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1 **Waste peat ash mineralogy and transformation to microporous zeolites**

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8
9 **Abstract**

10 The combustion of peat fuel for industrial scale power generation and domestic heating
11 produces toxic ash, most of which is presently buried in landfill. In this study, the mineralogy
12 of waste peat ash was determined, followed by its successful use as a starting reagent to prepare
13 zeolites. X-ray diffraction (XRD) confirmed the presence of quartz, anhydrite, calcite, lime,
14 merwinite and magnetite in peat ash, and that a single extraction step using mineral acid was
15 sufficient to remove all non-quartz crystal phases. Alkali fusion of the acid-extracted samples
16 produced GIS-type zeolite. LTA- and FAU-type were also prepared by altering the Si/Al ratio
17 and extending the ageing time. Experiments confirmed that the LTA- and FAU-type zeolites
18 were active in the simultaneous adsorption of lead, cadmium, cobalt, zinc and copper from
19 aqueous solutions, with similar quantities of metals removed to those using a reference zeolite.

20
21 **Keywords;** Peat ash utilisation; zeolite; pyrolysis; waste management; water purification.

26 **1. Introduction**

27 Peat is a carbon based material produced from partially decayed vegetation that builds up over
28 a duration typically up to approximately 12,000 years [1,2]. The deficiencies of oxygen and
29 nutrients in waterlogged bogs and fens (peatlands) limit the decay rate of vegetation such that
30 there is an accumulation of peat over time. These peatlands cover an estimated global area of
31 4m km², which equates to 2-3% of the total land area, and are found mainly in Russia, North
32 and South America, Northern Europe and South-East Asia, including lower quantities in
33 locations such as central Africa [1,2]. Peat is classified as an intermediate fuel i.e. between
34 biomass and fossil fuel (lignite). Total global consumption is estimated at 17m tons per annum,
35 over 99% of which is used in Northern Europe for the production of heat and electricity [3].
36 Ireland is the largest user, consuming 3.8m tons annually from peatlands that cover
37 approximately 20% of the national land area [4]. Most of this is used in thermal power plants
38 to generate 8.5% of Ireland's electricity [5,6]. While renewable fuel sources are increasingly
39 being used as a substitute for peat (at least partially in the short term), the production of
40 electricity in Ireland using peat based fuel is an established industry with a secure, indigenous
41 energy source, and will, therefore, continue for the foreseeable future.

42 Peat ash is the main waste product of combustion at thermal power stations, some of which is
43 disposed of by landfill burial. The alkalinity of peat ash alters the soil quality of the landfill site
44 such that only alkali tolerant plants can grow during the years immediately after disposal. The
45 composition of peat ash varies with location but typically contains a mixture of silicon-,
46 aluminium-, calcium- and iron-containing species, and a range of toxic elements including
47 arsenic and cadmium [7-10]. While its elemental composition has been well studied, a
48 definitive characterisation of peat ash mineralogy is lacking in the literature. The few papers
49 that discuss peat ash infer crystal phases from (a) elemental composition by scanning electron
50 microscopy/energy-dispersive X-ray spectroscopy (SEM/EDAX) or X-ray fluorescence (XRF)

51 only and/or (b) unseen XRD data; the reader is thus advised to treat such assertions with
52 caution. For example, quartz, microcline, albite and calcium sulfate were reported to be present
53 in peat ash samples, although no XRD results were shown [7, 8].

54 The transformation of peat ash to a useful value-added product with industrial applications
55 would be a significant improvement on the current method of disposal. One such possibility is
56 to use peat ash to prepare zeolites, which are high surface area aluminosilicates widely used
57 for water treatment and purification, humidity control, and heterogeneous catalysis [11]. The
58 combustion of fossil fuels and biomass produces ash residue that contains silicon and
59 aluminium based minerals in appropriate quantities to those used to prepare aluminosilicate
60 zeolites. Coal fly ash has been extensively studied as a zeolite synthesis reagent, and a variety
61 of zeolite architectures were successfully prepared using the alkali fusion method [12-23].
62 More recently, there are reports showing zeolite preparation using ash from the following
63 renewable biomass sources: rice husk [24-27] eucalyptus bark residue [28], pulp from paper
64 industry [29], sawdust and pine bark [30], bamboo [31] and cogon grass [32].

65 We now report the mineralogy of peat ash and its successful transformation to pure zeolite
66 using a single stage purification step. To our knowledge, this is the first report of zeolite
67 prepared using peat ash. The zeolites formed removed heavy metals from aqueous solution
68 with practically similar quantities to those of a reference zeolite.

69

70 **2. Materials and Methods**

71 **2.1 Materials**

72 Peat ash, from Ireland, was collected and combusted as follows: (a) sample A (lime added),
73 *Bord na Móna Ltd.*, industrial boiler (b) sample B, air-dried peat sods from county Roscommon,
74 domestic stove. The following is a list of the materials' source/supplier and purity; hydrochloric
75 acid (HCl), concentration >37%, Fluka; nitric acid 70% w/w; sodium hydroxide (NaOH)

76 pellets (anhydrous), extra pure, Sigma-Aldrich; sodium aluminate (NaAlO_2), general purpose,
77 Fischer; sodium silicate solution, general purpose, Merck. Copper(II) nitrate trihydrate
78 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, cobalt(II) nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, lead nitrate $\text{Pb}(\text{NO}_3)_2$, zinc
79 nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and cadmium nitrate tetrahydrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were
80 all 99.99% purity and supplied by Sigma-Aldrich.

81

82 **2.2 Zeolite synthesis**

83 The samples were calcined in air at 600 °C (sample A) and 800 °C (sample B) for 4 h to remove
84 organic matter. Acid extraction was conducted by treating 30 g of calcined peat ash in 500 cm³
85 acid for 5 h as follows: Sample A was stirred in 5 M HNO_3 at room temperature, and sample
86 B was refluxed in 5 M HCl at 95 °C. The product was recovered by filtration and dried at 80
87 °C. Unless otherwise stated, 1 part of the acid extracted ash was ground in a mortar and pestle
88 with 2.4 parts (by mass) NaOH , heated at 600 °C in air for 3 h in a furnace, and crushed to
89 powder form after cooling to ambient temperature. 1 part alkali fused ash was then added to 10
90 parts water in a polypropylene bottle, stirred at room temperature for 3 days, and
91 hydrothermally treated at 90 °C for 24 h. Sodium aluminate was added prior to alkali fusion to
92 give Si/Al ratios (of synthesis reagents) of 5 and 1 to produce GIS and LTA, respectively.
93 Additional ageing of the Si/Al ratio 1 suspension was done for 4 days at 35 °C to produce FAU.
94 Products were recovered by filtration and calcined in air at 550 °C for 4 h using a ramp rate of
95 5 °C min⁻¹. A reference FAU zeolite was prepared from a synthesis solution with the molar
96 composition $8\text{NaOH} : 0.2\text{Al}_2\text{O}_3 : 1.0\text{SiO}_2 : 200\text{H}_2\text{O}$ [33]. The hydrothermal treatment was
97 performed at 80 °C for 24 h.

98

99 **2.3 Characterisation**

100 XRD was conducted in ambient conditions using a Panalytical X'Pert Powder diffractometer
101 with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). All powder diffraction patterns were recorded from 4 to
102 $120^\circ 2\theta$ with step size 0.013° and step time 50 s, using an X-ray tube operated at 40 kV and
103 30 mA with fixed $\frac{1}{4}^\circ$ anti-scatter slit. A Rigaku NEX-CG (XRF) spectrometer was used for
104 elemental analysis using the loose powder method under vacuum. Nitrogen
105 adsorption/desorption measurements were carried out using a Micromeritics ASAP 2020
106 surface area analyser at -196°C . Samples were degassed under vacuum ($p < 10^{-5}$ mbar) for 5
107 h at 200°C prior to analysis. Brunauer–Emmett–Teller (BET) surface areas of the samples
108 were calculated in the relative pressure range 0.05–0.30. Microscopic images were recorded
109 using a JEOL JSM-5600LV SEM.

110

111 **2.4 Adsorption study**

112 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were
113 dissolved together in water and diluted to give a solution that was 100 ppm in each of Cu, Co,
114 Pd, Zn and Cd. 20 cm^3 of this solution were added to 0.1 g LTA (sample A), stirred at 180 rpm
115 for 1 h at room temperature and the solid removed by filtration. The concentrations of metals
116 before and after adsorption were determined using a Thermo Scientific iCAP 6000 Series
117 inductively coupled plasma-optical emissions spectrometer (ICP-OES).

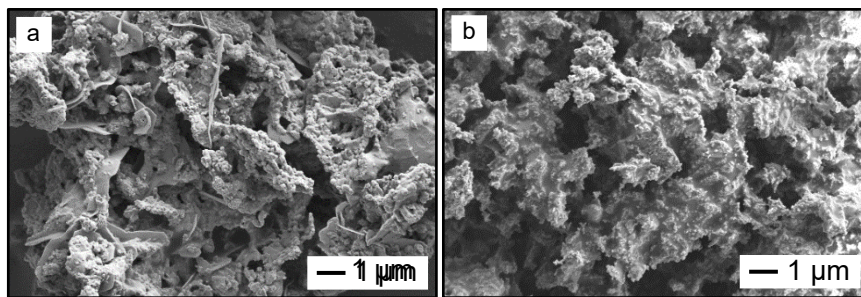
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119 **3. Results and Discussion**

120 **3.1 Crystallography and elemental composition**

121 SEM images, Fig. 1, show that both raw and calcined peat ash lack any regular morphology,
122 which is in contrast to the spherically shaped particles routinely observed for coal fly ash [12].
123 Results also showed that calcination did not cause an observable transformation in particle
124 morphology. Phase identification, performed by matching the XRD peak positions in Fig. 2

125 against the Crystallography Open Database, confirms that the major phases detected for sample
 126 A are anhydrite (CaSO_4), quartz (SiO_2), calcite (CaCO_3), lime (CaO) and merwinite
 127 ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$). Sample B contains anhydrite, quartz and magnetite (Fe_3O_4). A quantitative
 128 elemental analysis using XRF, Table 1, shows the 10 most concentrated elements present (for
 129 sample A) and confirms that the major ‘impurities’ (in terms of zeolite synthesis) are Ca and
 130 Fe based species. The major element present in Sample A is Ca at 53.9 wt% (as oxide) in
 131 agreement with the XRD analysis (Fig. 2). Sample B contains 21.2 wt% CaO and 22.0 wt%
 132 Fe_2O_3 . The greater quantity of CaO in sample A is due to the addition of lime to commercial
 133 peat to reduce SO_x emissions, which may have reacted to produce anhydrite. It is interesting
 134 then that sample B, which has not been treated with lime, also contains anhydrite.



140 Fig. 1. Typical SEM images of peat ash: (a) raw and (b) calcined.

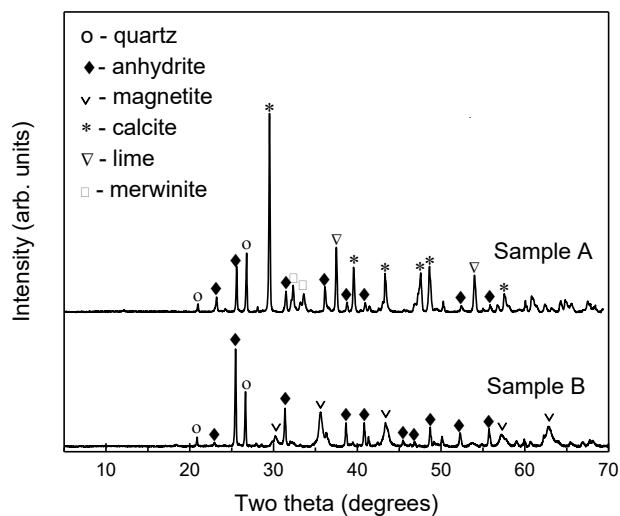


Fig. 2. XRD powder patterns of calcined peat ash.

143

144 It is not possible to make a meaningful comparison of the XRD results presented here with
145 published data on peat ash mineralogy, as such reports contain insufficient results [7,8].
146 However, all such studies confirm that the main elements present in peat ash are Ca, Fe, Si and
147 Al, which correlates well with our XRD and XRF results.

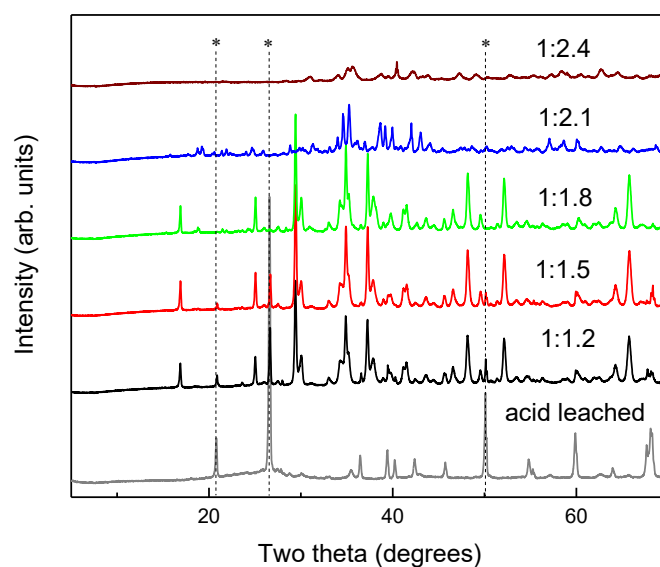
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149 Table 1: XRF elemental composition of peat ash in wt% following calcination and acid extraction.

	A		B	
	Calcined	Acid extracted	Calcined	Acid extracted
CaO	53.9	0.81	21.2	0.77
SiO ₂	9.47	71.4	12.7	76.9
SO ₃	7.32	0.58	22.4	0.26
Fe ₂ O ₃	4.81	1.29	22.0	0.61
MgO	2.20	0.12	10.4	0.35
Al ₂ O ₃	1.63	2.55	6.58	3.77
MnO	0.35	0.03	0.30	0.02
P ₂ O ₅	0.26	0.05	1.87	0.05
K ₂ O	0.19	0.97	0.97	1.12
TiO ₂	0.15	0.50	0.45	0.90

150

151 Dissolution by acid extraction considerably reduced the quantities of Ca and Fe in both
152 samples. The Si/Al ratios of acid extracted peat ashes are 28.0 for sample A and 20.4 for sample
153 B. XRD patterns confirm that acid extraction removes all detectable non-quartz crystalline
154 phases, Fig. 3. The majority of zeolite preparations using coal ash do not remove impurities by
155 acid extraction, so it is not surprising that a greater ratio of NaOH to ash is required for the peat
156 ash samples explored here to achieve full quartz decomposition due to the higher quantity of
157 quartz [12]. Fig. 3 shows that the mass ratio of 1.2:1 NaOH to ash (chosen as a starting point
158 based on reference [22]) was insufficient but that higher ratios removed quartz completely; a
159 mass ratio of 2.4:1 was used in all further preparations. The other peaks in Fig. 3 confirm the
160 presence of silicates and aluminosilicates, as reported in the literature [34].



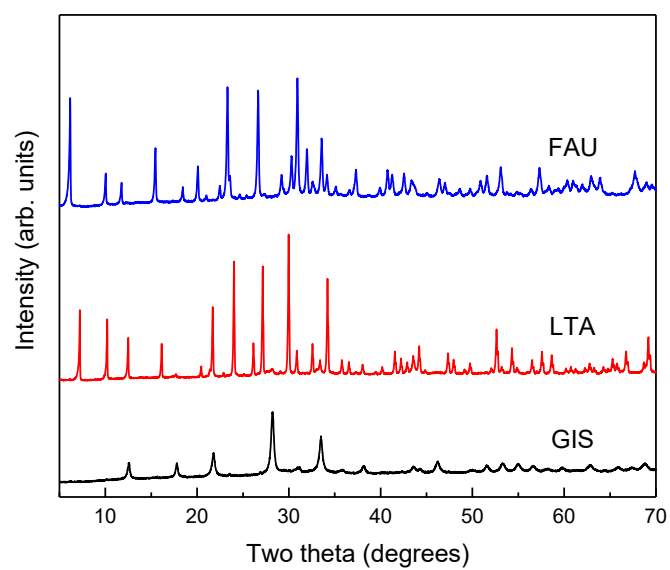
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162 Fig. 3. XRD patterns of sample A after acid leaching and the acid-leached sample after alkali fusion at
 163 600 °C using different sample:NaOH mass ratios as indicated on the figure; the asterisks indicate
 164 quartz peaks.

165

166 3.2 Zeolite formation

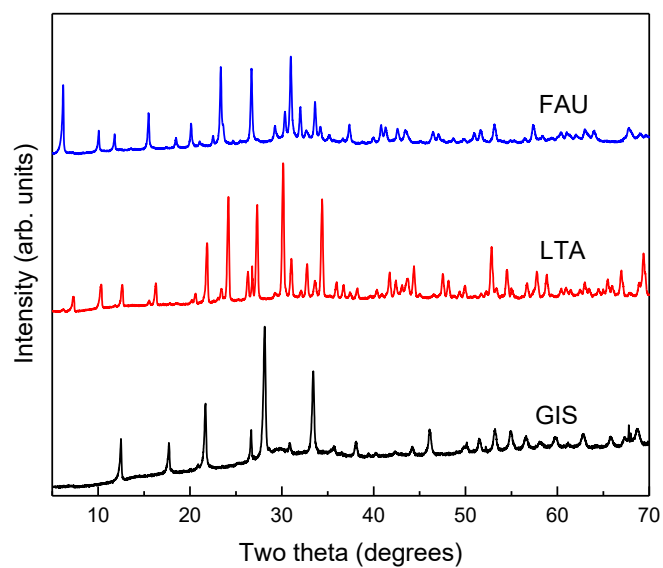
167 The XRD patterns in Figs. 4 and 5 confirm that peat ash was transformed to zeolite frameworks
 168 GIS, LTA and FAU through changes in the synthesis parameters viz. addition of sodium
 169 aluminate for LTA, and extended ageing time for FAU. Non-zeolitic crystalline phases were
 170 not observed by XRD in any detectable quantities. The effect of altering the Si/Al ratio by
 171 adding external silica was found to alter the crystal phase produced in a study of the
 172 crystallisation mechanism of zeolite from coal fly ash, where FAU was not formed until the
 173 Si/Al ratio was reduced to approximately 1.5 [35]. SEM images, Fig. 6, show the morphology
 174 of GIS, the characteristic cubic ca. 1 μm sized particles of LTA and the sub-micron
 175 agglomerated FAU particle morphology, providing further evidence of the presence of these
 176 phases. The Si/Al ratios are shown in Table 2: the Si/Al ratios of FAU are 1.32 and 1.35, so
 177 these samples are zeolite X. The highest BET surface areas were recorded for the FAU
 178 structures, which were calculated to be 486 and 319 $\text{m}^2 \text{g}^{-1}$.



179

180

Fig. 4 XRD patterns of zeolites prepared using sample A.



181

182

Fig. 5 XRD patterns of zeolites prepared using sample B.

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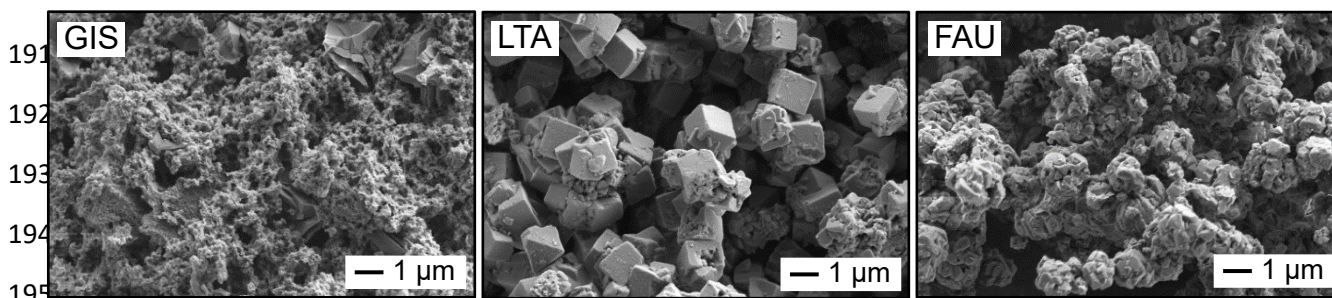
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Table 2: BET surface areas and Si/Al elemental ratios.

	Surface area ($\text{m}^2 \text{g}^{-1}$)		Si/Al	
	A	B	A	B
Raw	24	25	4.04	1.55
Calcined	6	22	4.94	1.64
FAU	486	319	1.32	1.35
LTA	84	55	1.41	1.35
GIS	77	104	2.83	2.83

189

190



196 Fig. 6. Typical SEM images of different zeolites types prepared from peat ash.

197

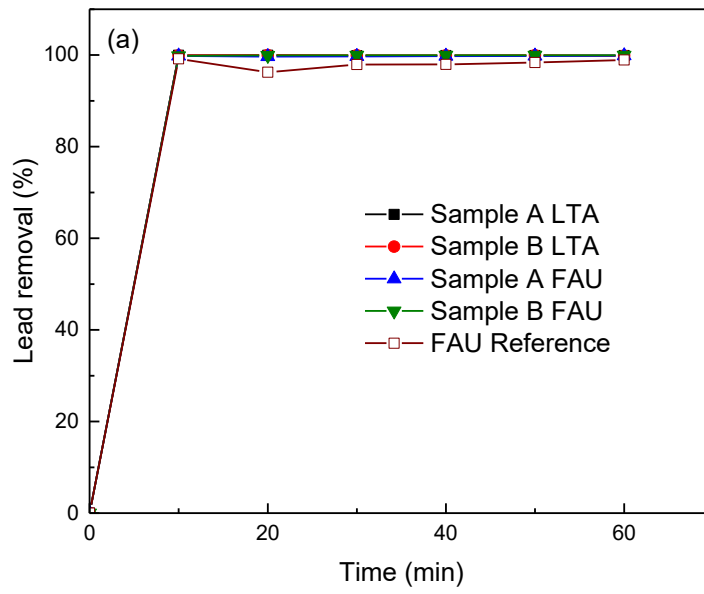
198 The characteristics of zeolites prepared from peat ash also compare well with analogous studies
 199 using fly ash. For example, the highest surface area reported by Tosheva et al. for FAU
 200 prepared from fly ash was $441 \text{ m}^2 \text{g}^{-1}$, relative to $486 \text{ m}^2 \text{g}^{-1}$ for that prepared here [23]. The
 201 classification of coal is based on the relative amounts of organic and inorganic materials, age,
 202 and quantity of heat energy that can be produced. Most reports in the literature describing coal
 203 ash to zeolite conversions are for sub-bituminous (up to 45% carbon) bituminous (86%) and
 204 anthracitic (97%) coal types. Lignite has lower carbon content than sub-bituminous coal and,
 205 because it is formed over time from compressed peat, which has carbon content less than 40-
 206 55%, seems the most appropriate comparison to the results presented here [1-3]. Kunecki et al.
 207 used lignite, containing quartz, anhydrite and gehlenite, to prepare zeolite [36]. Both LTA and
 208 FAU frameworks were prepared by varying experimental conditions, but not in pure form. The
 209 highest BET surface area for FAU was $256 \text{ m}^2 \text{g}^{-1}$, which was significantly lower than the FAU

210 from either sample in this study, 486 and 319 m² g⁻¹. The increased crystal purity and surface
211 area for zeolite prepared using peat ash is tentatively attributed to the removal of impurities in
212 the starting material by acid extraction. Anhydrite is highly soluble in aqueous solution and its
213 presence during zeolite crystallisation, as in the case of lignite to zeolite, reduces the solubility
214 of silicates and aluminosilicates, which will negatively impact both the formation of zeolite
215 nuclei and the subsequent dissolution and crystallisation of zeolite during hydrothermal
216 treatment. Furthermore, ions in solution are known to interact with zeolite frameworks during
217 crystallisation, so the Ca²⁺ and SO₄²⁻ ions from anhydrite may have a negative effect on the
218 formation of zeolite [37].

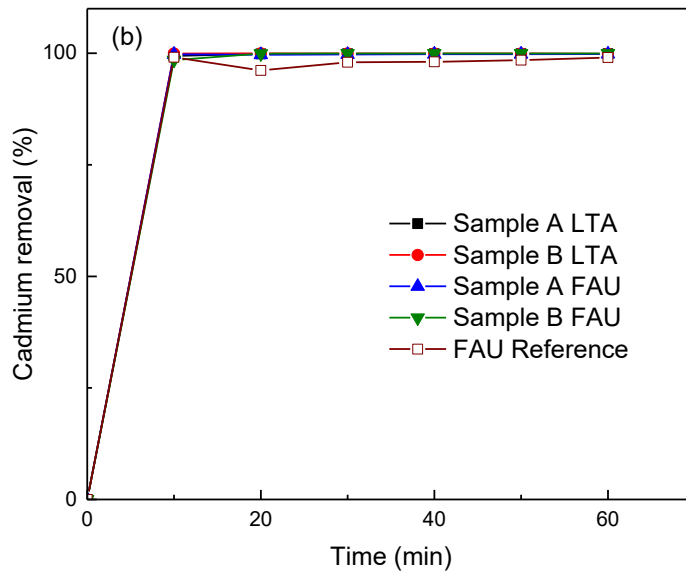
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220 **3.3 Adsorption study**

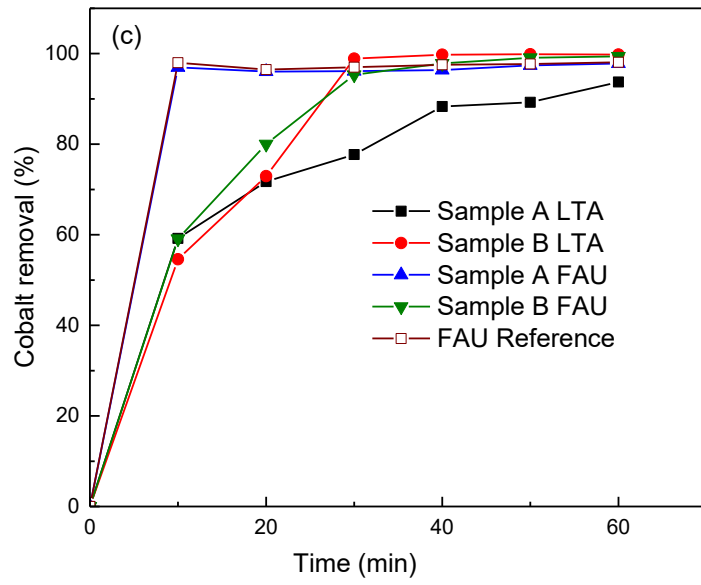
221 The prepared zeolites were tested as adsorbents in the removal of heavy metals lead, cadmium,
222 cobalt, zinc and copper from aqueous solution; these metals were chosen on the basis of their
223 toxicity and presence in wastewater streams [38]. The results, Fig. 7, showed that all zeolites
224 actively removed the range of metals between 10 and 60 minutes, in which the quantities of
225 lead, cadmium, zinc and copper adsorbed using peat ash prepared zeolites were slightly higher
226 than those measured for the FAU- reference. In the case of cobalt, adsorption was higher using
227 FAU-type zeolites than LTA-, while the most active adsorbent was that prepared from sample
228 A, which showed near identical properties to that of the reference zeolite. A more in-depth
229 study of metals adsorption on zeolites viz. influence of concentration, temperature, and kinetics
230 is currently underway and will be published as a follow up to this paper. While the focus of
231 this paper is the preparation of pure zeolite from peat ash, the adsorption results are included
232 to validate the efficacy of such materials in real applications.



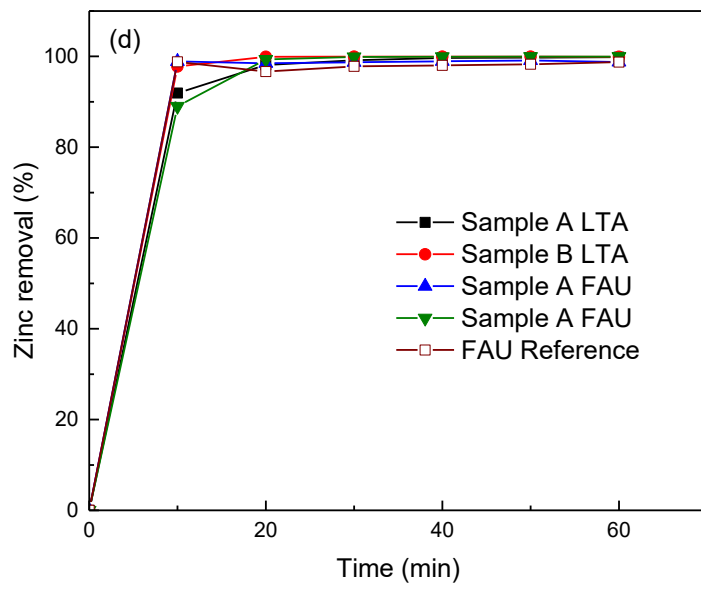
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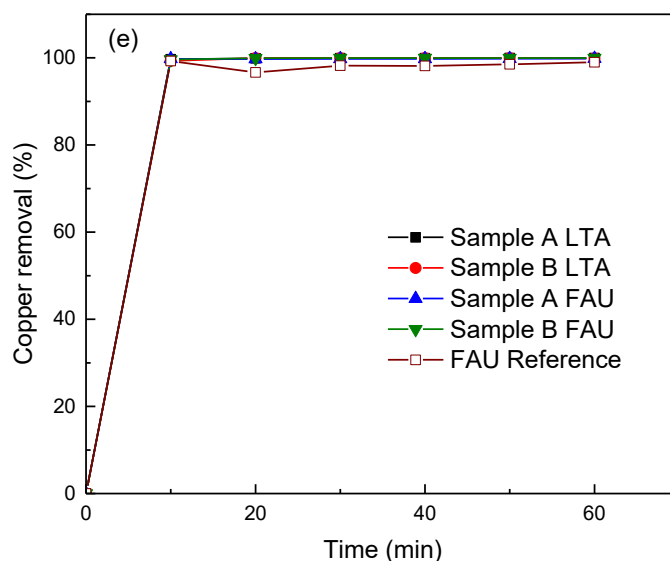
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236



237

238 Fig. 7. Metal removal (as % of original concentration) of (a) lead (b) cadmium (c) cobalt (d) zinc and
 239 (e) copper on LTA- and FAU-type zeolites prepared from peat ash and an FAU- reference.

240

241 4. Conclusions

242 Zeolites were successfully prepared from peat ash using a combination of acid leaching, alkali
 243 fusion and hydrothermal treatment. The framework structure was systematically varied such
 244 that crystal phases of GIS, LTA and FAU-type zeolites were each prepared. The prepared
 245 zeolites were active in the removal of a range of metals from aqueous solution.

246

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253

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