

1 **The use of Lightweight Expanded Clay Aggregate (LECA) as Sorbent for PAHs Removal**
2 **from Water**

3 Marian Asantewah Nkansah ^{1*}, Alfred A. Christy ¹, Tanja Barth², George William Francis²

4 ¹Department of Science, Faculty of Engineering and Science, University of Agder Service Box
5 422, NO - 4604, Kristiansand, Norway

6 ²Department of Chemistry, University of Bergen, Allegaten 41,
7 N-5007 Bergen, Norway

8 *** Corresponding author: Tel.: 0047-96843489. Email: maan4gr@yahoo.co.uk**

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24 **Abstract**

25 LECA has been explored as a sorbent for the removal of PAHs (phenanthrene, fluoranthene and
26 pyrene) from water. The efficacy of LECA as a sorbent for PAHs was assessed using contact
27 time, mass of sorbent and sorption isotherms in a series of batch experiments. Maximum
28 (optimum) sorption was reached at 21 h after which the amount of PAHs sorbed remained almost
29 constant. Batch experiments were conducted by shaking a 100 ml solution mixture of individual
30 PAHs (containing 0.02 mg/l) with LECA. The maximum sorption was 70.70, 70.82 and 72.12%
31 respectively for phenanthrene, fluoranthene and pyrene when a mass of 0.2 g of sorbent was
32 used. There was an increase in sorption as a result of an increase in mass of sorbent until a
33 maximum was reached at a mass of 4.0 g LECA with 92.61, 93.91 and 94.15% sorption of
34 phenanthrene, fluoranthene and pyrene respectively. Sorption data were fitted to the linearised
35 forms of the Freundlich and Langmuir isotherm models to determine the water-LECA
36 partitioning coefficient. Physical sorption caused by the aromatic nature of the compounds was
37 the main mechanism that governed the removal process while the hydrophobicity of the PAHs
38 also influenced the sorption capacity. LECA can be used as an alternative method for aqueous
39 PAHs removal.

40 ***Keywords: PAHs, Sorption, contaminated water, LECA***

41

42

43

44

45

46

47 **1. Introduction**

48 Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds containing
49 two or more fused aromatic rings of carbon and hydrogen atoms [1]. They are ubiquitous
50 pollutants formed from the combustion and pyrolysis of organic matter such as coal, oil, wood
51 and fossil fuels like diesel and petrol [2]. PAHs are also released during oil spills where their
52 types and quantities depend on the nature of the petroleum involved. Lighter oils have small but
53 detectable amounts of PAHs while the heavier petroleum products can have elevated levels [3].
54 PAHs exposure usually occurs in the form of mixtures rather than individual compounds [4].
55 PAHs are compounds of environmental importance because of their carcinogenicity and
56 mutagenicity [5]. There is a recent global concern about the increase in PAHs contamination of
57 water systems [6]. The PAHs detected in highest concentration in drinking water are
58 fluoranthene, phenanthrene, pyrene and anthracene [7]. Their presence in surface water or
59 groundwater is an indication of a source of pollution [8]. Due to their low solubility in water and
60 high affinity for particulate matter, PAHs are not usually found in water in high concentrations.
61 The concentrations of total PAHs in water vary between 2.5 - 9.0 ng/L in tap water, 1.0 - 10 ng/L
62 in groundwater, 2.7-7.3 ng/L rainwater and about 10 - 830 ng/L in surface water [9]. The
63 European Union, EEC Directive 98/83/EC has set a limit of 0.1 ng/L for total PAHs in drinking
64 water [10].
65 PAHs are generally resistant to biodegradation and are not easily removed by traditional
66 physicochemical methods like flocculation, coagulation, sedimentation, filtration or ozonation
67 [11]. Methods like chemical or biological oxidation, ion exchange, electrolysis and solvent
68 extraction can be complicated to operate and sometimes prove inefficient for removing trace
69 levels of pollutants [12]. Sorption however has been proved to be effective for the removal of

70 persistent organic pollutants, and activated carbon is extensively used for this purpose [6, 13].
71 When compared to other methods of PAH removal, sorption is simple, convenient, easy to
72 design and can be operated with very little technical know-how [14].
73 In the last decade, studies on the use of sorption methods for removing PAHs (and other
74 organics) from water include the use of oil shale ash and mineral particles [15], commercially
75 available fibrous sorbents like Zylon [16], immature clay, leonardite [6], kapok and cattail fibres
76 [17], agricultural waste such as sugar cane baggase, green coconut shells etc [18], silica gel [19]
77 and petroleum coke-derived porous carbon [20].
78 Isotherms are generally used to predict and evaluate the sorption capacity of sorbents [21]. The
79 Freundlich isotherm is the most widely used model for quantifying the sorption of dilute organic
80 chemicals from aqueous solutions. This non-linear model is based on the assumption that the
81 sorption system involves heterogeneous surfaces, limited sorption sites and potential energy
82 interactions [22]. The Langmuir isotherm has also gained popularity due to its ability to fit a
83 wide variety of sorption data quite as well as the Freundlich isotherm [23]. The Langmuir
84 isotherm is based on the assumptions that sorption is limited to one monolayer where all surface
85 sites are equivalent [24].
86 Lightweight Expanded Clay Aggregate (LECA) is a special type of clay that has been pelletised
87 at high temperature. As it is fired, the organic compounds in the clay burn off forcing the pellets
88 to expand and become honeycombed while the outside surface of each granule melts and is
89 sintered. The resulting ceramic pellets are lightweight, porous, chemically inert, have a neutral
90 pH value and non-biodegradable. They are also non-combustible, have excellent sound and
91 thermal insulation properties, contain no harmful substances, are resistant to frost and chemicals
92 and will not break down in water. LECA filters have uniform pore distribution and are not

93 significantly lost when backwashed. LECA is used in gardening to retain moisture in the soil, in
94 concrete for building purposes and in water treatment facilities for the filtration and purification
95 of municipal wastewater and drinking water [25, 26, 27, 28]. There are no known disadvantages
96 of LECA as a material for water treatment. Though LECA has successfully been used for
97 removal of heavy metals in water [29], its use as a sorbent for aqueous PAH removal has not
98 been reported.

99 This study investigates the sorption properties of LECA for the removal of PAHs like
100 phenanthrene, fluoranthene and pyrene from water.

101

102 **2. Materials and methods**

103 **2.1 Standards, solvents, reagents and Materials**

104 Phenanthrene (98%), fluoranthene (98%) and pyrene (98%) were obtained from Aldrich, St.
105 Louis, MO 63103-USA. Analytical grade chemicals were used as received in all other cases.
106 Analytical HPLC grade dichloromethane was used for extraction. The LECA used in this study
107 was obtained from the Saint-Gobain Weber Company, Filtralite Department in Oslo, Norway.
108 The physicochemical properties of LECA and PAHs are presented in Tables 1 and 2.

109

110

111

112

113

114

115

116 **Table 1: Typical characteristics / properties of LECA**

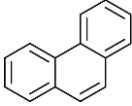
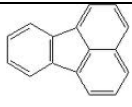
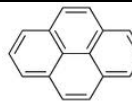
Parameter	Value
Particle size , mm	1.5-2.5
Surface area m ² /m ³	~2200
Specific surface area m ² /Kg	~2.93
Bulk density, Kg/m³	750
Particle density	1600
Fire resistance	High
Thermal conductivity coefficient , W/m-K	0.07 - 0.10
Resistance to acids	high
Resistance to alkali	high
pH resistance	high
SiO₂ (%)	62
Al₂O₃ (%)	18
FeO₃ (%)	7
CaO (%)	3
MgO (%)	3
K₂O (%)	4
Na₂O (%)	2
C (total) (%)	0.02
Loss on ignition	1.36

117 ***Source: Saint-Gobain Weber Company, Filtralite Department in Oslo, Norway and Dansk**
 118 **Leca A/S, Randers, 8900-Denmark [30, 31]**

119

120

121 **Table 2: Physicochemical properties of PAHs used in the study**

Compound	MF	MW	Mp °C	CP	log K_{ow}	Vp, torr	S _{H2O} (mg/L)	Chemical structure
Phenathrene	C ₁₄ H ₁₀	178.23	110	3	4.57	6.8 x 10 ⁻⁴ at 20 °C	1.6 at 25 °C	
Fluoranthene	C ₁₆ H ₁₀	202.25	111	3	5.22	10 ⁻⁶ -10 ⁻⁴ at 20 °C	0.265 at 25 °C	
Pyrene	C ₁₆ H ₁₀	202.25	149 -156	3	5.18	6.9 x 10 ⁻⁹ at 20 °C	0.135 at 25 °C	

122 *MF: Molecular formula, MW: Molecular weight, Mp: Melting point, Vp: Vapour

123 pressure, CPS: Solubility (Adopted from, IARC: International Agency for Research on

124 Cancer; US EPA: US Environmental Protection Agency)

125

126 2.2 Experimental Procedure

127 2.2.1 Properties of LECA

128 The surface image (Figure 1) and elemental composition of LECA were determined with a Zeiss

129 Supra 55 VP FEG scanning electron microscope (SEM).

130 2.2.2 Treatment of LECA

131 In order to remove any contamination that might have occurred during the handling and transport

132 of the LECA particles and to ensure the elimination of a possible complication in the

133 interpretation of analytical results, LECA pellets were washed twice in methanol and rinsed with

134 deionised water. They were air dried at room temperature and then baked in a pre-heated oven at

135 320 °C for 3 hours. The pellets were then stored in a dry air - tight container.

136 **2.2.3 Preparation of PAHs spike solution**

137 Approximately 2.5 mg each of phenanthrene, fluoranthene and pyrene were dissolved in
138 dichloromethane (DCM) to the mark of a 25 ml volumetric flask. The resultant standard solution
139 had a concentration of ~ 0.1 mg/ml of each of the three compounds. An aliquot of 0.2 ml was
140 transferred into a 1000 ml volumetric flask and made to the mark with distilled water to give a
141 final concentration of 0.02 mg / l (DCM is highly volatile and 0.2:1000 ml of water is negligible
142 and does not contribute to solvent effect). The resultant spike solution was transferred into a
143 stopped borosilicate bottle and shaken at 300 rpm for 2 hours to ensure a homogeneous
144 distribution of the PAHs. Aliquots of 100 ml each of the resultant aqueous solution were used for
145 the LECA sorption experiments.

146 **2.2.4 Extraction and analyses of PAHs**

147 After each batch experiment, the spiked water was decanted and centrifuged. Determination of
148 levels of PAHs in water before and after treatment with LECA was performed by liquid-liquid
149 extraction. PAHs were extracted by shaking with dichloromethane, first with 3ml at 300 rpm in a
150 borosilicate glass for 30 minutes, then 4 ml and 3 ml respectively in a separating funnel. The
151 dichloromethane extracts were combined and dried with anhydrous Na_2SO_4 before GC-MS
152 analysis.

153 GC-MS analysis was carried out using Agilent Technologies 7820B GC / 5975 MSD system
154 with an Agilent 190915 - 433 capillary column (30 m x 250 μm x 0.25 μm). Samples were
155 injected at a rate of 1 $\mu\text{l min}^{-1}$ by pulsed splitless injection and helium was used as the carrier gas
156 at a constant flow rate of 1.2 ml min^{-1} . The oven program was started at 50 $^\circ\text{C}$ and held for 1
157 min, increased at a rate of 15 $^\circ\text{C min}^{-1}$ up to 300 $^\circ\text{C}$ and held for 2.5 min. Mass detection was
158 operated in a SIM mode with MS source temperature at 230 $^\circ\text{C}$. Quantification was done using

159 calibration curves of standard phenanthrene, fluoranthene and pyrene which gave R^2 values of
160 1.000, 0.999 and 1.000 respectively.

161 A recovery of 90.1% was obtained for the extraction method as judged by the results of spiking.

162 **2.2.5 Effect of contact time on sorption**

163 Batch experiments were performed with 100 ml aliquots of 0.02 mg/l solution. Aliquots were
164 transferred into borosilicate glass bottles and 0.2 g aliquots of LECA were added. The bottles
165 were covered with aluminium foil, screw capped and shaken for durations between 1 and 21
166 hours at 300 rpm. For each batch, a blank containing only distilled water and LECA was
167 performed. Extraction of PAHs remaining in the solution after each LECA interaction was done
168 as described in section 2.2.4.

169 **2.2. 6 Effect of mass of sorbent on sorption**

170 Different masses of LECA between 0.2 - 4.0 g were shaken with 100 ml of 0.02 mg/l of PAHs
171 spiked water for 21 hours in each case and the residual aqueous PAHs were quantified.

172 **2.2.7 Sorption isotherms**

173 In order to determine the sorption capacity of LECA for removing PAHs from untreated water,
174 solutions of PAHs (phenanthrene, fluoranthene and pyrene) of concentrations 0.0005, 0.0025,
175 0.005, 0.01 and 0.02 mg/l were shaken with 0.2 g each of LECA for 6 hours (the time period
176 during which the most rapid sorption occurs, see section 2.2.5). These concentrations are lower
177 than the solubility of the individual PAHs in water (Table 2). The amount of PAHs before and
178 after LECA interaction was determined as in section 2.2.4.

179

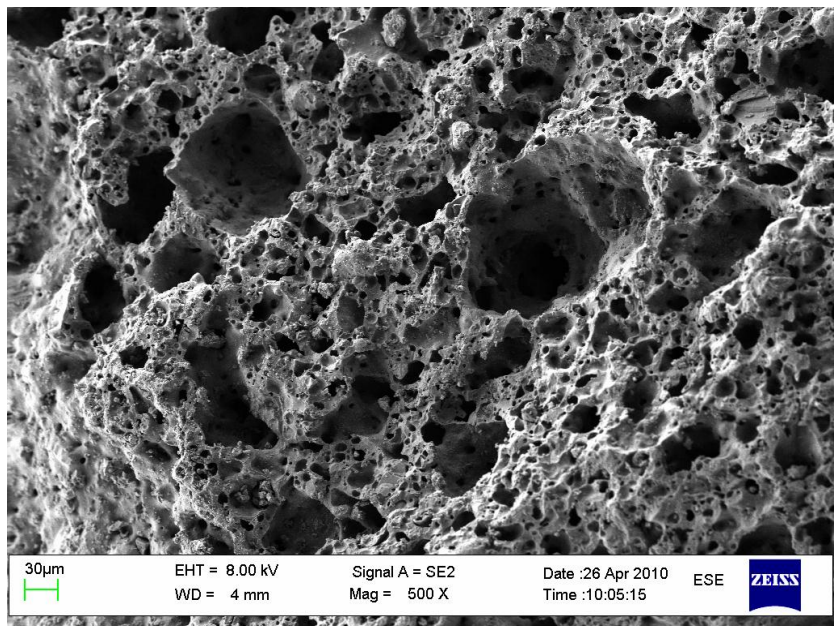
180

181

182 **3. Results and discussion**

183 The size of the LECA used was in the range of 1.5-2.5 mm. Elemental analysis with Zeiss Supra
184 55 VP FEG scanning electron microscope (SEM) showed the presence of C, O, Na, Mg, Al, Si,
185 K, Ca, Ti and Fe. The SEM surface image shows a rough surface with many pores (Figure 1).
186 The outcome of the sorption studies with LECA are presented in Figures 2 (PAHs sorbed versus
187 contact time), Figure 3 (Amount of PAHs sorbed versus mass of LECA at 21 h), Figure 4
188 (Maximum amount (%) of PAHs removed at maximum time of 21h) and Figure 5 (The
189 linearised form of the Freundlich and Langmuir sorption isotherms). Table 3 shows the
190 Freundlich and Langmuir parameters for the PAHs studied.

191



192

193 **Figure 1: Surface image of a LECA particle under a scanning electron microscope (SEM)**
194 **showing pores**

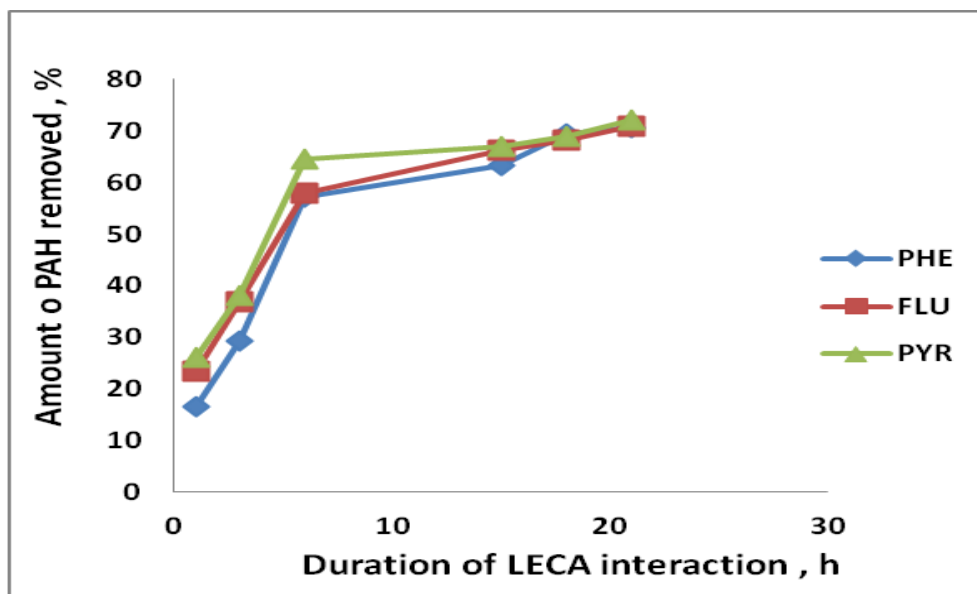
195

196

197

198 **3.1 Effect of contact time on sorption**

199 When batch experiments were conducted to determine the rate of uptake of PAH by LECA at
200 room temperature (25 °C), it was observed that the rate of sorption increased with contact time
201 (Figure 2). The results show that all PAHs were removed at a rapid rate during the first 1-6 h, by
202 which time approximately 60% of all PAHs had been removed (57.3 ,57.8 and 64.6 % of
203 phenathrene, fluranthene and pyrene respectively). This was the basis for the selection of a 6 h
204 duration for the isotherm experiments. After 6 h , the uptake efficiency decreased gradually as
205 sorption increased until it reached a maximum at 21 h. At this time , 70.7, 70.83 and 72.12 % of
206 phenathrene, fluoranthene and pyrene respectively had been removed. Considering the similarity
207 of the sorption curves, it is very clear that molecular weight is not a determinant for the rate of
208 sorption. Sorption occurred in two stages regardless of molecular weight, a fast interaction in the
209 first 6 hours and a slower one for the remaining period. The main sorption mechanism seem to be
210 based on a fast attraction of the PAH with high hydrophobicity or low polarity towards the
211 hydrophobic sites of the LECA surface immediately on exposure. This mechanism was enhanced
212 with contact time. Hence PHE was less removed at the maximum sorption time than FLU and
213 PYR which had similar sorption patterns with contact time. This similarity could be attributed to
214 their being structural isomers. Only 70.7 % of PHE had been removed at 21 h , while 70.83 and
215 72.12 % of FLU and PYR had been removed (Figures 2, 4). This trend is consistent with
216 sorption mechanisms that are driven by PAH hydrophobicity. Similar trends for sorption
217 processes based on hydrophobicity of PAHs have been reported in a case where leonardite was
218 used as sorbent [6] and also when lignin-based sorbents were used [18].
219



220

221 **Figure 2: PAH sorbed versus contact time**

222

223 3.2 Effect of sorbent mass on sorption

224 The sorbent mass was varied for the maximum sorption time of 21 h for a 100 ml solution
 225 containing 0.02 mg/l of PAHs, and the removal of PAHs was improved from masses of 0.2 g to

226 4.0 g. In the time series for a mass of 0.2 g, there was no further sorption beyond 21 hours,

227 although a very rapid sorption was observed for 0.5 g of sorbent at 81.24, 81.58 and 82.57 %

228 (PHE, FLU, PYR) to 2.5 g at 90.88, 91.82 and 91.59 % (PHE, FLU, PYR) (Figure 3). The

229 removal process proceeded gradually from this point until a maximum was reached at 92.61,

230 93.91 and 94.15 % for 4.0 g of sorbent. Further removal was impossible beyond this point.

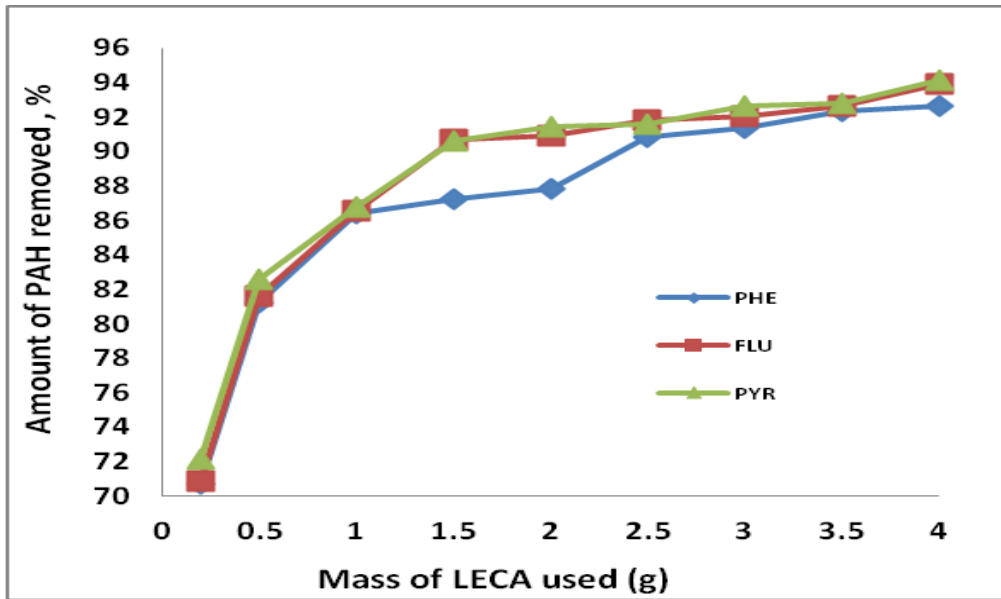
231 Several results which support the increase in sorption with mass of sorbent have been reported

232 for different systems including the use of 1-amino-2-naphthol-4-sulfonate as a selective solid-

233 phase sorbent for the extraction of gold [32] and the use of green coconut shells as sorbent for

234 the removal of toxic metal ions [33]. However, these are inorganic materials and may have

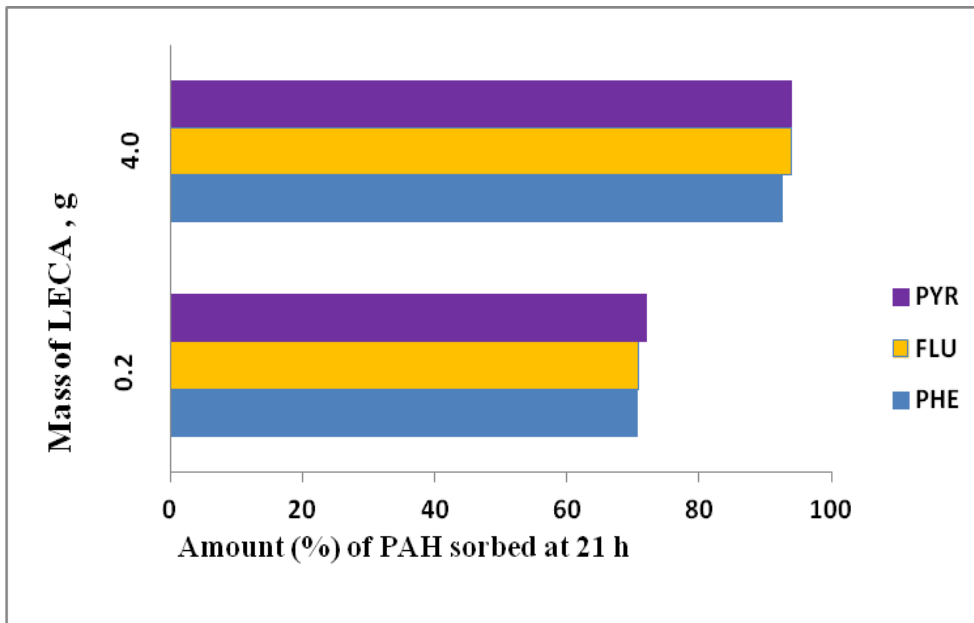
235 different sorption mechanisms.



236

237 **Figure 3: Amount of PAH sorbed versus mass of LECA at 21 h**

238



239

240 **Figure 4: Maximum amount (%) of PAHs removed at 21h**

241

242

243

244 3.3 Sorption Isotherms

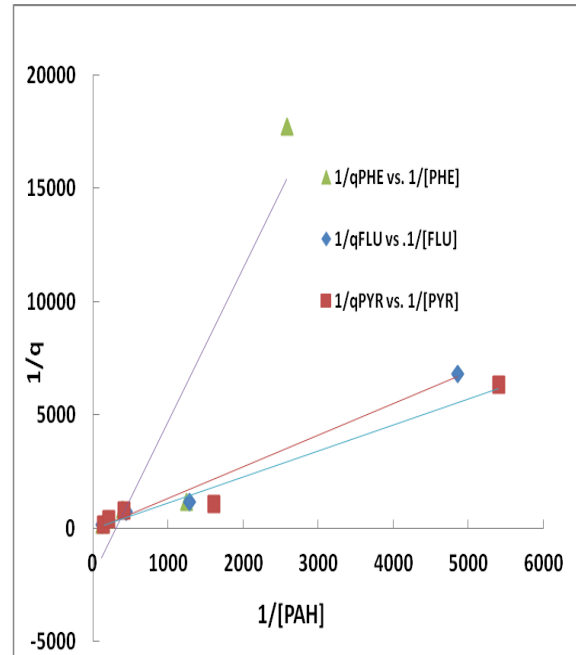
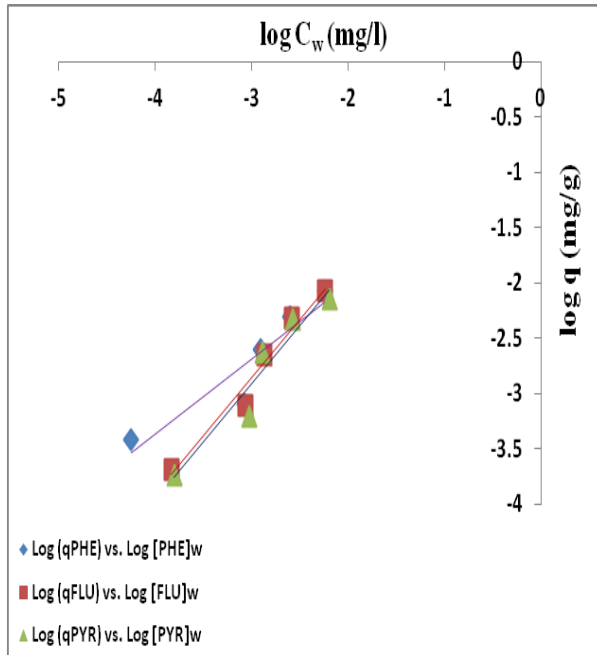
245 In a solid-liquid system where effective interaction occurs, the uptake of PAHs consists of the
246 following steps (i) diffusion transport of molecules from the solution to the exterior surface of
247 sorbent through a boundary layer, (ii) intra-particle diffusion of molecules through the interior
248 pores of sorbent and (iii) sorption of molecules onto the active sites on the interior surface [20].

249 In this study, the linear forms of the Freundlich and Langmuir isotherms were used in plotting
250 the graphs in Figure 5. Regarding the Freundlich isotherm, reasonable correlation coefficients of
251 0.86, 0.97 and 0.92 were obtained for phenanthrene, fluoranthene and pyrene respectively (Table
252 3). The equation is given as $\text{Log } q = \log K_f + 1/n \log C_w$; where q is mass of sorbed pollutant per
253 unit of sorbent (mg/g), C_w (mg/l) is the dissolved PAH in water, n is the measure of linearity and
254 K_f is Freundlich constant. The values of K_f and $1/n$ are obtained from the intercept and slope of
255 the plot of $\log q$ versus $\log C_w$. K_f is related to the sorption capacity while n is related to the
256 sorption intensity. The Freundlich isotherms in Figure 5a can be considered as barely nonlinear
257 for Flu and Pyr and explicitly nonlinear for Phe with n values (Table 3) outside the range of 0.95
258 $< n < 1.05$, as within these boundaries, the isotherms are considered linear [34].

259 When $n = 1$, a similarity is indicated to the Langmuir isotherm, while $n \geq 10$ indicates that
260 heterogeneous sorption is favoured [19]. This is also confirmed by the heterogeneous surfaces of
261 LECA particles (Figure 1). Nonlinear isotherms have also been obtained for several PAHs using
262 sorbents such as aspen wood, leonardite, black, carbon-free biopolymers, coconut shell, sugar
263 cane etc. [18, 35]. Sorption coefficients of 0.22, 2.02 and 1.70 were obtained for PHE, FLU and
264 PYR respectively.

265 In the case of the Langmuir isotherm (Figure 5b), correlation coefficients of 0.85, 0.99 and 0.97
266 were obtained for phenanthrene, fluoranthene and pyrene respectively. These figures are very

267 similar to those obtained for the Freundlich isotherm (Table 3). The linear equation is given as
268 $1/q = 1/Q_0 b \cdot 1/C_w + 1/Q_0$, where q and C_w have the same meanings as above; Q_0 is the Langmuir
269 constant analogous to maximum amount of sorption corresponding to complete monolayer
270 coverage (mg/g) and b is the Langmuir constant which is related to the rate of sorption intensity
271 [36]. The values of b and Q_0 (Table 3) are obtained from the intercept and slope of the plot of $1/q$
272 versus $1/C_w$. The Langmuir isotherm is usually interpreted with an equilibrium parameter R_L ,
273 given as $R_L = 1 / (1 + bC_0)$ where C_0 is the highest PAH concentration (mg/l), in this case 0.02
274 mg/l. The R_L values obtained for PHE, FLU and PYR are - 0.19, -15.67 and 6.00 respectively.
275 These R_L values do not favour Langmuir predictions since when $R_L > 1$ (unfavourable), $R_L = 1$
276 (linear), $R_L = 0$ (irreversible) and $0 < R_L < 1$ is favourable [19]. Therefore results of our study
277 indicate that the sorption of PHE, FLU and PYR by LECA are more similar to the Freundlich
278 than the Langmuir model. Regarding the lack of correspondence of the isotherms, it has been
279 reported that the sorption of organic solutes in solution is generally dependent on various
280 solute/sorbent interactions like Van der Waals and dipole interactions as well as weak
281 intermolecular forces [37, 38].
282



283

284 a) Freundlich

b) Langmuir

285 **Figure 5: Sorption isotherms of phenanthrene, fluoranthene and pyrene on LECA**

286

287 **Table 3: Freundlich and Langmuir parameters for phenanthrene, fluoranthene and**

288 **pyrene**

PAH	Freundlich			Langmuir			
	K_f (mg/g)	n	R^2	b (l/mg)	Q_0 (mg/g)	R^2	R_L
Phenanthrene (Phe)	0.22	1.48	0.86	-312.50	-4.75×10^{-4}	0.85	-0.19
Fluoranthene (Flu)	2.02	0.95	0.97	-53.19	-1.35×10^{-2}	0.99	-15.67
Pyrene (Pyr)	1.70	0.95	0.92	-41.67	-2.10×10^{-2}	0.97	6.00

289

290

291

292

293 **3.4 Comparison of the performance of LECA with other sorbents**

294 When the fibrous synthetic sorbent *p*-phenylene-2, 6-benzobisoxazole sold under the trade names
295 Zylon and PBO was used for aqueous PAH (including phenanthrene and pyrene) sorption
296 studies, an average of 95 % removal was achieved in 24 h when an average of 351.95 mg of fiber
297 was shaken in batch experiments with 20 ml aliquots of 50 µg/l of solution. The mass of 10 cm
298 of PBO fiber (containing 322 filaments) was equated to 0.01 g. The maximum sorption of 95%
299 can be presented as 2.7 µg/g removal [16]. Also a study involving the use of natural coal
300 leonardite as sorbent (0.5 g of sorbent to 0.5 l of solution) for the removal of 5 PAHs including
301 pyrene and benzo[k]fluoranthene resulted in 82% removal of a 100 µg/l solution in 24 h
302 equilibrium time. This figure can be presented as 82 µg/g removal [6]. In the case of LECA, the
303 92.61, 93.91 and 94.15 % (section 3.2) removal of PHE, FLU and PYR from 100 ml solution of
304 0.02 mg/l concentration by 4.0 g sorbent can be presented as 0.4631, 0.4696 and 0.4708 ug/g
305 removal respectively at 21 h. However when 0.20 g of LECA was used, the 70.7, 70.83 and
306 72.12 % removal of phenathrene, fluoranthene and pyrene respectively obtained can be presented
307 as 7.070, 7.083 and 7.212 µg/g. The removal efficiency of PBO is lower while that of Leonardite
308 is higher when compared to that of LECA. Among these three sorbents PBO is a speciality fibre
309 with a generally high production and sale cost [39]. The price of leonardite is around US \$5/Kg
310 [40] and that of LECA is around 0.15 US\$/Kg [41]. Though it may not be reasonable to compare
311 prices from two different companies selling different types of sorbents, it appears that LECA is a
312 much cheaper alternative. The low cost of LECA also affords the use of several folds of the
313 particles to increase the sorption of PAHs in field applications. Furthermore, LECA is heat
314 resistant and therefore can be regenerated by incineration at high temperatures.

315

316 **4. Conclusion**

317 The study has revealed that phenanthrene, fluoranthene and pyrene can be effectively removed
318 from water by batch sorption experiments using LECA as sorbent. The extent of removal was
319 enhanced with an increase in the mass of LECA from 70.7, 70.83 and 72.12% of PHE, FLU and
320 PYR for a mass of 0.2 g of LECA to 92.61, 93.91 and 94.15 % of PHE, FLU and PYR for a
321 mass of 4.0 g of LECA for 100 ml aliquots of 0.2 mg/l solution. The extent of sorption also
322 increased with contact time. The sorption of the PAHs tested followed the order $PYR > FLU >$
323 PHE , which is consistent with the sorption mechanism driven by PAH hydrophobicity. The
324 sorption isotherms followed the Freundlich model with correlation coefficients of 1.48, 0.95 and
325 0.95 for PHE, FLU and PYR respectively. The precision and accuracy of the methods used in the
326 study were satisfactory with a recovery of 90.1%. The price of LECA compares favourably with
327 other natural sorbents. LECA can thus be used as an effective alternative material for PAH
328 removal from contaminated water.

329

330 **5. Acknowledgement**

331 The authors are grateful to the Agder Fund and the University of Agder, Kristiansand (UiA) for
332 financing this research, to Egil Sev. Erichsen and Stein-Erik Lauritzen of University of Bergen
333 for their help in the arrangement and use of the SEM facility and to Benjamin Bandowe of
334 University of Bern, Switzerland for his technical advice on sorption studies.

335

336

337

338

339 **6. References**

- 340 [1] F.S.A. (Food Safety Authority of Ireland) Polycyclic aromatic hydrocarbons (PAHs) in food
341 toxicology, Factsheet Series, (2009)1-9.
- 342 [2] N. Rajput, A. Lakhani, Measurements of polycyclic aromatic hydrocarbons in an urban
343 atmosphere of Agra, India, *Atmósfera* 23 (2), 165-183.
- 344 [3] M.C. Pelletier, R.M. Burgess, K.T. Ho, A. Kuhn, R.A. McKinney, S.A. Ryba, Phototoxicity of
345 individual polycyclic aromatic hydrocarbons and petroleum to marine invertebrate larvae and
346 juveniles, *Environ. Toxicol. Chem.* 16, 10 (1997) 2190-2199.
- 347 [4] Y. C. M. Staal, D.G.A.J. HeBELS, M. H. M. Van Herwijnen, R. W. H. Gottschalk, F. J. Van
348 Schooten, J. H. M. Van Delft, Binary PAH mixtures cause additive or antagonistic effects on
349 gene expression but synergistic effects on DNA adduct formation, *Carcinogenesis* 28, 12 (2007)
350 2632 - 2640.
- 351 [5] W. Kanchanamayoon, N. Tatrahun, Determination of polycyclic aromatic hydrocarbons in
352 water samples by solid phase extraction and Gas Chromatography, *World J. Chem.* 3, 2 (2008)
353 51-54 in E. Martinez, M. Gros, S. Lacorte, D. Barcel, Simplified procedures for the analysis of
354 polycyclic aromatic hydrocarbons in water, sediments and mussels, *J. Chromatogr. A.*, 1047
355 (2004) 181-188.
- 356 [6] Z.C. Zeledon-Toruno, C. Lao-Luque, F.X.C. De las Heras, M. Sole-Sardans, Removal of
357 PAHs from water using an immature coal (leonardite), *Chemosphere* 67 (2007) 505-512.
- 358 [7] WHO. Polynuclear aromatic hydrocarbons: Guidelines for drinking-water quality, 2nd ed.
359 Health criteria and other supporting information, Geneva, World Health Organization, 2(1996)
360 495-505.
- 361 [8] WHO. Polynuclear aromatic hydrocarbons in Drinking-water: Background document for
362 development of WHO Guidelines for Drinking-water Quality, WHO/SDE/WSH/03.04/59, 2003.

363 [9] C. A. Menzie, B. B. Potocki, J. Santodonato, Exposure to carcinogenic PAHs in the
364 environment, *Environ. Sci. Technol*, 26 (1992) 1278 in A.K.M. Kabzinski, J. Cyran, R.
365 Juszczak, Determination of polycyclic aromatic hydrocarbons in water (including drinking
366 water) of Lotz, *Pol. J. Environ. Stud.* 11, 6 (2002) 695-706.

367 [10] The Council of the European Union, On the quality of water intended for human
368 consumption, *Off. J. Eur. Communities*, Council Directive 98/83/EC.

369 [11] R.E. Hinchee, B.C. Alleman, 1994. in R. Crisafully, M. A. L. Milhome, R.M. Cavalcante,
370 E.R. Silveira, D. De Keukeleire, R.F. Nascimento, Removal of some polycyclic aromatic
371 hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin,
372 *Bioresour. Technol.* 99 (2008) 4515 - 4519.

373 [12] A. Bhatnagar, A. K. Monicha, Conventional and non-conventional adsorbents for removal of
374 pollutants from waste: A review, *Indian J. Chem. Technol.* 13 (2006) 203-217.

375 [13] D.O. Cooney, Adsorption designer for wastewater treatment. Lewis Publishers, London,
376 England, UK, 1999, pp.45 - 190 in Crisafully, R., Milhome, M. A. L. Cavalcante, R.M. Silveira,
377 E.R. De Keukeleire, D. Nascimento, R.F. Removal of some polycyclic aromatic hydrocarbons
378 from petrochemical wastewater using low-cost adsorbents of natural origin, *Bioresour. Technol.*
379 99 (2008) 4515 - 4519.

380 [14] S.D. Faust, O.M. Aly, Adsorption process for water treatment, Butterworths Publishers,
381 Stoneham, 1987. , in A. Bhatnagar, A. K. Monicha, Conventional and non-conventional
382 adsorbents for removal of pollutants from waste: A review, *Indian J. Chem. Technol.* 13 (2006)
383 203-217.

384 [15] N. Irha, Sorption of pyrene from water by oil shale ash and mineral particles. *Toxicol.*
385 *Environ. Chem.* 74 (2000) 105-110.

- 386 [16] Y. J. Jung, Y. Kiso, T. Oguchi, T. Yamada, H. Takagi, K. Nashimura, Fibrous adsorbent for
387 removal of aqueous aromatic hydrocarbons, *Environ. Sci.* 14, 2 (2007) 067-077.
- 388 [17] E. Khan, S. Khaodhir, P. Rotwiron, Polycyclic aromatic hydrocarbon removal from water
389 by natural fiber sorption, *Water Environ. Res.* 79, 8 (2007) 901-911.
- 390 [18] R. Crisafully, M. A. L. Milhome, R.M. Cavalcante, E.R. Silveira, D. De Keukeleire, R.F.
391 Nascimento, Removal of some polycyclic aromatic hydrocarbons from petrochemical
392 wastewater using low-cost adsorbents of natural origin, *Bioresour. Technol.* 99 (2008) 4515 -
393 4519.
- 394 [19] S. Hall, R. Tang, J. Baeyens, R. Dewil, Removing polycyclic aromatic hydrocarbons from
395 water by adsorption on silica gel, *Polycyclic Aromat. Compd.* 29 (2009) 160 -183.
- 396 [20] M. Yuan, S. Tong, S. Zhao, C.Q. Jia, Adsorption of polycyclic aromatic hydrocarbons from
397 water using petroleum.coke-derived porous carbon, *J. Hazard. Mater.* 181 (2010) 1115-1120.
- 398 [21] P.C. Chiang, H. You, T. F. Ling, P. Chang, in *Proc. 4th int. Conf. on Fundamentals of*
399 *Adsorption*, (Ed. Suzuki, M.) Kodansha , Tokyo, 1993, p. 90.
- 400 [22] S. Ahn, D. Werner, H. K. Karapanagioti, D. R. Mcglothlin, R. N. Zare, R.G. Luthy,
401 Phenanthrene and pyrene sorption and intraparticle diffusion in polyoxymethylene, coke and
402 activated carbon, *Environ. Sci. Technol.* 39 (2005) 6516 - 6526.
- 403 [23] D.G. Kinniburgh, General purpose adsorption isotherms, *Environ. Sci. Technol.* 20 (1986)
404 895-904.
- 405 [24] D.S. Karpovich, G.J. Blanchard, Direct measurement of the Adsorption Kinetics of
406 Alkanethiolate Self-Assembled Monolayers on a Microcrystalline Gold Surface. *Langmuir*, 10
407 (1994) 3315-3322.

408 [25] Claytek, 2011. LECA [http://www.claytek.co.uk/leca_home.htm , accessed: 25th March,
409 2011)]

410 [26] Future garden, 2011. Lecastone [http://futuregarden.com/propagation/media_lecastone.html,
411 accessed on: 24th March, 2011)].

412 [27] Laterlite, 2011. Light weight concrete made with leca structural.
413 [<http://www.laterlite.com/pagina.aspx?idmenu=58&idlingua=eng&idpadre=63&livello=3>,
414 accessed on: 24th March, 2011]

415 [28] Shanghai Tiandouxin Industrial Development (STID) Co., Ltd, 2010.
416 (http://tdxsy.com/english/news_info.asp?nid=3, accessed: 17th /February, 2012)

417 [29] M. Malakootian, J. Nouri, H. Hossaini , Removal of heavy metals from paint industry's
418 wastewater using Leca as an available adsorbent, Int. J. Environ. Sci. Tech., 6, 2 (2009) 183-190.

419 [30] Saint-Gobain Weber Company, Filtrate Datasheet. Filtralite Department in Oslo, Norway.

420 [31] Dansk Leca A/S (<http://www.gpnm.org/e/uploads/131-b810984952.pdf>, accessed: 20th
421 February, 2012)

422 [32] L. Zhang, Z. Li, X. Du, X. Chang, Activated carbon functionalized with 1-amino-2-
423 naphthol-4- sulfonate as a selective solid-phase sorbent for the extraction of gold (III),
424 Microchim Acta. 174 (2011) 391-398.

425 [33] F.W. Sousa, A.G. Oliveira, J. P. Ribeiro, F. R. Morsyleide, D. Keukeleire, R.F. Nascimento,
426 Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed bed
427 column technology, J. Environ. Manage. 91 (2010) 1634 -1640.

428 [34] J. Pignatello, Y. Lu, E.J. LeBoeuef, W. Huang, J. Song, B. Xing, Nonlinear and competitive
429 sorption of a polar compounds in black carbon-free natural organic materials, J. Environ. Qual.
430 35 (2006) 1049 -1069.

431 [35] M. A. Olivella, P. Jové, A. Oliveras, The use of cork waste as a biosorbent for persistent
432 organic pollutants–Study of adsorption/desorption of polycyclic aromatic hydrocarbons, J.
433 Environ. Sci. Health, Part A, 46, 8 (2011) 824 - 832.

434 [36] C. Tien, Adsorption calculations and modeling, Butterworth-Heinemann-Boston, USA,
435 1994.

436 [37] A. A. Mackay, P.M. Gschwend, Sorption of monoaromatic hydrocarbons to wood, Environ.
437 Sci. Technol. 34 (2000) 839 - 845.

438 [38] D.O. Cooney, Adsorption designer for wastewater treatment, Lewis Publishers, London,
439 England, UK, 1999, pp. 45-190.

440 [39] Committee on High-Performance Structural Fibers for Advanced Polymer Matrix
441 Composites, National Research Council and National Academy of Sciences, High-performance
442 Structural Fibers for Advanced Polymer Matrix Composites, National Academies Press,
443 illustrated ed., Washington,D.C.-USA, 2005, p.15.

444 [40] Vermi Technology Unlimited, Leonardite.
445 (<https://www.vermitechnology.com/index.php?productID=108>, accessed: 20th February, 2012)

446 [41] Mike Wye & Associates Ltd, LECA.
447 (<http://www.mikewye.co.uk/naturalproducts.htm#leca>, accessed : 20th February 2012)

448

449

450

451

452

453