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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  $\text{PO}_4^{3-}$  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 Abeynaïke *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 (Abeynaïke *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 ( $\text{KH}_2\text{PO}_4$ ) 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,  $\text{Ca(OH)}_2$  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  $\text{cm}^{-1}$ , 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 $\alpha$  X-ray source. Scans were carried out in the 2 $\theta$   
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 CaCO<sub>3</sub> 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<sup>-1</sup>, 877 cm<sup>-1</sup>  
241 and 700 cm<sup>-1</sup> 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<sup>-1</sup> correspond to an aragonite polymorph (Kuriyavar *et al.*, 2000; Nan

244 *et al.*, 2008). The FTIR spectrum in 3(c) shows a band around  $3640\text{ cm}^{-1}$  attributed to hydroxyl  
245 stretching where this band appears due to adsorbed water and  $\text{-OH}$  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  $875\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$   
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  $\text{CO}_2$  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<sup>-1</sup> corresponds to the CO<sub>3</sub><sup>2-</sup> group. The existence of CO<sub>3</sub><sup>2-</sup> ions  
280 in the HAP could also be due to the adsorption of CO<sub>2</sub> 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 CO<sub>3</sub><sup>2-</sup> 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  $\text{CO}_3^{2-}$  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  $\text{PO}_4^{3-}$   
293 and  $\text{OH}^1$  groups characteristic of HAP: the bands at 962, 874 and 559  $\text{cm}^{-1}$  correspond to the  
294  $\text{PO}_4^{3-}$  group (Tanaka *et al.*; Reddy *et al.*, 2007; Wang *et al.*, 2010). Based on several studies done  
295 on HAP as photocatalyst, the  $\text{PO}_3^{4-}$  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  $\text{PO}_3^{4-}$  group changes and create a vacancy on the HAP and consequently will cause  
298 the formation of  $\text{O}_2^\bullet$  through the electron transfer to  $\text{O}_2$  in the atmosphere. The FTIR spectra of  
299 the as-synthesised HAP (Fig. 6a), showed a broad band around 3300  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  seen in both the heat treated and  
310 commercial HAP, which correspond to the  $\text{PO}_4^{3-}$  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  $\text{CO}_3^{2-}$  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  $\text{PO}_4^{3-}$   
444 group at 1087, 960, 594 and 470  $\text{cm}^{-1}$  are drastically decreased after photocatalytic reaction. A  
445 similar trend was observed for the band at 1019  $\text{cm}^{-1}$  which corresponds to the  $\text{HPO}_4^{2-}$  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  $\text{PO}_4^{3-}$  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  $\text{PO}_4^{3-}$  and  $\text{HPO}_4^{2-}$  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  $2.5 \times 10^{-8}$   
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  $\text{PO}_4^{3-}$  and  $\text{HPO}_4^{2-}$ , 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

527 **References**

- 528 Abeynaike, A., Hanley, B., Wang, L., Jones, M.I., Patterson, D.A., 2008. Investigating the  
529 Potential of Using Mussel Shells for the Synthesis of Hydroxyapatite, Chemeca 2008 (36th :  
530 2008 : Newcastle, N.S.W.). Engineers Australia, [Barton, ACT], pp. 615-629.
- 531 Abeynaike, A., Wang, L., Jones, M.I., Patterson, D.A., 2011. Pyrolysed powdered mussel shells  
532 for eutrophication control: effect of particle size and powder concentration on the mechanism  
533 and extent of phosphate removal. *Asia-Pacific Journal of Chemical Engineering* 6, 231-243.
- 534 Akpan, U.G., Hameed, B.H., 2009. Parameters affecting the photocatalytic degradation of dyes  
535 using TiO<sub>2</sub>-based photocatalysts: A review. *Journal of Hazardous Materials* 170, 520-529.
- 536 Ali, A.M., Emanuelsson, E.A.C., Patterson, D.A., 2011. Conventional versus lattice  
537 photocatalysed reactions: Implications of the lattice oxygen participation in the liquid phase  
538 photocatalytic oxidation with nanostructured ZnO thin films on reaction products and  
539 mechanism at both 254nm. *Applied Catalysis B: Environmental*  
540 106, 323-336.
- 541 Ali, A.M., Emanuelsson, E.A.C., Patterson, D.A., 2010. Photocatalysis with nanostructured zinc  
542 oxide thin films: The relationship between morphology and photocatalytic activity under  
543 oxygen limited and oxygen rich conditions and evidence for a Mars Van Krevelen  
544 mechanism, *Applied Catalysis B: Environmental*, pp. 168-181.
- 545 Al-Qasas, N.S., Rohani, S., 2005. Synthesis of pure hydroxyapatite and the effect of synthesis  
546 conditions on its yield, crystallinity, morphology and mean particle size. *Separation Science*  
547 *and Technology* 40, 3187-3224.
- 548 Belkacemi, B., Larachi, F., Sayari A., 2000. Lumped Kinetics for Solid-Catalyzed Wet  
549 Oxidation: A Versatile Model. *Journal of Catalysis* 193, 224–237.

550 Boiarkina, I., Pedron S., Patterson, D.A., 2011. An experimental and modelling investigation of  
551 the effect of the flow regime on the photocatalytic degradation of methylene blue on a thin  
552 film coated ultraviolet irradiated spinning disc reactor. *Applied Catalysis B: Environmental*,  
553 110, 14-24.

554 Boucetta, C., Kacimi, M., Ensuque, A., Piquemal, J.-Y., Bozon-Verduraz, F., Ziyad, M., 2009.  
555 Oxidative dehydrogenation of propane over chromium-loaded calcium-hydroxyapatite.  
556 *Applied Catalysis A: General* 356, 201-210.

557 Castello, G.K., 2009. *Handbook of Photocatalysts: Preparation, Structure and Applications*.  
558 Nova Science Pub Incorporated.

559 Chong, M.N., Jin, B., Chow, C.W.K., Saint, C., 2010. Recent developments in photocatalytic  
560 water treatment technology: A review. *Water Research* 44, 2997-3027.

561 Cullity, B.D., 1956. *Elements of X-Ray Diffraction*. Addison-wesley Publishing Company, Inc.

562 Currie, J.A., Harrison, N.R., Wang, L., Jones, M.I., Brooks, M.S., 2007. A preliminary study of  
563 processing seafood shells for eutrophication control. *Asia-Pacific Journal of Chemical*  
564 *Engineering* 2, 460-467.

565 Dannacher, J., Schlenker, W., 1996. The mechanism of hydrogen peroxide bleaching. *Textile*  
566 *chemist and colorist* 28, 24-28.

567 Davis, B.L., Adams, L.H., 1965. Kinetics of the Calcite $\rightleftharpoons$  Aragonite Transformation. *Journal of*  
568 *Geophysical Research* 70, 433-441.

569 De Groot, K., Klein, C., Wolke, J., de Blicck-Hogervorst, J., 1990. Chemistry of calcium  
570 phosphate bioceramics. *Handbook of bioactive ceramics* 2, 3-16.

571 De Lasa, H.I., Serrano, B., Salaices, M., 2005. *Photocatalytic Reaction Engineering*. Springer.

572 Domínguez, M.I., Romero-Sarria, F., Centeno, M.A., Odriozola, J.A., 2009. Gold/hydroxyapatite

573 catalysts: Synthesis, characterization and catalytic activity to CO oxidation. Applied Catalysis  
574 B: Environmental 87, 245-251.

575 Ferná ndez, E., Gil, F.J., Ginebra, M.P., Driessens, F.C.M., Planell, J.A., Best, S.M., 1999.  
576 Calcium phosphate bone cements for clinical applications. Part I: Solution chemistry. Journal  
577 of Materials Science: Materials in Medicine 10, 169-176.

578 Galvan-Ruiz, M., Hernandez, J., Banos, L., Noriega-Montes, J., Rodriguez-Garcia, M.E., 2009.  
579 Characterization of Calcium Carbonate, Calcium Oxide, and Calcium Hydroxide as Starting  
580 Point to the Improvement of Lime for Their Use in Construction. Journal of Materials in Civil  
581 Engineering 21, 694-698.

582 Gaya, U.I., Abdullah, A.H., 2008. Heterogeneous photocatalytic degradation of organic  
583 contaminants over titanium dioxide: A review of fundamentals, progress and problems.  
584 Journal of Photochemistry and Photobiology C: Photochemistry Reviews 9, 1-12.

585 Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W., 1995. Environmental applications  
586 of semiconductor photocatalysis. Chemical reviews 95, 69-96.

587 Houas, A., Lachheb, H., Ksibi, M., Elaloui, E., Guillard, C., Herrmann, J.-M., 2001.  
588 Photocatalytic degradation pathway of methylene blue in water. Applied Catalysis B:  
589 Environmental, 31, 145–157.

590 Hu, A., Li, M., Chang, C., Mao, D., 2007. Preparation and characterization of a titanium-  
591 substituted hydroxyapatite photocatalyst. Journal of Molecular Catalysis A: Chemical 267, 79-  
592 85.

593 Ji, S., Murakami, S., Kamitakahara, M., Ioku, K., 2009. Fabrication of titania/hydroxyapatite  
594 composite granules for photo-catalyst. Materials Research Bulletin 44, 768-774.

595 Jones, M.I., Wang, L.Y., Abeynaike, A., Patterson, D.A., 2011. Utilisation of waste material for

596 environmental applications: calcination of mussel shells for waste water treatment. *Advances*  
597 *in Applied Ceramics* 110, 280-286.

598 Jun, J.H., Lee, T.-J., Lim, T.H., Nam, S.-W., Hong, S.-A., Yoon, K.J., 2004. Nickel-calcium  
599 phosphate/hydroxyapatite catalysts for partial oxidation of methane to syngas: characterization  
600 and activation. *Journal of Catalysis* 221, 178-190.

601 Khachani, M., Kacimi, M., Ensuque, A., Piquemal, J.-Y., Connan, C., Bozon-Verduraz, F.,  
602 Ziyad, M., 2010. Iron-calcium-hydroxyapatite catalysts: Iron speciation and comparative  
603 performances in butan-2-ol conversion and propane oxidative dehydrogenation. *Applied*  
604 *Catalysis A: General* 388, 113-123.

605 Khataee, A.R., Kasiri, M.B., 2010. Photocatalytic degradation of organic dyes in the presence of  
606 nanostructured titanium dioxide: Influence of the chemical structure of dyes. *Journal of*  
607 *Molecular Catalysis A: Chemical* 328, 8-26.

608 Koutsopoulos, S., 2002. Synthesis and characterization of hydroxyapatite crystals: A review  
609 study on the analytical methods. *Journal of Biomedical Materials Research* 62, 600-612.

610 Kuriyavar, S.I., Vetrivel, R., Hegde, S.G., Ramaswamy, A.V., Chakrabarty, D., Mahapatra, S.,  
611 2000. Insights into the formation of hydroxyl ions in calcium carbonate: temperature dependent  
612 FTIR and molecular modelling studies. *Journal of Materials Chemistry* 10, 1835-1840.

613 Lixiong Li, L., Chen, P., Gloyna, E.F., 1991. Generalized kinetic model for wet oxidation of  
614 organic compounds. *AIChE Journal*, 37, 1687-1697.

615 Liu, Y., Liu, C.Y., Wei, J.H., Xiong, R., Pan, C.X., Shi, J., 2010. Enhanced adsorption and  
616 visible-light-induced photocatalytic activity of hydroxyapatite modified Ag-TiO<sub>2</sub> powders.  
617 *Applied Surface Science* 256, 6390-6394.

618 Mills, A., Le Hunte, S., 1997. An overview of semiconductor photocatalysis. *Journal of*

619 photochemistry and photobiology. *A, Chemistry* 108, 1-35.

620 Mills, A., 2012. An overview of the methylene blue ISO test for assessing the activities of  
621 photocatalytic films. *Applied Catalysis B: Environmental* 128, 144-149.

622 Mostafa, N.Y., 2005. Characterization, thermal stability and sintering of hydroxyapatite powders  
623 prepared by different routes. *Materials Chemistry and Physics* 94, 333-341.

624 Nan, Z., Shi, Z., Yan, B., Guo, R., Hou, W., 2008. A novel morphology of aragonite and an  
625 abnormal polymorph transformation from calcite to aragonite with PAM and CTAB as  
626 additives. *Journal of Colloid and Interface Science* 317, 77-82.

627 Nishikawa, H., 2003. Surface changes and radical formation on hydroxyapatite by UV irradiation  
628 for inducing photocatalytic activation. *Journal of Molecular Catalysis A: Chemical* 206, 331-  
629 338.

630 Nishikawa, H., 2004a. A high active type of hydroxyapatite for photocatalytic decomposition of  
631 dimethyl sulfide under UV irradiation. *J. Mol. Catal. A: Chem.* 207, 149-153.

632 Nishikawa, H., 2004b. Radical generation on hydroxyapatite by UV irradiation. *Materials Letters*  
633 58, 14-16.

634 Nishikawa, H., 2007. Photo-induced catalytic activity of hydroxyapatite based on photo-  
635 excitation. *Phosphorus Research Bulletin* 21, 97-102.

636 Nishikawa, H., Omamiuda, K., 2002. Photocatalytic activity of hydroxyapatite for methyl  
637 mercaptane. *Journal of Molecular Catalysis A: Chemical* 179, 193-200.

638 Parker, J.E., Thompson, S.P., Lennie, A.R., Potter, J., Tang, C.C., 2010. A study of the  
639 aragonite-calcite transformation using Raman spectroscopy, synchrotron powder diffraction  
640 and scanning electron microscopy. *CrystEngComm* 12, 1590-1599.

641 Patterson, D.A., Metcalfe, I.S., Xiong, F., Livingston, A.G., 2001a. Wet air oxidation of linear

642 alkylbenzene sulfonate 1. Effect of temperature and pressure. *Industrial & Engineering*  
643 *Chemistry Research* 40, 5507-5516.

644 Patterson, D.A., Metcalfe, I.S., Xiong, F., Livingston, A.G., 2001b. Wet air oxidation of linear  
645 alkylbenzene sulfonate 2. Effect of pH. *Industrial & Engineering Chemistry Research* 40,  
646 5517-5525.

647 Perić, J., Vučak, M., Krstulović, R., Brečević, L., Kralj, D., 1996. Phase transformation of  
648 calcium carbonate polymorphs. *Thermochimica Acta* 277, 175-186.

649 Pratap Reddy, M., Venugopal, A., Subrahmanyam, M., 2007. Hydroxyapatite-supported Ag-  
650 TiO<sub>2</sub> as *Escherichia coli* disinfection photocatalyst. *Water Research* 41, 379-386.

651 Rakovan, J., 2002. Growth and surface properties of apatite. *Reviews in mineralogy and*  
652 *geochemistry* 48, 51-86.

653 Rauf, M.A., Meetani, M.A., Khaleel, A., Ahmed, A., 2010. Photocatalytic degradation of  
654 methylene blue using a mixed catalyst and product analysis by LC/MS. *Chemical Engineering*  
655 *Journal* 157, 373-378.

656 Reddy, M.P., Venugopal, A., Subrahmanyam, M., 2007. Hydroxyapatite photocatalytic  
657 degradation of calmagite (an azo dye) in aqueous suspension. *Applied Catalysis B:*  
658 *Environmental* 69, 164-170.

659 Resende, N.S., Nele, M., Salim, V.M.M., 2006. Effects of anion substitution on the acid  
660 properties of hydroxyapatite. *Thermochimica Acta* 451, 16-21.

661 Rodriguez-Lorenzo, L., Vallet-Regi, M., 2000. Controlled crystallization of calcium phosphate  
662 apatites. *Chemistry of materials* 12, 2460-2465.

663 Sheng, G., Qiao, L., Mou, Y., 2011. Preparation of TiO<sub>2</sub>/hydroxyapatite composite and its  
664 photocatalytic degradation of methyl orange. *J. Environ. Eng.*, 137, 611-616.



665 Sivakumar, M., Manjubala, I., 2001. Preparation of hydroxyapatite/fluoroapatite-zirconia  
666 composites using Indian corals for biomedical applications. *Materials Letters* 50, 199-205.

667 Solhy, A., Tahir, R., Sebti, S., Skouta, R., Bousmina, M., Zahouily, M., Larzek, M., 2010.  
668 Efficient synthesis of chalcone derivatives catalyzed by re-usable hydroxyapatite. *Applied*  
669 *Catalysis A: General* 374, 189-193.

670 Soon, A.N., Hameed, B.H., 2011. Heterogeneous catalytic treatment of synthetic dyes in aqueous  
671 media using Fenton and photo-assisted Fenton process. *Desalination* 269, 1-16 Soon, A.N.,  
672 Hameed, B.H., 2010.

673 Tanaka, H., Tsuda, E., Nishikawa, H., Fuji, M., 2012. FTIR studies of adsorption and  
674 photocatalytic decomposition under UV irradiation of dimethyl sulfide on calcium  
675 hydroxyapatite. *Advanced Powder Technology* 23, 115-119.

676 Tsuchida, T., Kubo, J., Yoshioka, T., Sakuma, S., Takeguchi, T., Ueda, W., 2008. Reaction of  
677 ethanol over hydroxyapatite affected by Ca/P ratio of catalyst, *Journal of Catalysis*, pp. 183-  
678 189.

679 Wang, P., Li, C., Gong, H., Jiang, X., Wang, H., Li, K., 2010. Effects of synthesis conditions on  
680 the morphology of hydroxyapatite nanoparticles produced by wet chemical process. *Powder*  
681 *Technology* 203, 315-321.

682 Zahouily, M., Abrouki, Y., Bahlaouan, B., Rayadh, A., Sebti, S., 2003. Hydroxyapatite: new  
683 efficient catalyst for the Michael addition. *Catalysis Communications* 4, 521-524.

684 Zhang, Y., Li, Z., Sun, W., Xia, C., 2008. A magnetically recyclable heterogeneous catalyst:  
685 Cobalt nano-oxide supported on hydroxyapatite-encapsulated  $[\gamma]\text{-Fe}_2\text{O}_3$  nanocrystallites  
686 for highly efficient olefin oxidation with  $\text{H}_2\text{O}_2$ . *Catalysis Communications* 10, 237-242.

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