Accepted Manuscript

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Please cite this article as: Hou, P., Yan, Z., Cannon, F.S., Yue, Y., Byrne, T., Nieto-Delgado, C., Enhancement of perchlorate removal from groundwater by cationic granular activated carbon: Effect of preparation protocol and surface properties, *Chemosphere* (2018), doi: 10.1016/ j.chemosphere.2018.03.024.

Enhancement of Perchlorate Removal from Groundwater by Cationic Granular Activated Carbon: Effect of Preparation Protocol and Surface Properties

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Abstract: In order to obtain a high adsorption capacity for perchlorate, the epoxide-forming quaternary ammonium (EQA) compounds were chemically bonded onto granular activated carbon (GAC) surface by cationic reaction. The optimum preparation condition of the cationic GAC was achieved while applying softwood-based Gran C as the parent GAC, dosing EQA first

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17 at a pH of 12, preparation time of 48 hours, preparation temperature of 50 ℃, and mole ratio of

18 EQA/oxygen groups of 2.5. The most favorable cationic GAC that had the QUAB360 pre-

19 anchored exhibited the highest perchlorate adsorption capacity of 24.7 mg/g, and presented the

20 longest bed volumes (3,000 BV) to 2 ppb breakthrough during rapid small scale column tests

21 (RSSCTs), which was 150 times higher than that for the pristine Gran C. This was attributed to

22 its higher nitrogen amount (1.53 At%) and higher positive surface charge (0.036 mmol/g) at pH

23 7.5. Also, there was no leaching of the quaternary ammonium detected in the effluent of the

24 RSSCTs, indicating there was no secondary pollution occurring during the perchlorate removal

25 process. Overall, this study provides an effective and environmental-friendly technology for

26 improving GAC perchlorate adsorption capacity for groundwater treatment.

27 **Keywords:** Perchlorate removal, Cationic GAC, Epoxide-forming quaternary ammonium, Rapid

28 Small Scale Column Test, Surface charge

29 **1. Introduction**

30 Perchlorate, which originates primarily from rocket fuel, fireworks and explosives, is of

31 priority concern in drinking water of USA and other countries, since it is widespread, difficult to

32 treat and harmful to humans at low concentrations (Waldman, 2002). Perchlorate has been

33 detected within drinking waters in USA, Canada, Japan, Korea and China (Kucharzyk et al.,

34 2009, Backus et al., 2005, Kosaka et al., 2007, Quinones et al., 2007, Wu et al., 2010). In 2011,

35 the USEPA determined that perchlorate meets the Safe Drinking Water Act criteria for

36 regulation as a contaminant, and the best available scientific data, including best available

37 treatment methods, for perchlorate have been under review since that time. (USEPA, 2011).

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38   Conversely, California and Massachusetts have already implemented action levels of 6 ppb and 2

39   ppb, respectively (Renner, 2001). In response to these regulatory actions, many technologies

40   have been developed to remove perchlorate from water (Gu et al., 2002, Min et al., 2004, Xu et

41   al., 2003, Na and Cannon, 2002, Chen et al., 2005a, 2005b, Parette et al., 2005a, 2005b,

42   Patterson et al., 2010, 2011, Hou et al., 2013, Byrne et al., 2014). Compared to biological

43   treatment and ion exchange methods, the advantages of tailored GAC are: 1) it has the potential

44   to simultaneously adsorb organic contaminants while removing perchlorate due to its

45   hydrophobic basal planes and high surface area; 2) many water utilities are familiar with using

46   activated carbon (AC), as it has been widely practiced in the United States and other countries

47   for over 50 years (Chen et al., 2005b).

48   Previous work has demonstrated that the GAC pretreated with surfactant-quaternary

49   ammoniums and nitrogen exhibited higher perchlorate adsorption capacity compared to the

50   virgin carbon (Parette et al., 2005a, 2005b, Patterson et al., 2010, 2011, Byrne et al., 2014).

51   However, some of that physically loaded surfactant could desorb during water treatment and

52   cause subsequent environmental pollution. Therefore, the work herein aimed at circumventing

53   this leaching issue by chemical bonding the quaternary ammonium compounds onto GAC

54   surface by cationic reaction, in a manner that would preclude them from subsequently leaching

55   out of the GACs, while also maintaining a high adsorption capacity for perchlorate.

56   Prior researchers have chemically bonded 3-Chloro-2-hydroxypropyl trimethyl ammonium

57   chloride (CHPTAC/QUAB188), one of the typical epoxide-forming quaternary ammonium

58   compounds (EQA), through cationic reaction onto natural polymers, such as cellulose (Song and

59   Zhang,2011), red microalga (Geresh et al., 1999), soybean hulls (Wayne and Lynda, 2004),

60   starch (Pal et al., 2005), konjac glucomannan (Yu et al., 2006), cotton (Mohammad et al.,

61 2009), chitosan (Warayuth and Supawan, 2009) , agarose and polysaccharides (Prado and

62 Matulewicz, 2011 and 2014) . These EQAs have been observed to primarily combine with

63 alcoholic or phenolic –OH groups on the polymers (Wayne and Lynda, 2004); and activated

64 carbon also hosts such oxygenated groups. Therefore, it was hypothesized that the cationic

65 quaternary ammonium which has specific selectivity to perchlorate could be chemically bonded

66 other than physically loaded into the GAC backbone, through the reaction between the oxygen-

67 containing functional groups of GAC and the cationic quaternary ammonium.

68 The proposed process herein for anchoring EQA onto granular activated carbon by cationic

69 reaction per Hou et al. (2013) includes three steps: 1) adsorbing the chlorohydrin form of the

70 reagent onto the GAC, promoted by the surfactant tail of the reagent; 2) converting the

71 chlorohydrin form of the reagent to the epoxy intermediate in the presence of sodium hydroxide

72 (Fig. S1(a)); 3) reacting the epoxy with hydroxyls or other oxygen functional groups on the

73 graphene layer under alkaline conditions, so as to effectively attaches the quaternary ammonium

74 cation via the epoxide anchor to the GAC surface (Fig. S1(b)). The authors note that the epoxy

75 can be also converted to 2,3-dihydroxy derivatives, and these hydroxyls can react with other

76 epoxides in a manner that creates a multi-branched non-leachable extended structure within the

77 GAC pores, precluding secondary pollution during perchlorate removal process in practical

78 water treatment plant.

79 The objectives of this paper were to: 1) chemically bond the epoxide-forming quaternary

80 ammonium compounds onto GAC surface by cationic reaction, in a manner that would obtain a

81 high perchlorate removal, while also precluding them from subsequently leaching out of the

82 GACs; 2) discern the more favorable protocols for anchoring EQA onto GAC, by measuring

4

83 perchlorate removal from groundwater via adsorption isotherms and RSSCTs; and 3) investigate

84 the effect of surface properties of EQA-anchored GACs on perchlorate adsorption capacity.

2. Experimental

85

2.1. Materials

86

87 This study applied four different granular activated carbons: coconut-based Aquacarb

88 1240C (AC-1240) and bituminous Ultracarbon 1240C (UC-1240), supplied by Siemens Water

89 Technologies (now Evoqua), hardwood-based RGC-40 manufactured by MeadWestvaco

90 Specialty Chemicals (now Ingevity), and softwood Gran C (GC) manufactured by CABOT

91 NORIT Americas Inc. Prior to the tailoring process, the carbons were ground and sieved to a

92 U.S. mesh size of #200 × 400 (38 × 75 µm) in order to be the appropriate size for rapid small

93 scale column tests (RSSCTs), which employed the proportional diffusivity similitude equation,

94 per Crittenden et al. (1989). The sieved carbons were then washed, dried and stored under

95 vacuum in a desiccator until use.

96 The experiments employed four cationic reagents with molecular weights of 188, 342, 360

97 and 426 Daltons. These compounds came in aqueous solutions manufactured by QUAB

98 Chemical Company, and were 3-chloro-2-hydroxylpropyltrimethylammonium chloride

99 ($C_6H_{15}Cl_2NO$, QUAB188, 65 wt %), 3-chloro-2-hydroxyl-propyldodecyldimethylammonium

100 chloride ($C_{17}H_{37}Cl_2NO$, QUAB342, ≥ 38 wt %), 3-chloro-2-hydroxyl-

101 propylcocoalkyldimethylammonium chloride ($C_{13-23}H_{29-49}Cl_2NO$, QUAB360, ≥ 38 wt %) and 3-

102 chloro-2-hydroxyl-propylstearyldimethylammonium chloride ($C_{17-32}H_{37-49}Cl_2NO$, QUAB426, ≥ 38

103 wt %). Each of these contained a quaternary ammonium chloride (R-$\overset{|}{\underset{|}{N}}$-$^+$), which was the active

104 exchange site for perchlorate adsorption. Also, each contained a 3-chloro-2-hydroxy- group (Cl-

105 C-C-OH), which could participate in an epoxide reaction at high pH (Fig. S1). Yet further, each

106 contained an alkyl hydro carbon chain tail (-R), with width dimensions of about 4-6 Å, and

107 length dimensions of about 10-30 Å, and these tails facilitated extensive QAE adsorption into the

108 GAC pores.

109 Deionized (DI) water ($\geq$18.1 MΩ) was used for preparing analytical standards of perchlorate

110 solutions and for adsorption isotherm experiments. The water used in RSSCT experiments was

111 Penn State groundwater that had been spiked with 30 ppb perchlorate, per Hou et al. (2013).

2.2. Preparation and Optimization of Cationic GACs

113 The cationic GACs were prepared per the method of cationized polymers (Pal et al., 2005):

114 1.5g granular activated carbons (Gran C) were suspended in the solution of QUAB188,

115 QUAB342, QUAB360 and QUAB426 (QUAB chemicals), and stirred at room temperature for

116 24h. Sodium hydroxide solution was added into the pretreated mixture and stirred at different

117 temperatures for 8-72h. After that, dilute hydrochloric acid was added to lower the pH below 7 to

118 stop the cationization process. The solution were thereafter cooled to room temperature and

119 washed with DI water and reagent alcohol several times to remove the cationic agent residual.

120 Finally, samples were dried in a vacuum oven at 50°C for 24h.

121 The preparation conditions of cationic GACs were optimized by single-factor experimental

122 method, including the dosing sequence of sodium hydroxide, the reaction pH, the reaction time,

123 the reaction temperature and the dosage of quaternary ammonium reagents.

2.3. Characterization

125 The pore volume distributions and BET surface area of GACs were determined per Moore et

126 al. (2001), by adsorption of argon vapor onto GAC samples that were immersed within a glass

127 tube into liquid argon at a temperature of 87 K.

128   A Kratos Analytical Axis Ultra X-ray Photoelectron Spectroscopy (XPS) instrument was used

129   for XPS analysis. Casa XPS software was then used for peak fitting of N 1s (398.3-405.8 $\pm$0.2

130   eV), C 1s (284.8-288.9$\pm$0.2 eV), and O 1s (531.1-536 eV) signals (Vickerman and Gilmore,

131   2009).

132   Surface charge distributions were measured by the modified method from Chen et al. (2005b).

133   This method employed a Mettler Toledo DL53 titrator, which measured the total net surface

134   charge distribution over a broad pH range.

135   Boehm titrations for oxygenated surface functional groups of the pristine activated carbons

136   were conducted in triplicate according to the Boehm method (Boehm et al., 1964).

137   The slurry pH method used was adopted from Byrne (2012). All pristine and oxidized GACs

138   were tested by this protocol. Samples were tested in triplicate.

139   **2.4. Perchlorate Adsorption and Chemical Analysis**

140   2.4.1. Perchlorate Batch and Kinetic Adsorption Tests

141   Adapted batch adsorption tests were conducted using a bottle-point method (Hou et al., 2013).

142   The test was repeated at each perchlorate concentration for three times.

143   Perchlorate kinetic adsorption capacity was evaluated by RSSCTs per prior Penn State

144   research (Patterson et al., 2010, 2011, Byrne et al., 2014). During RSSCT operation, initial

145   breakthrough corresponded to when there was consistently detectable perchlorate in the effluent,

146   with specific emphasis on 2 ppb (the Massachusetts standard), or 6 ppb (the California standard).

147   Per prior experiments, duplicate RSSCTs have exhibited breakthroughs within 3-5% standard

148   error of one another.

149   2.4.2. Perchlorate and Quaternary Ammonium Analyses

7

150   Perchlorate concentrations were measured by a Dionex ICS-1100 Ion Chromatography unit

151   per Hou et al. (2013). This unit was equipped with a 4-mm AS16 column, a 4-mm AG16 guard

152   column, a 4-mm ASRS 300 ultra suppressor, and a DS3 detection stabilizer. An eluent

153   concentration of 25 mM NaOH was used with a 1000 µL injection loop. Method detection limit

154   (MDL) of perchlorate was around 2 ppb. For perchlorate concentrations in the range above 1

155   ppm, a 25 µL loop was used. Standard calibration curves were run for each new eluent

156   produced, with R^2 maintained above 0.99. The leaching of quaternary ammonium off the QAE-

157   anchored activated carbons was screened during several key RSSCTs. This screening employed

158   the Tsubouchi dye protocol (1981), as adapted by Parette et al. (2005a). This dye protocol

159   offered a detection sensitivity of 0.1 to 0.2 mg/L.

160   **3. Results and Discussion**

161   **3.1. Characterization of the Pristine GACs**

162   In order to better discern the impact of the starting GAC material, the characteristics of the

163   parent GACs were explored.

164   First, the cumulative porosities and surface areas of the parent GACs were examined to assess

165   the importance of porosity on tailoring and perchlorate removal (Fig. S2, Table 1). The DFT

166   surface area, micropore volume and mesopore volumes can be found in Table 1.

167   **Table1. Physical chemical properties of the pristine GACs**

Method	Sample	GC	AC1240C	UC1240	RGC
ASAP argon adsorption	Micropore volume (cm³/g)	0.348	0.399	0.313	0.371
	Mesopore volume (cm³/g)	0.615	0.022	0.115	0.679
	DFT-SA(m²/g)	915	1077	852	1118
X-ray PS	N (at.%)	0.48	ND*	ND*	ND*
	O (at.%)	12.3	7.77	5.29	4.22
Boehm	Carboxylic-like O (mmol/g)	0.356	0.015	-0.008	0.005
	Lactonic-like O (mmol/g)	0.336	0.053	0.075	0.080

8

titrations	Phenolic-like O (mmol/g)	0.310	0.055	0.059	0.034
	Sum (mmol/g)	1.002	0.123	0.126	0.119
Slurry pH		4.00±0.02	8.95±0.21	6.43±0.04	9.00±0.01

168   * ND means not detected.

169   The pristine AC1240 (coconut-based GAC) hosted the highest micropore volume (0.399 cm^3/g)

170 and high cumulative surface area (1077 m^2/g), even though it had low cumulative pore volumes.

171 The pristine UC1240 (bituminous-based GAC) displayed an even distribution of pores across the

172 micropore and lower mesopore range. Thus, the pristine RGC has the most balanced distribution

173 of porosity throughout the micropore and mesopore range (1.050 cm^3/g) and the highest total

174 density functional theory (DFT) surface area (1118 m^2/g) of all the starting GACs (Table 1).

175 The pristine GC exhibited the second largest cumulative pore volume (0.999 cm^3/g), though the

176 DFT surface area was somewhat low relative to the other GACs. The pristine GC also appeared

177 to be somewhat bimodal with a large amount of micropores in the 4-7 Å and 10-20 Å pore width

178 range, and almost none in the 7-10 Å range (Fig. S1).

179   Second, the slurry pH and external (top 10 nm) elemental compositions measured by XPS of

180 these parent GACs are shown in Table 1. Among the four parent GACs, the pristine GC hosted

181 the highest oxygen content (12.3%) and the lowest slurry pH (4.00 ± 0.02), whereas the

182 pristine RGC hosted the lowest oxygen content (4.2%) and the highest slurry pH (9.00 ± 0.01).

183 Across all four pristine GAC types, a higher oxygen content generally corresponded with lower

184 slurry pH (Table 1). This is because the pristine GC was chemically activated with phosphoric

185 acid from lignocellulosic materials, which resulted in a large amount of oxygen groups and a

186 low slurry pH; however, the pristine RGC was post-treated which resulted in a decrease in

187 acidic oxygen functional groups and an increase in slurry pH (Redding et al., 2009). Typically,

188 a low slurry pH indicates a surface with functionalities having low pKa values (i.e. oxidized

189   functional groups such as lactones and carboxyl groups). In contrast, a high slurry pH could be

190   indicative of nitrogen functionality, such as quaternary ammonium, pyridinium, and amines.

191   Therefore, slurry pH was used as an indicator of the extent of the oxidation or amination of the

192   carbon surface. In addition, the pristine GC likely contains nitrogen (0.48 at %) from the acid

193   activation process. The values were decreased after washing with boiling water.

194   Finally, the acid oxygen groups of the pristine carbon samples were measured by Boehm

195   titration. Table 1 also shows that the pristine GC hosted the highest acid oxygen groups (1.002

196   mmol/g), including carboxyls (0.356 mmol/g)，lactones (0.336 mmol/g) and phenolics (0.310

197   mmol/g). This result is consistent with that obtained by XPS, in which the pristine GC exhibited

198   the highest oxygen contents among the four pristine GACs.

199   It is suggested that the quaternary ammonium compounds would primarily combine with

200   alcoholic or phenolic –OH groups in cellulose or the lignin moieties by cationic reaction (Wayne

201   and Lynda, 2004). Therefore, in order to introduce the maximum quaternary ammonium

202   compounds into the GAC pores by the cationic reaction, the pristine GC, which was measured to

203   have the highest amount of oxygen groups, was applied as the parent GAC in the optimization of

204   the cationic GACs for perchlorate removal.

205 **3.2. Effect of preparation conditions of cationic GACs on perchlorate removal**

206 3.2.1 Effect of dosing sequence and preparation pH

207   Cationic GACs were prepared with pristine GC and epoxide-forming quaternary ammonium

208   (EQA) compounds under basic environment (pH >8) with different dosing orders. Fig. 1(a)

209   presents the effect of dosing sequence of QUAB188 and sodium hydroxide on perchlorate

210   removal through adsorption isotherms. When adsorbing an initial perchlorate concentration of

211   100 ppm, cationic GACs prepared with QUAB188 dosed first exhibited higher perchlorate

212 removal efficiency (4.0 mg/g) than that prepared with sodium hydroxide dosed first (1.1 mg/g).

213 This result indicates that when positively-charged QUAB188 was dosed first, it allowed

214 QUAB188 to penetrate into GAC pores sufficiently, resulting in higher QUAB188 loading

215 amount onto the negatively-charged GC surface which could subsequently react with NaOH. In

216 comparison, when dosing NaOH first, it would not only decrease the contact time between

217 QUAB188 and GC, but also lead to a change in the surface characteristics of wood-based GC,

218 such as increase of basic functional groups on the carbon surface, which would further decrease

219 the cationic reaction rate.
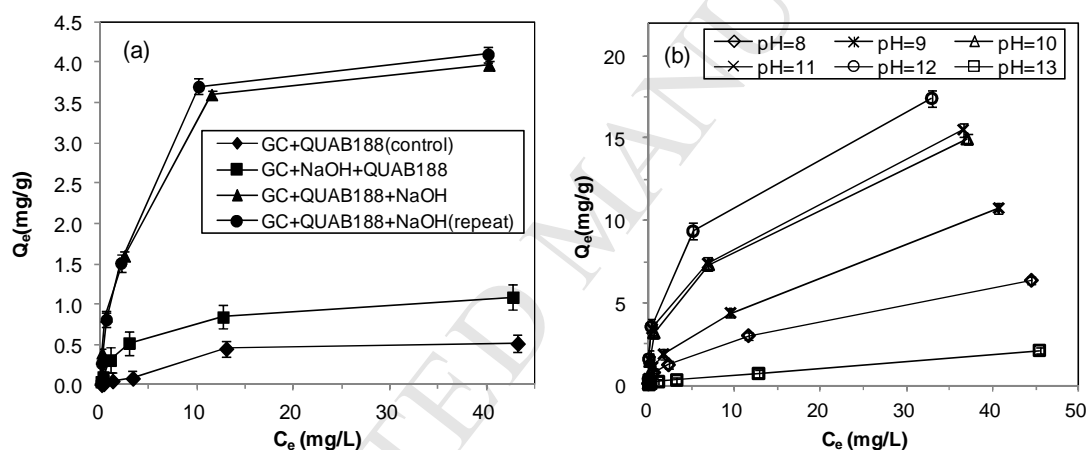
220

221 **Fig. 1. Effects of dosing sequence (a) and preparation pH (b) on perchlorate adsorption of**

222 **cationic GAC（C_o = 102.3 ppb, 350 ppb, 1.2 ppm, 4 ppm, 13.5 ppm, 50 ppm and 100 ppm, error bars**

223 **indicate standard deviations obtained from triplicate experiments.）**

224 In addition, cationic GACs prepared with QUAB188 dosed first were repeatable, as shown in

225 Fig. 1(a). As a control, pristine GC was dosed with only QUAB188. There was negligible

226 perchlorate removal for the control, indicating that the adsorbed QUAB188 residual can be

227 washed off during the cationic reaction without NaOH. This conclusion was confirmed through

228 the element analysis of nitrogen amount before and after dosing QUAB188 onto GC surface

229 (Table 2).

230 The pH value played the most important role in the cationic reaction, since it is not only the

231 necessary condition to form epoxide quaternary ammonium in the first step (Fig. 1a), but also the

232 "catalyst" to induce QUAB188 anchoring onto GAC surface through cationic reaction.

233 Therefore, the effect of pH on perchlorate removal of cationic GACs is investigated in Fig. 1 (b),

234 and the pH variation from 8 to 13 was adjusted by changing the mole ratio of NaOH/QUAB188.

235 In all of these experiments, the QUAB188 was absorbed into the activated carbon first; and then

236 the NaOH base was added to catalyze the epoxide-forming linkage reaction. Fig. 1 (b) shows

237 that the perchlorate adsorption capacity (Q_e) of QUAB188 anchored GAC increased while the

238 pH value increased from 8 to 12, but decreased dramatically with a pH value higher than 12.

239 The maximum perchlorate uptake was 17.4 mg/g, achieved at pH of 12 (mole ratio of 1.21

240 NaOH/QUAB188) when the initial perchlorate concentration was 50 ppm.   This result

241 corresponds to that exhibited by the modified biopolymers (Geresh et al., 1999).

242 It is noted that sodium hydroxide has the function of swelling, activating and catalyzing

243 etherification, and greatly enhancing nucleophilic ability of the hydroxyls of cellulose, but excess

244 sodium hydroxide can also decrease reaction efficiency (Wang and Ma, 2009, Kavaliauskaite et

245 al., 2008).   These results indicate that the optimum pH of this cationic reaction between

246 QUAB188 and GC was 12, when it was lower than 12, the activating and catalyzing

247 etherification ability of QUAB188 was increased with increasing pH; however, when it was

248 higher than 12, the side reaction was prominent and reduced the reaction rate, which led to

249 decreased perchlorate adsorption capacity.

250 3.2.2 Effect of preparation time and temperature

251 Fig. 2 (a) presents the effect of preparation time on perchlorate adsorption capacity of

252 cationic GAC. The cationic GACs was prepared at pH of 12, preparation temperature of 50 ℃,

253 and the preparation time varied from 8 to 72 hours. As shown in Fig. 2 (a), the perchlorate

254 adsorption capacity increased when the preparation time increased from 8 to 48 hours, but

255 declined rapidly after 48 hours. This is because, when the preparation time was longer than 48

256 hours, the side reaction would be induced by the extra reagent, such that the QUAB188 loading

257 amount would be affected to some extent. Therefore, the optimum preparation time was found

258 to be 48 hours, which generated the maximum adsorption capacity of 17.4 mg/g, while the initial

259 perchlorate concentration was 50 ppm (Fig. 2 (a)).
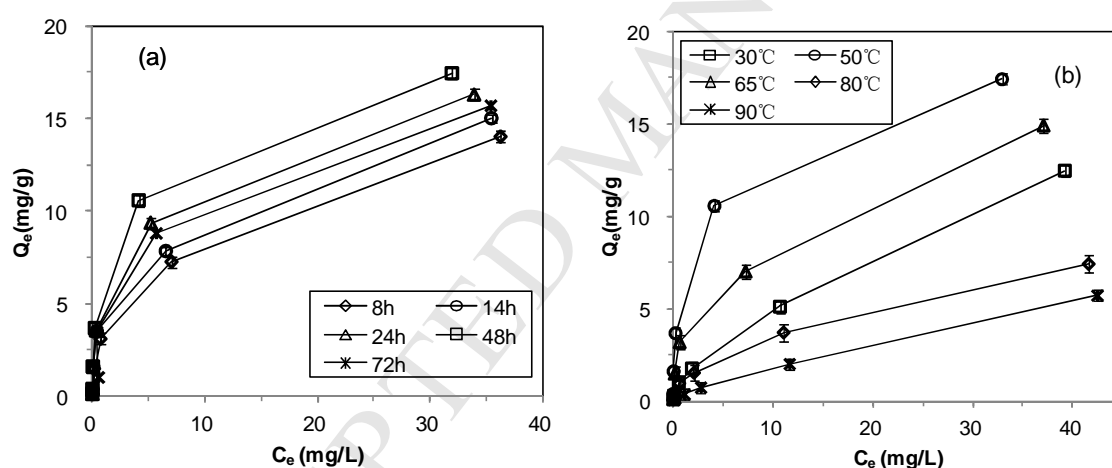
260

261 **Fig. 2. Effect of preparation time (a) and temperature (b) on perchlorate adsorption of cationic GAC（**
262 **C_o = 102.3 ppb, 350 ppb, 1.2 ppm, 4 ppm, 13.5 ppm, 50 ppm and 100 ppm, error bars indicate standard**
263 **deviations obtained from triplicate experiments.）**

264 The effect of preparation temperature on perchlorate adsorption of cationic GACs was also

265 evaluated in this study. Fig. 2 (b) shows that the maximum perchlorate adsorption capacity was

266 17.4 mg/g, achieved at the pH of 12, the preparation time of 48 hours, and the preparation

267 temperature of 50 ℃, while the perchlorate initial concentration was 50 ppm. In comparison,

268 lower adsorption values were observed for either lower (30 ℃) or higher temperature (65-90 ℃).

13

269 These results are due to 1) when the temperature is lower than 50℃, the increase of temperature

270 would improve the epoxide-forming and the cationic reaction rate (Siau et al., 2004); 2) when the

271 temperatures exceed 50 ℃, the higher energetic of a boiling reaction may damage the pore and

272 surface structure of activated carbon (Kuo and Lai, 2009), which would result in lower cationic

273 reaction rate thereafter. Hence, the optimum preparation temperature of 50℃ was applied for the

274 remainder of the study.

275 3.2.3 Effect of mole ratio of QUAB188/Oxygen groups and cationic reagents

276   In order to further increase the perchlorate adsorption capacity, the effect of QUAB188 dosage

277 was also evaluated in Fig. 3 (a). According to the etherification reaction equation, the proportion

278 of QUAB188 and primary hydroxyl group of alkali cellulose was 1:1 (Wang and Ma, 2009).

279 The reactants would be insufficient if too low a content of QUAB188 was added at the beginning

280 of the cationic reaction. Therefore, the QUAB188 dosage applied herein increased from 6 mL to

281 12 mL, corresponding to the mole ratio of QUAB188/oxygen groups increased from 2.5 to 5. As

282 shown in Fig. 3 (a), the perchlorate adsorption capacity decreased with the increase of the

283 QUAB188 dosage, and the maximum adsorption capacity (17.4 mg/g) was achieved at the

284 QUAB188 dosage of 6 mL, corresponding to the mole ratio of QUAB188/oxygen groups of 2.5.
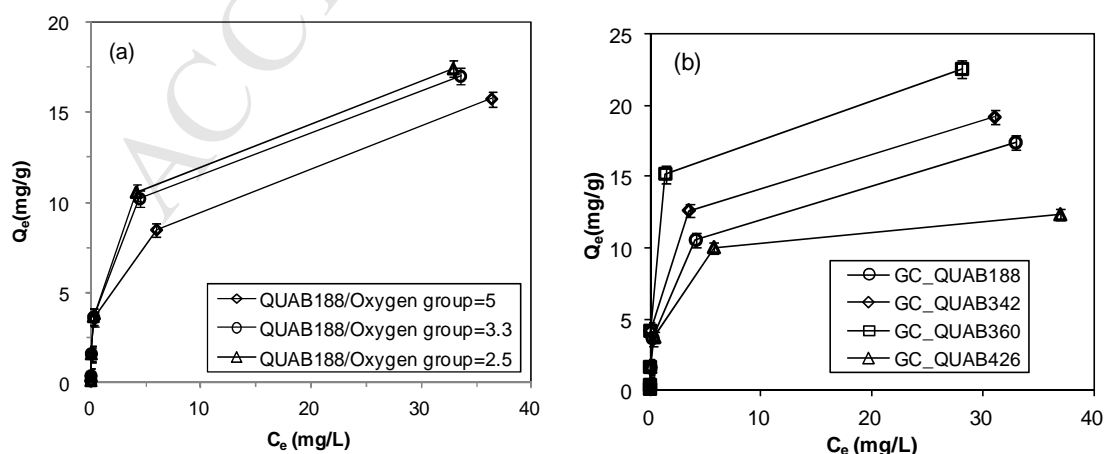
285

286   **Fig. 3. Effects of the mole ratio of QUAB188/oxygen groups and different cationic reagents on**

287   **perchlorate adsorption of cationic GAC（C_o = 102.3 ppb, 350 ppb, 1.2 ppm, 4 ppm, 13.5 ppm, 50 ppm**

288   **and 100 ppm, error bars indicate standard deviations obtained from triplicate experiments.）**

289   This result indicates that the cationic reaction is supposed to be completed when the mole ratio

290   of QUAB188/oxygen groups is 2.5, excess dosage of QUAB188 will only provide sufficient

291   conditions for the side reaction, and reduce the cationic reaction rate. Moreover, the lower

292   dosage of QUAB188 will reduce the preparation cost of the cationic GACs, which is good for

293   the practical application when commercialized. As a result, the optimum condition for the

294   preparation of cationic GACs is achieved at the pH of 12, preparation time of 48 hours,

295   preparation temperature of 50 ℃, and the mole ratio of QUAB188/oxygen groups of 2.5.

296   It was reported that the greatest perchlorate selectivity is attributed to its unique structure of

297   the trialkylammonium functional groups, where each nitrogen (the binding site) is surrounded by

298   three extended alkyl chains (Xiong et al., 2007). Therefore, in order to further enhance the

299   perchlorate adsorption capacity, the study herein also applied three extended chain quaternary

300   ammonium chemicals, QUAB342, QUAB360 and QUAB426, as the cationic reagents to react

301   with Gran C activated carbon at the above optimum condition.

302   Fig. 3 (b) presents the effect of different cationic reagents on perchlorate adsorption capacity

303   (Q_e) of cationic GC. When the perchlorate initial concentration was 50 ppm, the cationic GAC

304   preloaded with QUAB360 exhibited the highest perchlorate adsorption capacity (Q_e) of 24.7

305   mg/g, whereas the cationic GAC preloaded with either higher (QUAB 426) or lower (QUAB 188,

306   QUAB 342) molecular weight of quaternary ammonium chemicals exhibited lower perchlorate

307   adsorption capacity (Fig. 3 (b)).

308   In addition, the cationic GACs preloaded with EQA that containing extended alkyl chains

309   (QUAB342, QUAB360) displayed higher perchlorate uptake than that containing three methyl

310 groups (QUAB 188). These results indicate that the EQA that containing extended alkyl chains

311 hosted more attractive sites for perchlorate adsorption than did that containing three methyl

312 groups, since the extended chain structure creates a more hydrophobic local environment and

313 hinders sorption of more hydrophilic ions such as sulfate (Gu et al., 2001). It was also found that

314 this type of functionality is highly specific for anions with large size and low hydration energy

315 (such as ClO_4^- and TcO_4^-) (Gu et al., 2001). Moreover, it is noted that the perchlorate adsorption

316 capacity increased when the carbon amount of the extended alkyl chain increased from 4-7 to 16,

317 but decreased when it exceed 16, addressed by Parette et al. (2005b) in perchlorate removal with

318 quaternary ammonium preloaded GACs. This suggests that when carbon amount of the extended

319 alkyl chain exceeds 16, the large molecular size may kinetically hinder the diffusion of EQA to

320 the oxygen functional groups in the GAC micropores, thus reducing the perchlorate removal

321 efficiency of these cationic GACs. Therefore, among the four different cationic reagents, it was

322 QUAB360 when anchored on to Gran C presented the highest capacity for perchlorate

323 adsorption.

324 **3.3. Rapid small scale column tests for the pristine and optimized cationic GACs**

325 RSSCTs appraised the bed volumes to perchlorate breakthrough for the pristine GC and the

326 optimized cationic GACs that had been pre-anchored with QUAB188 and QUAB360 at the pH

327 of 12, preparation time of 48 hours, preparation temperature of 50 ℃, and the mole ratio of

328 QUAB188/oxygen groups of 2.5. Columns used in RSSCTs were 8.2 cm long and 0.36 cm in

329 diameter, with carbon mass of 0.23 to 0.58 g and flow rate of 1.05 minute empty bed contact

330 time (EBCT) (Fig. S3).

331 The RSSCT perchlorate breakthrough behavior showed that the GC with QUAB360 pre-

332 anchored exhibited the longest bed life for perchlorate removal (Fig.4 (a)). Specifically, the GC

16

333   that had the QUAB360 pre-anchored removed perchlorate in the effluent to below 2 ppb (the

334   Massachusetts standard) for 3000 bed volumes (BV), when processing Penn State ground water

335   that had been spiked with 30–35 ppb perchlorate at pH 7.5. This corresponds to 42 days of

336   perchlorate removal at a full scale water treatment plant. In addition, this BV capacity is 5 times

337   higher than that for the QUAB188 pre-anchored GC (600 BV), and 150 times higher than that

338   for the pristine GC (20 BV), which indicates that the perchlorate removal performance evaluated

339   by RSSCT is consistent with that conducted by adsorption isotherms (Fig. 3 (b)). Therefore, the

340   GC that had the QUAB360 pre-anchored exhibited the highest perchlorate adsorption capacity

341   (24.7 mg/g) and the longest bed volumes to 2 ppb perchlorate breakthrough (3,000 BV).

342   In addition, it is noted that there was no leaching of the quaternary ammonium detected when

343   the RSSCT column effluent was monitored by the Tsubouchi (1981) dye protocol. Thus, the

344   epoxide-based anchoring of these EQA molecules overcame the leaching issues that had been

345   posed with mere quaternary ammonium surfactants (Parette et al., 2005a, 2005b, Patterson et al.,
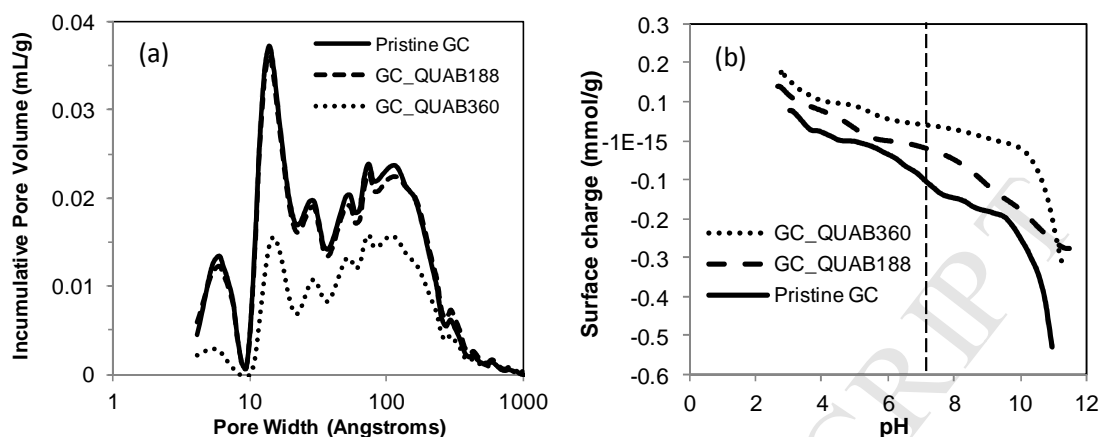
346   2010, 2011).
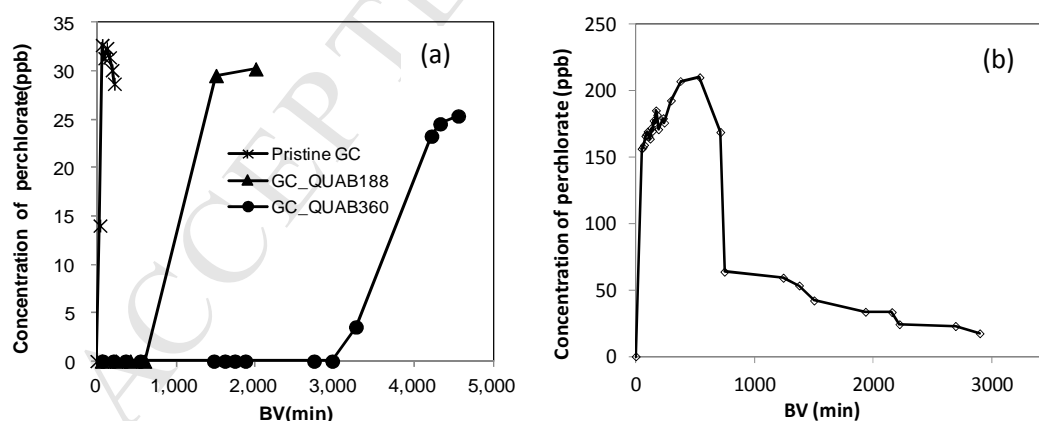
348   **Fig. 4. Perchlorate breakthrough for pristine and cationic GACs (a) and regeneration of perchlorate-**
349   **exhausted cationic GAC by RSSCT (b)**

350   Moreover, the regeneration of perchlorate-exhausted cationic GC was evaluated by RSSCT in

351   Fig.4 (b). It shows that 80% of the perchlorate spent cationic GAC could be regenerated by 3000

352 ppm Sodium bicarbonate after 3,000 BV treatment. The perchlorate desorption rate is fast before

353 750 bed volume, but becomes slow after that. This is probably due to the low ionic selectivity of

354 bicarbonate on the adsorption medium in the later stage of regeneration, such that the perchlorate

355 adsorption site on activated carbon is difficult to be replaced by bicarbonate.

356 **3.4 Effect of surface properties of the cationic GACs on perchlorate removal**

357 Pore volume distributions of pristine GC and the cationic GACs that preloaded with EQA are

358 displayed in Fig. 5 (a) to provide evidence for the mechanism of the EQA and the GAC during

359 the cationic reaction. Compared to Pristine GC, the cationic GAC that was preloaded with

360 QUAB188 had slightly lower mesopores (20-500 Å) volume, whereas the cationic GAC that was

361 preloaded with QUAB360 had approximately 50% diminished incremental pore volumes

362 throughout the full range of pores from 4 to 500 Å (Fig. 5 (a)). This result indicates that 1) the

363 EQA has been successfully preloaded into the cationic GAC pores, as evidence by a consistent

364 lose of porosity throughout the entire pore volume distribution, as compared to the pristine GC;

365 2) the QUAB 360 that contains one alkyl long chain exhibited more favorable attraction onto

366 GAC surface than the QUAB 188 that contains three methyl groups, such a higher volume of

367 micropore and mesopores were occupied by QUAB360 which has a larger molecular weight than

368 that can be occupied by QUAB188 which has smaller molecular weight, and this results in much

369 more perchlorate removal capacity for QUAB 360 versus QUAB188. This can also be

370 confirmed by the elemental analysis of nitrogen amount that showed in Table 2.

Fig. 5. Pore volume (a) and Surface charge (mmol H$^+$/g pristine or cationic GAC) (b) distributions of the pristine and cationic GACs

The surface charge distributions of the pristine and cationic GACs were characterized, as shown in Fig. 5 (b). There was a significant increase in positive surface charge for the cationic GAC that was preloaded with QUAB360, as compared with pristine GC, for a pH from 3 to 12. The particular interest of this work was the surface charge at pH 7.5, which corresponded to the pH of the groundwater applied in RSSCT below. Specifically, the cationic GAC preloaded with QUAB360 hosted the positive surface charge of 0.036 mmol/g at pH 7.5, whereas the cationic GAC preloaded with QUAB188 and pristine Gran C exhibited negative surface charge at pH 7.5 (Fig. 5 (b)). These results confirm the previous conclusions that EQA (QUAB360) contains positively-charged functional groups has been successfully introduced into the carbon by the reaction with hydroxyl groups in carbons, and also confirm that the increase of the loading amount of EQA that has specific selectivity for perchlorate results in the increase of the perchlorate adsorption capacity for the cationic GAC with preloaded EQA.

Table 2 summarizes the nitrogen fraction of pristine and cationic GACs by XPS analysis. It can be observed that nitrogen peaks of cationic GACs appeared at the binding energy of 402.9 eV and 403.4 eV, whereas that of the pristine GC appeared earlier at 400.2 eV. As mentioned in

19

389 previous study, the binding energy for quaternary ammonium is between 402 eV and 403 eV,

390 and the binding energy for oxygen-containing nitrogen is at 400.2 eV, which indicates that the

391 EQA (QUAB188 and QUAB360) has been successfully introduced into the carbon by the

392 reaction with hydroxyl groups in carbons and the EQA. This is consistent with the result

393 obtained in Fig. 5.

394 **Table 2. Nitrogen fraction of pristine and cationic GACs**

sample	Nitrogen(At%)		Binding Energy (eV)
	NQ-type*	NO-type**	
Pristine GC	ND***	0.48	400.21
GC+QUAB188	ND***	0.52	399.8
GC+QUAB188+NaOH	0.87	ND***	403.4
GC+QUAB360+ NaOH	1.53	ND***	402.9

395 * means quaternary ammonium, ** means oxygen-containing nitrogen, *** means not detected

396 In addition, compared to the pristine GC, the cationic GAC that preloaded with QUAB188

397 increased nitrogen amount by 0.87 At% at the binding energy of 403.4 eV, whereas that

398 preloaded with QUAB360 increased by 1.53 At% at the binding energy of 402.9 eV . This result

399 suggests that the higher loading amount of NQ-type nitrogen (EQAs) leads to the more

400 perchlorate adsorption, which is corresponding to the result observed in the isotherm data (Fig 3

401 (b)) and RSSCT data (Fig 4 (b)). Moreover, for the control GAC that only adsorbed QUAB188

402 previously and washed out thereafter, the similar NO-type nitrogen (0.52 At%) were observed as

403 for the pristine GC at binding energy of 399.8 eV, this result confirms the previous conclusion

404 that the adsorbed EQA residual can be washed off during the cationic reaction, in a manner that

405 reduces the possible secondary pollution during the water treatment.

406 **4. Conclusions**

407   1) Adsorption experiments and characterization results demonstrated that EQAs had been

408   successfully chemically bonded to softwood-based Gran C surface through cationic reaction

409   between the expoxide-forming groups on the EQAs and the oxygen groups on the Gran C

410   surface.

411   2) The optimum preparation condition of cationic Gran C was achieved while dosing EQA first

412   (before adding NaOH) at the pH of 12, preparation time of 48 hours, preparation temperature of

413   50 ℃, the mole ratio of EQA/oxygen groups of 2.5, when the softwood-based Gran C was

414   anchored with QUAB360.

415   3) Perchlorate adsorption tests and RSSCTs suggested that the optimized cationic Gran Cs

416   considerably improved the perchlorate adsorption capacity, compared to the pristine GC. The

417   cationic GC that had the QUAB360 pre-loaded (GC-QUAB360) exhibited the highest

418   perchlorate adsorption capacity of 24.7 mg/g, and presented the longest bed volumes (3000 BV)

419   of perchlorate breakthrough at 2 ppb, during rapid small scale column tests with ground water

420   that contained 30-35 ppb perchlorate, which was 150 times higher than that for the pristine GC.

421   4) As compared to the pristine GC, the cationic GC that pre-loaded with QUAB360 hosted the

422   highest nitrogen (quaternary ammonium) amount of 1.53 At% at the binding energy of 402.9 eV

423   and highest positive surface charge of 0.036 mmol/g at pH 7.5. These results confirmed that

424   EQA (QUAB360) contains positively-charged functional groups has been successfully

425   introduced into the carbon by the reaction with hydroxyl groups into the GAC surface, and also

426   confirm that the increase of the loading amount of EQA that has specific selectivity for

427   perchlorate results in the increase of the perchlorate adsorption capacity for the cationic Gran C

428   that pre-loaded with EQA.

429   5) There was no leaching of the quaternary ammonium detected when the RSSCT column

430   effluent was monitored, indicating that the epoxide-based anchoring of these EQA molecules

431   overcame the leaching issues that had been posed with mere quaternary ammonium surfactants.

432   Overall, this study provided an effective and environmental-friendly technology of improving the

433   perchlorate adsorption capacity from groundwater.

434   **Acknowledgements**

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1   **Highlights:**

2   1. Epoxide-forming quaternary ammonium had been successfully chemically bonded onto

3   GAC surface by cationic reaction for improving perchlorate removal.

4   2. The most favorable preparation protocols of the cationic softwood-based Gran C were

5   revealed.

6   3. The best-performing cationic Gran C exhibited 3000 bed volume compared to 20 bed

7   volume of pristine GranC during RSSCTs.

8   4. Effects of surface properties of the cationic GAC on perchlorate removal were studied.