Optimisation of zeolite LTA synthesis from alum sludge and the influence of the sludge source

Alexandra Rozhkovskaya¹, Jay Rajapakse¹,*, Graeme J. Millar²

¹ School of Civil and Environmental Engineering, Science and Engineering Faculty, Queensland University of Technology, Brisbane, Queensland 4000, Australia
² Institute for Future Environments and School of Mechanical, Medical and Process Engineering, Queensland University of Technology, Brisbane, Queensland 4000, Australia

ABSTRACT

Generation of alum sludge (AS) at drinking water treatment plants represents an environmental liability and adds to the cost of water purification. Consequently, this study explored the feasibility of using low and high carbon containing alum sludge from two water treatment plants to synthesize zeolite LTA. The hypothesis was that zeolite LTA synthesis was dependant upon alum sludge source and that a range of strategies may be required to optimize zeolite crystallinity. Zeolite characteristics such as morphology, phase composition, crystallinity, and particle size distribution were recorded. “One pot” hydrothermal synthesis of precursor gel with molar composition 4.2Na₂O:Al₂O₃:1.2SiO₂:168H₂O at 80°C for 3 hr resulted in 25 and 46 wt.% zeolite LTA from high and low carbonaceous sludge, respectively. Prior to hydrothermal reaction stage it was discovered that ageing of the gel, addition of zeolite LTA seeds, ultrasonic treatment and calcination all promoted zeolite LTA formation. Calcination of the alum sludge at 700°C for 2 hr before hydrothermal synthesis resulted in particle size reduction and the highest amount of crystalline zeolite LTA: 79 wt.% from low carbon sludge and 65 wt.% from high carbon sludge. Notably, the zeolite crystallinity reported in this study was the higher than previous studies on this topic. The outlined approach may allow value adding of alum waste and produce a commodity which could be used locally by the water treatment plant as a water softener.

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Introduction

Zeolites are versatile minerals, which have been extensively used in a wide range of industrial processes including water treatment (Wen et al., 2018), catalysis (Alkhlel and De Lasa, 2018), gas purification (Poursaeidesfahani et al., 2019), agriculture (Nakhli et al., 2017) and others. To date, more than 235 unique types of zeolite structures, both natural and synthetic, have been identified according to the International Zeolite Association Database of Zeolite Structures (IZA-SC, 2016). Of these materials, the highest ion-exchange capacity value is attributed to low silica zeolites such as LTA (also commonly known as “NaA zeolite” or “4A”) (Bhatia, 1990; Petrov and Michalev, 2012). High cation exchange capacity and particular affinity towards calcium cations make zeolite LTA one of the largest volume zeolites employed (Collins et al., 2020); with a market value of 250 million USD in the USA alone (Hegde, 2018). Zeolite LTA is mainly used commercially as an effective water softener in the detergent and water treatment industries (Muratiev et al., 2004; Tomaszewska et al., 2018). The industrial production of zeolite LTA involves the hydrothermal reaction of an aqueous solution of sodium hydrox-
ide with chemicals such as sodium metasilicate and sodium aluminate (Brockh et al., 2012).

Taking into account not only the substantial industrial demand for zeolite LTA but also a growing trend towards environmentally friendly and sustainable manufacturing processes; there is a need to develop alternative ways of synthesising zeolite LTA which utilise relatively inexpensive sources of silica and alumina, such as waste materials. Consequently, numerous studies have reported synthesis of zeolite LTA from various industrial wastes such as fly ash (Iqbal et al., 2015; Yang et al., 2019), rice husk (Azizi and Yousef, 2010; Nut, 2001), coal gangue (Qian and Li, 2015), bauxite tailings (Ma et al., 2015a; others (Chen et al., 2020)). However, results of these studies are available that the employment of alumin sludge in zeolite synthesis (Anuwattana and Khummongkol, 2009; Espejel-Ayala et al., 2013; Wongsrichien et al., 2014). Alumin sludge refers to a waste product at water treatment plants which use alum (hydrated aluminium sulphate \( \text{Al}_2(\text{SO}_4)\cdot(14-18)\text{H}_2\text{O} \)) as a coagulant to reduce water turbidity. The production of alumin sludge constitutes a key waste management issue, as up to 2000 ton/year of alumin sludge is generated from a typical drinking water treatment plant with a capacity of 180 ML/day (Alumin Sludge Reuse Investigation Working Technical Report, 2015). The composition of the alumin sludge varies and depends on the water source, alumin dosage and the treatment plant process configuration (Babatunde and Zhao, 2007; Tantawy, 2015). Typically, this sludge consists of main water (moisture content above 80 wt.% (Tantawy, 2015)), alumina (29.7 ± 13.3 wt.% dry weight), and silica species (33.4 ± 26.2 wt.% dry weight), which may be potentially reused instead of being dumped into landfills (Babatunde and Zhao, 2007).

Several research articles have reported that conventional hydrothermal zeolite synthesis methods were not effective to obtain zeolite LTA of high purity and crystallinity from sludge (Anuwattana and Khummongkol, 2009; Wongsrichien et al., 2014). The precise reasons relating to the relative inactivity of sludge are unclear. One key aspect contributing to such a result may be the fact that sludge is an industrial waste material, which contains significant levels of impurities such as soil organic matter, iron, and calcium (Espejel-Ayala et al., 2013; Kuwahara et al., 2010). Consequently, it has been suggested that the presence of impurities in sludge might be a negative factor for nucleation of aluminosilicate gels (Kuwahara et al., 2010). Hence, it appears logical to examine additional pre-treatment stages prior to hydrothermal synthesis of sludge. In general, there are two approaches to pursue: waste purification (to eliminate impurities) and nucleation-promotion (to increase the rate of zeolite nucleation) methods. One example of purification involves leaching of waste with sulphuric (Anuwattana and Khummongkol, 2009) or hydrochloric (Ma et al., 2014) acids to remove impeding species such as potassium, calcium and iron prior to zeolite crystallisation. However, acid leaching generates substantial volumes of potentially hazardous, low pH liquid wastes. Alternately, waste purification can be facilitated by calcination, which is a more environmentally beneficial method of waste pre-treatment. Calcination at 500-700°C can eliminate water and other volatile impurities from waste residues (Lukeshevich et al., 2011; Qian and Li, 2015; Wongsrichien et al., 2014). This method increases the weight percentage of the main components and removes impurities (e.g. harmful halogens, inorganic anions, and organic matter) which can negatively influence zeolite quality. Fusion treatment of waste at elevated temperature with sodium hydroxide has also been reported (Anuwattana and Khummongkol, 2009; Anuwattana et al., 2015; Espejel-Ayala et al., 2013). The highest degree of zeolite crystallisation was attained by Anuwattana and Khummongkol (2009) after fusion pre-treatment at 700°C for 1 hr. However, the final product comprised of only 64 wt.% zeolite LTA with 3 wt.% of sodalite also detected. With regards to the second approach, i.e. acceleration of nucleation in the starting aluminosilicate gel used for zeolite synthesis; there exist several strategies including: precursor ageing (Kuwahara et al., 2010), seeding (Diaz et al., 2006), ultrasonic treatment (Farias et al., 2017) and microwave irradiation (Li et al., 2017). Nucleation promotion has been widely researched due to positive benefits such as reduction in zeolite particle size, increase of crystalline zeolite content and higher purity of the products (Abdullahi et al., 2017; Zeng et al., 2015).

Surprisingly, efforts to optimize synthesis of zeolite LTA from sludge using the aforementioned approaches to purify the waste and enhance the nucleation of pre-cursors to zeolites have not been described. Furthermore, as outlined above the variation in sludge constitution has not been accounted for when trying to make zeolite materials from this waste source. Therefore, the aim of this study was to synthesise zeolite LTA from alumin sludge which was of high crystalline content and investigate the influence of alumin sludge source. The hypothesis was that it may be possible to promote the synthesis of zeolite LTA from alumin sludge by tailoring pre-treatment strategies which cope with the inherent compositional variation in alumin waste sources. The following research questions were addressed to support the hypothesis: (1) How sensitive is zeolite LTA formation to the source of the alumin sludge? (2) How can we optimise zeolite LTA crystalline content? (3) What are the preferred pre-treatment conditions for alumin sludge samples? In order to explore the influence of water treatment plant process design upon LTA zeolite formation, this study investigated alumin sludge samples from two different water treatment plants. To increase the amount of zeolite LTA present, several pre-treatment techniques were conducted including ageing, seeding, ultrasonic treatment and calcination. Zeolite products were analysed by techniques such as quantitative X-ray diffraction (qXRD), scanning electron microscopy (SEM) and particle size distribution (PSD) to investigate their mineral composition, presence of crystalline material and morphology. Optimun conditions for pre-treatment of aluminosilicate gels resulted in the formation of high quality zeolite LTA.

1. Materials and methods

1.1. Materials and chemicals

Dewatered alumin sludge (AS) from two different water treatment plants located in Queensland, Australia was used. Samples were collected after centrifugation from the Capalaba water treatment plant (Redland region) (AS01) and from the Mount Crosby West Bank water treatment plant (Ipswich region) (AS02). The Capalaba plant raw water had an average turbidity of 3 NTU (nephelometric turbidity unit) and alumin dosage of 8.2 mg/L as Al2O3, while the parameters of the Mount Crosby West Bank plant were: raw water turbidity 2.3 NTU and alumin dosage 7.6 mg/L as Al2O3, respectively. The process flow diagram for the operations at Capalaba and Mount Crosby West Bank water treatment plants are presented in Appendix A Fig. S1.

The major process difference was that at the Capalaba water treatment plant, depending on the seasonal variation of influent water quality, powdered activated carbon (PAC) was added to feedwater prior to the coagulation process. PAC is usually added at an early stage of the treatment process in order to remove odour and taste compounds as well as organic matter from drinking water.
Conventional hydrothermal synthesis was conducted at 80°C for 2–7 hr (Palčić et al., 2012; García-Soto et al., 2013). Once the reaction was complete, the bottle was removed from the heat source and cooled to room temperature. The solid product was separated from the alkaline solution using a vacuum filtration unit and washed with deionized water until the filtrate pH was below 9. Then the resultant zeolite was dried in an oven overnight at 102°C.

1.2.2. Pre-treatment of gel and alum sludge

1.2.2.1. Ageing of gel pre-cursor The synthesis of the pre-cursor solution was conducted as outlined in Section 1.2.1. In this instance the thick gel formed was aged at room temperature with no stirring for 5, 10, 16 and 24 hr in a sealed alkaline resistant Naigene® bottle. It was experimentally determined that stirring while ageing had no positive effect on zeolite crystallisation, which was supported by previous studies (García-Soto et al., 2013). In addition, experiments were also conducted at increased ageing temperatures of 30, 40 and 60°C for 16 hr. Crystallisation of zeolite LTA was conducted after the ageing process at 80°C for 3 hr.

1.2.2.2. Ultrasoication of gel Ultrasound has been demonstrated to provide benefits in terms of accelerated ageing of the pre-cursor gel (Farias et al., 2017). Hence, the gel described in section 1.2.1 was in this instance sealed in a Teflon vessel and placed in a 100 W laboratory ultrasonic bath (Digitech, Germany) for 10, 20, 40, and 100 min. Then the hydrothermal reaction was again conducted at 80°C for 3 hr.

1.2.2.3. Seeding of gel with zeolite LTA Preparation of the gel described in Section 1.2.1 was modified by addition of a commercial sample of zeolite LTA supplied by Tosoh (1, 5, and 10 wt.% of the alum sludge mass). The hydrothermal reaction at 80°C for 3 hr was then completed with no ageing stage.

1.2.2.4. Calcination of alum sludge Calcination of alum sludge was used as a pre-treatment option in order to improve the reactivity. High temperature treatment was expected to remove volatile impurities such as organic matter (Espejel-Ayala et al., 2013). Dry pulverized alum sludge of fixed mass (15 g) was placed in a nickel crucible and calcined in a furnace (AAT 11/3, Carbolite Gero, Germany) at 600, 700, and 900°C for 2 and 4 hr. After being cooled to room temperature, the sample (5 g) was mixed with 50 mL of 2.3 mol/L NaOH solution and stirred using a magnetic stirrer at 300 r/min at room temperature until homogenised. Sodium metasilicate was dissolved in NaOH solution and then poured into the sludge mixture. The doses of NaOH and Na₂SiO₃ were calculated for every sludge sample individually in order to obtain the following molar chemical composition of the gel: 4.2 Na₂O:Al₂O₃:1.2 SiO₂:168 H₂O. After ageing for 16 hr at room temperature, hydrothermal synthesis was conducted on this gel at 80°C for 3 hr.

1.3. Characterisation of solid materials

1.3.1. X-ray fluorescence (XRF) The chemical composition, including SiO₂/Al₂O₃ molar ratios of zeolite samples, and loss on ignition (LOI) of solids were analysed by X-ray fluorescence spectroscopy (XRF) using an Axios FAST simultaneous X-ray fluorescence spectrometer (Malvern Panalytical, UK). Samples were analysed in the form of glass disks prepared by fusion of the sample with mixed flux (49.75% Li₂B₂O₄, 49.75% LiBO₂ – 0.5% LiBr by Claisse) in an electronic fusion instrument at 1050°C (Claisse TheOX, Malvern Panalytical, UK). The chemical composition was presented in terms of the oxide forms of elements.
1.3.2. Quantitative X-ray diffraction (qXRD)
To determine the crystalline and amorphous content of the materials, the quantitative Powder X-ray diffraction (qXRD) method was applied using TOPAS (Total Pattern Analysis Solution) version 5 software (Tanaka et al., 2008). This method is more precise than “the sum of area under the peaks” used in previous studies (Iqbal et al., 2019) for phase quantification. The software utilizes a complex logarithm based on nonlinear least squares approach. To conduct quantitative XRD, a solid sample was first micronized with an internal standard corundum (10% of the sample weight). Then, XRD analysis was performed using a Xpert PRO Cu Kα powder diffractometer (Malvern Panalytical, UK) using CoKα radiation (λ = 1.789 Å). The XRD patterns were collected at a scan range between 2θ = 2° and 90° 2θ with a scan speed of 4°/min with a 2θ step size of 0.0167°. Then the patterns were refined by the Rietveld method using TOPAS software. Weight percentage of phases was calculated as an average from two repetitive experiments.

1.3.3. Carbon/Nitrogen/Sulphur (CNS) analysis
The amount of total carbon, nitrogen, and sulphur in an alum sludge sample was determined by CNS analysis. The powdered sample of approximately 0.5 g was analysed using a Trumac CNS instrument (LECO, USA) alongside with a standard reference soil (LECO® 502–309).

1.3.4. Scanning electron microscopy (SEM)
Sample imaging was conducted using a JEOL 7001F scanning electron microscope (Japan). Sample preparation included ultrasonication of samples in 99% ethanol for 5 min. Then, three drops of the ethanol/particle mix were put on a specimen stub. When dry, the samples were coated with 10 nm thick carbon using a 206HR Carbon Coater (Cressington, UK) prior to the analysis.

1.3.5. Particle size distribution
Particle size distribution curves were obtained using a laser diffraction particle size analyser Mastersizer 3000 (Malvern Panalytical, UK). The samples were mixed with deionized (DI) water and subsequently treated with ultrasound for 30 min.

2. Results and discussion

2.1. Characterization of alum sludge samples
Alum sludge from water treatment plants was described as a dark grey (with activated carbon added) or light brown (with no carbon) paste with a “river odour”. This colour may be attributed to presence of soil particles and natural organic matter removed from the treated water. The chemical composition of the wastes was analysed by X-ray fluorescence spectroscopy (XRF) and CNS (Table 1).

It was seen from Table 1 that the compositions of the sludge used in this study (which were from the same geographical region but from different treatment plants); varied in terms of iron, aluminium, and carbon content. AS02 consisted of ca. 7% more aluminium and 2% less iron than AS01. However, the major difference was the amount of carbon present. As was mentioned in Section 1.1, at one of the plants PAC was added to the feed water prior to the coagulation process. This strategy resulted in the carbon concentration of AS01 to be substantially greater (23.3 wt.%) than that of AS02 (14.06 wt.%). According to the International Zeolite Association (Kühl, 2001), the presence of iron should not significantly influence zeolite crystallisation. Studies have confirmed that even high amounts of iron in the initial material did not affect the quality of a final zeolite product (Espejel-Ayala et al., 2013). Loss of ignition (LOI) values of AS01 and AS02 were 51.72 and 44.83 wt.%, respectively. Such high percentages of volatile substances may be explained by the fact that the majority of impurities removed by coagulation from raw water were probably organic matter and biomaterials. The water content of alum sludge was also high and reached 76 wt.% (AS01) and 80 wt.% (AS02), which was in agreement with literature (Barakwan et al., 2019).

Also evident in Table 1 was the surprising fact that the silica/alumina ratio was less than 1 for the Australian samples and greater than 1 for the samples from Iran, Mexico, and Thailand. This data highlighted the impact of factors such as differences in alum dose and the specific nature of the treated water source. In terms of zeolite formation, zeolite LTA requires as a minimum a molar SiO₂/Al₂O₃ ratio equal to 1 due to the constraints of Lowenstein’s rule (Garcia-Soto et al., 2013). The SiO₂/Al₂O₃ molar ratios for AS01 and AS02 were calculated as 0.61 and 0.57, respectively. Consequently, it was inferred that addition of an external silica source was required if zeolite LTA was to be synthesised from alum sludge. Overall, the mineral compositions of all the sludge samples were within the range reported by Babatunde et al. (2007).

The mineral composition of alum sludge samples was investigated by the quantitative XRD method. The XRD patterns and weight percentage of phases present in the initial alum sludge samples are shown in Fig. 1. The phase composition of alum sludge from different treatment plants showed that the dominant phase was amorphous material (~90 wt.%). There were differences in the amount of crystalline impurities such as kaolinite, quartz, and albite. The presence of such minerals was attributed to the natural mineral composition of the riverbed and, therefore, of a turbid water sample (Singh and Schulze, 2015). The XRD patterns of received alum sludge were in agreement with those obtained by Espejel-Ayala (2013) who identified kaolinite, quartz and albite as major crystalline phases (albeit, only qualitative XRD analysis was conducted and not quantitative). It was previously claimed that zeolite materials are preferably formed from amorphous aluminosilicate precursor in a strongly alkaline solution (Deng et al., 2006). Thus, the high amorphous content and low percentage of crystalline impurities in alum sludge suggest it may be a favourable waste material for zeolite production.

![Fig. 1 – X-ray diffraction (XRD) patterns of alum sludges AS01 and AS02. K: kaolinite; Q: quartz; A: albite.](image-url)
Table 1 – Chemical composition of alum sludge samples (wt.%).

<table>
<thead>
<tr>
<th>Origin of the sludge</th>
<th>Australia Alum sludge carbonaceous (AS01)</th>
<th>Iran Alum sludge (AS02)</th>
<th>Thailand Foroughi et al., 2018</th>
<th>Mexico Espejel-Ayala et al., 2013 Wongwichien et al., 2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>11.30</td>
<td>12.85</td>
<td>37.41</td>
<td>33.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>31.22</td>
<td>38.05</td>
<td>27.75</td>
<td>31.98</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.10</td>
<td>2.36</td>
<td>5.42</td>
<td>4.94</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.11</td>
<td>0.20</td>
<td>0.45</td>
<td>0.41</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.28</td>
<td>0.31</td>
<td>2.23</td>
<td>0.43</td>
</tr>
<tr>
<td>MgO</td>
<td>0.37</td>
<td>0.45</td>
<td>1.83</td>
<td>0.63</td>
</tr>
<tr>
<td>CaO</td>
<td>0.35</td>
<td>0.50</td>
<td>3.59</td>
<td>0.64</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>0.14</td>
<td>0.17</td>
<td>0.32</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.17</td>
<td>0.26</td>
<td>0.51</td>
<td>0.48</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.17</td>
<td>0.36</td>
<td>0.25</td>
<td>0.40</td>
</tr>
<tr>
<td>Loss of ignition</td>
<td>51.72</td>
<td>44.83</td>
<td>20.05</td>
<td>26.1</td>
</tr>
<tr>
<td>Carbon</td>
<td>23.30</td>
<td>14.06</td>
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<td>No data</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.91</td>
<td>0.82</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.16</td>
<td>0.60</td>
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<td>No data</td>
</tr>
<tr>
<td>Water content</td>
<td>76</td>
<td>80</td>
<td>No data</td>
<td>No data</td>
</tr>
</tbody>
</table>

AS01: alum sludge from the Capalaba water treatment plant (Redland region); AS02: alum sludge from the Mount Crosby West Bank water treatment plant.

2.2. Influence of alum sludge source on zeolite LTA formation

2.2.1. Conventional hydrothermal synthesis without pre-treatment

First, a “one pot” hydrothermal synthesis procedure was applied to both sludge samples under the same conditions of 80°C for 2–7 hr reaction time. Quantitative XRD (qXRD) method was used in this study, which allowed to recognize a difference in crystalline content in zeolite products. Due to crystalline impurities from alum sludge (quartz, kaolinite and albite) were stable under examined hydrothermal conditions and original XRD patterns were found to be similar, the results are shown as weight percent of LTA zeolite measured by quantitative XRD (Fig. 2).

No significant correlation was found between the amount of crystalline zeolite material and reaction time. This finding was contrary to previous studies which have shown that hydrothermal time was the major influence on the extent of zeolite formation (Qian and Li, 2015; Anuwattana and Khummongkol, 2009). As shown in Fig. 2, already after 2 hr of hydrothermal reaction the zeolite LTA content in AS01 and AS02 samples reached 21 and 41 wt.%, respectively. After 3 hr of treatment the presence of crystalline zeolite plateaued at 25 wt.% for AS01 and 46 wt.% for AS02; further extension of reaction time did not markedly facilitate zeolite crystallisation. These results reflect those of Anuwattana and Khummongkol (2009) who found that the highest percentage of crystalline zeolite LTA was obtained from alum sludge after 3 hr of crystallisation. Wu et al. (2018) also demonstrated that complete conversion of opal waste rock into NaA zeolite occurred after 3 hr of hydrothermal reaction. Nevertheless, a range of longer crystallisation times at 80°C have been reported as optimum, including 50 (Bronić et al., 2012) and 160 hr (Moisés et al., 2013). However, extension of reaction time was not warranted...
in this study and 3 hr reaction time was adopted for further experiments.

Fig. 3 presents XRD patterns of the zeolite products obtained after hydrothermal treatment of AS01 and AS02 at 80 °C for 3 hr. From the XRD data it was concluded that the peak profiles of zeolites from both sludge samples were similar. It appeared that the quartz and albite phases were not significantly transformed into other materials under the applied synthesis conditions. However, a sodalite peak (ca. 1.5 wt.%) was detected in the product from the carbonaceous sludge (AS01), which was an impurity zeolite phase.

In order to investigate the morphology of zeolite LTA crystals, SEM micrographs of zeolite LTA samples (from AS01 and AS02 obtained after hydrothermal crystallisation at 80 °C for 3 hr) are shown in Fig. 4. It can be seen from Fig. 4 that both samples were represented by poorly crystalline cubic particles integrated with large clusters of amorphous material. Despite exhibiting a typical cubic morphology of zeolite LTA, the amount of crystalline materials was low, and samples consisted of mostly amorphous matters, which was in agreement with qXRD data (Fig. 2).

Taken together, the results in Figs. 2–4 indicated that sludge (AS01) which contained a greater initial quantity of carbonaceous material displayed reduced conversion to zeolite LTA. The results were consistent with those of previous studies (Selim et al., 2018). Previously, zeolite LTA with poor crystallinity and a large amount of amorphous matter was obtained in the presence of carbon. It was postulated that activated carbon interacted with dissolved aluminium and silicon species via Van der Waals forces, impeding gel formation (Kudravceva and Salnikova, 2012). In addition, oxides on the surface of activated carbon converted into ion-exchange centres when hydrated (Kudravceva and Salnikova, 2012). These centres could react with aluminium and silicon species, thus causing a negative effect on zeolite nucleation. This result provided evidence that the identity of the sludge was indeed critical when attempting to convert this waste to zeolite LTA.

It was also apparent that “one pot” hydrothermal reaction did not result in substantial zeolite LTA crystallization as was previously stated (Anuwattana and Khunmongkol, 2009). The degree of crystalline material formation did not surpass 46 wt.% for a regular sludge and 25 wt.% for a carbonaceous sludge. Despite the reaction parameters (crystallisation time, temperature, and composition of the gel) being in theory favourable for zeolite LTA formation (Breck, 1984), the majority of the sample remained amorphous. Notably, sludge contained a significant amount of organic and inorganic impurities (see Table 1). It was previously reported that the presence of impurities in zeolite precursors usually impedes nucleation and the following crystallisation stage; which resulted in a zeolite with low cation exchange capacity and irregular-shaped crystals (Kuwahara et al., 2010).

2.2.2. Improvement of zeolite LTA formation by introduction of pre-treatment strategies

2.2.2.1. Ageing AS01 and AS02 alum sludge derived aluminosilicate gel samples

Ageing of zeolite precursor can be defined as the process of storing aluminosilicate gel prior to crystallisation, for a period of time at a temperature lower than that employed in the hydrothermal synthesis stage. Previous studies have confirmed the effectiveness of preliminary ageing of amorphous aluminosilicate gels (Abdullahi et al., 2017; Jafari et al., 2013; Pašič et al., 2012). It was reported that this process resulted in an increase of the nucleation rate and hence, reduction of the particle size and increase of BET surface area and specific number of crystals (Khosravi et al., 2016; Pašič et al., 2012). Moreover, ageing of alumina silica gel favours kinetics of zeolite crystallisation during the hydrothermal step (Kerr, 1966; Pašič et al., 2012). Consequently, the feed mixture comprising of alum sludge, sodium silicate, sodium hydroxide, and water with the molar ratios 4.2 Na₂O·Al₂O₃·1.2 SiO₂·168 H₂O was aged at room temperature for 5 to 24 hr prior to hydrothermal treatment for 3 hr at 80 °C (Fig. 5).

Fig. 5 shows the creation of crystalline zeolite LTA from alum sludge AS01 increased by 10% after ageing for 5 hr, but
then levelled off at around 38 wt.%. Another important finding was that the sodalite content gradually decreased with increasing ageing time. Indeed, after ageing of the AS01 based gel at room temperature for 16 hr no sodalite was observed in the system. According to these results, it can be inferred that reorganisation of the gel during the ageing step led to more stable zeolite LTA nuclei and thus, slower conversion into sodalite, which was consistent with existing literature (Cundy and Cox, 2005). In the case of the AS02 based gel, no sodalite phase was detected in the samples. A slight rise of zeolite LTA crystallinity from 43 to 48 wt.% occurred after 5 hr of ageing. Albeit, the maximum value of 51 wt.% was reached after 16 hr. Generally, taking into account TOPAS error margin (±1%) (Tamer, 2013), minimal significant difference was observed in zeolite LTA concentration with increase of ageing time after 5 hr.

More detail regarding the influence of ageing upon formation of zeolite LTA was acquired by examination of the particle size of the zeolite LTA material (Fig. 6). Consistent with previous literature, this study found that increased ageing time led to the reduction of the average zeolite crystal size (Jafari et al., 2013). From the data in Fig. 6, it was seen that extension of the ageing time from 1 to 16 hr resulted in the average particle size being reduced from 0.8 to 0.5 and 0.6 μm for AS01 and AS02, respectively. During the ageing of the zeolite precursors, the structure of the gel rearranged causing formation of more nuclei with time (Jafari et al., 2013). Small crystal size (<1 μm) can be a beneficial parameter for zeolites used in water treatment and gas separation due to improved diffusion and higher surface area per volume; and thus, higher cation exchange capacity (Slanget al., 1997). Further extension of ageing time to 24 hr did not lead to significant differences in particle size. Thus, an ageing time longer than 16 hr was not justified for zeolite LTA synthesis from alun sludge. Therefore, an ageing time of 16 hr was selected for the following experiments.

SEM images of zeolite LTA samples from carbonaceous alun sludge AS01 and regular alun sludge AS02 after ageing for 16 hr are presented in Fig. 7a1 and b1. Notably, typical cubic morphology of NaA zeolite was observed in every micrograph in Fig. 7 (Sharma et al., 2012).

Regarding the presence of crystalline material, SEM data was consistent with the quantitative XRD data presented in Fig. 5. Introduction of ageing improved the crystallinity of zeolite LTA particles leading to more defined crystals and a reduction of amorphous matter, compared to zeolite with no pre-treatment (Fig. 4). However, the cubes after 16 hr of ageing still exhibited undefined edges and coarse surfaces, covered by amorphous matter. In the case of particle size distribution, SEM images indicated that generally the zeolite crystals were considerably less than 1 μm (Fig. 7a1, b1). It was apparent from the micrographs that reduction of particle size occurred after the gel was aged for 16 hr, which was consistent with PSD curves (Fig. 6).

Ageing at elevated temperature might be another advantageous approach for zeolite LTA synthesis from alun sludge. Therefore, the influence of elevated ageing temperature on zeolite formation was investigated. The precursors were aged for the optimum 16 hr time period at 30, 40, and 60°C. The results of qXRD analysis are presented in Fig. 8. With regards to AS02, an increase of the ageing temperature led to negative correlation with zeolite LTA content; which was in agreement with previous studies (Park et al., 1996). Park et al. (1996) found that a rise in ageing temperature of precursor gel suppressed nucleation of various zeolite types, including RHO, zeolite LTA, faujasite, and sodalite. The reason for this observation was suggested to relate to adsorption of aluminate anions on the silica surface, which inhibited silica dissolution and thus, formation of aluminosilicate species. In contrast, the amount of zeolite LTA synthesised from AS01 increased significantly from 38 to 55 wt.% as ageing temperature was elevated. Nevertheless, a possible drawback of elevated temperature ageing was the simultaneously recorded growth of sodalite content. This result was consistent with the fact that zeolite LTA was a metastable phase, which may transform into sodalite followed by cancrinite with a rise of crystallisation temperature or time (De LeON et al., 2011; Deng et al., 2006; Qian and Li, 2015). Interestingly, no sodalite was formed using AS02 sludge as zeolite precursor. The observed contradiction could be attributed to the distinction in amorphous composition of two sludges, specifically, presence of activated carbon. Phase transformation of zeolite LTA into more stable sodalite probably occurred according to Ostwald’s rule to stabilise the system. Thus, the fact that carbonaceous system converted faster might be explained by the presence of activated carbon making it less stable.

The SEM micrographs of zeolite LTA samples from AS01 and AS02 after ageing at 60°C for 16 hr are presented in Fig. 7a2 and b2. Regarding carbonaceous alun sludge AS01, significant
improvement of crystallinity was detected with an increase of ageing temperature, which was in agreement with XRD data (Fig. 8). Zeolite crystals were found to have more defined edges and less amorphous flakes compared to the sample with no ageing. However, formation of sodalite occurred on the surface of LTA zeolite cubes, which was explained above. With respect to AS02, the observed morphology of zeolite LTA after ageing for 16 hr at 60°C was found to be similar to that obtained with no ageing. Compared with ageing of aluminosilicate gel from AS02 at room temperature for 16 hr, crystallinity of the cubes in this experiment was noted to be lower, while the amount of amorphous flakes was higher. This result implied no positive effect of ageing of AS02 gel at elevated temperature on zeolite LTA crystallisation. It was also interesting to note that particle size of both alum sludge samples increased after elevation of the ageing temperature. These results were in accord with Bayati et al. (2008), who claimed that an increase of reaction time and, particularly, temperature were the major factors, which resulted in an increase of zeolite crystal size. This behaviour was explained by Ostwald’s step rule, which implied a phase transformation of small crystals into more energetically stable large ones, especially with the excess of energy in the system (Van Santen, 1984). Taken together, these results suggested ageing at room temperature for 16 hr was the optimum ageing conditions for AS02 pre-treatment (51 wt.%), while 16 hr ageing at 60°C was found to be the optimum for zeolite LTA synthesis from carbonaceous AS01 (55 wt.%).

2.2.2. Ultrasonication Ultrasonic treatment is a technique which has recently been introduced into the field of zeolite synthesis. Ultrasound application has been shown to favour the kinetics of the reaction, increasing crystallinity, and the surface area of the product (Bukhari et al., 2016; Dere Ozdemir and Piskin, 2017; Farías et al., 2017; Vaiciukyniene et al., 2015). Fig. 9 presents the experimental data regarding crystalline zeolite LTA formation after hydrothermal crystallisation of alum sludge with preliminary ul-
trasonic treatment of the gel. In the case of alum sludge AS02, significant growth of zeolite content was observed after the first 10 min of ultrasonication, which was significantly shorter than in previous studies (Bukhari et al., 2015). During the first 10 min of treatment, the crystallinity of zeolite LTA increased from 43 to 62 wt.%. With further rise of ultrasonication time up to 100 min, the zeolite content remained steady and no further growth was observed.

An ultrasonic field triggers formation of micro bubbles filled in with vacuum in a liquid phase. Subsequent collapse of these bubbles releases energy, which locally heats up the gas and liquid phases as well as homogenises the mixture (Syed Salman Bukhari et al., 2015). This effect improves mass transfer and, thus, potentially the zeolite nucleation rate. With regard to carbonaceous alum sludge, ultrasonic treatment also had a positive effect on zeolite LTA crystallisation. The amount of zeolite LTA increased by 10 wt.% after 20 min of ultrasonication and reached a peak of 46 wt.% after 40 min. Extending the period of ultrasonic treatment negatively impacted zeolite LTA formation, which slightly dropped to 43 wt.% after 100 min. The observed decrease can be explained by the fact that ultrasonic pre-treatment of carbonaceous favours transformation of zeolite LTA into the more stable sodalite phase (Fig. 9). Thus, extension of ultrasonication time longer than 40 min was not justified. The data from ultrasound experiments can be compared with those of ageing at the elevated temperature (Fig 8), which shows that increasing the temperature of ageing led to a rise of sodalite content. In terms of ultrasonic treatment, the process also provided extra energy for the reaction. In general, therefore, it seems that the presence of activated carbon inhibited the thermodynamic stability of the system, favouring its conversion into a more stable phase.

The particle size distribution of the zeolite LTA product after ultrasonic treatment is shown in Fig. 10. Interestingly, ultrasonication for 40 min caused minimal crystal size reduction in the case of carbonaceous source AS01. The value dropped from 0.8 μm for a sample with no pre-treatment to 0.7 μm. Although, after extension of the contact time up to 100 min, no reduction was found, and particle size increased back to 0.8 μm. This finding was contrary to previous studies which suggested that an increase of ultrasonication time leads to a subsequent decrease of zeolite crystal size (Askari et al., 2012). This inconsistency may be due to decline in zeolite content and, thus, increase in number of clusters formed by amorphous matter. Moreover, activated carbon particles impaired the homogeneity of aluminosilicate gel. This observation might cause an interference of zeolite nucleation. In contrast, for AS02 sludge no correlation was found between the time of treatment and particle size. After 20 min of ultrasonic treatment the crystal size value decreased to 0.55 μm, and the value remained the same with an extension of ultrasonic time up to 100 min.

2.2.2.3. Seed application to synthesis mixture “Seeding” is an extensively used method of zeolite synthesis, in which zeolite crystals (seeds) are added into the aluminosilicate gel prior to hydrothermal reaction. This method is used especially for high silica zeolites such as ZSM-5 (Javadani et al., 2019), and MEL (Iyoki et al., 2014; Zhang et al., 2019). The kinetic study by Kerr (1966) reported that the reaction rate and crystallinity of zeolites could be significantly increased by seeding. Once added to a precursor mixture, seed crystals work as a structural directing catalyst and a growth centre facilitating formation of nuclei of particular zeolite type. Based on classical nucleation theory (Karthika et al., 2016), a supersaturated solution tends to decrease its high Gibbs free energy through formation of nuclei. The presence of a seed crystal in the amorphous system reduces the energy barrier for nucleation and eventually, promotes zeolite crystallisation (Khosravi et al., 2016).

Fig. 11 shows SEM images of zeolites obtained after ultrasonic pre-treatment at optimum conditions. With introduction of ultrasonication as a nucleation promotion method, crystallinity of both zeolites increased, which was consistent with XRD analysis (Fig. 9). While crystals of AS01 sample after ultrasonication (Fig. 11a) still had rough surfaces and undefined edges, the surface of zeolite particles from AS02 after ultrasonic treatment (Fig. 11b) visibly smoothed out, and the particle size decreased. In addition, it was important to note that SEM and particle size analysis of both sludge samples (AS01 and AS02) confirmed a broad particle size distribution. This situation was particularly obvious in the SEM micrograph of LTA zeolite from AS02 after 10 min of ultrasonic treatment, where crystals of a range of sizes were clearly seen. This result may be explained by the low homogeneity of the original aluminosilicate gel due to the presence of impurities. In general, it appeared that ultrasonic pre-treatment was an advantageous approach to significantly increase crystallinity of LTA zeolite from regular alum sludge AS02 with no carbon.
Regarding carbonaceous sludge AS01, there was a positive correlation between the amount of seeds added and final zeolite LTA crystallinity from the sludge. Fig. 12 shows a linear growth of zeolite crystallinity with addition of 0.5 and 1 wt.% zeolite seeds. Contrary to alum sludge AS02, 0.5 wt.% of seed did not cause a major improvement of zeolite LTA crystallisation from carbonaceous alum sludge (only 4%). Addition of 1 wt.% of zeolite seeds resulted in 42 wt.% of NaA zeolite. Following this, zeolite LTA phase gradually increased with the rise of seed weight until it reached 51 wt.% with 10 wt.% of commercial crystals added. However, considering relatively low crystallinity of the product and high seed dose, using 10 wt.% of commercial zeolite LTA to promote carbonaceous sludge crystallinity was found to be unjustified. Another significant finding was the absence of sodalite phase in seeding experiments. As shown in Fig. 12, sodalite content declined sharply with addition of 0.5 wt.% of seeds and returned to zero after 1 wt.% seeding. In accordance with the present results, previous studies have reported that seeding method effectively prevents formation of undesirable zeolite phases (Bouizi et al., 2007; Iyoki et al., 2014). In summary, these results suggested that 1 wt.% of seeds was the optimum quantity for carbonaceous alum sludge due to the highest crystallinity growth with the reasonably low amount of commercial zeolite required.

SEM micrographs of zeolite samples at optimum seeding dosage are shown in Fig. 13. In accord with XRD results (Fig. 12), zeolite samples after seeding showed higher crystallinity than the ones with no seeds added. Zeolite particles from AS01 sludge after seeding were covered with amorphous clusters, whereas cubic crystals of zeolite sample from no carbon sludge AS02 were well developed and had a smooth surface. This observation implied more complete transformation of alum sludge into LTA zeolite, compared with the samples with no seeding. Moreover, a slight decrease of particle size and broad size distribution was observed for both sludges after addition of seeds. The observed reduction in particle size could be attributed to increased amount of nucleation centres available due to the introduction of seeds into the system.

2.2.2.4. Calcination To investigate the effect of thermal treatment of the alum sludge upon zeolite LTA formation, alum sludge samples were calcined in the temperature range 500 – 900°C for 2 and 4 hr, respectively. Following this procedure, the amount of total carbon in the calcined samples was determined by CNS (carbon, nitrogen, sulphur) analysis using standard soil LECO® 502–309 as a reference. Fig. 14a illustrates the differences in carbon amount in the calcined alum sludge samples. The calcination process eliminated the carbon species from both AS01 and AS02 sludge samples, which based on our hypothesis probably impeded zeolite crystallisation (Hagemann et al., 2018). For sludge AS02, no significant difference between 2 and 4 hr of calcination was discerned upon carbon content. Complete elimination of carbon occurred after 2 hr at 600°C. In contrast to sludge AS02, calcination of carbonaceous sludge AS01 for 2 hr led to total car-

Fig. 11 – SEM images of zeolite material from AS01 and AS02 sludge samples at optimum ultrasonic time: (a) from AS01 after 40 min of ultrasound and (b) from AS02 after 10 min of ultrasound.

Fig. 12 – Influence of seeding on zeolite LTA crystallisation from alun sludge.

Fig. 13 – SEM images of zeolite material from AS01 and AS02 sludge samples with optimum amount of seeds added: (a) from AS01 with 1 wt.% of LTA zeolite crystals and (b) from AS02 with 0.5 wt.% of LTA zeolite crystals.
bon elimination only at 900°C and after calcination at 700°C for 4 hr. This behaviour suggested the identity of the carbon in the sludge was inherently different. The data in Fig. 14a was consistent with the fact that activated carbon and natural organic material (NOM) was present in AS01 sludge but only NOM in AS02 sludge. Evidently, the activated carbon removal was more dependant upon calcination conditions than NOM.

One interesting finding was that after calcination of raw sludge at 900°C, crystalline phase transformations in the sludge were observed (Fig. 14b). Initially, alum sludge samples consisted of mainly quartz, kaolinite, and albite (Fig. 1). XRD data after calcination at 900°C for 2 and 4 hr (Fig. 14b) showed that alum sludge transformed into an unreactive mixture of silicon and α-aluminium oxides and mullite according to Eqs. (5) (Matori et al., 2012) and (6) (Guatame-García et al., 2018).

\[
\begin{align*}
\text{Al(OH)}_3 & \rightarrow \text{AlOOH} \rightarrow \gamma-\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \alpha-\text{Al}_2\text{O}_3 \\
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 & \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \\
\end{align*}
\]

These results reflected those of Matori et al. (2012) who also found that once calcined at 900°C, alum (\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}) lost its crystallinity and transformed into an amorphous mix of aluminium oxides. However, transformation of pure \(\theta-\text{Al}_2\text{O}_3\) into \(\alpha-\text{Al}_2\text{O}_3\) usually occurs at a temperature higher than 1100°C. This discrepancy could be attributed to the presence of impurities, which may alter the phase transition (Matori et al., 2012). In previous studies it was shown that direct conversion of \(\gamma-\text{Al}_2\text{O}_3\) into \(\alpha-\text{Al}_2\text{O}_3\) excluding intermediate phases might take place at 900°C due to the presence of sulphate (Mishra, 2002) or organic (Lee et al., 2013) anions, which were potentially present in both sludge samples (Table 1).

Fig. 15 additionally showed the influence of sludge calcination time and temperature on zeolite LTA crystallisation. In general, as the calcination temperature was increased the degree of zeolite NaA formed after hydrothermal reaction was notably enhanced. Albeit, calcination at 900°C resulted in no zeolite NaA production. Quartz, mullite, and \(\alpha-\text{Al}_2\text{O}_3\) phases remained stable and did not dissolve, which led to no change in phase compositions. This result may be explained by the fact that both oxides identified were chemically inert in dissolved caustic solution at low temperature of 80°C.

In the case of carbonaceous alum sludge AS01, the degree of zeolite LTA formation was influenced by calcination time as well as temperature. This behaviour correlated to the fact that increasing calcination temperature and time were both shown to decrease the amount of carbon present (Fig. 14a). As such zeolite LTA crystallinity was dramatically promoted from 38 to 65 wt.%. However, taken together, the results were found to be contrary to expectations: calcination of carbonaceous alum sludge AS01 did not lead to similar amounts of zeolite LTA from regular and carbonaceous sludges. It was clear from the Figs. 14a and 15 that, despite no carbon detected in both systems at 700°C, 4 hr test; there was still a gap of 14 wt.% in zeolite crystallinity. The reason for this observation was not clear. This rather contradictory result may be due to simultaneous formation of inert oxides, which limits dissolution of aluminosilicate gel. In addition, such a discrepancy could be attributed to sub-optimal hydrothermal reaction conditions.

SEM images of zeolites obtained from alum sludge samples calcined at 700°C for 2 hr are presented in Fig. 16. SEM analysis revealed high crystallinity of zeolite materials, compared to those where no calcination was conducted; with few
amorphous clusters observed. In contrast to nucleation promotion methods (ageing, seeding, ultrasonication), thermal purification of the sludge by calcination at 700°C for 2 hr resulted in formation of highly crystalline cubes with truncated edges and smooth surfaces. The change in the surface might be a result of sludge purification, which caused alteration of the general composition of amorphous matter. Both raw alum sludge samples had high LOI values (see Table 1), which implied the presence of a large amount of natural organic matter and other volatile impurities. On the other hand, after calcination at 700°C for 2 hr LOI values dropped to 13.5 wt.% for AS01 and 4 wt.% for AS02 (data not shown). It can therefore be assumed that the amorphous content of zeolite sample after calcination consisted mostly of non-volatile impurities which did not interfere with LTA zeolite crystallisation. In addition, one surprising finding was a significant reduction of particle size in the zeolite sample obtained from AS02 and its broad size distribution. These effects may be a consequence of elimination of volatile impurities from the original gel and, thus, improved homogeneity of the system. Purification of the raw alum sludge by calcination was found to be an effective method to improve alum sludge conversion to zeolite LTA.

Comparison of pre-treatment methods at optimum conditions for both sludge samples is presented in Appendix A. The data in Appendix A Table S1 describe the experiments at the optimum pre-treatment conditions with the maximum zeolite LTA crystallinity obtained throughout the study. Appendix A Fig. S2 compares particle size distribution curves of zeolite products after various pre-treatment techniques for both sludge samples. Appendix A Figs. S3 and S4 show the original XRD patterns of zeolite samples from AS01 and AS02 respectively collected in comparison with commercial zeolite LTA by Tosoh.

3. Conclusions

This investigation showed the benefits of various pre-treatment strategies to synthesise zeolite LTA from two alum sludge samples. Notably, the obtained zeolite LTA yields were greater than previously reported in literature. Remarkably, it was revealed for the first time that the carbon content and identity of carbon in alum sludge was critical when attempting to convert alum sludge waste to valuable zeolite LTA.

Water treatment plants using activated carbon resulted in a sludge which was challenging to convert into zeolite LTA. Application of pre-treatment strategies such as ageing, seeding, and ultrasonication improved the formation of crystalline zeolite LTA. However, the greatest yield of zeolite was obtained from calcined alum sludge. It was postulated that calcination reduced the inhibitory effect of carbon initially present in the alum sludge and thus further promoted zeolite LTA yield. Indeed, the formation of zeolite LTA was substantially increased when using both alum sludge types (65 wt.% LTA zeolite for carbonaceous sludge and 79 wt.% LTA zeolite for regular sludge). However, it was revealed that even with no carbon detected in calcined samples, the presence of crystalline zeolite LTA from sludge originally containing the highest carbon content was 14% less than the one produced using the lower carbon sludge. As an outcome, it was inferred that another factor was important in terms of zeolite LTA synthesis apart from carbon content. A precise answer was difficult to provide based upon the present investigation. One possibility was the formation of inert oxides during the calcination step which may interfere with zeolite nucleation. Additional research is required to understand in more detail the mechanism of sludge conversion into zeolite to clarify our idea. Overall, this new information enhances the prospect of drinking water plants globally to convert alum sludge into a material which may be used locally for a variety of applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.06.019.

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