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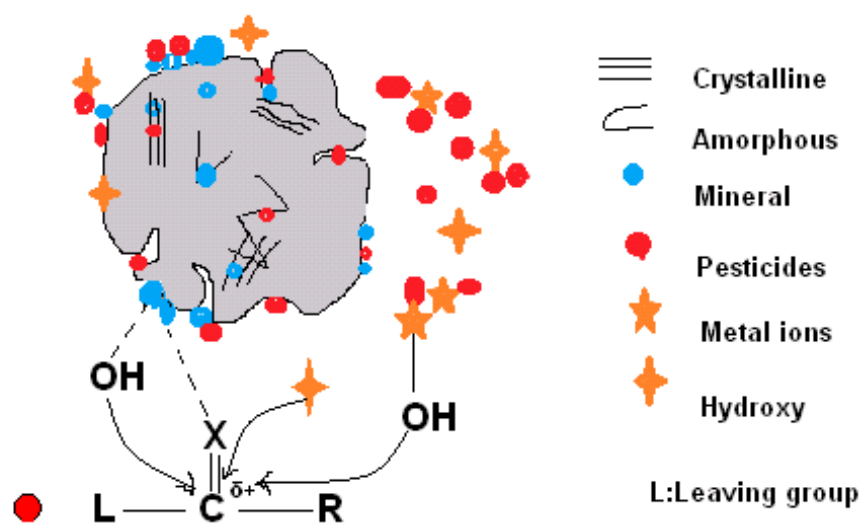
Highlights of the manuscript:

- High ash content biochar can increase solution pH and released metal ions.
- Ash in biochar can combine pesticide through specific interactions.
- Composition and structure of biochar is favor for the hydrolysis of pesticides.

1 **Adsorption and Catalytic Hydrolysis of Carbaryl and Atrazine on Pig Manure –**

2 **Derived Biochars: Impact of Structural Properties of Biochars**

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26 **Adsorption and Catalytic Hydrolysis of Carbaryl and Atrazine on Pig Manure –**

27 **Derived Biochars: Impact of Structural Properties of Biochars**

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32 **Abstract:** Biochars were produced from pig manure to elucidate the influence of biochars

33 with high ash contents on the fate of pesticides. Adsorption and catalytic hydrolysis of

34 carbaryl and atrazine on original biochars and deahed biochars were investigated. The

35 two pesticides were substantially adsorbed by the biochars, with organic carbon

36 normalized sorption coefficient (K_{oc}) values of $10^{2.65}$-$10^{3.66}$ L/kg for carbaryl and

37 $10^{1.90}$-$10^{3.57}$ L/kg for atrazine at C_e of 0.5 mg/L. Hydrophobic effect alone could not explain

38 the sorption, and several other processes including pore-filling and π-π electron

39 donor-acceptor interactions were involved in pesticide adsorption. Adsorption increased

40 greatly on the deashed biochar, indicating that some organic sorption sites in the original

41 biochars were blocked or difficult to access due to their interactions with inorganic moiety.

42 The pesticides were found to hydrolyze faster in the presence of biochars, and in the

43 presence of biochar pyrolyzed at 700 ℃, carbaryl and atrazine were decomposed by

44 71.8% and 27.9% in 12 h, respectively. The elevated solution pH was the main reason for

45 the enhanced hydrolysis; however both the mineral surface and dissolved metal ions

46 released from the biochars were confirmed to catalyze the hydrolysis.

47 **Keywords:** Biochar; Carbaryl; Atrazine; Sorption; Hydrolysis

2

1. Introduction

48

49   Biochar is a carbonaceous material produced from oxygen–limited pyrolysis of

50 biomass [1]. Interest in biochars has recently increased because the application of

51 biochars on farmland has been advocated to provide a means of sequestering carbon and

52 increasing soil fertility [2-4]. Biochars show extraordinarily strong adsorption affinities for

53 contaminants [5-8]. The adsorption of hydrophobic organic chemicals (HOCs) on biochars

54 and other carbonaceous materials has been well documented [5, 9, 10], with adsorption

55 coefficients (K_d) of 10^3-10^8 L/kg. The highly aromatic and porous structures in biochars,

56 which favor both hydrophobic effect and specific interactions, have been suggested to

57 contribute to the high adsorption coefficients [11,12].

58   Until now, the majority of studies concerning the adsorption of organic chemicals

59 have been limited on biochars derived from plant residues [13-17]. Plant-derived biochars

60 commonly contain low amounts of inorganic moiety (ash), so the effect of ash on HOC

61 adsorption has usually been neglected. Livestock manure is an important agricultural

62 waste biomass, and using such manure to produce biochar is a possible approach to

63 recycling livestock manure [18]. Biochars derived from livestock manures may have quite

64 different compositions compared to those from plant residues. One important difference is

65 that biochars derived from livestock manures usually contain high ash content [19-20].

66 The high content of ash and its interaction with organic moieties may influence the

67 interactions of biochars with organic pollutants. The influence of the interaction between

68 inorganic and organic moieties on sorption capacity has been extensively studied on

69 natural geosorbents [21, 22], with conflictive results. Generally, mineral surfaces inhibit

3

70   the non-specific adsorption of organic moieties by reducing the accessibility of organic

71   sorption sites [23]; this is particularly true for the partitioning of apolar organics [24].

72   However, mineral surfaces can also enhance sorption of polar organic chemicals through

73   specific interactions, such as electron donor-acceptor [25] and H-bonding interactions [26].

74   For ionizable organics, they may provide sites for additional interactions of cation or anion

75   binding. Though these mechanisms have been proposed previously, the influence of

76   biochars of high ash content on the fate of organic pollutants has seldom been studied

77   [27-29].

78   Pesticides are common soil pollutants. Adsorption on biochars has been studied for

79   some pesticides, such as diuron [30], triazine [31], and dieldrin [32]. Though the

80   adsorption capacity of biochars for polar pesticides was not as large as those for apolar

81   HOCs [33], biochars are generally good adsorbents for pesticides, with K_d values ranging

82   between 10^1 and 10^3 L/kg [30-32]. Hence, the application of biochars to soils can have

83   great impact on the fate of pesticides. Moreover, modern pesticides are designed to be

84   easily degraded. Hydrolysis is an important mechanism for abiotic degradation of

85   pesticides. Many factors influence pesticide hydrolysis, which include the pH, dissolved

86   ions as well as the presence of clay and metal oxides that can catalyze the hydrolysis

87   reaction [34-36]. Manure–derived biochar contains a high ash content, which is expected

88   to influence the hydrolysis of pesticides. However, there is no prior study on this aspect of

89   biochars.

90   The objective of this study was to obtain a thorough understanding about the effects

91   of biochars with high ash content on the fate of pesticides. Two biochar samples were

4

92   produced from pig manure by pyrolysis at different temperatures. One carbamate

93   insecticide, carbaryl and one *S* – triazine herbicide, atrazine were selected as model

94   pesticides. The adsorption and the catalytic hydrolysis of these two pesticides were

95   studied on both original and deashed biochars. The mechanisms of adsorption and

96   catalytic hydrolysis were then discussed.

97   **2. Experimental Section**

98   **2.1 Materials.**

99   Carbaryl (98%) was obtained from Haili Chemical Company (Hunan, China), and

100   atrazine (97%) was obtained from Rainbow Chemical Company (Shandong, China). The

101   pesticides were used in batch experiments without purification. Analytical standards for

102   the pesticides were purchased from Accustandard (Connecticut, US). Other chemicals

103   used in this study were all analytical or HPLC grade.

104   **2.2 Biochars.**

105   Pig manure stock was collected from a hoggery in Jixian County, Tianjin, China. The

106   pig manure was air–dried and ground to pass through a 2–mm sieve. The manure was

107   then heated at 350 ℃ or 700 ℃ in a ceramic pot covered with a tight-fitting lid (where

108   oxygen was soon exhausted) in a preheated muffle furnace for 2 h [37]. The produced

109   biochars were ground to pass through 0.038 - 0.075 mm (200 - 400 mesh) sieves and

110   stored in amber glass bottles. Based on the temperature they were heated at, the

111   biochars were designated as BC350 and BC700.

112   To remove the ash (deashing) of the biochars, the samples of the original biochars

113   were treated with acid [38]. Batches consisting of 20 g of biochar were mixed and shaken

5

114   in 200 mL of 1 M HCl for 10 h. That treatment was carried out 4 times for each batch. The

115   entire procedure was then repeated using 200 mL of a 1 M: 1 M HCl – HF solution. The

116   treated biochars were rinsed with de–ionized water several times to remove residual acid

117   and soluble salts until the solution pH was neutral. The resulting biochar samples were

118   freeze–dried and stored in desiccators for later use. Base on the original heating

119   temperatures, these deashed biochar samples were referred to as DABC350 and

120   DABC700.

121   **2.3 Characterization of Biochars.**

122   Bulk organic elemental composition (C, H, and N) of the biochar samples was

123   determined by an element analyzer (Elementar Vario EL, Germany). Ash content of the

124   samples was measured by the residual weight after heating the biochars at 750 ℃ for 6 h

125   [37], and the O content was calculated by mass difference. Surface elemental composition

126   of biochars was quantified using an X–ray photoelectron spectrometer (XPS) (ULVAC-PHI

127   PHI 5000 VersaProbe II, Japan). Surface area and pore volume were measured by a

128   surface area analyzer (Quantachrome NOVA 2200e, USA). Solid-state ^{13}C NMR spectra

129   were obtained by using the cross-polarization and total-sideband suppression (cptoss)

130   method on a 7 mm magic angle–spinning (MAS) probe (BRUKER AVANCE III, Germany).

131   Fourier transform infrared spectroscopy (FTIR) spectra of biochars were recorded

132   between 4000 and 400 cm^{-1} wave numbers using an FTIR spectrometer (Perkin Elmer

133   1725 X, USA).

134   **2.4 Batch Sorption Experiments.**

135   A total of four sorbents, i.e., BC350, BC700, DABC350, and DABC700, were studied.

6

136   Sorption isotherms for each sorbent were determined at six different initial solution

137   concentrations, with duplicate measurements at each concentration point. An aliquot of 50

138   mg of each sorbent was weighted into a 40 mL vial (US EPA) with a

139   polytetrafluoroethylene (Teflon)–lined screw cap, followed by 40 mL of a background

140   solution. The background solution contained 5 mM $CaCl_2$ to maintain a constant ionic

141   strength and 200 mg/L $HgCl_2$ (pH 6.5) to inhibit aerobic biodegradation. After

142   pre-equilibration for 24 h, designated amounts of pesticide stock solutions were spiked

143   into each vial, with the volume percentage of methanol kept below 0.2% to minimize

144   possible cosolvent effects on sorption. Initial concentrations of carbaryl were 1, 2.5, 5, 8,

145   20, 40 mg/L; while those of atrazine were 2, 4, 8, 10, 20, 30 mg/L. All of the vials were left

146   with minimal head space and sealed with Teflon film. The vials were put in a shaker

147   operated at 150 rpm and 20 – 24 ℃ in the dark for 24 h. The equilibration time was

148   predetermined, and 24 h was confirmed to be enough to reach an apparent equilibrium.

149   After equilibration, the vials were centrifuged at 3000 rpm for 20 min. Before analyzing by

150   high performance liquid chromatography (HPLC), the supernatant was filtered through

151   0.45 μm PTFE syringe filters (Shanghai ANPLE, China), and external standards were also

152   filtered to correct the solute loss due to filtration (less than 4%). The results of control

153   samples without biochar indicated that the losses of pesticides by evaporation,

154   photochemical decomposition, and sorption to vials, etc. were less than 4%.

155   Details of pretreatment and analysis of samples were described in Supplementary

156   Information (SI).

157   **2.5 Hydrolysis in the Presence of Biochars.**

7

158   Hydrolysis of the two pesticides was investigated in suspensions containing the

159   original biochars. Aliquot of 50 mg BC350 and BC700 were suspended in 40 mL

160   background solution (the same as in sorption experiment) in US EPA vials. After 24 h of

161   pre–equilibrium, pesticide stock solution was added to each vial to obtain spiked

162   concentrations of 5 mg/L. The vials were capped and shaken in the dark at 150 rpm at 20

163   – 24 ℃ for 7 d. Pesticide concentrations in the liquid phase and on biochar particles were

164   then measured. In addition, hydrolysis in the presence of 500 mg of original biochar was

165   tested to investigate the influence of biochar dose. The residue pesticides both in

166   aqueous and on solid phase were measured using the methods described in the SI and

167   the hydrolysis extents of the pesticides were calculated based on mass balance. The pH

168   of each suspension was monitored during the entire experiment.

169   **2.6 Mechanisms behind the Enhanced Hydrolysis.**

170   To investigate mechanisms for the enhanced catalytic hydrolysis of the pesticides in

171   the presence of biochars, several hydrolysis experiments were designed. Firstly,

172   hydrolysis was performed in background solutions without biochars at pH values of 6.5

173   and 9.1, which were similar to the pH values measured in the suspensions with 50 and

174   500 mg of biochar, respectively. The pH values of the background solutions were adjusted

175   using phosphate or boric acid/ borax buffer solution as appropriate. Secondly, hydrolysis

176   was performed in biochar suspensions (500 mg) with the solution pH adjusted to neutral

177   pH (6.8) before the pesticides were spiked. Thirdly, hydrolysis tests were performed in

178   biochar leachate. For this set of tests, 500 mg samples of biochar were shaken in 40 mL

8

179   background solutions at 150 rpm and 20 - 24 ℃ for 24 h. The biochars were then

180   removed from the suspensions by filtration through 0.45 μm membranes. The leachate

181   solutions were divided into two groups, with the pH of one group adjusted to neutral (6.8)

182   and the other not adjusted. Other manipulations were the same as described above.

3   Results and Discussion

3.1 Characterization of Biochars.

185   The bulk chemical compositions of the original biochars derived from pig manure at

186   the two temperatures and the corresponding deashed biochars are shown in Table 1. The

187   ash content of the biochars was greater at higher pyrolyzing temperature (45.3% for

188   BC350 and 66.8% for BC700). These are much higher than the common ash contents of

189   biochars derived from plant sources [37]. The carbon content of BC700 (25.2%) was lower

190   than that of BC350 (31.6%). This finding is not in agreement with an earlier study on

191   biochars with low ash contents [33]. As the charring temperature increased, some

192   amorphous carbon was burn into carbon dioxide [39], resulting in the higher ash content

193   and lower carbon content in BC700 compared to BC350.

194   At higher temperatures, some of the amorphous carbon could also be transformed

195   into aromatic carbon [37]. The atomic ratios of H/C and [(O + N)/ C] are recognized as

196   indices for aromaticity and polarity, respectively [40]. In the present study, bulk aromaticity

197   of the biochar increased and polarity decreased with charring temperature, as indicated

198   by the decreasing H/C and [(O + N)/ C] ratios.

199   The ^{13}C NMR spectra showed that the proportion of alkyl carbon in the total organic

200   carbon of the biochars decreased from 30% to 13%, while the aromatic carbon proportion

9

201 slightly increased from 37% to 43% as the charring temperature increased. Deashing

202 treatment efficiently reduced the ash content of biochars (Table 1). As a result, organic

203 matter in the deashed biochars greatly increased (> 93%). The bulk polarity of the

204 deashed biochars decreased as indicated by the reducing [(O + N)/ C)]; while the

205 aromaticity increased as indicated by the reducing H/C. Deashing also increased the

206 number of acidic functional groups, such as phenolic and carboxyl groups (Table 1). This

207 observation is in agreement with previous findings showing that alkaline functional groups

208 are decreased by acid treatment [41].

209 Surface elemental compositions, surface areas and pore volume of the biochars are

210 presented in Table 2. The surface elemental composition of the original biochars was very

211 complex, with carbon as the dominant element, followed by oxygen. The results also

212 revealed the presence of mineral elements such as Al and Si on the surfaces of original

213 biochars. The surface polarity [(O + N)/ C] of BC350 was smaller than that for BC700,

214 which was opposite to the trend in the polarity for the bulk material. The different trends in

215 bulk and surface polarity between BC350 and BC700 indicated their heterogeneous

216 structure.

217 All surface element contents decreased after deashing except for C. The elements of

218 Al and P even could not be detected after deashing. Similar to the bulk biochar, the

219 surface polarity of the deashed biochars decreased, as indicated by the decreasing [(O +

220 N)/ C]. The reduction degree of polarity on the surface was greater than that of the bulk

221 biochar, suggesting that mineral oxides and salts (containing N, P, and S) were the main

222 components of ash covering the surface of biochars. The inorganic fraction was not

10

223 removed completely after deashing, indicating that some minerals were masked by

224 organic matter or were located deeper in the biochar.

225   The surface area of biochars increased from 23.8 to 32.6 m^2/g as charring

226 temperature increased. This increase was attributed to a greater transformation in the

227 elemental composition with increasing temperature. After deashing, the surface area and

228 pore volume increased due to the removal of surface minerals, and greater change

229 occurred in the BC700. The characteristics of surface area and pore volume of biochar

230 depend much on pyrolyzing temperature. At low temperature, amorphous carbon is the

231 main carbon, and pores are not well developed. Some pores are blocked by aliphatic or

232 volatile constitutes that also reduce surface area. Under high temperature, amorphous

233 carbons condense to crystalline carbons, more pores are formed, and aliphatic and

234 volatile constitutes are removed [37]. This is why greater change occurred in BC700 with

235 more micropores as compared to BC350 after the removal of inorganic constitutes by

236 deashing.

237   The FTIR fingerprints appear to be quite different for biochars derived at different

238 temperatures (Figure 1). In BC700, hydroxyl was oxidized as indicated by the loss of peak

239 intensity at 3665 cm^{-1}, while aliphatic carbon was transformed as indicated by the

240 reduction in intensity of peaks at 2885 – 2850 cm^{-1} and 1740 - 1700 cm^{-1} [37]. After

241 deashing, the amount of carboxyl groups increased slightly, as indicated by the increasing

242 height of peaks at 1500 – 1450 cm^{-1} and 1350-1300 cm^{-1}. These results are consistent

243 with the ^{13}C NMR results (Table 1).

244 **3.2 Sorption Isotherms**.

11

245   Sorption isotherms of carbaryl and atrazine on the original and deashed biochars are

246 presented in Figure 2. The adsorption data were fitted to the Freundlich model given by Q_e

247 = $K_f C_e^{n}$, where Q_e (mg/kg) and C_e (mg/L) are the adsorbed and aqueous – phase

248 equilibrium concentrations, respectively; K_f ((mg/kg)/ (mg/L)^{n}) is the affinity coefficient; and

249 n is the linearity index. All samples showed nonlinear isotherms except atrazine on BC350,

250 and the nonlinearity of sorption isotherm was greater at higher pyrolyzing temperature

251 (Table 3). Biochars could effectively sorb carbaryl and atrazine, and the corresponding K_f

252 values of on BC700 were $10^{2.85}$ and $10^{2.77}$, respectively, being significantly higher

253 ($P<0.001$) than those on BC350 ($10^{2.06}$ and $10^{1.40}$). After deashing, the sorption capacity of

254 biochars increased significantly ($P<0.001$). The K_f of carbaryl and atrazine increased to

255 $10^{3.35}$ and $10^{3.15}$ on DABC350, and to $10^{3.70}$ and $10^{3.55}$ on DABC700, respectively. Hence,

256 among the two biochars, BC700 had greater sorption capacity; and deashing further

257 enhanced the sorption.

258   It is well known that organic carbons play a crucial role in the sorption of organics. To

259 evaluate the sorption capacity of organic carbons in different biochars, the organic carbon

260 normalized sorption coefficients (K_{oc}) at equilibrium concentrations of 0.5 and 20 mg/L

261 were calculated (Table 3) by $K_{oc} = Q_e/(C_e f_{oc})$, where f_{oc} (C contents in Table1) is organic

262 carbon content of the sorbent [42,43]. Firstly, the K_{oc} values were $10^{2.65}$-$10^{4.00}$ L/kg for

263 carbaryl and $10^{1.90}$-$10^{3.85}$ L/kg for atrazine at C_e of 0.5 mg/L, being greater for biochars

264 acquired at higher temperature. This suggests that the organic carbon in biochars

265 generated at different temperatures have different sorption capacity. Secondly, K_{oc}

266 increased after deashing, suggesting that the removal of ash enhanced the accessibility of

12

267   sorption sites in organic moiety. Thirdly, K_{oc} decreased at higher solute concentration (20

268   mg/L), suggesting the heterogeneous nature of sorption sites. The sites with high sorption

269   affinity may have been saturated in face to high solute concentration. The K_{oc} in the

270   present study are higher than literature values of carbaryl ($10^{2.02}$-$10^{2.59}$) in soil [44] and

271   atrazine ($10^{1.91}$-$10^{2.42}$) in biochar amended soil [45].

3.3 Sorption Mechanisms.

273   To elucidate the controlling factor in biochar on sorption, K_{oc} values were correlated

274   with the structural parameters of the biochars. No significant correlation was found

275   between K_{oc} values of pesticides on biochars and the hydrophobic carbon contents (alkyl

276   and aromatic moieties, Table 1) in biochars. As hydrophobic carbon components,

277   aromatic carbon can provide sorption sites for hydrophobic effect and pore-filling, and

278   some studies have found that K_{oc} correlates positively with aromatic carbon contents in

279   sorbents [24, 46]. However, in this study, due to the high content of ash, the aromatic

280   carbon content of biochars is positively correlated with the O-alkyl and carboxyl carbon

281   content (Pearson correlation coefficient, r = 0.983, 0.988, $p < 0.05$). The surrounding polar

282   O-alkyl and carboxyl groups would have reduced the accessibility of aromatic domains to

283   pesticides. Hence, hydrophobic partition is not the only factor affecting pesticide sorption

284   on biochars, and other specific interactions may be involved.

285   To reveal the possible effect of porosity on sorption, surface area–normalized

286   adsorption isotherms of the two pesticides were drawn (Figure A.1 in Supplementary

287   Information). It can be seen that the normalized sorption on BC350 was obviously lower

288   than those on other biochars. This could be attributed to a lack of micropores in BC350

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289   compared to other biochars (Table 2). In addition, the normalized adsorption for atrazine

290   was slightly higher than that for carbaryl at low solute concentration; this could be related

291   to the smaller molecular size of atrazine compared to carbaryl (0.61 nm versus 0.71 nm,

292   Figure A.3 in Supplementary Information). These findings suggested that pore-filling effect

293   was a main mechanism for pesticide sorption on the biochars and contributed more at low

294   solute concentrations.

295   Strong adsorption of HOCs on micro- and mesoporous carbon is usually driven by

296   specific interactions [10-11, 24-25]. In the present study, the chlorine substituent in

297   atrazine and the ester group in carbaryl have electron–withdrawing natures, making the

298   associated aromatic π–structures electron acceptors, which could interact with the

299   aromatic carbon (electron–donors) on the biochar surface through $\pi-\pi$ electron

300   donor-acceptor (EDA) interactions. Previous studies have shown that $\pi-\pi$ interactions

301   are much stronger than Van der Waals forces [21]. Therefore, the high adsorption affinity

302   between the pesticides and the biochars may have resulted from specific interactions

303   between the pesticide molecules and the biochar surface.

304   Moreover, the polarity of sorbents has been elucidated to exhibit negative effect on

305   the sorption of organic compounds. Recent literature proposed that surface polarity is a

306   more important parameter affecting adsorption than bulk polarity [24]. In the present study,

307   K_{oc} values at two equilibrium concentrations (0.5 and 20 mg/L) on different biochars

308   displayed an insignificant negative correlation (P>0.05) with the bulk polarity index [(O +

309   N)/ C] for both pesticides, while no clear correlation was observed for surface polarity

310   (Figure A.2 in Supplementary Information). The surface polarity of BC700 was the highest

14

311   due to its highest ash content; while it exhibited a substantially high sorption capacity. This

312   is because the two pesticides can be adsorbed to mineral ash through specific

313   interactions. Carbaryl is a neutral insecticide that contains an ester group. It has been

314   reported that clay minerals can adsorb carbamate insecticide through site-specific

315   interactions between the carbamate functional group and exchangeable cations on solid

316   surface [47]. Atrazine is a weak base, with a pK_a of 1.68 [48]. At the pH used in this study,

317   atrazine existed as neutral molecules, therefore, they could form weak hydrogen bonds to

318   the clay surface or carboxyl groups through their heterocyclic nitrogen atoms [49]. In

319   addition, the surface of BC700 was not covered completely by ash, and uncovered

320   aromatic sites were available for sorption and contributed to the high sorption capacity.

321   After deashing, the sorption increased. To estimate the influence of ash and its

322   interaction with organic moieties in adsorption, the adsorption capacity of the deashed

323   biochars was taken as the adsorption capacity of the organic matter fraction in the original

324   biochars. Estimated isotherms fractionized by organic matter content in the original

325   biochars were then drawn (Figure 2). For carbaryl, the estimated isotherm for BC350 is

326   well above its measured isotherm; while the one for BC700 is close to the measured

327   isotherm. Similar trend was observed for atrazine. These results indicate that though the

328   ash could combine with the pesticides, the ash also reduced the sorption onto organic

329   matter by covering sorption sites or making the sorption sites more difficult to access. As a

330   result, the overall contribution of ash to adsorption in the original biochar, which was a

331   complex of ash and organic matter, was very weak or even negative [25]. The difference

332   between the measured and predicted isotherms was more obvious for BC350 compared

15

333   to BC700. This is because BC350 contained more amorphous carbons, which exhibit

334   mainly partition and weak interaction; while BC700 contained crystalline carbons of

335   specific interactions [50, 51]. Hence, the adsorption affinity of BC350 was weak compared

336   to BC700, and the negative effect of inorganic moiety in BC350 was greater than that in

337   BC700.

338   **3.4 Hydrolysis.**

339   Carbaryl was hydrolyzed markedly in the suspension of the original biochars ($P<0.05$),

340   and the hydrolysis occurred in two phases (Figure 3). The 7 d hydrolysis extents ranged

341   between 23.5% and 90.6%, being greater at higher biochar dose and in the presence of

342   biochar acquired at higher pyrolysis temperature ($P< 0.05$, Table 4). The hydrolysis of

343   atrazine was much weaker than that of carbaryl ($P<0.05$). The hydrolysis extents of

344   atrazine in the presence of different doses of the original biochars were less than 25%

345   except in the presence of 500 mg BC700, where a 7 d hydrolysis extent of 63.4% was

346   achieved (Figure 3b, Table 4). Deashing of the chars decreased the hydrolysis extents of

347   the two pesticides. The 7 d hydrolysis extents ranged between 14.3% and 16.6% for

348   carbaryl and 8.5% and 10.2% for atrazine in suspensions containing 500 mg deashed

349   biochars (Figure A.4, Table 4).

350   **3.5 Mechanisms behind the Enhanced Hydrolysis.**

351   The pH is a crucial factor affecting the hydrolysis. Both the residue minerals and

352   aromatic structure in biochars could lead to an elevation in pH [52]. As shown in Table 4,

353   at the low biochar dose (50 mg), the pH of the suspensions was weakly basic (7.1 for

354   BC350 and 7.6 for BC700). The pH increased significantly as the biochar dose increased

16

355   to 500 mg (7.9 for BC350 and 9.1 for BC700). Hydrolysis of the carbamate ester bond in

356   carbaryl is typically base–catalyzed [53]. Hence, the elevated pH could explain the

357   enhanced hydrolysis of carbaryl in the presence of biochar. Atrazine is a moderately

358   persistent herbicide that can be hydrolyzed in strong acidic or alkaline solutions [54]. The

359   pH values of biochar suspensions were only weakly basic except for BC700 at the dose of

360   500 mg, and these weakly basic suspensions could not efficiently catalyze the hydrolysis

361   of atrazine. The pH values of suspensions containing 500 mg deashed biochars were 6.5

362   and 6.6 for DABC350 and DABC700, respectively. This could partially explain the

363   decreasing hydrolysis of the pesticides in suspensions of the deashed biochars.

364   To confirm the effect of elevated pH on hydrolysis, the hydrolysis of the two pesticides

365   was examined in background solution with adjusted pH (Figure A.5). Two pH values (6.5

366   and 9.1) were selected based on the pH values of the biochar suspensions. Carbaryl was

367   hydrolyzed slowly at pH 6.5, with a 7 d hydrolysis extent of 14.5%; however, at pH of 9.1,

368   the hydrolysis became faster and 86.5% of carbaryl decomposed after 24 h. The

369   hydrolysis extent of atrazine was very weak, with less than 20% decreasing within 7 d

370   even at pH 9.1.

371   The hydrolysis extent of the pesticides in biochar suspensions differed a lot from

372   those in pure background solutions with the same pH values, and both enhancement and

373   inhibition occurred. The reduced hydrolysis in the presence of biochar, such as the case

374   for carbaryl in suspension containing 500 mg of BC700, could be explained by the

375   reduced availability of sorbed pesticides for chemical reaction. This result is consistent

376   with our other study, in which we found that Fenton oxidation of pyrene was significantly

17

377 reduced after pyrene was sorbed onto soils [55]. However, hydrolysis was markedly

378 greater in the presence of biochar for some cases, such as for atrazine in the suspension

379 containing 500 mg of BC700 (*P*<0.05). This result indicated that factors other than pH may

380 catalyze the hydrolysis of pesticides.

381 To find the catalytic effects of other factors, the hydrolysis of the two pesticides was

382 examined in the suspension containing 500 mg biochar with pH adjusted to neutral (6.8)

383 so that the effects of pH could be excluded (Figure A.6 and Table 4). Hydrolysis of both

384 pesticides occurred in neutral biochar suspensions, and the hydrolysis was greater in the

385 presence of BC700 compared to BC350. The 7 d hydrolysis extent was 59.3% and 33.5%

386 for carbaryl and atrazine in the neutral suspensions containing 500 mg of BC700,

387 respectively. Previous studies found that clay and metal oxides can catalyze the

388 hydrolysis in several ways [56]. Bound metal atoms present at solid surface may

389 coordinate a hydrolysable moiety by forming complexes with pesticides, which would

390 facilitate the nucleophilic attack of water molecules. In addition, hydroxo groups bound to

391 the surface may act directly as nucleophiles. Furthermore, adsorption on the surface (or in

392 vicinal water surrounding the surface) leads to accumulation of reactants (organic

393 compounds and nucleophiles), thus facilitating the reaction. The original biochars used in

394 this study, especially BC700, had high ash contents. This could explain the catalytic

395 capacity of the biochars for pesticide hydrolysis.

396 Moreover, biochars may release metal ions into solution, which can catalyze

397 hydrolysis via similar mechanisms as a mineral surface [56]. First, metal species may

398 facilitate the attack of a nucleophile, analogous to proton catalysis. Second, dissociation of

18

399   a leaving group may be promoted by interaction of the leaving group with a metal center.

400   Third, a nucleophile bound to metal centers (metal hydroxo species) may have a higher

401   nucleophilicity as compared to its nucleophilicity in bulk water. To illustrate the possible

402   effect of the dissolved ions, the hydrolysis of two pesticides in the leachate of 500 mg

403   original biochar was investigated (Figure A.7). Hydrolysis of carbaryl was more rapid than

404   that in the background solution at the same pH (Table 4). When the pH was adjusted to

405   neutral, the hydrolysis of carbaryl was still substantial, and a 7 d percentage hydrolysis of

406   40% was achieved. This result indicates that metal ions in the suspensions also contribute

407   to catalyze the hydrolysis of carbaryl. Metal ions were scanned by ICP-MS (Table A.1),

408   and alkali, alkali-earth, and transition metals were detected, with transition metals in

409   relatively lower amounts. After deashing, metal ions in the leachates were reduced by

410   three to five orders of magnitudes (Table A.1). The change in metal ions together with that

411   in pH could explain the decreasing hydrolysis in the presence of deashed biochars.

412   However, the hydrolysis of atrazine in the leachate of original biochars was weak, with all

413   samples less than 12%. This suggests that dissolved ions had less effect on atrazine

414   catalytic hydrolysis.

415   4 **Conclusions**

416   This research evaluated the impacts of biochars derived from pig manure, which have

417   high ash contents, on the fate of two pesticides (carbaryl and atrazine). In the original

418   biochar, which is a complex of organic matter and inorganic ash, pore-filling and specific

419   interactions contributed much to adsorption of the pesticides besides hydrophobic effects.

420   The ash can combine pesticides by specific interactions, however, its enhancement in

19

421   sorption was counteracted because the adsorption sites of organic moieties were masked

422   by ash. After deashing, sorption was enhanced significantly, and DABC700 has the

423   highest sorption capacity. Hydrolysis of carbaryl was enhanced in the suspensions of

424   biochar, due to the catalytic effects of elevated pH, released dissolved metal ions and the

425   mineral surface. However, hydrolysis of atrazine was mainly enhanced by high pH and

426   mineral surface. The influence of biochar on the fate of pesticides can vary greatly due to

427   different chemical compositions and steric conformations. Such influences should be

428   systematically studied.

429   **Support Information.** Details of pretreatment and analysis of the samples; One table

430   showing metal ions in the leachate of biochars; and seven figures, (1) Surface area -

431   normalized adsorption isotherms; (2)Correlations between K_{oc} of pesticides and polarity of

432   biochars; (3) Chemical structure and molecular size of the two pesticides; and (4-7)

433   Hydrolysis dynamics under different conditions.

434   **ACKNOWLEDGMENT**

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Table 1. Bulk Elemental Composition and Chemical Composition of the Original and Deashed Biochars

sorbents	bulk elemental composition (%)						atomic ratio[a]		chemical shift (ppm) and carbon assignment					
									0-50	50-109	109-145	145-163	163-190	190-220
	f_{om}[b]	C	H	N	O	ash	H/C	(O+N)/C	alkyl	O-alkyl	aromatic	phenolic	carboxyl	carbonyl
BC350	54.67	31.58	2.36	3.80	16.93	45.33	0.90	0.51	30	16	37	8	8	1
BC700	33.16	25.16	1.12	2.05	4.83	66.84	0.53	0.21	13	16	43	2	14	12
DABC350	98.73	66.68	4.44	7.58	20.03	1.27	0.80	0.32	30	12	33	10	10	5
DABC700	93.46	74.22	2.79	4.97	11.48	6.54	0.45	0.17	10	13	44	5	14	14

[a] Calculated from atomic ratio of the bulk elements [b] Organic matter content. Noted that the bulk elemental composition and carbon assignment of the original and deashed biochars were determined by elemental analyzer and ^{13}C NMR, respectively.

Table 2. Surface Elemental Composition, pH, CEC, Surface Area and Pore Volume Parameters for the Original and Deashed Biochars

sorbents	surface elemental composition (%)							atomic ratio[a]		S_{BET}[b] (m^2/g)	V_t[c](cm^3/g)	D_p[d](Å)	pH[e]	CEC (cmol/kg)
	C	N	O	Si	Al	P	S	O/C	(O+N)/C					
BC350	59.14	5.28	20.25	1.40	2.09	3.57	1.08	0.26	0.33	23.8	0.053	88.3	8.3	96.8
BC700	54.82	4.26	22.98	2.74	1.08	4.25	1.94	0.31	0.38	32.6	0.035	42.6	9.5	112.5
DABC350	76.23	6.22	16.72	0.37	N.D.[f]	N.D.	0.45	0.16	0.23	67.1	0.096	57.5	6.2	5.6
DABC700	81.13	2.93	13.62	1.23	N.D.	N.D.	1.10	0.13	0.16	218.1	0.315	57.8	6.4	8.7

[a] Calculated from atomic ratio of the surface elements [b] Surface area determined by N2 adsorption using the Brunauer – Emmett – Teller (BET) method. [c] Total pore volume, determined at P/P_0=0.99. [d] Average pore diameter. [e] pH of biochars measured in solution (biochar:water=2.5:1). [f] Not detected. Noted that surface element composition of the original and deashed biochars was measured by XPS.

Table 3. Freundlich Isotherm Parameters for the Sorption of the Two Pesticides onto Biochars

pesticides	Sorbents	lgK_f	n	R^2	lgK_{oc}[a]	lgK_{oc}[b]
carbaryl	BC350	2.06±0.029	0.718±0.033	0.991	2.65	2.19
	BC700	2.85±0.018	0.302±0.015	0.990	3.66	2.54
	DABC350	3.35±0.045	0.615±0.058	0.965	3.64	3.03
	DABC700	3.70±0.071	0.448±0.075	0.874	4.00	3.11
atrazine	BC350	1.40±0.082	0.999±0.080	0.969	1.90	1.90
	BC700	2.77±0.030	0.330±0.023	0.976	3.57	2.50
	DABC350	3.15±0.022	0.615±0.037	0.983	3.44	2.83
	DABC700	3.55±0.032	0.427±0.041	0.957	3.85	2.93

[a] K_d normalized by f_{oc}, L/ kg, calculated from Freundlich model at $C_e = 0.5$ mg/ L; b at $C_e = 20$ mg/ L.

Table 4. The 7 d Hydrolysis Extents of the Two Pesticides and pH Values of Different Experimental Systems. Values with the same letter are not significantly different from each other ($p < 0.05$).

| Experiment design	7 d degradation extent (%)		pH
	Carbaryl	Atrazine	
Suspension of 50 mg BC350	23.5±3.5a	12.6±1.5abc	7.1±0.1a
Suspension of 500 mg BC350	59.1±4.3b	21.2±4.2e	7.9±0.3c
Suspension of 50 mg BC700	67.9±3.3c	14.9±3.1bcd	7.6±0.2c
Suspension of 500 mg BC700	90.6±7.5d	63.4±6.5g	9.1±0.2d
Background solution without pH adjusted	14.1±5.6e	8.0±0.1a	6.5±0.1b
Background solution with pH adjusted	100±0.1f	16.1±3.0cd	9.1±0.3d
Suspension of 500 mg BC350 with pH adjusted	29.1±0.2g	21.8±2.3e	6.8±0.1ab
Suspension of 500 mg BC700 with pH adjusted	59.3±2.0b	33.5±0.1f	6.8±0.2ab
Suspension of 500 mg DABC350	14.3±0.8e	8.5±0.6a	6.5±0.3b
Suspension of 500 mg DABC700	16.6±2.3e	10.2±0.9ab	6.6±0.2b
Leachate of 500 mg BC350 without pH adjusted	65.2±0.6c	16.1±0.0cd	7.9±0.1c
Leachate of 500 mg BC700 without pH adjusted	100±0.1f	19.4±0.2de	9.1±0.1d
Leachate of 500 mg BC350 with pH adjusted	37.6±0.2h	8.5±1.7a	6.8±0.3ab
Leachate of 500 mg BC700 with pH adjusted	40.0±0.4h	11.8±1.4abc	6.8±0.3ab

Caption of Figures
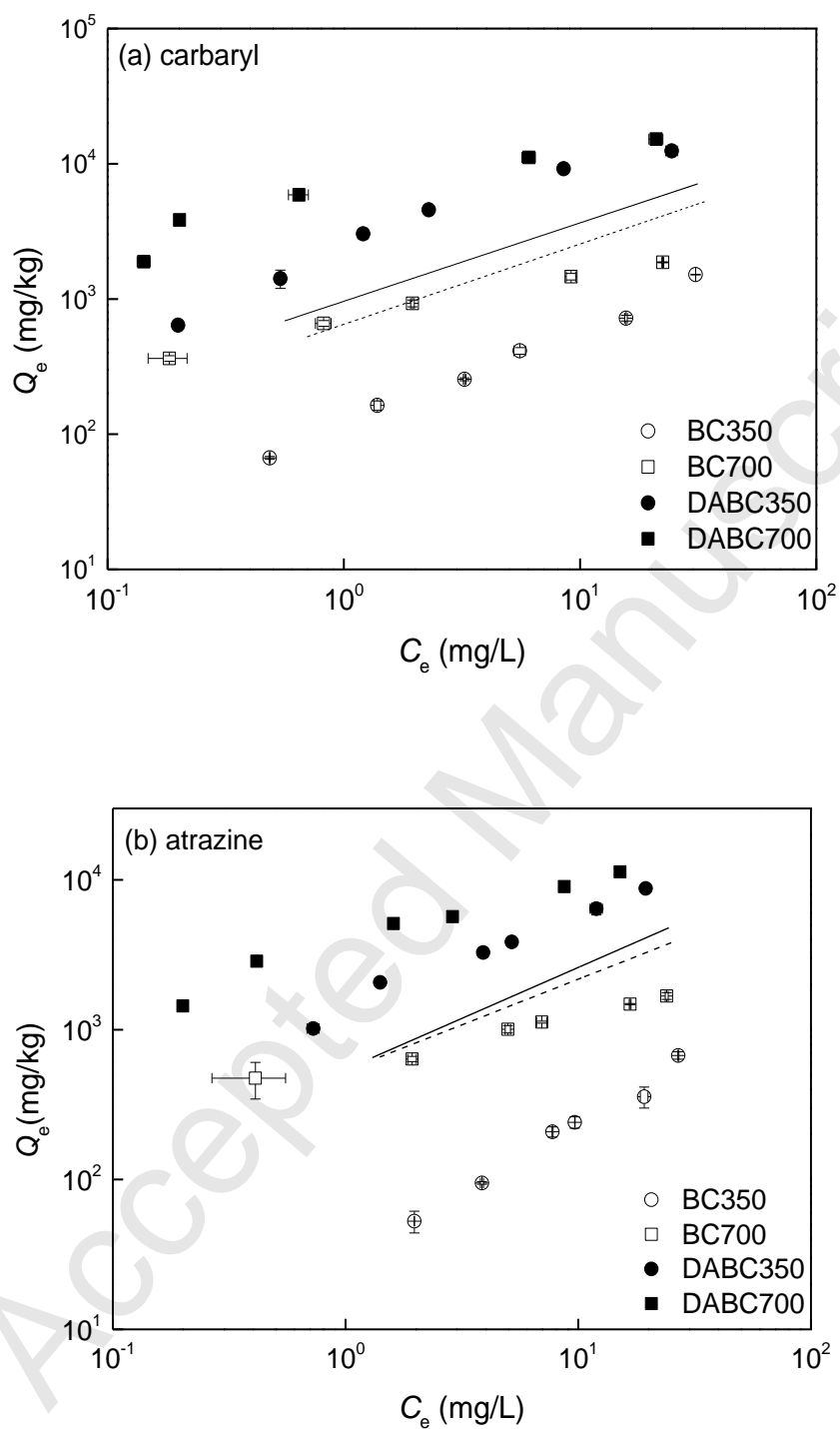
Figure 1. FTIR spectra of biochars

Figure 2. Adsorption isotherms of two pesticides by original and deashed biochars. The lines represent the calculated Freundlich model fitting to adsorption data for the deashed biochar fractionalized by to the organic matter content in the original biochar (solid line for BC350; dotted line for BC700).

Figure 3. Hydrolysis of the two pesticides in suspensions of original biochars
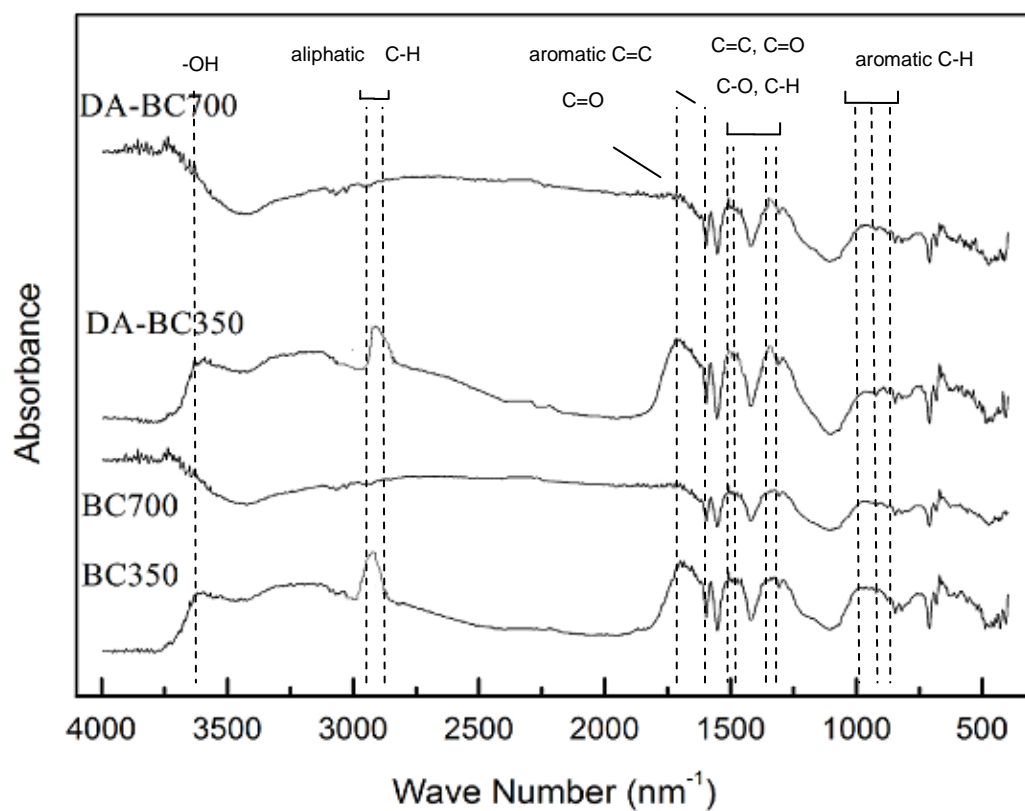
Figure 1. FTIR spectra of biochars

Figure 2. Adsorption isotherms of two pesticides by original and deashed biochars. The lines represent the calculated Freundlich model fitting to adsorption data for the deashed biochar fractionalized by the organic matter content in the original biochar (solid line for BC350; dotted line for BC700).
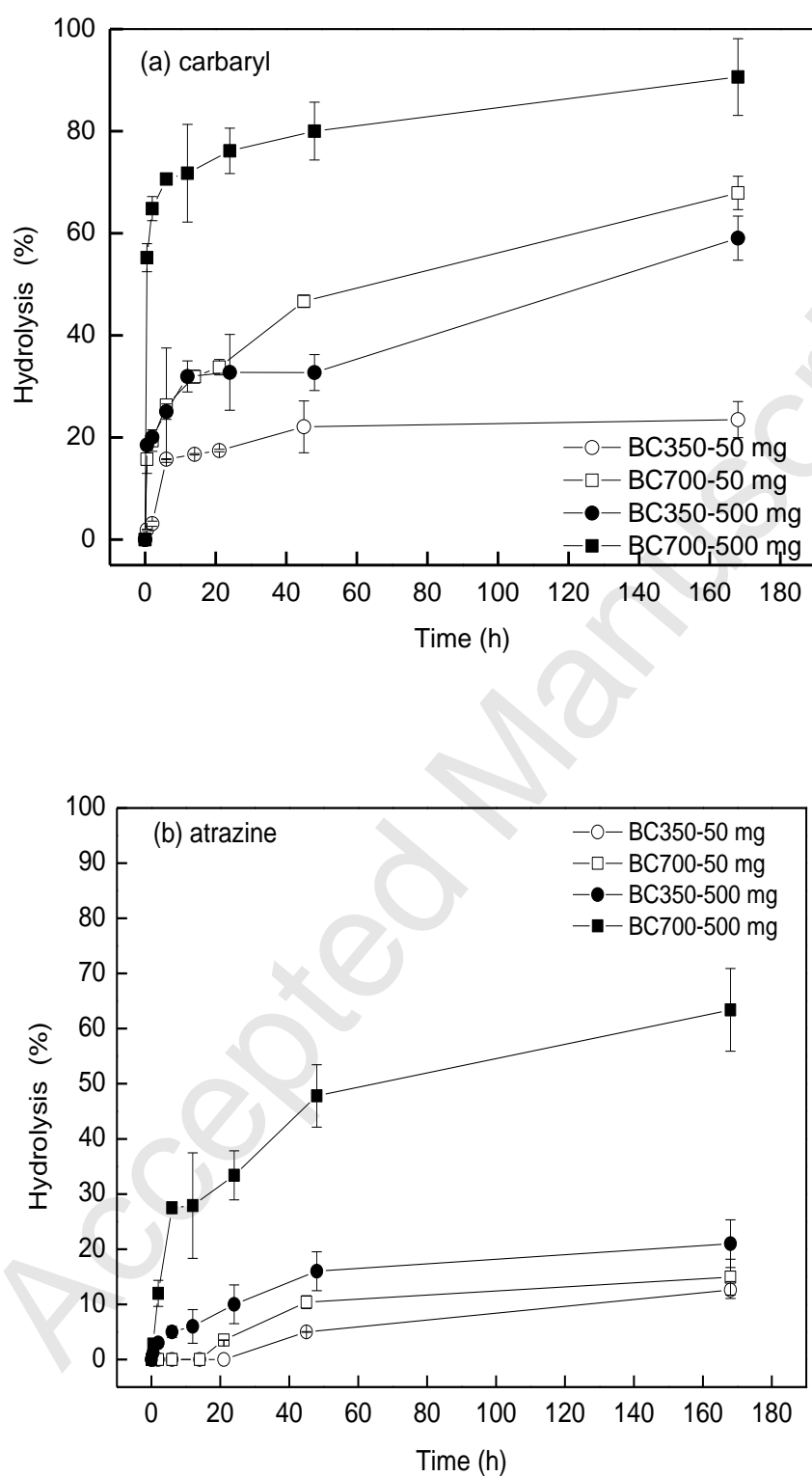
Figure 3. Hydrolysis of the two pesticides in suspensions of original biochars.