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1 **Greener Photocatalysts: Hydroxyapatite Derived from**
2 **Waste Mussel Shells for the Photocatalytic Degradation of a**
3 **Model Azo Dye Wastewater**

4
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16

17 Abstract

18 This paper demonstrates for the first time the feasibility of utilizing waste mussel shells for the
19 synthesis of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (denoted as HAP) to be used as a greener,
20 renewable photocatalyst for recalcitrant wastewater remediation. HAP was synthesised from
21 *Perna Canaliculus* (green-lipped mussel) shells using a novel pyrolysis-wet slurry precipitation
22 process. The physicochemical properties of the HAP were characterized using X-ray Diffraction
23 (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy
24 (SEM). The HAP produced was of comparable quality to commercial (Sulzer Metco) HAP. The
25 synthesized HAP had good photocatalytic activity, whereby methylene blue (a model textile
26 wastewater compound) and its azo dye breakdown products were degraded with an initial rate of
27 $2.5 \times 10^{-8} \text{ mol L}^{-1} \text{ min}^{-1}$. The overall azo dye degradation was nearly 54% within 6 hours and 62%
28 within 24 hours in an oxygen saturated feed in a batch reactor using a HAP concentration of 2.0
29 g/L, methylene blue concentration of 5 mg/L, UV irradiation wavelength of 254 nm and a
30 stirring speed of 300 rpm. The kinetics were well described by three first order reactions in
31 series, reflecting the reaction pathway from methylene blue to azo dye intermediates, then to
32 smaller more highly oxidised intermediates and finally degradation of the recalcitrants. The final
33 two steps of the reaction had significantly slower rates than the initial step (rates constants of 6.2
34 $\times 10^{-3} \text{ min}^{-1}$, $1.2 \times 10^{-3} \text{ min}^{-1}$ and approximately (due to limited data points) $1.6 \times 10^{-4} \text{ min}^{-1}$ for the
35 first, second and third step respectively), which tie in with this mechanism, however it could also
36 indicate that the reaction is either product inhibited and/or affected by catalyst deactivation.
37 FTIR analysis of the post-reaction HAP revealed surface PO_4^{3-} group loss. Since there is good
38 photocatalytic activity with oxygen in limited and excess supply during the photoreaction, this
39 indicates the possibility of lattice oxygen participation in the photocatalytic reaction, which

40 needs to be characterised more fully. However, overall, these results indicate that the HAP
41 derived from the mussel shells is a promising greener, renewable photocatalyst for the
42 photocatalytic degradation of wastewater components.

43

44 Keywords: Hydroxyapatite; photocatalysis; wastewater treatment; waste material recycle;
45 reaction mechanism, methylene blue.

46

47 **1. Introduction**

48 Mussel farming is a fast growing industry around the world (and especially in New Zealand
49 where this research is based), and the increase in the production of the mussels generates a
50 concomitantly large amount of mussel shell waste. Recent regulations and strategies on the
51 aquaculture waste have opened up new opportunities to sustainable development which has also
52 encouraged the application of environmental technologies (Gaya and Abdullah, 2008; Chong *et*
53 *al.*, 2010). In particular, mussel shells are a calcium-rich resource that can be used to produce
54 calcium oxide (lime). This lime can be used in several different ways in environmental
55 technologies, for example in a study conducted by Currie *et al.* (2007), lime from mussel shells
56 was shown to be able to remove about 90% of phosphates in water. A further study carried out
57 by Abeynaike *et al.* (2011) indicated that mussel shells can also be converted into hydroxyapatite
58 (HAP) with potential for use as value-added products. Therefore, by utilising shell waste for the
59 purposes of water and wastewater treatment, two existing problems can be solved: pollution
60 remediation and the transformation of a significant existing waste material into a useful
61 commodity.

62
63 HAP is widely used in bone regeneration and dental materials since it is the major inorganic
64 component in natural bones and teeth (Sivakumar and Manjubala, 2001; Ji *et al.*, 2009). It has
65 also been widely used as an adsorbent in various applications such as in hydrogenation and
66 wastewater treatment (Zahouily *et al.*, 2003; Reddy *et al.*, 2007). The stoichiometric form of
67 HAP is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ where the Ca/P molar ratio is 1.67. HAP has been applied as a catalyst
68 in various applications such as for dehydration and dehydrogenation reactions (Abeynaike *et al.*,
69 2008; Tsuchida *et al.*, 2008; Boucetta *et al.*, 2009; Khachani *et al.*, 2010), synthesis of chalcone

70 derivatives (Solhy *et al.*, 2010), gas-phase oxidation reactions (Jun *et al.*, 2004; Zhang *et al.*,
71 2008; Domínguez *et al.*, 2009) and also as a photocatalyst in a select few gas-phase
72 photocatalysis processes (Hu *et al.*, 2007; Reddy *et al.*, 2007; Ji *et al.*, 2009; Liu *et al.*, 2010).
73 Very few studies have evaluated HAP as an aqueous phase photocatalyst in its own right – those
74 that have (e.g. Sheng *et al.*, 2011) have only investigated a very limited range of reaction
75 conditions and reactants and have not looked at a wide range of reaction conditions, types of
76 HAP, different reactants and the reaction mechanism. This work therefore aims to begin to fill
77 this knowledge gap, where HAP will be evaluated more extensively than before as an aqueous
78 phase photocatalyst for the remediation of a model dye wastewater containing methylene blue.

79
80 Photocatalysis is a rapidly developing wastewater treatment technology, gradually attracting
81 more interest due to its ability to fully mineralise various compounds and so is a potentially
82 important application for HAP. Photocatalysis can be defined as acceleration of a photoreaction
83 by the presence of a catalyst (Mills and Le Hunte, 1997; Gaya and Abdullah, 2008; Castello,
84 2009). Photocatalysis is best applied when the more common wastewater treatment technologies
85 such as biological degradation, sedimentation, adsorption, flocculation, filtration and reverse
86 osmosis are insufficiently effective (Soon and Hameed, 2010) and where the compound cannot
87 be recovered and needs to be made less toxic and more biodegradable by the photocatalytic
88 oxidative degradation reaction. Three components must be present in order for the heterogeneous
89 photocatalytic reaction to take place: an emitted photon (with appropriate wavelength), a
90 catalytic material (usually a solid catalyst) and a strong oxidizing agent which in most cases is
91 oxygen (De Lasa *et al.*, 2005). The most commonly used and most active photocatalysts are
92 powdered semi-conductors such as titanium dioxide (Akpan and Hameed, 2009; Khataee and

93 Kasiri, 2010; Boiarkina *et al.*, 2011) and zinc oxide (Ali *et al.*, 2010, 2011). However the
94 problems with these catalysts are that they are expensive and consist of metals that have limited
95 availability on Earth. Using HAP as a photocatalyst overcomes this problem – it contains readily
96 and widely available atoms (Rakovan, 2002; Al - Qasas and Rohani, 2005), can be made from
97 renewable sources (such as waste mussel shells, as in the present work) and, depending on the
98 required purity, can be inexpensive to make.

99 In this work the model wastewater compound tested is methylene blue, which is a commonly
100 used compound as the exemplar for azo dye and textile dye wastewaters. It has been extensively
101 studied throughout photocatalysis literature (Houas *et al.*, 2001; Ali *et al.*, 2010, 2011; Boiarkina
102 *et al.*, 2011) and is even the model compound used in the standard method for assessing
103 photocatalysts (Mills, 2012). Therefore it is the ideal compound to benchmark the degradation
104 using the novel HAP photocatalysts synthesised in this work.

105 Therefore the aim of this paper is to characterise the feasibility of using HAP synthesised from
106 mussel shells as a renewable photocatalyst for the remediation of a model dye wastewater.

107

108 **2. Materials and Methods**

109 ***2.1. Materials***

110 Green Lipped Mussel shells were kindly donated by Sanford Ltd (New Zealand) and originate
111 from their Marlborough processing plant. Potassium dihydrogen phosphate (KH_2PO_4) from
112 Sigma-Aldrich (99% pure) was employed in the formation of HAP, methylene blue was obtained
113 from Sigma-Aldrich (85% pure) and 99.5% pure oxygen by BOC gases was used for
114 oxygenation of the reactant solution. A calcium carbonate standard (99.5% purity) was obtained

115 from Sigma-Aldrich. A reagent-grade commercially available HAP powder (Sulzer Metco,
116 Australia) was employed as a comparative standard. All reagents were used as received, unless
117 otherwise stated. The water employed in all the studies was deionised water (from an ELGA
118 Maxima Ultra purifier system).

119 **2.2. Methods**

120 *2.2.1. Synthesis of HAP*

121 Calcium oxide was produced by calcination of waste mussel shells in an in-house fabricated tube
122 furnace under nitrogen flow as described previously (Jones *et al.*, 2011). A wet precipitation
123 method was used in order to prepare the HAP. First, calcium hydroxide with a concentration of
124 0.1M was prepared from calcium oxide that was converted from the raw shell, then was left in
125 deionized water overnight in a sealed reactor. A 0.06M phosphate solution was prepared from
126 potassium dihydrogen phosphate dissolved in deionized water. Specific concentrations for the
127 calcium hydroxide suspension and the phosphate solution were used in order to produce
128 stoichiometric HAP (i.e. HAP with a Ca/P ratio of 1.67). The phosphate solution was added into
129 the HAP reactor by a peristaltic pump (Cole-Parmer MasterFlex, model 7519-06). The solution
130 was stirred over a period of 5 hours under a nitrogen atmosphere to produce a milky white
131 suspension containing a precipitate. The resultant solid was separated from the solution by a
132 centrifuge and dried in an oven at 110°C overnight. The resultant solid is designated as ‘as-
133 synthesised HAP’. Part of this material was further processed by heat treatment (pyrolysis in a
134 nitrogen atmosphere in the same tube furnace used for calcination) at 800°C for 5 hours. This
135 material is designated as ‘heat treated HAP’.

136

137 2.2.2. Photocatalytic Degradation Experiments

138 The photocatalysis experiments were carried out in an in-house custom-made stainless steel UV
139 reactor, described elsewhere (Ali *et al.*, 2010). Two 200 mL beakers were used as reaction
140 vessels. The beakers were filled with 150mL of methylene blue containing 2.0 g/L of heat treated
141 HAP powder as photocatalyst (as-synthesized HAP was not tested in this work).

142 **<Fig. 1 here>**

143 Photocatalysis experiments were conducted under both oxygen rich (saturated pure oxygen
144 bubbled into the reaction solution) and oxygen limited (no oxygen bubbled into the reaction
145 solution) conditions. Under limited oxidant supply conditions, the HAP photocatalysts were
146 effectively examined under the ‘toughest’ reaction regime, where the only oxidant is from the
147 dissolved oxygen within the reaction solution. Additional oxygen can only be provided by mass
148 transfer from the surface of this solution, meaning that the overall reaction rate could be mass
149 transfer limited by the supply of oxidant. In other work (Ali *et al.*, 2010, 2011), this has provided
150 an insight into the oxygen participation during photocatalysis. Prior to illumination, the
151 suspension was magnetically stirred in the dark for 30 min, corresponding to the time needed to
152 establish the adsorption/desorption equilibrium at room temperature. Stirring was maintained to
153 keep the mixture in suspension during the irradiation. At regular intervals, samples of 1.0 mL
154 were withdrawn. Before analysis, the samples were centrifuged to separate the HAP particles.
155 Methylene blue concentration was evaluated by UV-Vis spectroscopy (Lambda 35 UV-Visible
156 Perkin Elmer), measuring the peak at 662 nm. Note that this peak does not give a pure response
157 for methylene blue throughout the reaction and will also be contributed to by the absorbance of
158 azo dye photocatalytic reaction intermediates such as Azure A, Azure B and Azure C (Ali *et al.*,

159 2010, 2011). The strongest response is however from methylene blue, which has its strongest
160 absorbance at this wavelength (see Supplementary Material for peak wavelengths comparison of
161 the reaction intermediates), however because of the contributions from the other azo dyes (which
162 are formed by the photocatalytic reaction), the concentration derived from this measurement will
163 be presented and interpreted as ‘azo dye’ concentration rather than methylene blue alone.

164 To get a ‘pure’ concentrations, the aqueous azo dye reaction intermediates and products
165 concentrations (along with a pure methylene blue concentration) were evaluated by high
166 performance liquid chromatography using the method, reagents and instrument detailed in
167 Boiarkina *et al.* (2011). The concentration of methylene blue was determined by calibration
168 using external standards. Note that UV-Vis and HPLC determination of the reaction progress and
169 reaction intermediates and products is used in this work and not measures of mineralisation such
170 as total organic carbon (TOC), since mineralisation is not the aim of this photocatalytic
171 degradation; a partial oxidation to more biodegradable products is. This is desired, since the
172 authors believe that it is a waste of energy and reactor size to fully mineralise wastewater
173 pollutants, when a partial degradation can make most pollutants more biodegradable and
174 therefore amenable to inexpensive and widely available biological wastewater treatment (such as
175 by aerobic and anaerobic digestion in activated sludge wastewater treatment plants). This paper
176 does not address the biodegradability of the products formed however (since this is beyond the
177 scope of the work), but by determining what is being formed (via HPLC) puts the authors in a
178 good position to understand what reaction products are formed when and therefore quantify the
179 extent of partial degradation. Also by knowing the identities of the reaction products, more
180 biodegradable products can be identified through literature search (if required). The

181 biodegradability of the reaction products however is not a focus of the current paper and will be
182 explored in future publications.

183 The pH of the reaction solution was taken before and after reaction (pH 330i from WTW,
184 Germany). The intensity of the UV lamp was measured using a UV probe (SUV 20.1A2Y2 from
185 IL Metronic Sensortechnik). UV intensity measurements were monitored periodically to ensure a
186 consistent intensity was maintained over the experimental period.

187 Two sets of control experiments were also conducted under oxygen rich conditions: firstly an
188 evaluation of the photolysis of methylene blue at the same concentrations used during
189 photocatalysis – here reactions were run under equivalent conditions to the photocatalysis runs
190 but in the absence of photocatalyst; secondly reactions were run in the absence of UV (in the
191 dark) over the reaction period to quantify the effect of adsorption over this time.

192 Note that all reactions were repeated at least once and error bars the mean \pm one standard
193 deviation.

194

195 *2.2.3. Characterization of HAP*

196 Characterisation of the raw shell powder, pyrolysed powder, Ca(OH)_2 and HAP produced (both
197 as-synthesised and heat treated), as well as the HAP after the photocatalysis reaction, was carried
198 out using Fourier Transform Infra-red (FTIR) spectroscopy, X-Ray Diffraction (XRD) analysis
199 and Scanning Electron Microscopy (SEM). FTIR was carried out with a Perkin Elmer Spectrum
200 100 using powder on a KRS-5 diamond attenuated total reflectance (ATR) system with the
201 wavenumbers recorded from 380 to 4000 cm^{-1} , in line with other methods used for HAP

202 (Rodriguez-Lorenzo and Vallet-Regi, 2000; Al-Qasas and Rohani, 2005; Mostafa, 2005). The
203 spectra produced were compared to spectra from several references (Koutsopoulos, 2002;
204 Al-Qasas and Rohani, 2005; Resende *et al.*, 2006; Tanaka *et al.*, 2012) allowing the key peaks to
205 be identified.

206 The X-ray diffraction (XRD) analyses were performed using a Bruker D8 Advance X-ray
207 diffractometer operating with a 40-kV Cu K α X-ray source. Scans were carried out in the 2 θ
208 range of 10 to 80 $^\circ$ with a 0.02 $^\circ$ step size and a 1 s step time.

209 The morphologies of granular samples were observed using an FEI Quanta 200 FEG scanning
210 electron microscope (5 kV accelerating voltage). Prior to imaging, the samples were double
211 coated with platinum using a Polaron SC 7640 Sputter Coater (2 minutes coating time) to
212 prevent charging.

213

214 **3. Results and Discussion**

215 ***3.1. Conversion of shells to lime by pyrolysis***

216 Pyrolysis of mussel shells at a temperature of 800 $^\circ$ C results in the decomposition of the
217 limestone as per equation (1):



219

220 <Table 1 here>

221 The mass loss at 540°C was consistent with results reported by Jones *et al.* (2011) where typical
222 mass loss under the calcination temperature of 700°C was between 3 and 5%. Since there is no
223 lime formed at this temperature, the mass loss can be used to determine the amount of adsorbed
224 moisture and the proteinaceous content of the shell. The pyrolysis of raw shell at 800°C resulted
225 in mass loss ranging from 44 to 48% including the mass loss of organic material. Subtracting the
226 organic content determined from the mass loss of the sample heated at 540°C, allows
227 determination of the mass loss during the transformation of carbonate to oxide, and this can be
228 used to determine the extent of transformation from CaCO₃ to CaO based on a theoretical mass
229 loss on full conversion of 44%. As shown in Table 1, for these samples the transformation was
230 between 93.6 and 99.5 % complete.

231 Fig. 2 shows XRD patterns for the raw mussel shell powder and powder pyrolysed at 800°C. For
232 the raw shell powder, all the observed peaks were identified as calcium carbonate with an
233 aragonite crystal structure (Kuriyavar *et al.*, 2000; Nan *et al.*, 2008; Galvan-Ruiz *et al.*, 2009).
234 Following the pyrolysis process at a temperature of 800°C, the pattern was dominated by peaks
235 from lime, with a small amount of calcium carbonate remaining in the sample in the form of
236 calcite due to the polymorphic transformation of carbonate that takes place when heating the
237 shells above 400°C (Davis and Adams, 1965; Perić *et al.*, 1996; Resende *et al.*, 2006; Parker *et*
238 *al.*, 2010; Jones *et al.*, 2011). The FTIR spectra of raw mussel shells and calcium carbonate with
239 99.5% purity are shown in Fig. 3. Comparing the spectra from a commercial calcium carbonate
240 (with a purity of 99.5%) to the raw shells, the sharp intense bands around 1400 cm⁻¹, 877 cm⁻¹
241 and 700 cm⁻¹ confirm a very close similarity. These bands correspond to the C-O bond from
242 carbonate (Kuriyavar *et al.*, 2000; Nan *et al.*, 2008; Galvan-Ruiz *et al.*, 2009). In addition, the
243 bands around 700-704 cm⁻¹ correspond to an aragonite polymorph (Kuriyavar *et al.*, 2000; Nan

244 *et al.*, 2008). The FTIR spectrum in 3(c) shows a band around 3640 cm^{-1} attributed to hydroxyl
245 stretching where this band appears due to adsorbed water and -OH species perturbed due to
246 hydrogen bonding (Resende *et al.*, 2006; Galvan-Ruiz *et al.*, 2009). The band at 1416
247 corresponds to C-O bond from carbonate while the band around 875 cm^{-1} and 500 cm^{-1}
248 corresponds to Ca-O bonds (Galvan-Ruiz *et al.*, 2009). This again indicates that lime has formed
249 with an unconverted calcium carbonate residual.

250 <Fig. 2 here>

251 <Fig. 3 here>

252 The SEM images shown in Fig. 4 indicate that there are structural changes that occur during the
253 pyrolysis, consistent with those observed in previous studies (Abeynaike *et al.*, 2011; Jones *et*
254 *al.*, 2011). Fig. 4a and 4c show that the raw mussel shells have well-defined edges and are
255 fragmented to reveal a layered structure common in mollusks. In Fig. 4b, it can be seen that the
256 edges were not well-defined. In Fig. 4d, it can be seen that there are some relief lines on the
257 particle surfaces resulting from the high temperature during calcination. For the pyrolysed shells,
258 the coarsening of particles can be observed as shown in Fig. 4b and 4d. The morphology of the
259 raw mussel shells differed considerably from the calcium oxide indicating that the calcination
260 process releases CO_2 as shown in Equation (1) and creates some cavities. This structure of the
261 calcined shells helps to react with deionised water to hydrolyse the calcium oxide to calcium
262 hydroxide in order to form a solid suspension/slurry of calcium hydroxide for the preparation of
263 HAP.

264 <Fig. 4 here>

265

266 3.2. Formation of HAP from the shell-derived lime

267 HAP was synthesized in a semi-batch reactor via a heterogeneous reaction where the potassium
268 dihydrogen phosphate was being dosed into a stirred solid suspension of calcium hydroxide. The
269 precipitates from the reaction were washed several times using deionised water and further dried
270 overnight in an oven at 110°C. The overall reaction for this mechanism is shown by equation (2):



272 Characterization of as-synthesised and heat treated powders by FTIR and XRD (Fig. 5 and 6)
273 confirmed that HAP was produced. The XRD pattern for the as-synthesised HAP (Fig. 5a)
274 confirms that although HAP was formed (full peak match to reference XRD patterns as reported
275 by Koutsopoulos, S., 2002; N.S. Al-Qasas and S. Rohani; Tsuchida *et al.*, 2008; Wang *et al.*,
276 2010), there was still a small trace of calcite remaining from the original calcination process
277 since the transformation of the raw shell to lime is between 93.6 to 99.5% as shown in Table 1.
278 Similar findings were observed in the FTIR spectrum for the as-synthesised HAP as shown in
279 Fig. 6a where the band at 1417 cm⁻¹ corresponds to the CO₃²⁻ group. The existence of CO₃²⁻ ions
280 in the HAP could also be due to the adsorption of CO₂ in the atmosphere during the preparation
281 of HAP (Rodriguez-Lorenzo and Vallet-Regi, 2000; Tanaka *et al.*, 2012; Khalid *et al.*, 2013). It
282 should be noted that the synthesis of HAP done in this work were done in a nitrogen atmosphere
283 in order to minimise the possibilities of the incorporation of the CO₃²⁻ in the lattice. The calcite
284 was not detected for the heat treated HAP as shown by the XRD pattern in Fig. 5b however,
285 either indicating that some of the remain calcite was converted to lime via calcination during this
286 final heat treatment as in previous work (Jones *et al.*, 2011), or that the calcite or lime (that is
287 expected to form in the heat treated HAP) could not be detected by the XRD - the XRD detection

288 limit is 5-10% (Cullity, 1956). Note that Khalid *et al.* (2013) has similar findings on the decrease
289 in the intensity of CO_3^{2-} ions in the FTIR spectrum when HAP powders were heat treated.

290 **<Fig. 5 here>**

291 The FTIR analyses for the as-synthesised, heat treated and commercial (Sulzer Metco) HAP
292 shown in Fig. 6 again confirmed that HAP was formed from the shell material, with the PO_4^{3-}
293 and OH^1 groups characteristic of HAP: the bands at 962, 874 and 559 cm^{-1} correspond to the
294 PO_4^{3-} group (Tanaka *et al.*; Reddy *et al.*, 2007; Wang *et al.*, 2010). Based on several studies done
295 on HAP as photocatalyst, the PO_3^{4-} group is believed to play important roles in the photocatalytic
296 reactions (Nishikawa, 2004a; Pratap Reddy *et al.*, 2007; Reddy *et al.*, 2007). The electron state
297 of the surface PO_3^{4-} group changes and create a vacancy on the HAP and consequently will cause
298 the formation of O_2^\bullet through the electron transfer to O_2 in the atmosphere. The FTIR spectra of
299 the as-synthesised HAP (Fig. 6a), showed a broad band around 3300 cm^{-1} which is due to
300 absorbed water, whereas this broad band does not appear in either the heat treated or the
301 commercial HAP. This shows that this water is not strongly bound and can be removed via
302 drying if this is needed. The IR spectra for both the heat treated and commercial HAP (Fig. 6b)
303 show a band around 3572 cm^{-1} assigned to the hydroxyl group (Tanaka *et al.*; Wang *et al.*, 2010).
304 Based on the study done by H. Tanaka *et al.* (2013), this hydroxyl group plays the important role
305 in the photocatalytic decomposition of dimethyl sulphide where this decomposition through UV
306 irradiation took place on the surface P-OH groups of HAP, which may be due to the formation of
307 surface P-OH radicals.

308 **<Fig. 6 here>**

309 The intense sharp bands around 1087, 962, 600 and 474 cm^{-1} seen in both the heat treated and
310 commercial HAP, which correspond to the PO_4^{3-} group, confirm that the HAP synthesised from
311 the shell waste material was similar to that of the commercial powder. From the EDS spectrum
312 for the as-synthesised and heat treated HAP, shown in Fig. 7a and 7b respectively, it can be seen
313 that both materials are composed of calcium, carbon, oxygen and phosphorous. However, traces
314 of potassium were also observed in both samples. This is perhaps due to the material being
315 insufficiently washed with water and future work will look at optimising this washing stage. It is
316 important to wash the precipitate with high water purity because the apatite lattice readily
317 incorporates foreign elements into the structure (Gross and Berndt, 2002).

318 <Fig. 7 here>

319 From the EDS analysis, the Ca/P ratio for both samples were calculated and for the as-
320 synthesised HAP, the Ca/P ratio was 1.61 while for the heat treated sample the ratio was 1.66
321 which is very close to the stoichiometric HAP ratio of 1.67.

322

323 ***3.3. Photocatalytic Degradation of Methylene Blue by HAP***

324 The results of the degradation of Methylene Blue in photolysis (UV lit in the absence of
325 catalyst), under dark (i.e. adsorption only) and with UV lit oxygen limited and oxygen rich
326 conditions are shown in Fig. 8.

327 <Fig. 8 here>

328 Fig. 8 shows that photolysis of methylene blue was negligible, indicating that the degradation of
329 methylene blue in the presence of HAP is likely to be due to photocatalysis. The photolytic

330 degradation of methylene blue in this reactor has been also shown to be negligible in previous
331 work in the same laboratory (Ali *et al.*, 2010).

332 The dark adsorption experiments shown in Fig. 8 show that adsorption to the HAP at the loading
333 used (methylene blue at 5 mg/L and heat treated HAP at 2.0 g/L) was negligible. This indicates
334 that adsorption is likely to be a minor methylene blue removal mechanism in this system
335 (assuming that adsorption properties do not change significantly in the presence of UV light).

336 When UV light (at 254 nm) was present, photocatalysis occurred under both oxygen rich and
337 oxygen limited conditions. Degradation (here monitored via decolorisation at a UV-Vis
338 wavelength of 662 nm which is characteristic of the primary degradation of methylene blue) was
339 observed for the first 90 minutes only with an overall degradation of only 1.8% and no further
340 decrease with time. It can be seen that the degradation was higher when oxygen (the oxidant) is
341 present and the reasons for this are discussed below. Under oxygen limited conditions the
342 degradation was around 39% after 6 hours and showed no further change when extending the
343 time to 24 hours. For the oxygen rich conditions, at 6 hours the degradation was around 54% and
344 increased further with time, reaching 62% after 24 hours.

345 Overall Fig. 8 therefore shows that HAP derived from mussel shells is a photocatalyst in the
346 presence of UV light when used in aqueous solutions. This therefore opens up the possibilities of
347 using HAP for pollution remediation through the transformation of a significant existing waste
348 material - waste sea shells. Furthermore, this shows that a greener photocatalyst is available,
349 produced from readily and widely available atoms and synthesised from renewable and
350 potentially recycled sources (if for example the phosphates are taken from wastewaters).
351 However, the key issue is – how good a photocatalyst is it?

352 When compared to another HAP, the shell-derived HAP appears to be a superior photocatalyst.
353 Fig. 9 shows a comparison of mussel shell derived heat treated HAP and the Sulzer Metco
354 commercially sourced HAP for the photocatalytic degradation of methylene blue under oxygen
355 rich conditions. This shows that the mussel shell derived HAP is the more effective photocatalyst
356 over the reaction period studied. The difference in performance between the two is most likely
357 due to the differences in material properties outlined in Sections 3.1 and 3.2. It is suspected that
358 the difference in performance is from the CO_3^{2-} ions in the shell-derived heat treated HAP as
359 shown in Fig. 6b. The exact nature of this performance enhancement has yet to be determined.

360 <Fig. 9 here>

361 <Fig. 10 here>

362 A kinetic analysis of the data with the heat treated HAP as photocatalyst in Fig. 8 is shown in
363 Fig. 10 and Table 2. A first order kinetic model analysis is used as these are commonly used in
364 photocatalysis research (as the simplification of the Langmuir-Hinshelwood kinetic model when
365 there are dilute reactant concentrations) and have in particular been used in several studies
366 quantifying the kinetics of photocatalytic dye oxidation in aqueous systems (Houas *et al.*, 2001;
367 Rauf *et al.*, 2010). Fig. 10 is the resulting first-order-reaction analysis of methylene blue
368 degradation with heat treated HAP. Note that the semi log data does not produce a single straight
369 line, hence does not fit a simple first order reaction model for the entire period of the reaction. A
370 series of first order reactions (as shown in Fig.10) is often found to be appropriate for advanced
371 oxidation reactions, since the degradation can be broken down in to several different dominant
372 reaction steps, such as primary degradation of the reactant, several secondary degradation steps
373 corresponding to the oxidation to major stable/recalcitrant classes of reaction intermediate and

374 finally mineralization (Houas *et al.*, 2001; Ali *et al.*, 2011). This is an accepted kinetic modeling
375 strategy for both non-catalytic and heterogeneously catalyzed wet oxidation reactions (Li *et al.*,
376 1991; Belkacemi *et al.*, 2000), a technology which also degrades compounds via a free radical
377 oxidation mechanism (Patterson *et al.*, 2001b). It is not widely used for photocatalysis since the
378 primary degradation of the reactant is often dominant and so fast that many reactions can be
379 fitted with a single first order expression – this is however not the case for the HAP
380 photocatalysis reactions here and so the reactions of the intermediates need to be accounted for
381 in the kinetics. It is found that the degradation of methylene blue and its azo dye reaction
382 intermediates is well modeled by a three step series of first order reactions. This reflects the
383 expected reaction pathway: first from methylene blue to azo dye intermediates (which should
384 have the fastest rate, since methylene blue has the strongest response in the UV-Vis
385 measurement used in this work), then secondary degradation of the azo dyes to smaller more
386 highly oxidised intermediates (that do not show UV absorbance at 662 nm) and finally
387 degradation of the recalcitrant coloured reaction intermediates. This directly relates to the
388 currently understood pathways of methylene blue photocatalytic degradation (Ali *et al.*, 2011).
389 Fig. 11 shows the concentration of MB and the peak areas of the reaction intermediates/products
390 as measured by HPLC during the course of a typical reaction and indicates that these pathways
391 most likely apply for the photocatalysis of MB with HAP also. In particular, these results show
392 that like many other studies of the photocatalytic degradation of MB, azure B is the major
393 reaction intermediate/product (Ali *et al.*, 2011). Fig. 11 also indicates that the reaction rate for all
394 of the component reactions slows considerably between the 5 and 10 hour reaction time – this is
395 inclusive of the degradation of MB as well as the formation and degradation of azure A, azure B,

396 azure C and thionin. A full analysis of these reaction pathways and kinetics will be covered in a
397 future publication.

398 **<Fig. 11 here>**

399 The first order reaction rate constants for three first order kinetic regions are shown in Table 2.
400 These show the trend expected from the methylene blue reaction mechanism: fast primary
401 degradation, slower secondary degradation, with the degradation of the recalcitrant intermediates
402 being the slowest reaction stage. However it also could indicate that the reaction is either product
403 inhibited and/or affected by catalyst deactivation – and so this was therefore investigated further.
404 Note that due to limited data in the final stages of the reaction, the authors are less confident on
405 the value with the rate constant for the third and final reaction stage, compared to the first two
406 stages of the reaction. Further work is needed to refine this value. However, the rate and rate
407 constants are representative of the overall change in concentration seen during this time and
408 serve to demonstrate that the rate is slower during this period.

409 **<Table 2 here>**

410 Fig. 12 shows a comparison between heat treated HAP photodegradation of MB at two different
411 stirring speeds: 300 and 600 rpm. These results show that there is no significant difference in
412 degradation extent and therefore reaction rate between the two sets of data (within the error
413 range of the data). This indicates that external mass transfer resistances are not significant at the
414 stirring speeds used. The true photocatalytic reaction kinetics have therefore been measured and
415 quantified in the preceding analysis.

416 **<Fig. 12 here>**

417 Overall, these results are consistent with the fact that dissolved oxygen can easily scavenge an
418 electron at the surface of a UV-irradiated semiconductor metal oxide, which aids in the
419 separation of photo-generated charges and decreases the recombination of generated electron-
420 hole pairs (Nishikawa and Omamiuda, 2002). In other words, oxygen provides the oxidant
421 source in indirect oxidation through the production of radical species (most likely hydroxyl
422 radicals here) and so having an excess of it present should increase the oxidation rate, as
423 observed. There is an analogy to this in previous gaseous HAP photocatalytic work where
424 Nishikawa & Omamiuda (2002) reported that an increase in the photocatalytic degradation of
425 methyl mercaptane by hydroxyapatite corresponded to an increase in the amount of superoxide
426 ($O_2^{\bullet-}$) species which were generated due to the UV irradiation – the main species that would be
427 generated by indirect oxidation in a dry gas phase photooxidation. The formation of radicals on
428 HAP through UV irradiation in the gas phase is also reported in other papers from the same
429 research group (Nishikawa and Omamiuda, 2002; Nishikawa, 2003; Nishikawa, 2004a;
430 Nishikawa, 2004b, 2007). Nishikawa & Omamiuda (2002) have indicated that the oxygen
431 vacancy is formed on HAP by UV irradiation and suggest that the activation of oxygen takes
432 place by the formation of the labile superoxide radicals due to electron transfer to O_2 in the
433 atmosphere (Nishikawa and Omamiuda, 2002). It is likely that in the aqueous environment of the
434 current experiments, a similar mechanism is occurring, but with hydroxyl radical species (such
435 as HO^{\bullet}) being formed instead of the superoxide radicals, as dictated by the expected aqueous
436 equilibrium reactions of these species (Dannacher and Schlenker, 1996; Patterson *et al.*, 2001a,
437 b) and as found in conventional semi-conductor photocatalysis (Hoffmann *et al.*, 1995).
438 However, if this is the case, then this mechanism cannot be used to explain the photocatalytic
439 reaction proceeding in the absence of sufficient oxygen, as in the oxygen limited case. Here, the

440 only available oxygen is from the residual oxygen within the reaction solution and any that can
441 mass transfer from the surface of the solution into the bulk solution.

442 Comparative FTIR spectra of the heat treated HAP powder before and after the photocatalytic
443 reaction are shown in Fig. 13. This figure reveals that the absorbance intensity due to the PO_4^{3-}
444 group at 1087, 960, 594 and 470 cm^{-1} are drastically decreased after photocatalytic reaction. A
445 similar trend was observed for the band at 1019 cm^{-1} which corresponds to the HPO_4^{2-} in non-
446 stoichiometric HAP. The formation of radicals on HAP by a photocatalytic reaction have been
447 reported by several researchers. The changes of surface PO_4^{3-} group and generation of trapped
448 electron suggest the appearance of oxygen vacancy by UV irradiation (Nishikawa and
449 Omamiuda, 2002; Nishikawa, 2003; Nishikawa, 2004a). This indicates that the phosphate group
450 (the moiety containing oxygen in HAP) could be dissolved during the reaction. This is not
451 expected at the pH that the HAP was subjected to in this reaction (the pH of the solution before
452 the photocatalytic reaction was 6.7 and following the reaction was slightly higher at 7.8), since
453 HAP is sparingly soluble at pHs above 4.2 (De Groot *et al.*, 1990; Ferná'ndez *et al.*, 1999). This
454 may therefore indicate that there is photocatalytic dissolution of HAP. Furthermore, since there
455 is photocatalytic activity in the absence of an oxidant, this may also indicate that the lattice
456 oxygen is being used instead, in a Mars van Krevelen type mechanism. A parallel to this lies in
457 the work of Ali *et al.* (2010; 2011) who used nanostructured ZnO thin films in methylene blue
458 photocatalysis. In this work, it was demonstrated that photocatalysis occurred in the absence of
459 oxidant (as it does here) and through confirming more rapid dissolution of the ZnO under these
460 conditions, it was hypothesized that this was likely to be through a Mars Van Krevelen type
461 mechanism, where lattice oxygen from the ZnO films were consumed under oxygen limited
462 conditions. The effect was more pronounced in less crystalline structures (i.e. more defects,

463 which aid photo-dissolution). Similar results are seen in this work, so it is therefore possible that
464 the same may also be happening with the HAP here.
465 Therefore, the decrease in the absorbance intensity due to PO_4^{3-} and HPO_4^{2-} in Fig. 13 may
466 indicate that these groups are being photo-dissolved in order for the lattice oxygen to participate
467 in the redox reactions degrading the methylene blue. This is perhaps due to the trapped electron
468 generated by the UV irradiation forming surface P-OH radicals on HAP. This photo-degradation
469 would also deactivate the HAP photocatalyst, which may also be a contributing factor to the drop
470 in reaction rate in the latter stages of the reaction as outlined earlier.

471 **<Fig. 13 here>**

472 This all indicates that like the ZnO photocatalysts, the HAP photocatalytic reaction mechanism
473 in both the solid and liquid phases are not fully understood and is different to what is expected
474 from the currently available photocatalysis literature. Further work is therefore continuing,
475 characterising a full range of HAP structures and photocatalytic reaction mechanisms in both the
476 solid and liquid phases, determining the optimal conditions and operating envelope for
477 stabilising this photocatalyst deactivation pathway whilst maintaining acceptable photocatalytic
478 activity.

479

480 **4. Conclusions**

481 It has been demonstrated that it is possible to use waste mussel shells (*Perna Canaliculus*) as a
482 calcium source to form lime (calcium oxide) and then hydroxyapatite (HAP) by first pyrolysis at
483 800°C and then a wet precipitation method at room temperature and without pH control in a short
484 5 hours reaction time. A further heat treatment at 800°C increased the crystallinity of the HAP

485 formed. The HAP produced was comparable to a commercial HAP, although the as-synthesised
486 material contained residual calcite due to incomplete calcination. This calcite was removed by
487 the subsequent heat treatment step following HAP production.

488 It has been shown for the first time that this mussel derived HAP can be used as a photocatalyst
489 for the degradation of aqueous pollutants. Methylene blue was successfully degraded (primarily
490 measured as decolourization at a UV-Vis wavelength of 662 nm) by the heat treated HAP
491 photocatalyst under both oxygen limited and oxygen rich conditions. Under oxygen limited
492 conditions, the degradation of methylene blue was approximately 39% after 6 hours and showed
493 no further increase with longer durations. For the oxygen rich conditions, degradation during the
494 initial 6 hours was approximately 54% and increased to 62% after 24 hours. The
495 photodegradation of methylene blue in the presence of HAP as photocatalyst is well modelled by
496 a series of three first-order- reactions with the first stage reaction rate constant is $6.2 \times 10^{-3} \text{ min}^{-1}$,
497 followed by $1.2 \times 10^{-3} \text{ min}^{-1}$ for the second stage and finally approximately (due to limited data
498 in this kinetic stage) $1.6 \times 10^{-4} \text{ min}^{-1}$ for the third stage with an average reaction rate of 2.5×10^{-8}
499 $\text{mol L}^{-1}\text{min}^{-1}$ over all three stages. These three reaction stages reflect the currently understood
500 photocatalytic reaction pathway: primary degradation of methylene blue to azo dye
501 intermediates, then secondary degradation to smaller more highly oxidised intermediates and
502 finally degradation of recalcitrants. The final two steps of the reaction had significantly slower
503 rates than the initial step, which tie in with this mechanism, however it also could indicate that
504 the reaction is either product inhibited and/or affected by catalyst deactivation. FTIR analysis of
505 the HAP before and after the photocatalysis experiments showed a decrease in the absorbance
506 intensity of PO_4^{3-} and HPO_4^{2-} , indicating photo-dissolution of the HAP. This is perhaps due to
507 trapped electrons generated by the UV irradiation forming surface P-OH \cdot radicals on HAP, which

508 can participate as the oxygen and/or oxidant source for the reactions under oxygen limited
509 conditions, but therefore also causing catalyst deactivation through dissolution. This indicates
510 that the photocatalytic reaction mechanism in both the solid and liquid phases is different to what
511 is normally expected from the currently available photocatalysis literature, providing a platform
512 for future work exploring the materials and operating envelopes for stabilising this photocatalyst
513 deactivation pathway whilst maintaining acceptable photocatalytic activity.

514 Overall this project indicates that waste mussel shells can be converted into a HAP photocatalyst
515 with good photocatalytic activity. This potentially provides a greener route for recovering and
516 recycling waste shells into hydroxyapatite which can be used as alternative photocatalyst in the
517 photocatalytic degradation of wastewater components.

518

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526

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725

726 Fig. 9 - Comparison of the Sulzer Metco commercially sourced HAP (■) and mussel shell
727 derived heat treated HAP (▲) for the photocatalytic degradation under oxygen rich conditions
728 of methylene blue and its azo dye reaction products with concentration of the azo dyes measured
729 using UV-Vis spectroscopy. Both catalysts were loaded at 2.5 g/L.

730

731 Fig. 10 - Three stage first order plot for the kinetic photodegradation of azo dye in the presence
732 of heat treated HAP as photocatalyst under oxygen rich conditions based on the data in Figure 8.

733

734 Figure 11 – HPLC determined reaction profile of the degradation of initially 5 mg/L MB with
735 2.5 g/L of heat treated HAP photocatalyst under oxygen rich conditions, showing the
736 concentration of MB and its degradation intermediates/products over the reaction period.
737 Reaction intermediates/products are: Azure A (AA), Azure B (AB), Azure C (AC) and Thionin
738 (Th). (a) Methylene blue concentration (b) Overall reaction profile with HPLC peak area as a
739 proxy for concentration, (b) close-up of the intermediate/products without major reaction species
740 MB and AB with HPLC peak area as a proxy for concentration.

741
742 Fig. 12 - Comparison of the degradation of the azo dye compounds from methylene blue and its
743 reaction intermediates by photocatalysis at two different stirring speeds with 2.5 g/L heat treated
744 HAP under oxygen rich conditions with concentrations measured using UV-Vis spectroscopy.
745 This shows that external mass transfer resistances are likely to be insignificant at the stirring
746 speeds used.

747
748 Fig. 13 - FTIR spectra for the heat treated HAP powder: (a) before photocatalytic reaction, (b)
749 after photocatalytic reaction.