

Original research Articles

Brazilian Kaolin Wastes: Synthesis of Zeolite P at Low-Temperature

Abstract

The synthesis of zeolite in forms suitable for industrial applications is of great importance, mainly as ion exchange material, molecular sieves, adsorbents and catalyst. This paper deals with synthesizing zeolite P using waste kaolinite as starting material (from Brazilian industry ores). The material was characterized by chemical element analysis (FRX), X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared and Raman spectroscopies. With promissory results, although traces of other zeolitic products, such as Zeolite LTA and Zeolite Y, the XRD characteristic peaks attributed to the formed zeolite were confirmed by the 39-0219 (NaP1) cards of JCPDS. The synthesis products are of interest as they can be used in several environmental applications. The prepared material was used as a catalyst in the photodecolorization process of Remazol Golden Yellow (RNL) dye in aqueous solution under UV irradiation.

Keywords: Low-temperature synthesis, kaolin waste, fluoride media, zeolitic products.

1. Introduction

In Brazil, in three regions (south, north and northwest) stands out for having the most important international kaolin deposits for the paper and ceramics industries. During the processing steps for purifying raw kaolin, waste is produced and stored in settling ponds which occupy large area. This situation presents a problem due to the impact on the environment. Kaolin waste is unsuitable for use in paper-making industries; however, this material has the potential of being used in other applications, such as: alumina production, refractories, pozzolans and synthesis of zeolitic materials [1]. Zeolites are crystalline aluminosilicates with a 3-dimensional, open anion framework consisting of oxygen-sharing TO_4 tetrahedral, where T is Si or Al. Their framework contains interconnected voids which can be occupied with adsorbed molecules or cations. The general empirical formula is $M_x/nAl_xSi_{2-x}O_4 \cdot mH_2O$ where n is the valence of the exchangeable cation M, m water content and $0 \leq x \leq 1$. The flexibility of the zeolite Si-O-Si bond explains the fact that more than 200 structures have been determined. Since the pioneering work [2] the conditions for zeolite synthesis have changed little. Zeolite synthesis has been extensively reviewed in several books and literature on this subject is abundant [3-5]. The general method of zeolite production involves dissolving an aluminium source (metal or oxide) into an alkaline solution. Most zeolites probably could be obtained at temperatures $<100^\circ C$ in alkaline solutions. This is generally the case for zeolites with low Si/Al ratios. However, in order to reduce reaction times (especially for zeolites with high Si/Al ratios) and to control crystallite sizes, morphologies and compositions, some syntheses are performed at temperatures $>100^\circ C$ under autogeneous pressure in autoclaves. Typical precursor materials include: SiO_2 and Al_2O_3 sources, mineralizer and structure directing agents (SDAs). Other synthetic variables including the source of the inorganic precursors, the mineralizing agent (OH^- or F^-) and the reactant concentrations have also resulted in new crystalline materials. Corma, 2004, using F^- as mineralizing agent allows one to carry out the synthesis at lower pH than when using OH^- , and opens new possibilities such as: the incorporation of elements in the framework which have low solubility in alkaline medium, adequate stability of many possible templates in this medium, expanding the number of potential templates especially when working with concentrated gels [6]. Finally, the synthesis in the presence of fluoride produces high silica zeolites with a smaller number of defects than in alkaline media and also one has the possibility of growing single crystals large enough for direct structure determination [7-15].

Additionally, several groups have reported a catalytic role of fluoride species for silicate hydrolysis and condensation [16]. Kim et al. (2004) developed the synthesis of zeolite beta in fluoride media under microwave irradiation as an efficient and fast route of synthesis. The synthesis of crystalline aluminosilicate zeolites can be carried out from clay minerals [1-2, 17-20]. Previous work has shown that the improvement of the properties of the kaolinite by chemical methods is difficult due to its low reactivity. It is not significantly affected by acid or alkaline treatments, even under strong conditions [21-27]. Therefore, kaolinite is usually used after calcination at temperatures between 550-950 °C [28] to obtain a more reactive phase (metakaolinite) under chemical treatments, with the loss of structural water and associated reorganization of the structure. Several authors have reported the synthesis of kaolinite- and metakaolinite-based zeolitic materials [29-34]. Zeolite P can be synthesized from various silica-aluminium sources and methods, for examples, using Brazilian kaolin from various sources at 100 °C in 4 days, by the alkaline fusion procedure [35]; from coal fly ash by agitation at 120°C [36] or from sodium aluminate and sodium silicate solution by hydrothermal treatment in microwave oven [37]. The characterisation and crystal chemistry of NaP zeolites has been controversial for many years. Owing to what was referred to by Hansen *et al.*, it has been difficult to distinguish between different NaP phases and to understand their composition and structure. Although all P zeolites are characterised by the same framework topology, which is the GIS net (named after the natural zeolite gismondine), the formula, symmetry and structure of samples of different composition—which means samples of different Si–Al ratio, Na content and hydration level—were found to be difficult to establish. The main reason for this state of affairs is the high flexibility of the Si–Al linkage in a framework, which has been described being ‘the most open (tetrahedral) framework type generated so far [38-39]. A phase called Na-P1 was refined in *I4* [40]. For this phase, a unit cell content of $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot 12\text{H}_2\text{O}$ was adopted. Barrer *et al.* [41] claimed apparently three polymorphs of zeolite Na-P: cubic (Na-P1), tetragonal (Na-P2) and more rarely orthorhombic (Na-P3). Na-P1 has been described as being body-centered tetragonal with a unit cell of pseudo-cubic geometry. Many salient features of zeolites dynamics and structure can be deduced from vibrational spectroscopy data, such as infrared (IR) and Raman spectroscopy, and the two kinds of spectroscopies are often complementary [42-43]. In zeolite science Raman spectroscopy seems rather underdeveloped compared with infrared spectroscopy. Therefore, the main purpose of this study was to synthesize zeolite NaP using kaolin waste from the northwest region as the main source of silicon and aluminium, improving crystallization time for lower values at low temperature. The characterization by XRD, FRX, SEM, TG/DTA, Raman and FTIR supported this work. Other primary objective was to determine the activity catalytic for decolorization and mineralization extents of dye wastes. Reactive azo dyes are the largest group of organic dyes with –N=N– group as a chromophore in the molecular structure. They represent more than a half of the global dye production especially because of their wide usage in dyeing industries due to the simple dyeing procedure [44, 45]. Normally zeolites have applications in many technological fields such as catalysis and wastewater treatment [46]. Zeolites can serve as hosts to activate transition metal ions, offering a unique ligand system with multiple types of coordination for cations. Zeolites are three-dimensional aluminosilicates containing exchangeable cations that act as Lewis acid sites. The framework oxygen atoms of alkali exchanged zeolites bear partial negative charge and behave as Lewis base [47]. Zeolite P which was synthesized in this paper has a Si/Al ratio of 3.5 which is located in the range of 1–5 for zeolite P.

2. Experimental

2.1. Materials

Kaolin waste was used as the starting material for this work, after steps grinding by mechanical milling. This material well crystallized, fine grained ($\leq 74\ \mu\text{m}$) is the silica and alumina sources used in the synthesis of zeolites. Without contaminants (muscovite and quartz), kaolinite $[\text{Al}_2\text{SiO}_5(\text{OH})_4]$ may be a good alternative to reuse. Thus, economic advantages would be obtained over chemical reagents used in processes to obtain zeolites that are relatively

expensive. Metakaolinite ($\text{Al}_2\text{Si}_2\text{O}_7$) was obtained from calcination of kaolinite at 700 °C for 3 h. Other reagents used in the activation of the starting materials were: sodium fluoride, NaF (99%, Fluka) and distilled water. Dye RNL, $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_{10}\text{S}_3\text{Na}_2$, were kindly provided by a textile manufacturer located in Brazil. The YR chemical structure is shown in Fig.1

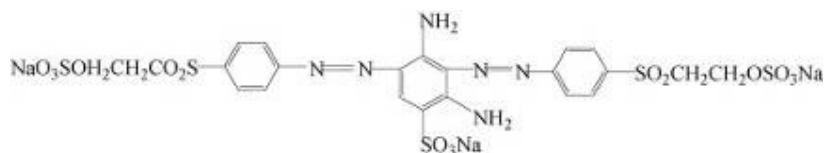


Figure 1. Chemical structure of Remazol Yellow Gold RNL dye.

2.2. Synthesis

Low-temperature zeolite synthesis (modified standard procedure established by IZA) involves pre-treatment and mild-temperature thermal treatment under reflux at approximately 100 °C. In the first step, 12,7 g of metakaolinite was mixed with a sodium fluoride, prepared by dissolving 10,4g of NaF pellets in 87,7 mL of distilled water. The resulting synthesis slurry was aged at 50 °C by stirring the mixture for 4 h. After this ageing, the slurry then underwent a thermal treatment by heating at a temperature of approximately 100 °C under reflux system for 96 h. At the end of the thermal treatment, the synthesised solid product was washed with deionized water until the rinsing water reached a pH of about 9. The solid product was washed and centrifuged at 3500 rpm he was reached and dried at 105 °C overnight.

2.3. Methods and Characterization

Powder X-ray diffraction patterns were recorded on a SIEMENS D5000 diffractometer using $\text{CuK}\alpha 1$ radiation and the 2θ range between 5–50°, degree 2θ at 0.1° intervals and a counting speed of 0.05°/s. and operating at 40 KV and 30 mA. The mineral phases present in the sample were identified by comparison with the *Joint committee on powder diffraction standards – International centre for diffraction* (JCPDS-ICD) reference library that was supplied with the XRD instrument.

The major oxides and trace elements in solid residue feedstock were measured by X-ray fluorescence (XRF) spectroscopy, using a RIX 3000 model, wavelength dispersive spectrometer (Rigaku), with six crystals and a rhodium X-ray tube target. To prevent interaction of the X-rays with air particles, samples were analysed within a vacuum.

The infrared analyses were carried out in a MB 102 Bomem spectrometer in the 4,000-400 cm^{-1} region (mid-infrared), scan and 4 cm^{-1} resolution, using a diffuse reflectance cell.

The Raman analyses were done in a spectroscopy were measured by a Renishaw inVia Raman Microscope with an argon laser operating at 512 nm as the excitation source.

The synthesized Zeolite P were coated with gold and the morphology was analyzed by Scanning Electron Microscopy (SEM) using a Shimadzu SSX-550 Super Scan Scanning Electronic Microscope, with energy dispersive spectrometer (EDS), at 5.0 keV.

The characterization of the precursor (kaolin) was performed by thermogravimetry (TG) and differential thermal analysis (DTA), using a TA Instruments SDT 2960 thermal analyzer. Samples of about 10 mg were heated at 10 °C min^{-1} up to 1000 °C, in an air atmosphere, inside alumina pans, with a flow rate of 100 mL min^{-1} .

2.4. The photocatalytic activity

Photodecolorization experiments were performed with a photocatalytic reactor system (Figure 2). During the photocatalytic tests, 10.0 mg of the zeolite P powders was added to a Petri dish containing 15.0 mL of a 10 ppm aqueous solution of RNL with no stirring. All of the analyses were performed in triplicate at pH = 6.0. Experiments were conducted in a 10 x 10 x 100 cm^3

163 lab-made reactor for 5 h using a UVC lamp ($\lambda = 254$ nm), SuperNiko, model ZG-30T8.
 164 Evaluation of the adsorption and of the photocatalysis was performed by measurement of the
 165 discoloration percentage. The decolorization of Remazol dye was analysed by UV-vis
 166 spectrophotometer (UV-2550 Shimadzu). The analysis of the resulting solution was performed
 167 after centrifugation and filtering of the suspension. The discoloration percentage was obtained
 168 from the band at 410 nm, which is assigned to the $=N=N-$ bond, i.e., the azo bond. The values
 169 were calculated using a calibration (based on Beer's law) were established with the absorbance
 170 and the concentration of dye) curve obtained from the intensity of the absorption band at 410
 171 nm of solutions with known concentrations of RNL. Discoloration due to photolysis was
 172 subtracted from the discoloration percentage.
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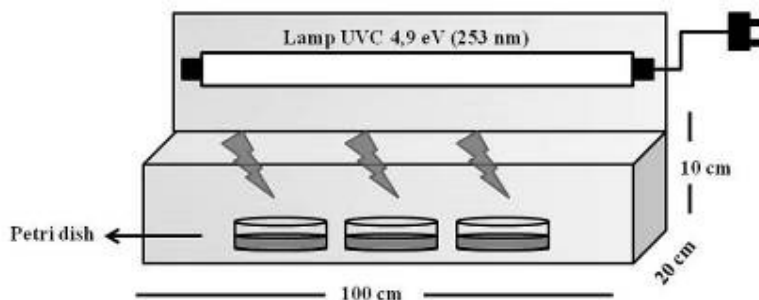


Figure 2. Apparatus used in the photocatalytic test.

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3. Results and discussion

179
 180 The thermal decomposition of kaolinite is illustrated in the Figure 3. Both TGA and DTA traces
 181 indicate a three stage desorption process. At < 150 °C, low temperature release of absorbed
 182 water in pores, on the surfaces, (water desorption), which depends on the nature of the kaolinite
 183 and the degree of disorder of stacking, and the corresponding weight loss amounts were about
 184 13%. Between ~ 150 – 400 °C, a weight loss that can be correlated with a pre-dehydration process
 185 takes place as a result of the reorganization in the octahedral layer, first occurring at the OH of
 186 the surface. After dehydration, kaolinite goes through a pre-dehydroxylation state, at 400 – 650
 187 °C. According to literature [48], between ~ 400 – 650 °C, the kaolinite dehydroxylation occurs,
 188 with the transformation to a non-crystalline phase, metakaolinite. Although the thermal
 189 transformation of kaolinite has been investigated for many years, controversy about the process
 190 of dehydroxylation (elimination of the OH groups from the kaolinite structure) remains.

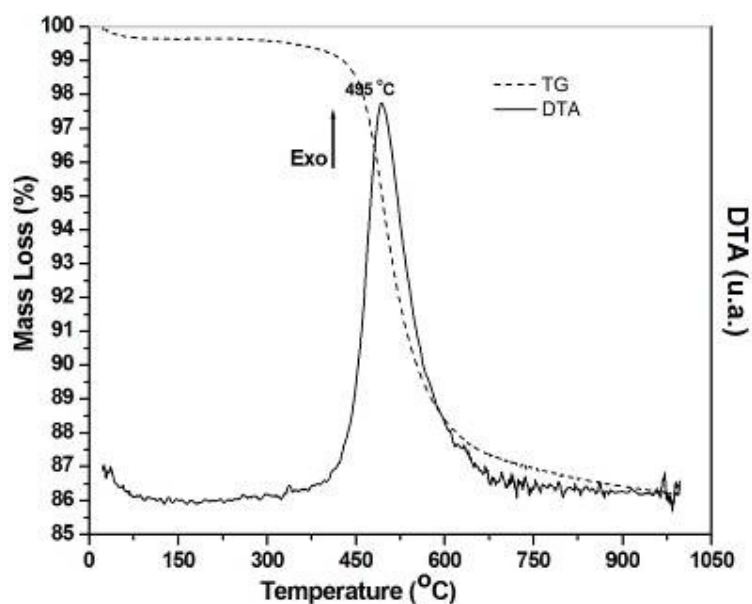


Figure 3. TG/DTG curves between 10-1000 °C for kaolinite.

The elemental analysis of sample was conducted by X-ray fluorescence spectrometer (XRF). This analysis was chosen instead of other techniques due to its simpler sample preparation, ability to determine some non-metals and improved precision. The chemical composition of the kaolin waste was determined by means of element chemical analysis by using the X Ray Fluorescence (XRF) technique, and it is shown in Table 1. As can be seen from Tab. 1, the kaolin sample with SiO_2 , Al_2O_3 and K_2O , as the major constituents and content of Fe_2O_3 less than 1%. The amount of SiO_2 and Al_2O_3 within zeolite was lower when compared to waste kaolin. This is may be due to the dissolution of aluminium-silicate in glass phase into alkaline solution during alkaline treatment and the aluminate and silicate ions are condensed to form an aluminosilicate gel, which is prematerial of zeolite crystal, covering the other surface of waste kaolin and so, aluminate and silicate ions are not supplied from waste kaolin due to its coverage onto the particle surface. An increase in Na_2O contents of the products is caused by captured sodium ions, to neutralize the minus charge on aluminate in zeolite structure when zeolite crystal is formed [49]. The amount of Mg, Fe, Ca, K and others, which are impurities, were reduced. This indicated that this impurities were dissolved into alkaline solution during alkaline treatment. Zeolites contain natural molecular water as an intracrystalline fluid, which can be removed by elevated temperature and evacuation. The water can normally be re-adsorbed by exposing the crystal to water vapour. The water content of sample which corresponded to the loss of ignition. In this case, extra amount of sodium content which was introduced into the zeolite by exhaustively exchange enhanced the water re-adsorption. The observation concluded that the water content partially attributed to the cation types and their amount present in the zeolite. In this study, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is equal to 3.5 mol, the X-ray diffraction analysis shows the presence of zeolite NaP in the synthesized sample as evidenced from reflections of low intensity near $2\theta = 12.4, 17.8, 21.7, 28.2, 33.3, 35.76, 38.01, 42.20$ and 44.18 . This result indicated that the solid residue from kaolin processing was successfully converted into zeolite-P structure with no amorphous materials. While the peaks positioned in $34.77, 42.19, 42.85$ may be zeolite A (LTA) or $34.69, 42.14$ and 42.66 zeolite Y (Figure 4).

Table 1 - Chemical composition of the starting material (waste kaolin) and Zeolite P

Constituents	kaolin	Zeolite-P
	Weight determined (%)	
SiO ₂	66.93	38.5
Al ₂ O ₃	24.2	18.7
K ₂ O	6.91	1.5
Fe ₂ O ₃	0.46	0.6
Na ₂ O	0.39	11.9
MgO	0.34	0.2
MnO	0.22	0.1
P ₂ O ₅	0.14	tr
CaO	0.08	0.6
TiO ₂	0.07	0.2
SO ₃	0.03	0.2
ZnO	0.017	0.0104
NbO	0.011	0.0085
ZrO ₂	0.043	0.0084
Cl	0.064	0.444
SrO	0.0035	tr

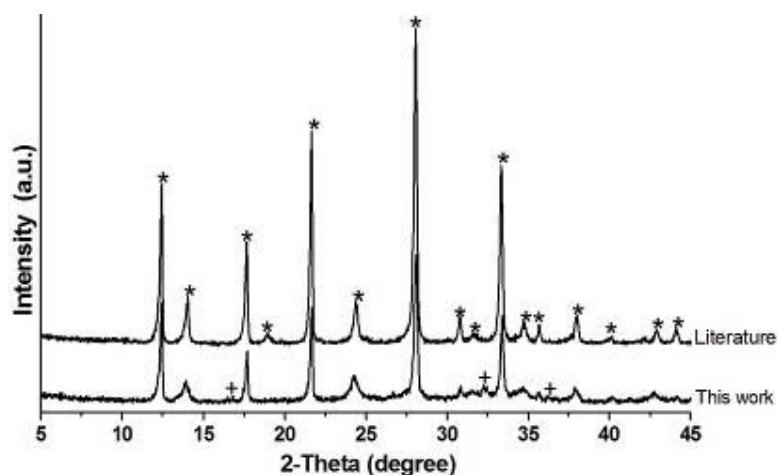


Figure 4: XRD pattern Zeolite-P synthesised at 100 °C. + others zeolitics phases

Table 2 - Result of Qualitative Analysis of Zeolite P

Phase name	Formula	Space group	DB card number
Zeolite P1, syn	Na ₆ Al ₆ Si ₁₀ O ₃₂ (H ₂ O) ₁₂	82 : I-4	01-071-0962
Zeolite LTA	Na ₁₂ Al ₁₂ Si ₁₂ O ₄₈ (H ₂ O) ₂₇	226 : Fm-3c	01-073-2340
Zeolite Y, syn	Na _{6,28} D _{44,23}	227 : Fd-3m,choice-2	01-079-1419

Scanning electron microscopy (SEM) was used to observe the morphology, size and shape of crystals in the zeolitic material synthesised. The energy dispersive X-ray spectroscopy (EDS) analyser (Phenom desktop Scanning Electron Microscope) that was coupled to the SEM was used to identify the chemical composition of a specific area of a sample. The SEM of zeolite NaP1 (Fig. 5) showed aggregates with no specific shapes (spherical particles appearance). Particle sizes of about 5 μm of diameter were obtained with a wide particle size distribution - the diameter of the smallest particle could be less than 2 μm . The chemical composition by EDS analysis indicates that the zeolite product was rich in aluminium, silica, oxygen and sodium, characteristic of a typical zeolite P. The presence of magnesium indicates its possible incorporation into the zeolite crystal lattice framework from the starting material (solid residue).

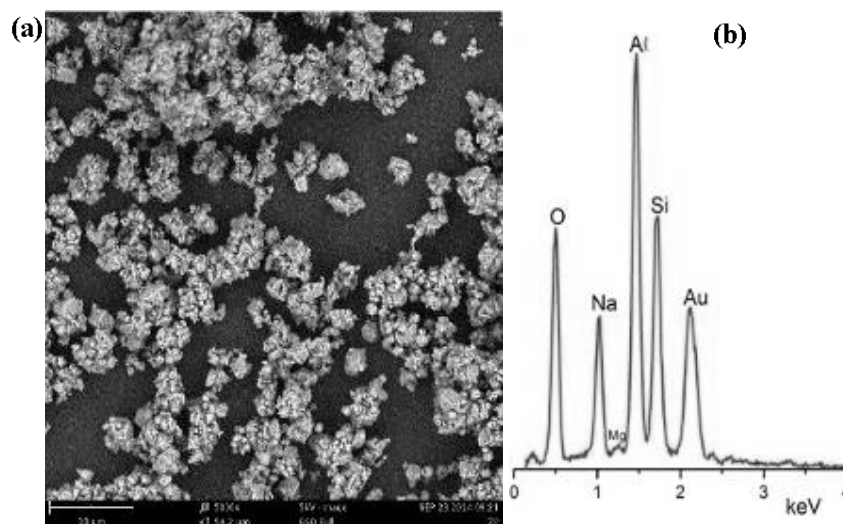


Figure 5: Zeolite-P synthesised at 100 $^{\circ}\text{C}$. (a) Scanning electron micrograph (b) EDS spectra.

Figure 6 illustrates the Raman spectrum of Zeolite P with an Si/Al ratio of 3.5. The bands appear at 280, 328, 398, 480 and 508 cm^{-1} [50]. There is a correlation between the ring sizes and the Raman spectra of crystalline zeolites. Structures that are built-up of four-membered rings as the smallest building block exhibit the Raman band around 480-520 cm^{-1} . One of these is zeolite NaP (gismondine) built-up of four-membered rings as the smallest building unit. The strongest band at 508 cm^{-1} is assigned to the bending mode of the characteristics 4-membered rings. Zeolites containing exclusively even numbered rings (4MR, 6MR, 8MR, 10MR or 12MR) have Raman frequencies of 390 and 460 cm^{-1} and the other band around 500 cm^{-1} . Therefore, the basic assignment of the bands in Raman Spectra for zeolite P should be similar to the one for zeolites A, X and Y. The band at 480 cm^{-1} is assigned to the bending mode of 4-membered Si-O-Al rings. All these results can be influenced and attributed to the difference in the Si/Al when compared with other zeolites with similar symmetries [51].

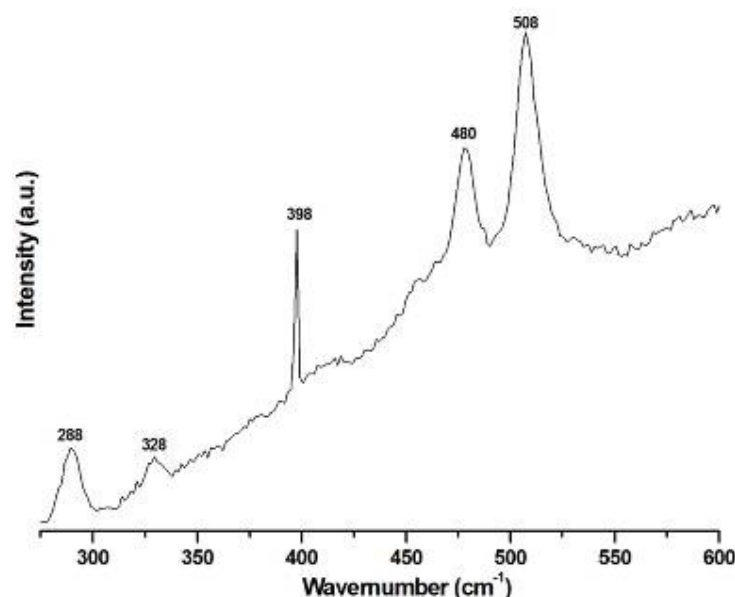


Figure 6: Raman Spectra of Zeolite-P synthesised at 100 °C.

Infrared spectroscopy (Figure 7) is another sensitive tool to explore the local chemical environment of atoms. NaP zeolite shown the bending vibration of TO_4 ($\text{T} = \text{Si}, \text{Al}$) was recorded at around $430\text{--}580\text{ cm}^{-1}$, this bands are related to the deformation mode of the same bonds. The symmetric stretching vibrations of zeolite NaP framework structure of Si–O and Al–O were noticed at, 669 and 710 cm^{-1} [52]. A medium shoulder at 868 cm^{-1} for zeolite NaP1. In addition, one T–O symmetrical stretching for external linkage as indicated by 740 cm^{-1} . [53]. According to Huo et al.[54], frequencies near 1000 cm^{-1} are ascribed to asymmetric stretching of bonds Si–O or Al–O. These bands are close to 1000 cm^{-1} in the, which in turn is a feature Si–O–Al bond of the tetrahedron TO_4 and confirm the presence of zeolitic material [55]. The bands with a maximum at 1646 cm^{-1} are peculiar of vibrations of functional groups of OH type and are ascribed to water with zeolitic nature. Similar behavior was found by Albert et al. [56]. Flanigen et al [7] preview this bands for zeolite P:

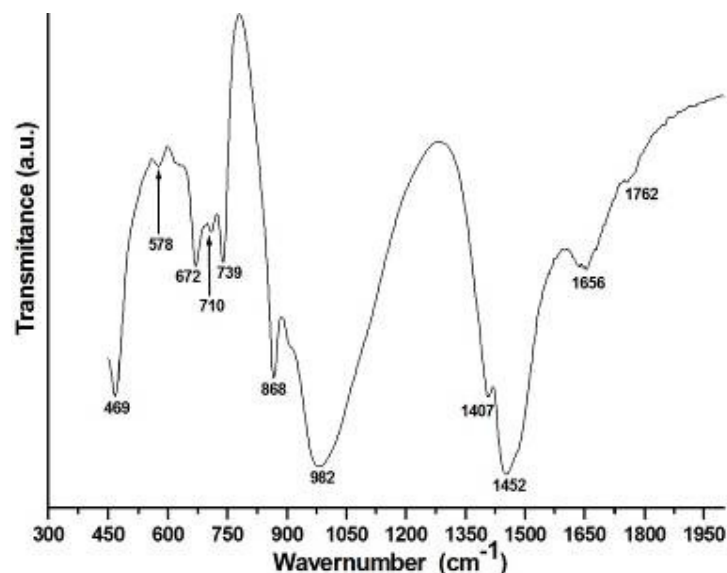


Figure 7: FT-IR spectra of Zeolite-P synthesised at 100 °C.

UV-vis spectra of the RNL solutions after photocatalytic test under irradiation in time interval of 15 min are presented in Figure 8. The decrease of absorption spectra and therefore absorbance of samples is indicated by decolorization of the dye, in applied conditions, due to the decrease in the concentration of dye. Since there are partial peaks appearing in the UV-vis spectra the dye isn't completely degraded, but, there was a softening of the bands located at 238 and 292 nm (3-amine-acetanilide group) [57]. Confirmation of the structure undergoes this process can be confirmed through the IR or chromatographic analysis dye. Azo and chromophore group's band (411 nm) has intensity decreased, demonstrating that the zeolite P in study presents some activity to the photodegradation process. This adsorption does not lead to the breaking of the -N=N- bond, and discoloration is simply related to the decrease in the concentration of the RNL adsorbed onto the catalyst after its removal from the solution [58]. A comparison of discoloration due to adsorption and discoloration due to photocatalysis reveals that the percentage increased 17.2%.

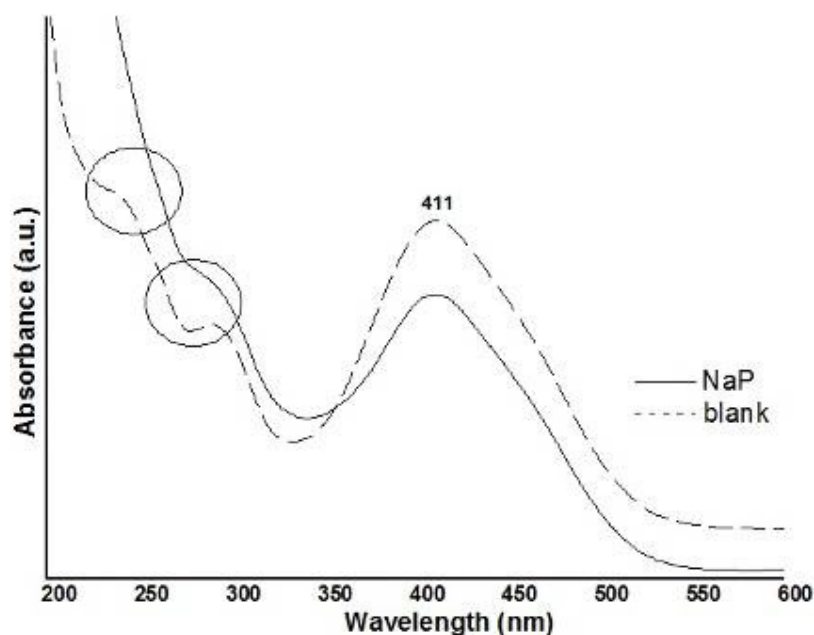


Figure 8: UV-visible absorption spectra of the textile dye, RNL, after photocatalysis in the presence of NaP irradiated with UV light, comparing to that of the blank.

4. Conclusions

In summary, kaolin wastes from Seridó of Brazilian northwest region refined by mechanical milling and thermally activated is a promising source of silicon and aluminum for the synthesis of zeolite NaP. Mineralogical analysis of the final zeolitic product not showed the presence of others feedstock phases of solid residue, which indicated complete change. The synthesised zeolite NaP was tested for photocatalytic degradation of Remazol Yellow Gold (commercial azo dye). This work demonstrates this materials showing significant potential for using as a photocatalytic material for effluent treatment.

References

- [1] P. K. Dutta, D.C. Shieh, M. Puri, Correlation of framework Raman bands of zeolites with structure. *Zeolites*, 8 (1988), 306-309.

- [2] R.M. Barrer, J. F. Cole, H. Sticher, Chemistry of soil minerals. Part V. Low temperature hydrothermal transformations of kaolinite. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical.* (1968) 2475-2485.
- [3] R.M. Barrer, *Hydrothermal Chemistry of Zeolites*, 1st ed., London: Academic Press, 1982.
- [4] P. A. Jacobs, J. A. Martens, *Synthesis of High-Silica Aluminosilicate Zeolites*, 1st Ed., New York: Elsevier Science, 1987.
- [5] R. Szoztak, *Handbook of Molecular Sieves*, 1st ed., London: Blackie Academic and Professional, 1998.
- [6] A. Corma, Towards a rationalization of zeolite and zeolitic materials synthesis. *Studies in Surface Science and Catalysis.* 154 (2004) 25-40.
- [7] E. M. Flanigen, *Advances in Chemistry.* 2nd ed., Washington: American Chemical Society, 121 (1973), A review and new perspectives in zeolite crystallization, p. 119-139.
- [8] A. Tavoraro, R. Mostowicz, F. Creaa, A. Nastro, R. Aielloa, J. B. Nagy, Formation of MFI crystalline zeosilites from fluoride-containing silicate gels. *Zeolites* 12; 6 (1992) 756-761.
- [9] L. V. C. Rees, S. Chandrasekhar, Hydrothermal reaction of kaolinite in presence of fluoride ions at pH less than 10. *Zeolites.* 13; 1 (1993) 534-541.
- [10] B. Férona, J. L. Guth, N. Mimouni-Erddalanea, Influence of the presence of NaF on the crystallization of zeolite A (LTA): First evidence for the existence of fluorosodalite, the missing end-member of the halosodalite series. *Zeolites.* 14; 3 (1994) 177-181.
- [11] H. Koller, A. Wolker, L. A. Villaescusa, M. J. Díaz-Cabañas, S. Valencia, M. A. Cambor, Five-Coordinate Silicon in High-Silica Zeolites. *Journal of the American Chemical Society.* 121; 14 (1999) 3368-3376.
- [12] P. A. Barrett, M. A. Cambor, A. Corma, R. H. Jones, L. A. Villaescusa, Synthesis and Structure of As-Prepared ITQ-4, A Large Pore Pure Silica Zeolite: The Role and Location of Fluoride Anions and Organic Cations. *The Journal of Physical Chemistry B.* 102; 21 (1998) 4147-4155.
- [13] D. P. Serrano, R. Van Grieken, P. Sanchez, R. Sanz, L. Rodriguez, Crystallization mechanism of all-silica zeolite beta in fluoride medium. *Microporous and Mesoporous Materials.* 46;1 (2001) 35-46.
- [14] M. Kato, K. Itabashi, A. Matsumoto, K. Tsutsumi, Characteristics of MOR-Framework Zeolites Synthesized in Fluoride-Containing Media and Related Ordered Distribution of Al Atoms in the Framework. *The Journal of Physical Chemistry B.* 107; 8 (2003) 1788-1797.
- [15] D. S. Kim, J-S. Chang, J-S. Hwang, S-E. Park, J. M. Kim, Synthesis of zeolite beta in fluoride media under microwave irradiation. *Microporous and Mesoporous Materials* 68; 1-3 (2004) 77-82.
- [16] P. Schmidt-Winkel, P. Yang, D. I. Margolese, B. F. Chmelka, G. D. Stucky, Fluoride-Induced Hierarchical Ordering of Mesoporous Silica in Aqueous Acid-Syntheses. *Advanced Materials.* 11; 4 (1999) 303 307.
- [17] D. Boukadir, N. Bettahar, Z. Derriche, Synthesis of zeolites 4A and HS from natural materials. *Annales de Chimie Science des Matériaux.* 27; 4 (2002) 1-13.
- [18] R. Klimkiewicz, E. B. Drag, Catalytic activity of carbonaceous deposits in zeolite from halloysite in alcohol conversions. *Journal of Physics and Chemistry of Solids.* 65; 2-3 (2004) 459-464.
- [19] A. Baccouche, E. Srasra, M. E. Maaoui, Preparation of Na-P1 and sodalite octahydrate zeolites from interstratified illite-smectite. *Applied Clay Science.* 13; 4 (1998) 255-273.
- [20] P. Cañizares, A. Durán, F. Dorado, M. Carmona, The role of sodium montmorillonite on bounded zeolite-type catalysts. *Applied Clay Science.* 16; 5-6 (2000) 273-287.
- [21] R. Lussier, A novel clay-based catalytic material-preparation and properties. *Journal of Catalysis.* 129; 1 (1991) 225-237.
- [22] M. Murat, A. Amokrane, J. P. Bastide, L. Montanaro, Synthesis of zeolites from thermally activated kaolinite. Some observations on nucleation and growth. *Clay Minerals.* 27; 1 (1992) 119-130.
- [23] D. Akolekar, A. Chaffee, R. F. Howe, The transformation of kaolin to low-silica X zeolite, *Zeolites.* 19; 5 (1997) 359-365.

- [24] M. Perissinotto, L. Storaro, M. Lenarda, R. J. Ganzerla, Solid acid catalysts from clays: Acid leached metakaolin as isopropanol. *Journal of Molecular Catalysis A: Chemical*. 121; 1 (1997) 1103-109.
- [25] S. Chandrasekhar, P. N. Pramada, Investigation on the synthesis of zeolite NaX from Kerala kaolin. *Journal of Porous Materials*. 1999, vol. 6, núm. 4, pp. 283-297.
- [26] A. Demortier, N. Gobeltz, J. P. Lelieur, C. Duhayon, Infrared evidence for the formation of an intermediate compound during the synthesis of zeolite Na-A from metakaolin. *International Journal of Inorganic Materials*. 1; 2 (1999) 129-134.
- [27] M. Xu, M. Cheng, X. Bao, X. Liu, D. Tang, Growth of zeolite KSO1 on calcined kaolin microspheres. *Journal of Materials Chemistry*. 9; 12 (1999) 2965-2966.
- [28] R. C. Mackenzie, *Differential Thermal Analysis*, vol. 1, 1st Ed., London: Academic Press, 1970.
- [29] J. Chorover, S. Choi, M. K. Amistadi, K. G. Karthikeyan, G. Crosson, K. T. Mueller, Linking Cesium and Strontium uptake to kaolinite weathering in simulated tank waste leachate. *Environmental Science Technology*. 37; 10 2003 2200-2208.
- [30] H. Zhao, Y. Deng, J. B. Harsh, M. Flury, J. S. Boyle, Alteration of kaolinite to cancrinite and sodalite by simulated hanford tank waste and its impact on cesium retention. *Clays and Clay Minerals*. 52; 1 (2004) 1-13.
- [31] D.-Ch. Lin, X.-W. Xu, F. Zuo, Y.-C. Long, Crystallization of JBW, CAN, SOD and ABW type zeolite from transformation of meta-kaolin. *Microporous and Mesoporous Materials*. 70; 1-3 (2004) 63-70.
- [32] C. Covarrubias, R. Garcia, R. Arriagada, J. Yanez, T. Garland, Cr(III) exchange on zeolites obtained from kaolin and natural mordenite. *Microporous and Mesoporous Materials*. 88; 1-3 (2006) 220-231.
- [33] C. A. Ríos, C. D. Williams, M. A. Fullen, Nucleation and growth history of zeolite LTA synthesized from kaolinite by two different methods. *Applied Clay Science*. 42; 3-4 (2009) 446-454.
- [34] S. Huang, S. Jing, J. Wang, Z. Wang, Y. Jin, White silica obtained from rice husk in fluidized propellant bed. *Powder Technology* 117 (2001) 232-238.
- [35] M. M. Acorsi, A. J. Schwanke, F.G. Penha, S. B. C. Pergher, D.I. Petkowicz, Transformação de caulim em zeólita tipo P. *Cerâmica Industrial*. 14 (2009) 28-33.
- [36] N. Murayama, H. Yamamoto, J. Shibata., Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. *Int. J. Miner. Process.*, 64 (2002) 1-66.
- [37] M. Sathupunya, E. Gularib, S. Wongkasemjit. ANA and GIS zeolite synthesis directly from alumatrane and silatrane by sol-gel process and microwave technique. *Journal of the European Ceramic Society* 22 (2002) 2305–2314.
- [38] S. Hansen, U. Hakansson, A. R. Landa-Canovas, L. Fälth, On the crystal chemistry of NaP zeolites. *Zeolites* 13 (1993) 276-280.
- [39] W. M. Meier, D. H. Olsen, *Atlas of Zeolite Structure Types*, 4th ed., Zeolites, 1996, Butterworth-Heinemann, London.
- [40] S. Hansen, L. Fälth, S. Andersson, “Structural relationships in tetrahedral frameworks: Reflections on Cristobalite”, *J. Solid State Chem.* 39 (1981) 137-141.
- [41] Ch. Baerlocher, W. M. Meier, Crystal-Structure of Synthetic Zeolite Na-P1, an Isotype of Gismondine. *Z. Kristallogr.* 135 (1972) 339.
- [42] R.M. Barrer, J. W. Baynham, F. W. Bultitude, W. M. Meier, Hydrothermal Chemistry of the Silicates Part VIII: Low Temperature Crystal growth of Aluminosilicates, and of Some Gallium and Germanium Analogues. *J. Chem. Soc.* (1959) 195-208.
- [43] D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, 1st Ed., New York: John Wiley, 1974.
- [44] C. Zhu, L. Wang, L. Kong, X. Yang, L. Wang, S. Zheng, F. Chen, F. MaiZhi, H. Zong, Photocatalytic decolorization of AZO dyes by supported TiO₂/UV in aqueous solution, *Chemosphere* 41 (2000) 303–309.
- [45] I.T. Pernal, N. Koprivanac, A. M. L. Bozic, H. M. Kusic, Comparative study of UV/TiO₂, UV/ZnO and photo-Fenton processes for the organic reactive dye decolorization in aqueous solution, *J. Hazard. Mater.* 148 (2007) 477–484.

- 458 [46] S. Anandan, M. Yoon, Photocatalytic activities of the nano-sized TiO₂-supported Y-
459 zeolites, *J. Photochem. Photobiol. C: Photochem. Rev.* 4 (2003) 5–18.
- 460 [47] I. Othman, R. Mohamady, I. A. Ibraheem, M. M. Mohamed, Synthesis and modification of
461 ZSM-5 with manganese and lanthanum and their effects on decolorization of indigo carmine
462 dye, *Appl. Catal. A* 299 (2006) 95–102.
- 463 [48] R. R. Menezes, R. R. Almeida, L. N. L. Santana, H. S. Ferreira, G. A. Neves, H. C.
464 Ferreira, Utilização do Resíduo do Beneficiamento do Caulim na Produção de Blocos e Telhas
465 Cerâmicos. *Revista Matéria* 12; 1 (2007) 226–236.
- 466 [49] E. A. Hildebrando, C. G. B. Andrade, C. A. F. R. Junior, R. S. Angélica, F. R. Valenzuela-
467 Diaz, R. F. Neves., Synthesis and Characterization of Zeolite NaP Using Kaolin Waste as a
468 Source of Silicon and Aluminum. *Materials Research.* 17; 1 (2014) 174-179.
- 469 [50] Y. Yu, G. Xiong, C. Li, F.-S. Xiao, Characterization of aluminosilicate zeolites by UV
470 Raman spectroscopy. *Microporous and Mesoporous Materials* 46 (2001), 23-34.
- 471 [51] Peter-Paul Knops-Gerrits, Dirk E. De Vos, Eddy J.P. Feijen, Peter A. Jacobs., Raman
472 spectroscopy on zeolites. *Microporous Materials* 8 (1997) 3-17.
- 473 [52] Albert BR, Cheetham AK, Stuart JA and Adams CJ. Investigations on P zeolites: synthesis,
474 characterisation, and structure of highly crystalline low-silica NaP. *Microporous and*
475 *Mesoporous Materials.* 1998; 21:133-142.
- 476 [53] G. G. Fuentes, A. R. Ruiz-Salvador, M. Mir, O. Picazo, G. Quintana, M. Delgado, Thermal
477 and Cation Influence on IR Vibrations of Modified Natural Clinoptilolite. *Micropor. Mesopor.*
478 *Mater.* 20 (1998) 269-281.
- 479 [54] Z. Huo, X. Xu, Z. Lv, J. Song, M. He, Z. Li, et al, Thermal study of NaP zeolite with
480 different morphologies. *Journal of Thermal Analysis and Calorimetry* (2012) 1-5.
- 481 [55] A. Demortier, N. Gobeltz, J. P. Lelieur, C. Duhayon, *Int. J. Inorg. Mater.* 1 (1999) 129-134.
- 482 [56] V. L. Zholobenko, J. Dwyer, R. Zhang, A. P. Chapple, N. P. Rhodes, J. A. Stuart,
483 Structural transitions in zeolite P: An in situ FTIR study. *Journal of the Chemical Society,*
484 *Faraday Transactions* 94; 12 (1998) 1779-1781.
- 485 [57] M. Catanho, G. R. P. Malpass, A. J. Motheo, Avaliação dos tratamentos eletroquímico e
486 fotoeletroquímico na degradação de corantes têxteis, *Quim. Nova* 29; 5 (2006) 983-989.
- 487 [58] H. B. Sales, V. Bouquet, S. Députier, S. Ollivier, F. Gouttefangeas, M. Guilloux-Viry, V.
488 Dorcet, I. T. Weber, A. G. Souza, I. M. G. Santos, Sr_{1-x}Ba_xSnO₃ system applied in the
489 photocatalytic discoloration of an azo-dye, *Solid State Sciences* 28 (2014) 67-73.
- 490