Zeolite Synthesis from Waste Materials for the Medical Field of Oxygen Concentrators: Focus on the African Scenario

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The property of zeolites to selective remove specific compounds from a fluid mixture was exploited in the medical field of oxygen concentrators for the removal of N2 from air in order to deliver almost pure oxygen to patient under Oxygen Therapy. Rising attention was given for zeolite synthesis from waste materials in order to abate the high costs related to such process. The latter approach constitutes also a valid support for the development of Oxygen Concentrators in rural countries such as the African one. In this work a systematic literature research was performed in order to detect all the low-cost/waste materials adopted in literature as aluminum and silicon sources for the synthesis of zeolites X (NaX) that are the ones used for the design of medical oxygen concentrators. Moreover, the African scenario was analyzed and Coal Fly Ash, with an estimated production of 12 Mtons/y by 2030, was selected as the best alternative for zeolite synthesis in this country.

1. Introduction

Zeolites or “molecular sieves” are crystalline aluminosilicates formed by the union of SiO4 and AlO4-type tetrahedrons. The basic structure of Zeolites can be described by the generic formula

\[ M_x(AI_2)_y(SiO_2)_z \cdot cH_2O \]  

where \( x \leq y \) and \( M \) represents the compensation cation (\( Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+} \)) which balances the negative charge introduced by every Al atom. The zeolitic structure can be thought of as an assemblage of polyhedral units made of several SiO4 and AlO4 tetrahedra on which the catalytic/adsorption active sites are available. Moreover, specific cavities or “windows” define the effective diameter of the zeolite pores and determine the access to the crystalline structure only to selected molecules. Zeolites found wide application in separation processes due to their ability to selective remove specific compounds from a fluid mixture (liquid or gaseous). Such property was exploited in the medical field of oxygen concentrators for the removal of N2 from air in order to deliver almost pure oxygen to patient under Oxygen Therapy. After several years of research, it was found out that the most performant Zeolites for this purpose were the types NaX, LiX and LiLSX (LiX with low Si content Si/Al=1) which are the ones that are currently employed in commercial oxygen concentrators.

Solvothermal synthetic method is a general term which indicates that the zeolite synthesis is occurring in a liquid solvent. Several researches reported a successful synthesis of zeolite using different solvents such as alcohols (e.g., methanol, ethanol, pentanol), ethylene glycol, hydrocarbons and pyridine (Khaleque et al., 2020). Moreover, when ionic solvents (ionic liquids) are adopted this term is assigned as ionothermal, while when water is employed as solvent it takes the name of hydrothermal. The Hydrothermal Method (HM) is considered one of the least costly for zeolite synthesis (De Magalhães et al., 2022) and hence it is one of the most used. It consists of three steps here explained. 1) Crystallization: a water solution of silicon and aluminum sources together with mineralizing agents such as OH- and F-, metal cations, and structure-directing agent (usually an organic
surfactant) (Liu and Yu, 2016) is prepared and placed into an autoclave reactor. The reaction (crystallization) takes place at a temperature range of 80-150°C at autogenous pressures up to 15 bar (Cocchi et al., 2020); 2) Filtering step: the reaction product is filtered and washed several times in order to collect the solid and remove from its surface the residual reagents; 3) Drying step: the material is oven dried.

The aim of this work is to detect with a systematic approach all the possible solution for zeolite synthesis starting from a waste raw material. Moreover, it was detected the most available waste material in the African region that could be used as both aluminium and silicon sources for zeolite synthesis.

2. Materials and Methods

The goal of the systematic research was to report all the low-cost/waste materials adopted in literature as aluminium and silicon sources for the synthesis of zeolites X (NaX) that are the ones used for the design of medical oxygen concentrators (when necessary with an ion exchange they can become LiX and LiLSX). Relevant works and papers were identified and selected by searching on Scopus database.

The first step of the study regarded the input of pertinent key-words that should not exclude for some reason relevant works from the search of the database. Observing the keywords of some relevant papers of the field (Abdelrahman, 2018; Flores et al., 2021; Khaleque et al., 2020; Ren et al., 2020b; Schwanke et al., 2022) the words “zeolite”, “synthesis”, “low-cost”, “waste”, always appear between the Title, the abstract or the keywords of the articles. For this reason, boolean combinations of the aforementioned words were chosen for the research. The research was conducted in September 2022.

The number of works found was 108. At this point the following criteria of selection (also shown as a schematic flow chart in Figure 1) were implemented:

1. The research was limited for paper published in the last 10 years (2012). The actual number of documents was 92;
2. The subject areas of Business, management and Accounting, Mathematics, Computer science, Earth and planetary Sciences, Pharmacology, Toxicology and Pharmaceutics were excluded because considered out of topic. The actual number of documents was 79;
3. Conference papers and conference reviews were omitted since conference works are partial findings of full articles. The number of resulting documents was 73.
4. The Title of each article (and when needed the abstract) was carefully screened to verify that it effectively deals with the synthesis of zeolite from a waste material. The number of resulting documents was 30.

![Flow chart of literature search: inclusion and exclusion criteria](image)

**Figure 1:** Flow chart of literature search: inclusion and exclusion criteria.

3. Results and discussion

In this section were described all the most relevant materials available for zeolite synthesis. All the waste materials used as Aluminium and silicon sources collected according to the systematic article criteria selected were reported in Table 1 together with their corresponding type of zeolite synthetized and solvo-thermal treatment working conditions.
3.1 Waste Materials

Coal Fly Ash (CFA)

Coal fly ash (CFA) is a by-product of coal combustion. Typically, 5–20 wt.% of feed coal turns into ash during the combustion process. Fine fly ash is captured from flue gas and collected by electrostatic or mechanical precipitation represents 85–95 wt.% of the total ash generated (Yao et al., 2015). The release of large amounts of CFA (coal fly ash) can cause air pollution and harm to human health. Consequently, there is a pressing need for appropriate CFA disposal. Currently, CFA is predominantly utilized as building materials, in the form of cement or concrete. The main components of CFA are Si- and Al-containing compounds, which are similar to zeolite. Hence, CFA is conducive to the synthesis of zeolite.

In this systematic research it was found out that 9 articles dealt with the synthesis of zeolites from coal fly ash. Zeolite A was successfully synthesized from Coal fly ash by Angaru et al. (Angaru et al., 2021) following the procedure of Choi et al. (Choi et al., 2019) which obtained also Zeolite X using the same method. Yadav et al. (Yadav et al., 2021) used for the same purpose an hydrothermal method conducted at 95°C for 16 h (in this work the type of zeolite obtained was not specified). Submicron Zeolite Y was obtained by Ren et al. (Ren et al., 2020a) using the hydrothermal method at 80°C for 12 h. NaA and Na-P1 zeolites were synthesized using an hydrothermal method at 90°C for 16h and 80°C for 36h respectively by Goscińska et al. (Goscińska et al., 2018) using fly ash belonging to class F (in the ASTM C 618 classification) according to their chemical composition. Moreover, coal fly ash was used to synthesize zeolite with an hydrothermal method by Maria Visa (Visa, 2016) and Sun et al. (Sun et al., 2010). A zeolite precursor for the synthesis of a zeolite-reduced graphene oxide composite was obtained by Soni et al. (Soni et al., 2019) using an hydrothermal method at 90°C for 6 h. Among all the works collected, it was found the review of Ren et al. (Ren et al., 2020b) on the synthesis of zeolites from coal fly ash which includes several other works on the same topic.

The previous works were all performed using the hydrothermal method. Instead, Bin Shi and Qing Chang (Shi and Chang, 2021) used coal fly ash for the production of Zeolite Y adopting a solvent-free crystallization (SFC). In this case the fly ash constitutes both a silicon and aluminum source but extra Si was added to obtain the desired Si/Al ratio to obtain the zeolite Y. In the work of Zhibin Ma et al. (Ma et al., 2022), the synthesis of Na-P1 zeolite was conducted via hydrothermal method using circulating fluidized bed combustion coal fly ash (CFBFA). The latter differ from the ordinary Coal Fly Ash for its high content of anhydrite (CaSO₄) and free calcium oxide (CaO). To remove such impurities, the CFBFA required a pre-treatment at 90°C with an HCl solution. The hydrothermal operating conditions were conducted in the temperature range of 90-130°C for 6-12 h.

Rice Husk Ash (RHA)

When rice is milled, it results in a by-product called husk, which makes up about 22% of the weight of the paddy grain. This husk contains organic volatile matter comprising 75% of its weight, and the remaining 25% turns into ash during firing, known as rice husk ash (RHA), which has around 85%-90% amorphous silica (Nagrale et al., 2012). Due to the significant amount of silica present in the husk, it is a commonly used source of silicon for synthesizing zeolites. In this systematic research it was found out that 4 articles dealt with the synthesis of zeolites from Rice husk. Rice husk was used only as silicon source by Gomes Flores et al. (Flores et al., 2021) for the hydrothermal (optimal conditions 125 °C 8 h) synthesis of potassium zeolites (Chabazite-K and Merlinite). Hydrothermal treatment was also adopted by Morales et al. (Morales et al., 2018) for the synthesis of zeolite NaA (Si/Al=1; 70°C for 6h) and NaX (Si/Al=2; 90°C for 12 h). Moreover, NaA and NaP zeolite powders were synthesized (Subba et al., 2014). (Bohra et al., 2013)) by hydrothermal condition at 100°C for 15-96 h using agro-waste material, rice husk ash as silica source in the presence of other organic-free low cost precursors like aluminum foil, sodium hydroxide and water.

3.2 African Prospective

In 2019 the African electrical capacity was estimated to be around 220 GW. Nearly 80% of Africa electricity generation is fossil-fueled and 21% are coal-based (46.2 GW). At the same time, Africa’s electricity demand is set to increase rapidly as it seeks to industrialize and achieve improved economic development for the world’s fastest growing population. As a matter of fact, by 2030 the total electrical capacity is expected to increase reaching the amount of 480 GW 15% of which derived by coal power plants (72 GW) (Aloa et al., 2021). According to the fraction of electrical energy produced from fossil fuels and in particular from coal (Eᵣ), the following assumptions were made to estimate the amount of coal fly ashes generated per year:

- African Coal calorific value (UHV) equal to 31 MJ/kg as reported in the study “The characteristics of Southern African coals” by Falcon et al. (Falcon R. & Ham, 1988);
- Thermal power plant global efficiency for electricity production (η) of 0.3 (conservative value);
- The fraction of coal fly ashes released respect to the total amount of carbon burned (ω) is (at least) of 5% as pointed out in the work of Yao et al. (Yao et al., 2015).
Finally, the calculation of the amount of coal fly ashes ($F_{CFA}$) produced in Africa per year was performed as shown in Equation 2

$$F_{CFA} = \frac{E_{C}}{LHV} \cdot \eta \cdot \omega$$

(2)

It resulted that in 2019 7.6 Mtons/y of CFA were (at least) generated, while in 2030 12 Mtons/y of CFA are expected to be produced. The high availability of CFA in African region sets it as valid candidate as waste material for zeolite synthesis.

Table 1: Output of the systematic review: Waste materials used as Aluminum and silicon Sources together with their corresponding type of zeolite obtained. Moreover, hydrothermal (HM) or solvent-free crystallization (SFC) synthesis technique working conditions were provided.

<table>
<thead>
<tr>
<th>Waste material</th>
<th>Source</th>
<th>Type of zeolite</th>
<th>Conditions</th>
<th>#Papers</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Fly Ash (CFA)</td>
<td>Si &amp; Al</td>
<td>A, X, Y, P1</td>
<td>($\text{HM}$) [80; 95]$^\circ$C [6; 36] h (SFC)</td>
<td>(9)</td>
<td>(Angaru et al., 2021) (Yadav et al., 2021) (Ren et al., 2020a) (Goscińska et al., 2018) (Visa, 2016) (Sun et al., 2010) (Son and Shukla, 2019) (Ren et al., 2020b) (Shi and Chang, 2021)</td>
</tr>
<tr>
<td>Fluidized Bed combustion Coal Fly Ash (CFBFA).</td>
<td>Si &amp; Al</td>
<td>P1</td>
<td>($\text{HM}$) [90; 130]$^\circ$C [6; 12] h</td>
<td>(1)</td>
<td>(Ma et al., 2022)</td>
</tr>
<tr>
<td>Rice Husk Ash (RHA)</td>
<td>Si</td>
<td>A, X, P, Chabazite-K and Merlinoite</td>
<td>($\text{HM}$) [90; 125]$^\circ$C [6; 96] h</td>
<td>(4)</td>
<td>(Flores et al., 2021) (Borrego Morales et al., 2018) (Bohra et al., 2014) (Bohra et al., 2013)</td>
</tr>
<tr>
<td>Bagasse Ash (BA)</td>
<td>Si &amp; Al</td>
<td>N.A.</td>
<td>($\text{HM}$)</td>
<td>(2)</td>
<td>(Noor-Ul-Amina et al., 2021) (Shah et al., 2012)</td>
</tr>
<tr>
<td>Aluminum Can</td>
<td>Al</td>
<td>A, X, Y</td>
<td>($\text{HM}$) $T = 150^\circ$C $t = 12$ h</td>
<td>(2)</td>
<td>(Abdelrahman et al., 2021) (Abdelrahman, 2018)</td>
</tr>
<tr>
<td>Red Mud</td>
<td>Si &amp; Al</td>
<td>P1</td>
<td>($\text{HM}$) $T = 120^\circ$C $t = 7$ h</td>
<td>(1)</td>
<td>(Cheng et al., 2021)</td>
</tr>
<tr>
<td>Geopolymers</td>
<td>Si &amp; Al</td>
<td>A</td>
<td>($\text{HM}$) [90; 100]$^\circ$C [6; 12] h</td>
<td>(3)</td>
<td>(Zhang et al., 2020) (Wang et al., 2019) (Meng et al., 2016)</td>
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<tr>
<td>Lithium–silicon-powder (LSP)</td>
<td>Si &amp; Al</td>
<td>Y</td>
<td>($\text{HM}$) $T = 100^\circ$C $t = 15$ h</td>
<td>(1)</td>
<td>(Shui et al., 2020)</td>
</tr>
<tr>
<td>Electrolytic manganese residue</td>
<td>Si &amp; Al</td>
<td>A</td>
<td>N.A.</td>
<td>(1)</td>
<td>(Li et al., 2015)</td>
</tr>
<tr>
<td>Expanded Perlite</td>
<td>Si &amp; Al</td>
<td>A, X, P1</td>
<td>N.A.</td>
<td>(1)</td>
<td>(Król et al., 2014)</td>
</tr>
<tr>
<td>Blast Furnace Slag (BFS)</td>
<td>Si</td>
<td>A</td>
<td>($\text{HM}$) $T = 100^\circ$C $t = 5$ h</td>
<td>(1)</td>
<td>(Guo et al., 2017)</td>
</tr>
<tr>
<td>Non-Burning Brick</td>
<td>Si &amp; Al</td>
<td>N.A.</td>
<td>N.A.</td>
<td>(1)</td>
<td>(Ai et al., 2022)</td>
</tr>
<tr>
<td>Waste Liquor</td>
<td>Si &amp; Al</td>
<td>ZSM</td>
<td>($\text{HM}$) $T = 140^\circ$C [3; 10] d</td>
<td>(1)</td>
<td>(Ning et al., 2019)</td>
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<td>Reviews</td>
<td></td>
<td></td>
<td></td>
<td>(2)</td>
<td>(Khaleque et al., 2020) (Narayanan et al., 2020)</td>
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<tr>
<td>TOT</td>
<td></td>
<td></td>
<td></td>
<td>(30)</td>
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4. Conclusions

In this work a systematic review was conducted to detect all the possible waste materials that could constitute a valid aluminum and silicon source for the synthesis of zeolites X to be applied in the medical field of oxygen concentrators. Among all the 13 waste materials revealed from the analysis, Coal Fly Ash was considered the best one for the African scenario due to the following reasons: CFA already contains both Si and Al for zeolite synthesis; synthesis of zeolites from CFA is the most investigated (and hence well-known) procedure; in line with the growing African energy demand, an increase of CFA production is expected to reach an amount of 12 Mtons/y by 2030.


