in the production of high value products.

The results demonstrated that fly ash from coal combustion in Presidente Medici Power Plant (Brazil) can be used as raw material in the synthesis of nanozeolite materials. The formation of the zeolite P1 and hydroxysodalite was confirmed using alkaline conventional hydrothermal treatment. The adsorption of cationic surfactant on zeolite surfaces resulted in insignificant changes to rigid cage structure, and the XRD spectra of non-modified and surfactant-modified nanozeolites was identical. CEC values for the zeolitic materials were 40 times higher than those of fly ash and nanozeolites can be used as ion exchangers. The experimental data suggest that the fly ash could be converted also into organonanozeolite, a beneficial product, which will be used in the future as a low cost adsorbent material in removing a wide range of pollutants from wastewaters.

Acknowledgements

The authors thank the National Council for Scientific and Technological Development (CNPq), Brazil for the financial support and Presidente Medici Thermal Power Plant for supplying the coal ash samples.

References


