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Zhang, Jin-Wei; Mariska, Sarah; Pap, Sabolc; Tran, Hai Nguyen; Chao, Huan-Ping

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# Separation and Purification Technology

## Enhanced separation capacity of carbonaceous materials towards potential toxic metals through grafting copolymerization --Manuscript Draft--

<b>Manuscript Number:</b>	SEPPUR-D-22-04028R1
<b>Article Type:</b>	VSI:Resource recovery
<b>Section/Category:</b>	Adsorbent synthesis (carbons, zeolites, metal organic frameworks) for gas or liquid applications
<b>Keywords:</b>	acrylic acid; Agricultural Waste; Adsorption; Desorption; Ion exchange; Heavy metal; Water treatment
<b>Corresponding Author:</b>	Hai Nguyen Tran Dai Hoc Duy Tan Ho Chi Minh, VIET NAM
<b>First Author:</b>	Jin-Wei Zhang
<b>Order of Authors:</b>	Jin-Wei Zhang
	Sarah Mariska
	Sabolc Pap
	Hai Nguyen Tran
	Huan-Ping Chao
<b>Abstract:</b>	<p>Oxygen-containing groups in the surface of materials (i.e., –COOH and –OH) often play a key role in adsorbing toxic metals. Acrylic acid (<math>\text{CH}_2 = \text{CHCOOH}</math>) is used as a green grafter for enhancing the density of those groups in carbonaceous materials, and ammonium cerium nitrate is used as an initiator. Hydrochar (prepared through hydrothermal carbonization at 190 °C), biochar (generated via pyrolyse at 800 °C, and activated carbon (AC; produced through chemical activation with <math>\text{K}_2\text{CO}_3</math> at 800 °C) derived from ginger residues were used as feedstock materials for the grafting process. The carbonaceous materials were characterized using scanning electron microscopy, X-ray photoelectron spectrometry, Brunauer–Emmett–Teller (BET) analyzer, Fourier transform infrared spectroscopy, and zeta potential. <math>\text{Cu}^{2+}</math>, <math>\text{Cd}^{2+}</math>, and <math>\text{Pb}^{2+}</math> were selected as adsorbates. Equilibrium adsorption experiments for the three metal ions on the un-grafted and grafted carbonaceous materials were conducted at 25 °C and pH 5.0. Results indicated that the oxygen content in the grafted materials was higher than that of un-grafted ones. The grafting process could increase the OH and COOH functional groups on the carbonaceous materials, which leads to increasing the adsorptive amounts of metal ions. The Langmuir maximum adsorption capacity (<math>Q_{\text{max}}</math>) of carbonaceous materials for toxic metal ions (mol/kg) followed <math>\text{Cu}^{2+} &gt; \text{Cd}^{2+} &gt; \text{Pb}^{2+}</math>. The adsorptive amounts of potentially toxic metal ions on the un-grafted and grafted (abbreviated as G) materials followed hydrochar &gt; AC &gt; biochar. The <math>Q_{\text{max}}</math> value of hydrochar (72.8, 74.7, and 109.3 mg/g), biochar (53.6, 69.1, 53.9 mg/g), AC (54.4, 73.1, 101.8 mg/g), G-hydrochar (130.9, 146.0, 271.4 mg/g), G-biochar (92.6, 143.6, 153.6 mg/g), G-AC (96.3, 146.1, 259.1 mg/g) for adsorbing metals (<math>\text{Cu}^{2+}</math>, <math>\text{Cd}^{2+}</math>, and <math>\text{Pb}^{2+}</math>) was higher than that of commercial activated carbon (21.83, 22.13, 25.15 mg/g, respectively). The adsorption capacity of the grafted hydrochar was restored after five adsorption/desorption cycles. The primary adsorption mechanisms were complexation and ion exchange.</p>
<b>Suggested Reviewers:</b>	<p>Ashleigh Fletcher University of Strathclyde ashleigh.fletcher@strath.ac.uk Expert in the area of study</p>
	<p>Adrián Bonilla-Petriciolet Instituto Tecnológico de Aguascalientes, Aguascalientes Institute of Technology petriciolet@hotmail.com Expert in the area of study</p>

	<p>Martin Hubbe North Carolina State University, NC State University hubbe@ncsu.edu</p>
Response to Reviewers:	<p>Reply to reviewer's comments/suggestions The authors hope that your comments were properly taken into account in the revised manuscript, and our responses would satisfy insightful comments and valuable suggestions of the reviewer. (The change is highlighted in the red color)</p> <hr/> <p>-</p> <p>Reviewer #1:</p> <p>In this study, the authors employed ginger as raw materials to produce activated carbon, hydrochar, and biochar, and then used NaOH and H<sub>8</sub>CeN<sub>8</sub>O<sub>18</sub> for producing respective grafting materials. The manuscript has been well written and the data were clearly discussed. The main concerns include:</p> <p>(1)Ginger is a valuable food product. The authors shall clarify the reason on using ginger as raw materials, instead of using other solid organic wastes.</p> <p>Reply: The reviewer has a correct observation. The authors apology for this misunderstanding because of not enough information. In this study, the authors used ginger residues collected from local markets. To avoid the confusion for readers, the authors have correct the information.</p> <p>(2)There are lacks of experiments illustrating re-adsorption capabilities and stability of the produced materials after multi-regeneration cycles.</p> <p>Reply: According the the reviewer's suggestions, the authors add the data to confirm re-adsorption capabilities and stability of the produced materials after multi-regeneration cycles (Figure 9) and added some new relevant discussion (i.e., Section 3.6, page 18)</p> <p>(3)Commercial activated carbon needs to be used as a baseline for a comparison with the produced adsorbents.</p> <p>Reply: Many thanks for your suggestion. The data of commercial activated carbon were added. The reviewer can checked the adsorption isotherm of CAC in Figure S3 (Supporting Information), Table 3, and some relevant information (i.e., lines 186-189 in page 8; lines 390-392 in page 18)</p> <hr/> <p>Reviewer #2:</p> <p>Overall, I consider that the paper can be accepted for publication after a major revision. In particular, authors should provide more details of the adsorption data modeling. I am expecting that a nonlinear regression approach was used for the data correlation. If this was not done, please perform recalculate the model parameters.</p> <p>Reply: Many thanks for your concern. All parameters of the models were obtained by the nonlinear method using the Origin software. We have disused on the problem of using the liner method at the paper (<a href="https://pubmed.ncbi.nlm.nih.gov/28478298/">https://pubmed.ncbi.nlm.nih.gov/28478298/</a>) According to the reviewer comment, the authors add the information in page 8 line 181-182 ("The nonlinear regression approach correlated adsorption equilibrium data using the Origin software.") On the other hand, I disagree with the classification of some isotherm as H-type. Please review this classification. Authors have not reported the results of these adsorbents after the heavy metal adsorption. This information will complement the analysis and discussion of adsorption mechanism.</p> <p>Reply: The information on the H-shape isotherm has been removed from the manuscript. The reviewer can see Figure 6 (no denoted for H-shape). Many thanks.</p>

Vietnam, April 3<sup>rd</sup>, 2023

Professor Ho Kyong Shon:

*Guest Editor*

Separation and Purification Technology

Elsevier publisher

**Dear Editor:**

Many thanks for sending the reviewers' report for our submitted manuscript titled "*Enhanced separation capacity of carbonaceous materials (hydrochar, biochar, and activated carbon) towards potential toxic metals through grafting copolymerization*", which is being submitted for potential publication as a research paper in the journal.

According to the reviewer's suggestion, the authors have paid more attention to revise our manuscript thoroughly. The authors hope that our thorough responses would satisfy insightful comments and suggestions of reviewers. Attached file showed the replies to reviewer's specific comments, and suggestions.

In addition, the authors would like to invite Dr. Sabolc Pap from University of the Highlands and Islands as a new co-author in this work. This is because he has a great contribution during the revision. The authors hope that the editor and publisher will accept this change.

I declared that all authors have agreed to the submission of this manuscript. We also declared that this work is original and has not been submitted or considered elsewhere. The authors declare no competing financial interest.

Looking forward to hearing good news soon.

Sincerely yours,



Tran Nguyen Hai, Ph.D.

Duy Tan University, Vietnam

E-mail: [trannguyenhai@duytan.edu.vn](mailto:trannguyenhai@duytan.edu.vn)

## Reply to reviewer's comments/suggestions

*The authors hope that your comments were properly taken into account in the revised manuscript, and our responses would satisfy insightful comments and valuable suggestions of the reviewer.*

(The change is highlighted in the red color)

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### Reviewer #1:

**In this study, the authors employed ginger as raw materials to produce activated carbon, hydrochar, and biochar, and then used NaOH and H<sub>8</sub>CeN<sub>8</sub>O<sub>18</sub> for producing respective grafting materials. The manuscript has been well written and the data were clearly discussed. The main concerns include:**

**(1) Ginger is a valuable food product. The authors shall clarify the reason on using ginger as raw materials, instead of using other solid organic wastes.**

#### Reply:

The reviewer has a correct observation. The authors apology for this misunderstanding because of not enough information. In this study, the authors used **ginger residues collected from local markets**. To avoid the confusion for readers, the authors have correct the information.

**(2) There are lacks of experiments illustrating re-adsorption capabilities and stability of the produced materials after multi-regeneration cycles.**

#### Reply:

According the the reviewer's suggestions, the authors add the data to confirm re-adsorption capabilities and stability of the produced materials after multi-regeneration cycles (**Figure 9**) and added some new relevant discussion (**i.e., Section 3.6**, page 18)

**(3) Commercial activated carbon needs to be used as a baseline for a comparison with the produced adsorbents.**

#### Reply:

Many thanks for your suggestion.

The data of commercial activated carbon were added. The reviewer can checked the adsorption isotherm of CAC in **Figure S3** (Supporting Information), **Table 3**, and some relevant information (i.e., lines 186-189 in page 8; lines 390-392 in page 18)

---



## Reviewer #2:

Overall, I consider that the paper can be accepted for publication after a major revision. In particular, authors should provide more details of the adsorption data modeling. I am expecting that a nonlinear regression approach was used for the data correlation. If this was not done, please perform recalculate the model parameters.

### Reply:

Many thanks for your concern. All parameters of the models were obtained by the nonlinear method using the Origin software.

We have disused on the problem of using the liner method at the paper (<https://pubmed.ncbi.nlm.nih.gov/28478298/>)

According to the reviewer comment, the authors add the information in page 8 line 181-182 (“The nonlinear regression approach correlated adsorption equilibrium data using the Origin software.”)

**On the other hand, I disagree with the classification of some isotherm as H-type. Please review this classification. Authors have not reported the results of these adsorbents after the heavy metal adsorption. This information will complement the analysis and discussion of adsorption mechanism.**

### Reply:

The information on the H-shape isotherm has been removed from the manuscript. The reviewer can see Figure 6 (no denoted for H-shape).

Many thanks.

# Enhanced separation capacity of carbonaceous materials (hydrochar, biochar, and activated carbon) towards potential toxic metals through grafting copolymerization

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30

31

## ABSTRACT

Oxygen-containing groups in the surface of materials (i.e.,  $-\text{COOH}$  and  $-\text{OH}$ ) often play a key role in adsorbing toxic metals. Acrylic acid ( $\text{CH}_2 = \text{CHCOOH}$ ) is used as a green grafter for enhancing the density of those groups in carbonaceous materials, and ammonium cerium nitrate is used as an initiator. Hydrochar (prepared through hydrothermal carbonization at  $190^\circ\text{C}$ ), biochar (generated via pyrolyse at  $800^\circ\text{C}$ , and activated carbon (AC; produced through chemical activation with  $\text{K}_2\text{CO}_3$  at  $800^\circ\text{C}$ ) derived from ginger residues were used as feedstock materials for the grafting process. The carbonaceous materials were characterized using scanning electron microscopy, X-ray photoelectron spectrometry, Brunauer–Emmett–Teller (BET) analyzer, Fourier transform infrared spectroscopy, and zeta potential.  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  were selected as adsorbates. Equilibrium adsorption experiments for the three metal ions on the un-grafted and grafted carbonaceous materials were conducted at  $25^\circ\text{C}$  and pH 5.0. Results indicated that the oxygen content in the grafted materials was higher than that of un-grafted ones. The grafting process could increase the OH and COOH functional groups on the carbonaceous materials, which leads to increasing the adsorptive amounts of metal ions. The Langmuir maximum adsorption capacity ( $Q_{\text{max}}$ ) of carbonaceous materials for toxic metal ions (mol/kg) followed  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ . The adsorptive amounts of potentially toxic metal ions on the un-grafted and grafted (abbreviated as G) materials followed hydrochar  $>$  AC  $>$  biochar. The  $Q_{\text{max}}$  value of hydrochar (72.8, 74.7, and 109.3 mg/g), biochar (53.6, 69.1, 53.9 mg/g), AC (54.4, 73.1, 101.8 mg/g), G-hydrochar (130.9, 146.0, 271.4 mg/g), G-biochar (92.6, 143.6, 153.6 mg/g), G-AC (96.3, 146.1, 259.1 mg/g) for adsorbing metals ( $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ ) was higher than that of commercial activated carbon (21.83, 22.13, 25.15 mg/g, respectively). The adsorption capacity of the grafted hydrochar was restored after five adsorption/desorption cycles. The primary adsorption mechanisms were complexation and ion exchange.

**Keywords:** Acrylic acid; Agricultural Waste; Adsorption; Desorption; Ion exchange; Heavy metal; Water treatment

## 1. Introduction

Wastewater discharged into rivers or irrigation ditches contains heavy metal ions that can lead to soil contamination or adverse effects on organisms. Although heavy metal ions can be removed through chemical precipitation, a small quantity is discharged into water bodies. For this reason, strict regulations have been set to limit the concentration of heavy metals in effluents. When effluent standards for heavy metals cannot be achieved using chemical precipitation, new methods are required to effectively remove heavy metals from the effluent. Various advanced treatment methods for heavy metal removal have been developed in the past [1, 2] and of these, using adsorbents is a low-cost and highly efficient treatment method. Minerals, biosorbents, and carbonaceous materials have been used to adsorb heavy metal ions [3-5]. Generally, carbonaceous materials (including activated carbon, biochar, hydrochar, carbon nanotubes, carbon spheres, and graphene oxide) are used as adsorbents in water or wastewater treatment procedures to adsorb heavy metal ions. Activated carbon with a high specific surface area is commonly used to remove contaminants [3, 4, 6, 7].

Activated carbon can be derived from agricultural waste rich in cellulose. The synthesis process for activated carbon is divided into two stages: carbonization and activation. Carbonization can be carried out through a hydrothermal method or calcination under oxygen-deficient conditions [8, 9]. Subsequently, acid, base, and other salts were frequently used as activators to increase the surface area of activated carbon specifically [4, 9]. When agricultural waste is carbonized using the hydrothermal method, the byproduct can also be called hydrochar [10]. Hydrochar possesses rich functional groups on its surface that can effectively adsorb heavy metals [9]. The agricultural waste was calcined under oxygen-deficient conditions to generate biochar [5]. Biochar has also been used to adsorb heavy metal ions [11]. Moreover, biochar has been mixed with soil, which can reduce the uptake of heavy metal ions by plants [5].

In this study, ginger wastes were selected as the raw material, and three-stage processes were

82 performed to synthesize activated carbon. First, hydrochar was produced using a hydrothermal  
83 method. Second, the hydrochar was calcined at 800 °C under oxygen-deficient conditions to obtain  
84 the biochar. Third, biochar mixed with K<sub>2</sub>CO<sub>3</sub> was calcined to increase the specific surface area to  
85 obtain activated carbon. The synthesized hydrochar, biochar, and activated carbon were used to  
86 adsorb the heavy metal ions Cu<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup>.

87 To further increase the adsorptive amounts of metal ions, the three carbonaceous materials were  
88 modified by a polymerization reaction, which effectively increased the OH or COOH functional  
89 groups on the surface of the carbonaceous materials [4, 12]. Acrylic acid was used to provide OH or  
90 COOH functional groups, and ammonium cerium (IV) nitrate was used as an initiator to complete  
91 the graft copolymerization reaction. Few studies have used grafted carbonaceous materials for the  
92 removal of potentially toxic metal ions. It is expected that the grafting process can effectively enhance  
93 the adsorption of potentially toxic metals on carbonaceous materials. Thus, the adsorptive amounts  
94 of the test metals on the modified carbonaceous materials were compared with those on unmodified  
95 carbonaceous materials in this study. Potential adsorption mechanisms were elucidated.

96 The authors emphasized that one raw material (ginger) produces three carbonaceous materials  
97 (hydrochar, biochar, and AC) to carry out the grafting process. Then, the authors compared the  
98 difference among the hydrochar, biochar, and AC. The increase in adsorptive amounts of three  
99 potentially toxic metals was discussed after the grafting process. The cost of biochar and hydrochar  
100 synthesis is far lower than that of activated carbon. The study can provide the best choice for  
101 wastewater treatment.

## 102 **2. Materials and methods**

### 103 **2.1. Materials**

104 All chemicals in the experiments were purchased from Merck or Sigma Aldrich (purity > 95 %)

105 and used without further purification. **Ginger residues were** used as the raw material in this study and  
106 purchased from a local market in Taiwan. Copper nitrate [Cu(NO<sub>3</sub>)<sub>2</sub>], cadmium nitrate [Cd(NO<sub>3</sub>)<sub>2</sub>],  
107 and lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] were used to prepare solutions for adsorption experiments. Acrylic acid  
108 (C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>) and ammonium cerium (IV) nitrate (H<sub>8</sub>CeN<sub>8</sub>O<sub>18</sub>) were selected for grafting, and potassium  
109 carbonate (K<sub>2</sub>CO<sub>3</sub>) was used as the activator to reduce secondary pollution. Sodium hydroxide  
110 (NaOH) and hydrochloric acid (HCl) were used to adjust solutions pH.

## 111 **2.2. Preparation of carbonaceous materials**

112 The **ginger wastes that were collected from local markets were** washed with deionized distilled  
113 water and dried in an oven at 90 °C for 4 h. The dried raw material was then ground and sieved through  
114 a 100-mesh screen. After the pre-treatment process, 15 g of raw materials mixed with 100 mL of  
115 deionized distilled water was added to a 100 mL Teflon vessel, sealed in a stainless-steel vessel, and  
116 heated at 190 °C for 24 h. When the reaction was complete, the sample was collected and washed with  
117 deionized distilled water to remove impurities. The sample was then oven-dried overnight at 60 °C,  
118 and the product was called **hydrochar**.

119 The 50-g hydrochar sample was placed in a crucible and covered. After calcination at 800 °C  
120 for 4 h under oxygen-deficient conditions, the sample was collected and washed with 0.1 N HCl and  
121 deionized distilled water until a near-neutral pH value was reached. The samples were oven-dried  
122 overnight at 60 °C and the product was called **biochar**.

123 The 50-g biochar was mixed with K<sub>2</sub>CO<sub>3</sub> at a weight ratio of 1:1 and then placed in a crucible  
124 and covered. The sample was calcined in an oven at 800 °C under oxygen-deficient conditions and  
125 then washed with 0.1 N hydrochloric acid and deionized distilled water until a near-neutral pH value  
126 was reached. **After that**, the sample was dried and called activated carbon (**AC**).

127 The three carbonaceous materials were modified using the same grafting copolymerization  
128 procedure at a room temperature 25 °C. A primary experiment was carried out to explore the optimal

129 conditions for the grafting copolymerization (data not shown). After the optimal experiment, the  
130 experimental procedure was obtained and reported in this study. Briefly, one gram of carbonaceous  
131 material was added to 200 mL of deionized distilled water, and the solution was heated to 90 °C.  
132 Twenty milliliters of acrylic acid and 20 mL of ammonium ceric nitrate (0.225 M) were added to the  
133 solution and allowed to react for 90 min. When the solution cooled to room temperature, the solid  
134 and solution were separated by centrifugation at 7000 rpm for 15 min. The samples were then oven-  
135 dried overnight at 60 °C. After the grafting copolymer reaction, the carbonaceous material samples  
136 were immersed in a 200 mL solution containing NaOH (0.2M) for 70 min. The samples were collected  
137 and rinsed with DD water until near-neutral pH values. Subsequently, the samples were dried  
138 overnight at 60 °C to generate grafted carbonaceous materials. The carbonaceous materials (hydrochar,  
139 biochar, and AC) after grafting were called G-hydrochar, G-biochar, and G-AC, respectively.

140 In summary, the procedure for the preparation of un-grafted and grafted carbonaceous materials  
141 is summarized in **Figure 1**.

142 **Figure 1**

### 143 **2.3. Properties of carbonaceous materials**

144 A field-emission scanning electron microscope (SEM, Hitachi S-4800, Japan) observed the  
145 surface morphologies of the synthesized adsorbents. An X-ray photoelectron spectrometer (XPS)  
146 device (ESCALAB 250, Thermo Scientific, USA) measured the elemental composition of the  
147 carbonaceous materials and chemical bonding on the surface of the carbonaceous materials. The  
148 functional groups on the surfaces of the adsorbents were analyzed using Fourier transform infrared  
149 spectroscopy (FTIR, FT/IR-6600, JASCO). Carbonaceous materials were mixed with potassium  
150 bromide (KBr) to obtain the FTIR spectra in the wavenumber range 400–4000 cm<sup>-1</sup>. The increased  
151 number of COOH groups on the grafted adsorbents can be observed in the FTIR spectra. Zeta  
152 potentials of the material were detected by a Zetasizer 3000HS (Malvern Co.)

153 Textural properties of the materials were calculated based on nitrogen adsorption/desorption  
154 isotherm at 77 K using an ASAP 2020 analyzer (Micromeritics, USA). The BET specific surface area  
155 ( $S_{\text{BET}}$ ) and Langmuir surface area ( $S_{\text{Lang}}$ ) of the materials were calculated from the Brunauer-Emmett-  
156 Teller (BET) equation and Langmuir equation, respectively. Their total pore volume ( $V_{\text{Total}} = Q_{0.99}/647$ )  
157 was computed based on the single point adsorption (quantity adsorbed  $Q_{0.99}$ ; cm<sup>3</sup>/g STP) at the highest  
158  $p/p^\circ$  value ( $\sim 0.99$ ) [13]. The  $t$ -plot method was applied for determining the micropore volume ( $V_{\text{Micro}}$ ;  
159 pore width <2 nm), micropore area ( $S_{\text{Micro}}$ ), external surface area ( $S_{\text{Ext}}$ ) of the materials [13]. Their  
160 ultra-micropore volume ( $V_{\text{Ultra-micro}}$ ) or narrow microporosity (pore width <0.8 nm) was determined  
161 by the Horvath–Kawazoe method [14].

## 162 2.4. Adsorption experiments

### 163 2.4.1. Adsorption isotherm of each metal

164 Adsorption isotherms for the potentially toxic metals on the un-grafted and grafted  
165 carbonaceous materials at 25 °C were obtained to evaluate the adsorption characteristics and estimate  
166 the maximum adsorption capacities. The concentrations of metal ions ranged from approximately 10  
167 to 1000 mg/L. To avoid precipitation, the pH values of the solutions were adjusted to 5.0 (pH<sub>eq</sub>) before  
168 and during the adsorption processes.

169 A dried mass of 0.02 g of each adsorbent was added to the solutions containing various  
170 concentrations of potentially toxic metal ions. The solutions were then placed on a reciprocal shaker  
171 at 120 rpm for 24 h. Following this, the solutions were passed through a 0.45-μm filter. The filtrate  
172 was collected, and the potentially toxic metal concentration was measured using a flame atomic  
173 absorption spectrometer (Avanta/AAS, GBC). To avoid competitive adsorption, only one potentially  
174 toxic metal was tested in the adsorption experiment. Each experiment was performed in duplicate,  
175 and the resulting data were averaged. If the bias of a repeated experiment exceeded 15%, a triplicate  
176 run was performed. Finally, the Langmuir equation estimated the maximum adsorption capacity of

177 the adsorbents.

178 The amount of contaminants adsorbed by carbonaceous materials at a given concentration at  
179 equilibrium is represented as  $q_e$ . The  $q_e$  (mg/g) was calculated using the mass balance equation.

$$q_e = \frac{(C_o - C_e)}{m} V \quad (1)$$

180 where  $C_o$  (mg/L) and  $C_e$  (mg/L) are the initial and equilibrium concentrations of the adsorbates,  
181 respectively;  $m$  (g) is the mass of the adsorbent; and  $V$  (L) is the volume of each adsorbate solution.

182 The Langmuir and Freundlich models are shown in Equations 2 and 3 to describe the  
183 characteristics of the selected adsorbates on the composite material. Those models are often applied  
184 for modeling the experimental data of adsorption equilibrium [3, 4, 9, 12, 15]. The nonlinear  
185 regression approach correlated adsorption equilibrium data using the Origin software.

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

186 where  $Q_{\max}$  (mg/g) is the maximum adsorption capacity of the adsorbate on the adsorbent;  $K_L$  (L/mg)  
187 is the Langmuir constant; and  $K_F$  [(mg/g)/(mg/L) <sup>$n$</sup> ] and  $n$  (dimensionless) are the Freundlich  
188 constants.

189 For comparison, a commercial activated carbon (CAC) purchased from Merck Company  
190 (SAFC, 102555) was utilized. Its BET specific surface area is higher than 1000 m<sup>2</sup>/g. The maximum  
191 adsorption capacity of CAC to each target metal was estimated through the adsorption isotherm.



## 2.4.2. Competitive adsorption

The adsorption capacity of the materials under mixture solutions was studied by competitive adsorption. The initial concentrations of metal ions in the mixture were prepared at 1, 10, and 50 mmol/L. Around 0.02 g of the material was added to the solution (50 mL) containing three metals ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ ) at different initial metal concentrations. The  $\text{pH}_{\text{eq}}$  of solution was maintained at 5.0 during the adsorption process. The competitive adsorption was fixed at a contact time of 24 h and 30 °C.

## 2.4.3. Study of adsorption–desorption cycle

The reusability of the metal-laden materials was evaluated through an adsorption–desorption cycle study. The selection of adsorption conditions (especially initial metal concentration) is very important these experiments. If the initial metal concentration is too low, the adsorption sites in the material might not be saturated by the metal ions. Therefore, the adsorption study was conducted at ~1000 mg/L of each toxic metal and under conditions: 0.4 g/L, pH 5.0, 24 h, and 30 °C. Because the adsorbates ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ ) are cations, an acid was used as a target desorbing agent. The experimental conditions for desorption study were 0.1 N HCl, 0.4 g/L, 30 °C, and 1 h. Desorption efficiency was calculated based on Equation 4.

$$\% \text{Desorption} = \frac{q_{e(2)}}{q_{e(1)}} \quad (4)$$

where  $q_{e(1)}$  and  $q_{e(2)}$  are the adsorption capacity of the material at the 1<sup>st</sup> and the 2<sup>nd</sup> cycles of adsorption and desorption, respectively.

# 3. Results and discussion

## 3.1. Characteristics of adsorbents

The textural characteristics of the six carbonaceous materials are presented in **Table 1**. The

hydrochar with its low  $S_{\text{BET}}$  and  $V_{\text{Total}}$  (3.078 m<sup>2</sup>/g and 0.022 cm<sup>3</sup>/g) was a typical non-porous material. The agricultural waste was produced by a hydrothermal process, which might generate a similar structure [9, 16]. In addition, the external surfaces of the hydrochar (Figure 2a) did not exhibit obvious pore structures because this carbonaceous material was not chemically activated or thermally treated. Activated carbon and biochar were expected to possess a higher  $S_{\text{BET}}$  value.

## Table 1

## Figure 2

In contrast to the hydrochar, the biochar (533.3 m<sup>2</sup>/g and 0.223 cm<sup>3</sup>/g) and AC (991.9 m<sup>2</sup>/g and 0.485 cm<sup>3</sup>/g) were porous materials with their high  $S_{\text{BET}}$  and  $V_{\text{Total}}$ . This is consistent with the observation of their surface morphology in Figure 2b–2c. Similarly, the other authors [9] reported that the  $S_{\text{BET}}$  values of activated carbons developed from hydrochar (derived from *Crocus sativus* petals) through a chemical activation (using KOH) ranged from 788 to 1497 m<sup>2</sup>/g. The  $S_{\text{BET}}$  and  $V_{\text{Total}}$  value of the AC (991.9 m<sup>2</sup>/g and 0.485 cm<sup>3</sup>/g) were close to that of commercial activated carbon (CAC; 1241 m<sup>2</sup>/g and 0.445) [4].

Notably, although the surface morphology of the grafted materials (Figure 2d–f) did not indicate a remarkable change compared to their pristine materials (Figure 2a–c), their  $S_{\text{BET}}$  and  $V_{\text{Total}}$  (especially for biochar and AC) decreased after the grafting process (Table 1). However, the change of textural properties of three materials after grafting was less important than others (i.e., surface chemistry and functionality) in determining the adsorption amounts of toxic metals. In essence, toxic metal ions adsorbed on carbonaceous materials are mainly correlated with the functional groups on their surface rather than their textural properties [12, 17]. Thus, the  $S_{\text{BET}}$  value was less relative to the adsorption amount. However, a high  $S_{\text{BET}}$  may increase the adsorption of other contaminants, such as organic contaminants [3]. In contrast, the adsorbent with a high  $S_{\text{BET}}$  value could provide more active sites to increase the grafting efficiency. In addition, it provides information to understand the

237 characteristics of carbonaceous materials.

238 For carbonaceous materials, the oxygen content is a critical factor in determining the adsorptive  
239 amounts of potentially toxic metal ions. The oxygen content correlates with the COOH or OH groups  
240 that might generate ion exchange or complexation reactions with metal ions [5, 9]. The carbon content  
241 can determine whether the synthesized material is carbonaceous. The main elements of the six  
242 carbonaceous materials that were measured by the XPS technique (Figure S1; full scan XPS survey)  
243 are listed in Table 2. All the carbonaceous materials in this study were mainly composed of C and O,  
244 and the other elements (i.e., Na and Ce) were present after grafting. The carbon contents of all samples  
245 exceeded 70%, demonstrating the successful production of carbonaceous materials. The oxygen  
246 content ranged from 18% to 25%, indicating that the adsorbents can uptake potentially toxic metal  
247 ions through feasible complexation mechanisms [5, 9, 12]. Since the grafting process requires the use  
248 of NaOH and H<sub>8</sub>CeN<sub>8</sub>O<sub>18</sub>, sodium, and cerium were present in the grafted carbonaceous materials.  
249 In addition, K<sub>2</sub>CO<sub>3</sub> was used as the activator, causing AC to possess a small amount of potassium.

## 250 Table 2

251 The main objective of the grafting process was to increase the number of oxygen-containing  
252 groups (–COOH or –OH) on the surface of carbonaceous materials. The oxygen content of the grafted  
253 material increased after grafting. The results exhibited that the oxygen on acrylic acid was transferred  
254 onto the carbonaceous materials to form the –COOH or –OH groups and that grafting was  
255 successfully performed. Because bivalent metals were used as adsorbates, the Na (I) and Ce (IV)  
256 contents affected the adsorptive amounts. The high Na content favored the adsorption of the tested  
257 metal ions on the adsorbents. In contrast, the high Ce content did not favor the adsorption of the  
258 potentially toxic metal ions on the adsorbents.

259 The main functional groups on the adsorbent surface are critical in determining the adsorption  
260 amounts of the tested contaminants. Although the high oxygen content of carbonaceous materials

could lead to high adsorptive amounts of potentially toxic metal ions, the functional groups on the un-grafted and grafted carbonaceous materials needed to be analyzed through the narrowed scan O 1s XPS and FTIR. Although the narrowed scan C 1s XPS (Figure 3 a–c) provides the information on the O–C=O group at around 288 eV, the majority is helpful for identifying the C–H/C–C and C=C group (at around 284 eV) in the aromatic structure of the materials [10, 15, 18]. In contrast, Figure 3 d–e provides the O 1s XPS spectrum of the un-grafted and grafted materials. In general, the peaks at approximately 531, 532, and 533 eV can be designed for the carbonyl, carboxylic, and hydroxyl groups, respectively [15, 18, 19]. For the hydrochar, the main peak was shifted from 532.6 eV to 531.5 eV after the grafting process. In contrast, negligible change was observed in the relevant peak in the O 1s spectrum of the biochar before (531.7 eV) and after (531.4 eV) the grafting process. Meanwhile, the peak at 531.6 eV in the AC was deconvoluted into two peaks at 563.4 eV and 529.4 eV. The results suggest that the presence of the oxygen-containing groups in the grafted materials was different in nature.

### Figure 3

The FTIR data showed that the functional groups of the grafted carbonaceous materials were similar to those of the un-grafted carbonaceous materials (Figure 4). The results indicate that the grafting process did not destroy the functional groups on the adsorbent. The bands at approximately 3450  $\text{cm}^{-1}$  are attributed to the OH group stretching vibrations [9, 18]. Alcoholic phenols and carboxylic acids can provide functional groups. The bands at nearly 1640  $\text{cm}^{-1}$  are potentially provided by C=O groups, such as carboxylic acids [3, 9, 18]. Meanwhile, the identified bands at 1080  $\text{cm}^{-1}$  are attributed to C–O groups [3, 4, 10, 15]. Moreover, the bands observed at 1650  $\text{cm}^{-1}$  and 650  $\text{cm}^{-1}$  are ascribed to the vibration of aromatic C=C and C–H [10, 15, 18]. As the main components of ginger contain lignin or cellulose, carbonaceous materials derived from ginger wastes were rich in the C=O and OH groups.

## Figure 4

In addition, the intensities of the C=O and OH functional groups on the surface of the grafted materials were higher than those of the un-grafted material (Figure 4). The other functional groups on the surface showed no significant changes. The intensities of the C=O and OH functional groups increased in the following order: hydrochar > AC > biochar. When adsorbents had more OH and COOH functional groups on their surfaces, they yielded more cation exchange sites to adsorb the tested metal ions. In contrast, oxygen in the OH and COOH functional groups could generate a complexation reaction with  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  [5, 9]. The results indicate that grafted materials can generate higher adsorptive capacities than un-grafted materials.

The zeta potentials the carbonaceous materials (Figure 5) provided information on the charge state (positive or negative) on their external surface within solutions pH. In general, the external surface charge of three materials indicated remarkable changes after the grafting process. However, the tendency of such change are different among hydrochar, biochar, and AC, which results from fundamental difference on their properties (i.e., their surface chemistry in Figure 3). For example, the pH at the isoelectric point ( $\text{pH}_{\text{IEP}}$ ) of AC decreased from 4.21 to 2.28 after the grafting process (Figure 5c). A similar decrease in this point was found in the case of hydrochar. In essence, a material (i.e., G-hydrochar) with its lower  $\text{pH}_{\text{IEP}}$  value often possesses higher actively functional groups and higher negatively charged surface than others (i.e., hydrochar).

## Figure 5

### 3.2. Adsorption isotherms of potentially toxic metal ions on carbonaceous materials

The adsorption isotherms of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  on the carbonaceous materials are illustrated in Figure 6. The curves were concave downward, indicating that the metal ions favor adsorption on the tested carbonaceous materials. Both the un-grafted and grafted adsorbents could be used to remove the three metal ions from the solution. The curves were denoted as an L-type isotherm for the

un-grafted materials (**Figures 6a–c**) and the grafted materials (**Figures 6d–f**). The classification for the shape of adsorption isotherm has been reported in the document [20]. In essence, this shaped isotherm indicates that adsorbent has a great adsorption affinity to adsorbate in solution (even at low initial adsorbate concentration). The result suggests that the grafted materials exhibited a higher adsorption affinity to the potentially toxic metals in the solution than the un-grafted materials.

### **Figure 6**

As expected, the adsorption capacities of the three metal ions on the grafted materials were higher than those on the un-grafted materials. The grafting process increased the amounts of metal ions adsorbed on the carbonaceous material. According to the surface characteristics, grafted materials with the high density of the OH and COOH groups generate higher adsorption capacities for potentially toxic metal ions. The un-grafted and grafted materials exhibited a negatively charged surface (**Table 1**) because their zeta potentials were negative and ranged from  $-21.2$  to  $-40.1$  mV (**Figure 5**). In the literature, the zeta potentials of CAC and tire wastes-derived AC reported were  $-36.1$  mV and  $-34.5$  mV [4]. Therefore, the adsorption of cation metals ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ ) through electrostatic attraction was highly feasible. Generally, the primary adsorption mechanism of  $\text{Pb}^{2+}$  on carbonaceous materials was ion exchange. The primary adsorption mechanisms of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  are ion exchange and complexation reactions, respectively. The ion exchange ability depends on the ion radius. Among the three metal ions, the ion exchange ability followed the order  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . In contrast, the ability of the complex reaction for the three metal ions follows the order  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$  based on the literature [21]. The amounts of the three metal ions adsorbed can be used to evaluate the potential adsorption mechanisms.

### **3.3. Adsorptive amounts of potentially toxic metal ions on carbonaceous materials**

When comparing the values of the adjusted coefficient of determination ( $\text{adj-}R^2$ ) and the reduced chi-square statistics ( $\text{red-}\chi^2$ ) for the two models, the Langmuir model ( $\text{adj-}R^2 = 0.9015$ –

0.9987 and  $\text{red-}\chi^2 = 1.2\text{E-}05\text{--}2.9\text{E-}03$ ; **Figure 6** and **Table 3**) fits well with the adsorption of the three metal ions on carbonaceous materials compared to the Freundlich model ( $\text{adj-}R^2 = 0.883\text{--}0.9939$  and  $\text{red-}\chi^2 = 66\text{E-}05\text{--}24\text{E-}03$ ; **Figure S2** and **Table S1**).

### **Table 3**

All  $\text{adj-}R^2$  values in the Langmuir model were greater than 0.90, indicating that the maximum adsorptive capacities of the metal ions could be estimated using the Langmuir model. In addition, all  $n$  values in the Freundlich model ( $n = 2.082\text{--}7.736$ ) were greater than 1.0, demonstrating that the test metal ions adsorbed on the synthesized materials were favorable. Generally,  $n$  values lie within the range of 1.0–10. This result is consistent with that of other studies [3, 4, 12, 15].

The maximum capacities of the three metal ions on the un-grafted carbonaceous materials followed the order of the hydrochar > AC > biochar (**Figure 7**). Similarly, the grafted carbonaceous materials exhibited the following order: G-hydrochar > G-AC > G-biochar (**Figure 7**). Functional groups, such as  $\text{--OH}$  and  $\text{--COOH}$ , are critical factors in determining the adsorptive amount of potentially toxic metal ions. The hydrochar derived from agricultural waste containing cellulose can maintain functional groups on the surface. It possessed the highest adsorptive amounts toward metal ions. The biochar was synthesized at 800 °C under oxygen-deficient conditions. The binding of the  $\text{--OH}$  and  $\text{--COOH}$  groups could be broken to form other functional groups. The results can be demonstrated by the intensities of the  $\text{--COOH}$  and  $\text{--OH}$  groups in the FTIR spectra and XPS data. The activator potassium carbonate mixed with the carbonaceous material under high-temperature and oxygen-deficient conditions can react with the functional groups on the surface of carbonaceous materials. Potassium may bond to the surface of carbonaceous materials. These results can be demonstrated through the potassium content measured by XPS. This can increase the cation exchange capacity of the adsorbent, leading to a higher adsorptive amount of metal ions.

### **Figure 7**

357 For the tested metal ions on all carbonaceous materials, the adsorptive amounts, based on the  
358 mol/kg ratio, were in the order of  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$  (Figure 7 and Table 3). As mentioned before,  
359 the primary  $\text{Pb}^{2+}$  adsorption mechanism in carbonaceous materials is ion exchange. Therefore,  $\text{Pb}^{2+}$   
360 generated the lowest amount of adsorption on the synthesized adsorbents. In addition to ion exchange,  
361  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  might generate a complexation reaction with the OH and COOH groups on the surface  
362 of the carbonaceous materials. However,  $\text{Cu}^{2+}$  possesses better complexation ability for the OH and  
363 COOH groups because it is a transition metal. The adsorptive amounts followed the order  $\text{Cu}^{2+} >$   
364  $\text{Cd}^{2+} > \text{Pb}^{2+}$ . These results demonstrate that both ion exchange and complexation reactions are the  
365 primary mechanisms in this study.

### 366 3.4. Effects of the grafting process on the adsorptive amounts

367 Although the grafting process can increase the –OH and –COOH groups on carbonaceous  
368 materials, the effects of the grafting process on different carbonaceous materials could generate a  
369 discrepancy in the results. Table 4 indicates the enhanced ratio of the adsorptive amounts of the three  
370 carbonaceous materials after the grafting process.

371 Table 4

372 The enhanced ratios for the adsorptive amounts of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  on the three adsorbents  
373 ranged from 1.727–1.797, 1.956–2.080, and 2.483–2.850, respectively. Although the  $S_{\text{BET}}$  values  
374 (Table 2) indicate the order  $\text{AC} > \text{biochar} > \text{hydrochar}$ , the enhanced ratios exhibit an approximate  
375 result for the specific metal ions in the three carbonaceous materials. The results showed that the  $S_{\text{BET}}$   
376 values are less important parameters for the increase in the –COOH and –OH groups during the  
377 grafting process. In addition, the high enhanced ratio for the adsorptive amounts of the three  
378 potentially toxic metal ions indicated that the grafting process is effective for increasing the removal  
379 of metal ions.

380 For the three carbonaceous materials, the enhanced ratios of the adsorptive amounts exhibited



the order  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . As  $\text{Pb}^{2+}$  barely undergoes a complexation reaction with oxygen-containing functional groups, the primary adsorption mechanism was regarded as ion exchange. In contrast, complexation is an important adsorption mechanism for  $\text{Cu}^{2+}$  on carbonaceous materials. The enhanced ratios of the adsorptive amounts for  $\text{Pb}^{2+}$  were higher than those for  $\text{Cu}^{2+}$ . These results indicated that ion exchange was the primary adsorption mechanism, and the complexation reaction was the secondary mechanism.

The results reveal that the grafting process can effectively increase the amounts of potentially toxic metal ions adsorbed on carbonaceous materials. The grafted hydrochar ( $Q_{\max} = 271.4, 146.0, 130.9 \text{ mg/g}$ ) could generate the highest adsorptive amounts of metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ ); and its values  $Q_{\max}$  were overwhelmingly higher than those of CAC (25.15, 22.13, 21.83 mg/g; Table 3) in this study and others reported the literature, such as powdered CAC (24.8, 1.12, and 3.18 mg/g) and granular CAC (6.21, 1.12, and 2.54 mg/g, respectively) [22].

Other researchers [4] reported that the values  $Q_{\max}$  of CAC for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  were 42.5 and 15.0 mg/g that was remarkably lower than the grafted hydrochar ( $Q_{\max} = 298.1$  and 136.3 mg/g). However, the hydrochar was seldom applied in real water or water treatment. The use of the grafted hydrochar may be more widely adopted in wastewater treatment in the future. Soil mixed with the biochar has been studied for its ability to reduce the uptake of potentially toxic metal ions by plants. The grafted biochar in the soil can effectively reduce harm to human beings. The AC is frequently used to remove organic compounds from wastewater or water. The grafted AC can simultaneously adsorb metal ions and organic contaminants to simplify the treatment process.

### 3.5. Competitive adsorption

The competitive adsorption was evaluated at three initial concentrations of the mixture metals (1, 10, and 50 mmol/L). Figure 8 shows that the reference ranking of three metals onto G-hydrochar was in the following order:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$  (when  $C_0 = 1 \text{ mmol/L}$ ),  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$  at higher

405 concentration ( $C_o = 10$  mmol/L), and  $Cu^{2+} > Cd^{2+} > Pb^{2+}$  ( $C_o = 50$  mmol/L). The result suggests that  
406 the adsorption order of the grafted hydrochar toward three target metals was strongly dependent on  
407 the initial concentrations of metals in the mixture. The adsorption sites in G-hydrochar were more  
408 favorable to the Cu ions than the Pb and Cd ions at high initial concentrations (10 and 50 mmol/L).

## 409 **Figure 8**

### 410 **3.6. Cycle of adsorption/desorption**

411 The stability of G-hydrochar was evaluated through studying adsorption/desorption cycles.  
412 Because the toxic metals ( $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Pb^{2+}$ ) are cations, hydrochloric acid ( $H^+$  ions) is selected  
413 as a target desorbing agent for removing them from G-hydrochar. The adsorption study was conducted  
414 at a high metal concentration (~1000 mg/L) to ensure that the adsorption sites in G-hydrochar were  
415 saturated or occupied by metal ions. **Figure 9** shows the desorption efficiency was higher than 98%.  
416 The adsorption capacity of G-hydrochar slightly decreased after each cycle. The result suggest that  
417 the grafting process of the co-polymers was successful and the active adsorption sites in G-hydrochar  
418 were highly stable.

## 419 **Figure 9**

### 420 **4. Conclusions**

421 Notably, an increase in the oxygen content along with the presence of Na and Ce on the surface  
422 of grafted materials (G-hydrochar, G-biochar, and G-AC) confirm success in grafting  
423 copolymerization into the surface of the carbonaceous materials.

424 In this study, ginger waste was used as a raw material to synthesize hydrochar, biochar, and

425 activated carbon. The grafting process was performed on the three materials to increase the density  
 426 of –OH and –COOH functional groups. The grafted carbonaceous materials possessed more –OH and  
 427 –COOH functional groups to increase the adsorptive amounts of the tested metal ions through  
 428 complexation reactions and ion exchange. The adsorptive amounts of the tested metal ions were in  
 429 the order of hydrochar > AC > biochar and G-hydrochar > G-AC > G-biochar. For the tested metal  
 430 ions, the adsorptive amounts followed the order  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ . The grafting process enhanced  
 431 the adsorptive amounts of metal ions by approximately 1.7–2.8 times. The grafted carbonaceous  
 432 hydrochar was the best adsorbent where the contaminants were potentially toxic metal ions. This  
 433 material can be applied for five adsorption /desorption cycles without significant change in its  
 434 adsorption capacity. When organic contaminants and potentially toxic metal ions exist in water bodies,  
 435 G-AC can be used to remove them.

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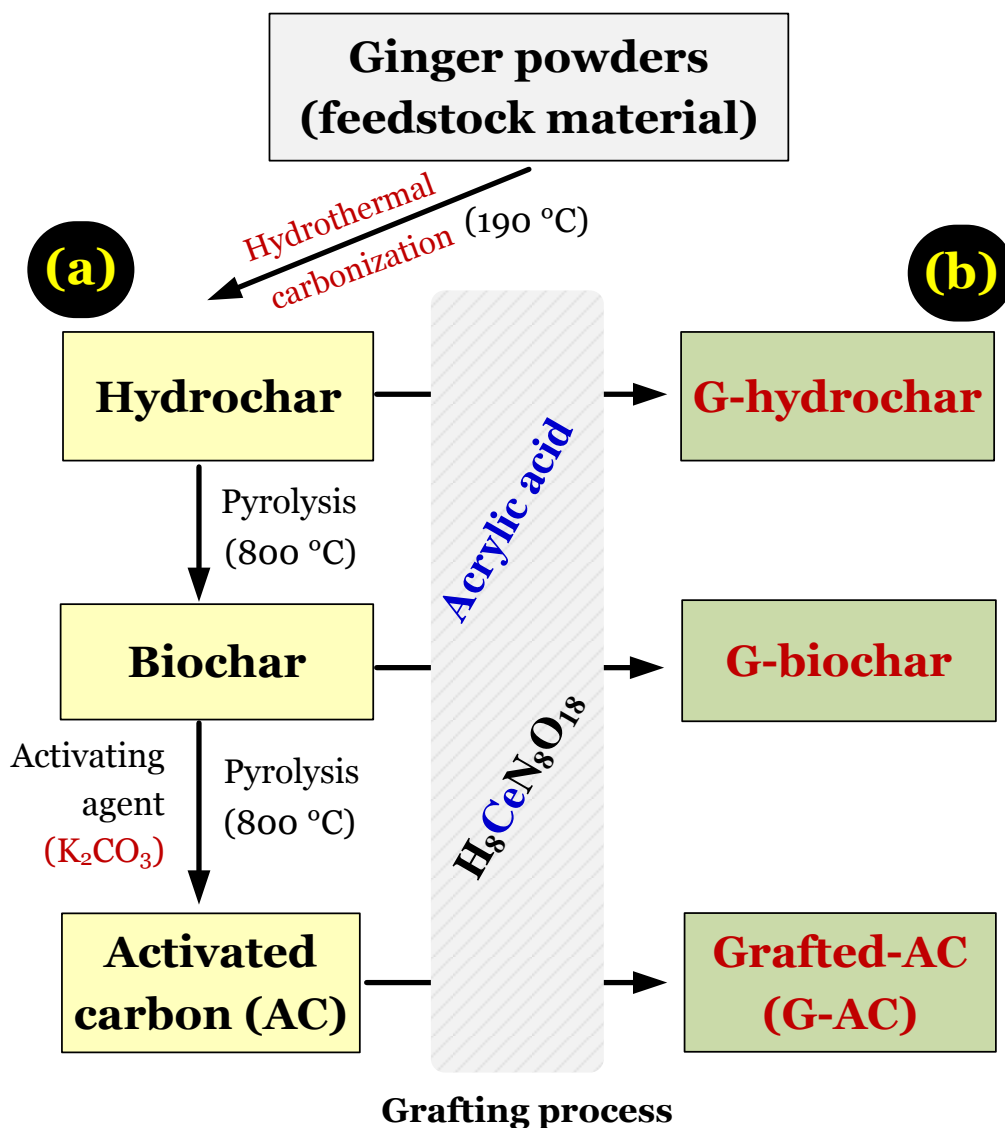
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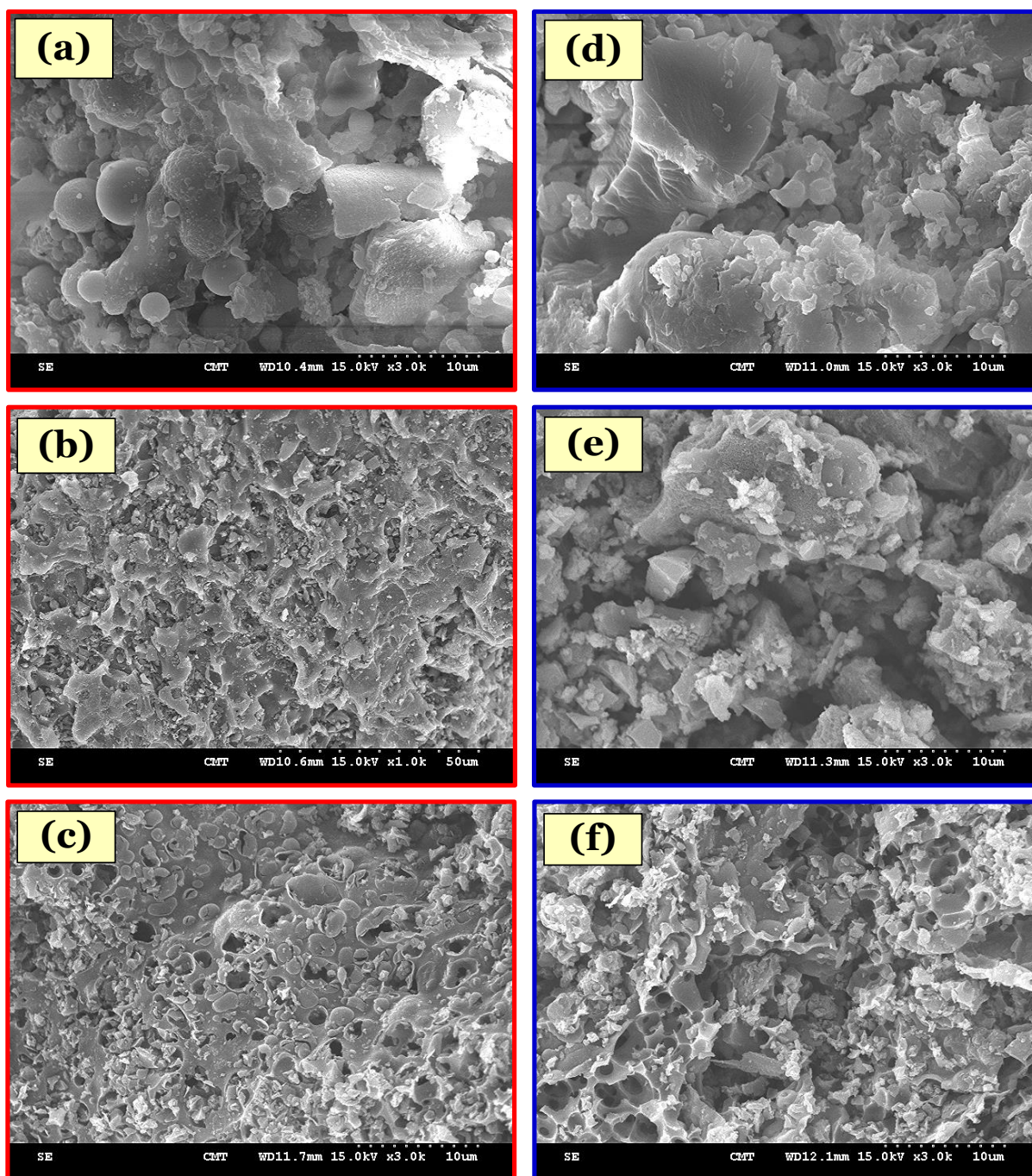
## Highlights

1. New grafting copolymerization using acrylic acid and ammonium cerium nitrate developed
2. Hydrochar, biochar, and activated carbon used as carbonaceous feedstocks for grafting
3. Grafting materials exhibiting excellent adsorption capacity than their feedstocks
4. The order for maximum adsorptive amounts (mol/kg):  $\text{Cu} > \text{Cd} > \text{Pb}$
5. Grafted hydrochar possessing the highest adsorption capacity



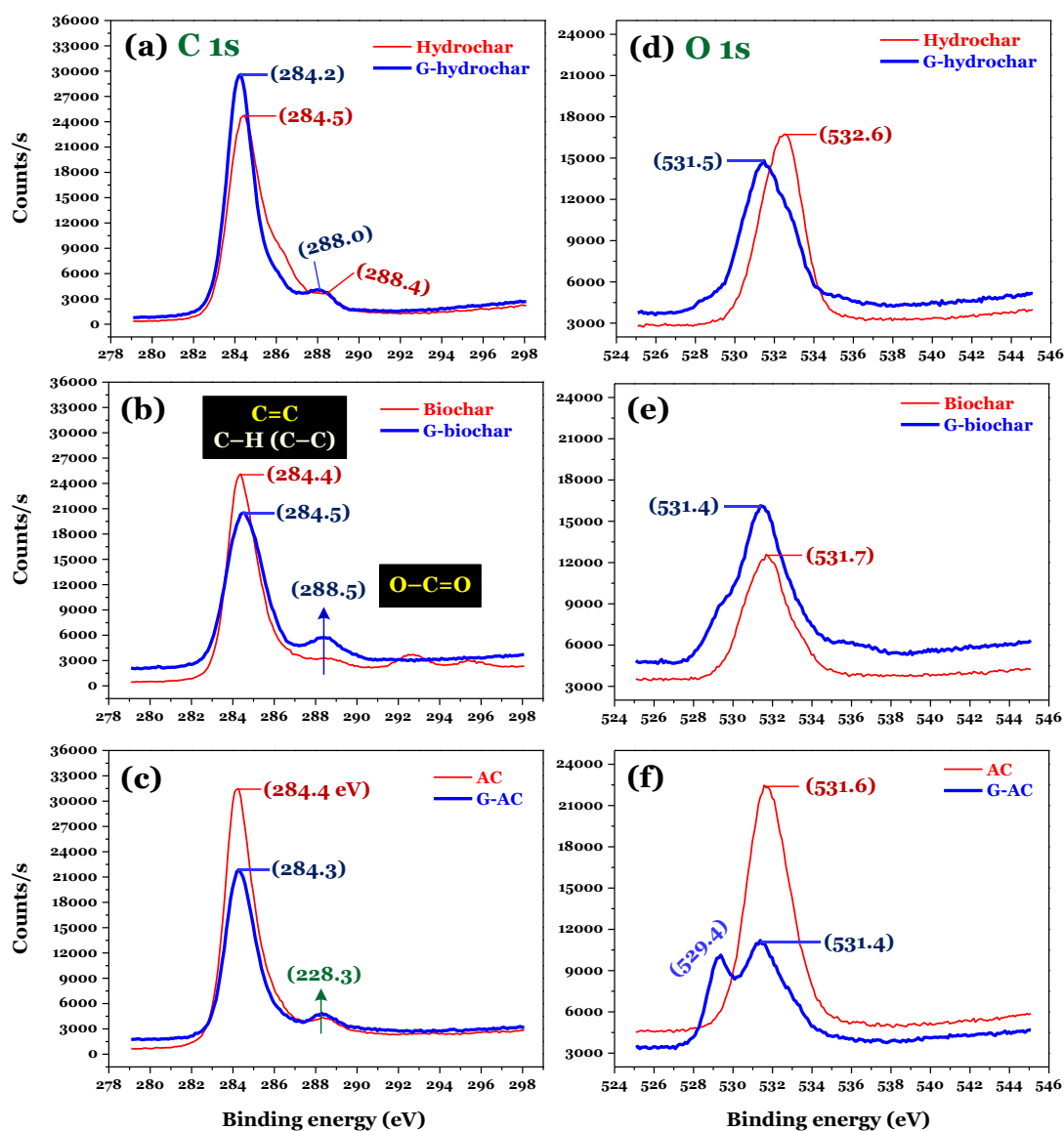
**Figure 1.** Schematic presentation for the preparation procedure of (a) pristine (or un-grafted) carbonaceous materials (hydrochar, biochar, and AC) and (b) un-grafted ones (G-hydrochar, G-biochar, and G-AC)



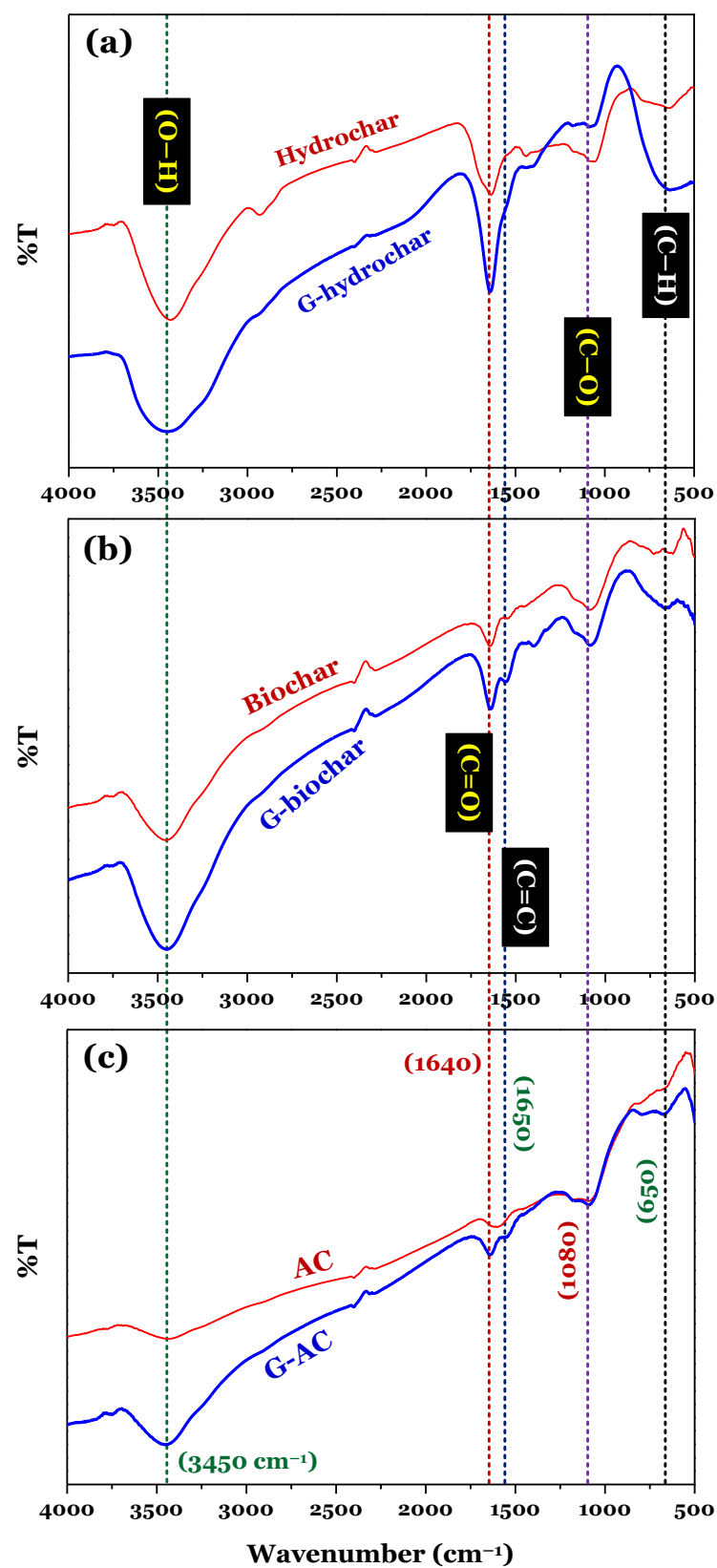


**Figure 2.** SEM image of the carbonaceous materials: un-grafted [(a) hydorchar, (b) biochar, and (c) AC] as well as grafted [(d) G-hydrochar, (e) G-biochar, and (f) G-AC]

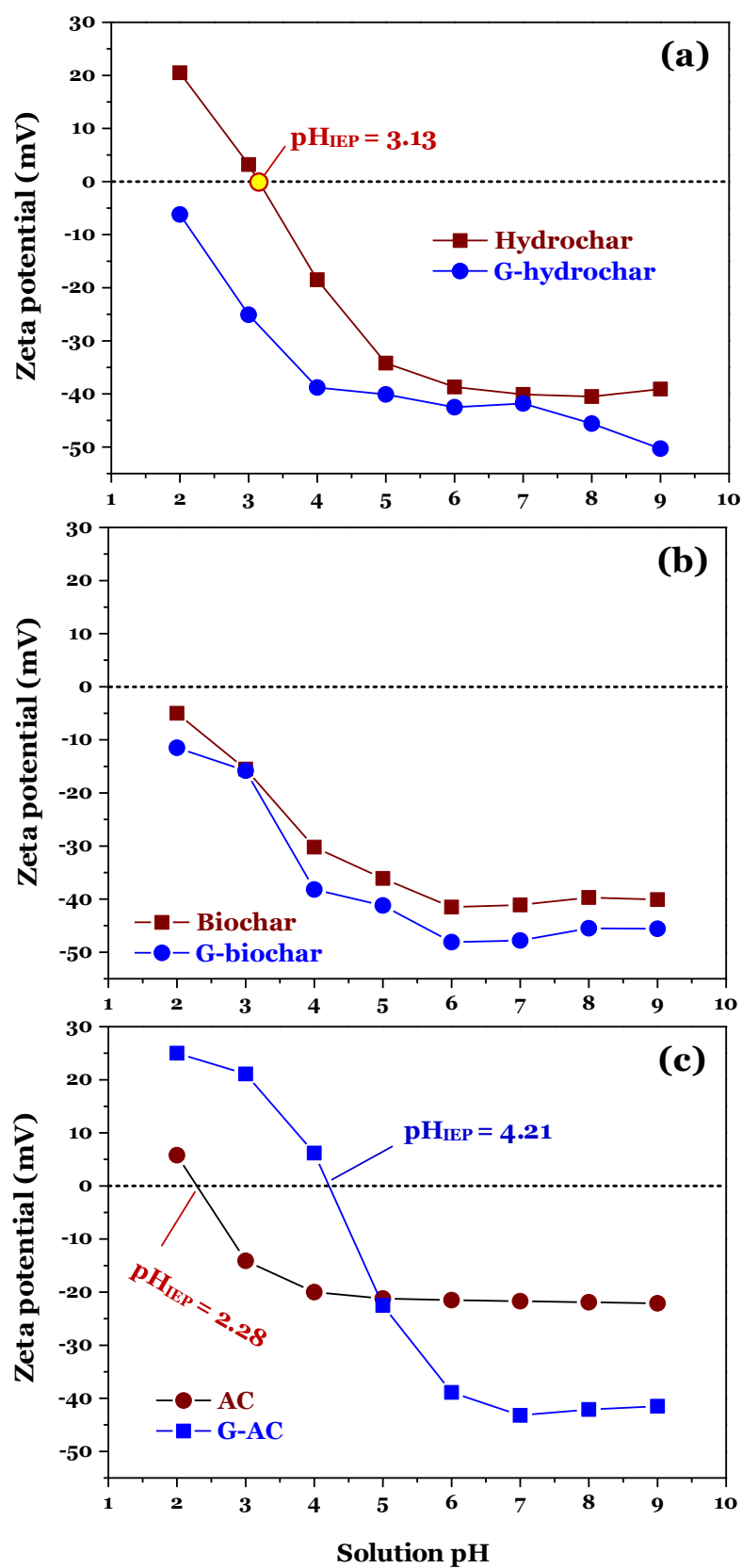




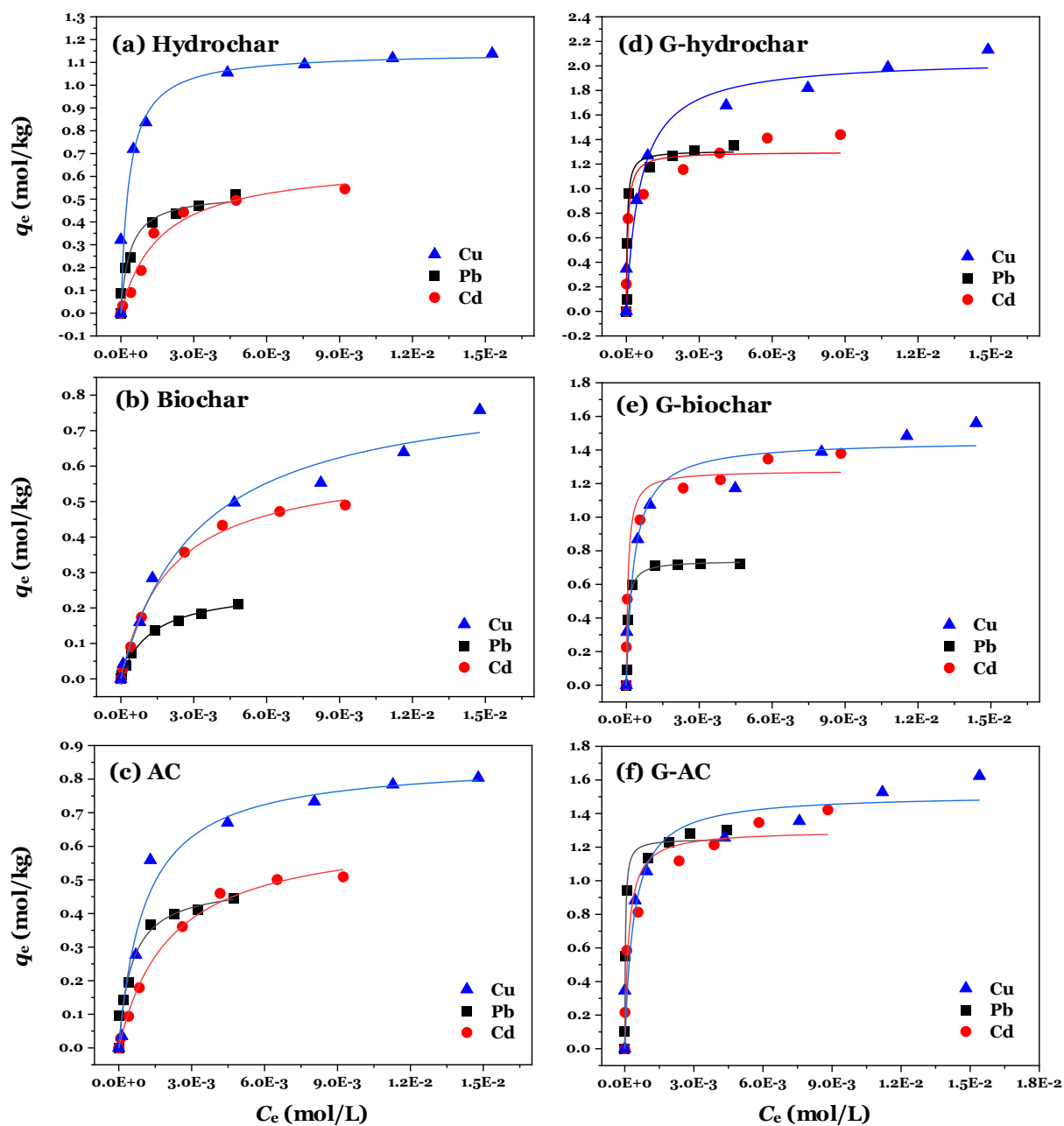
**Figure 3.** Narrowed scan XPS spectrum for C 1s (a–c) and O 1s (d–e) of the un-grafted and grafted carbonaceous materials



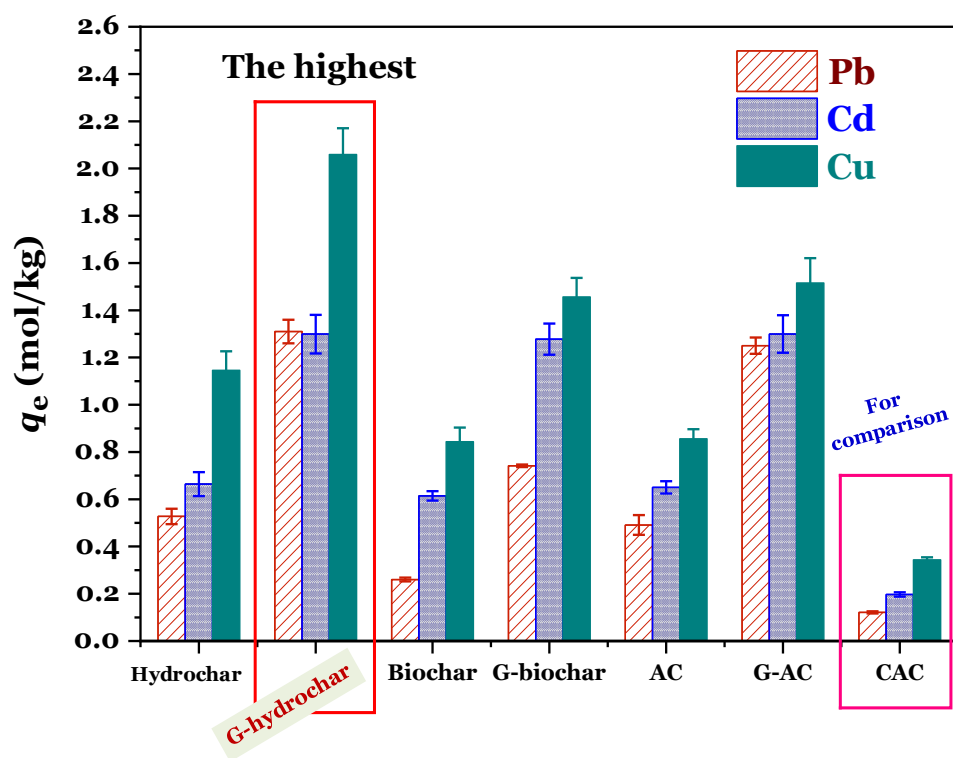
**Figure 4.** FTIR spectrum of (a) hydrochar (b) biochar, and (c) AC before and after grafting process



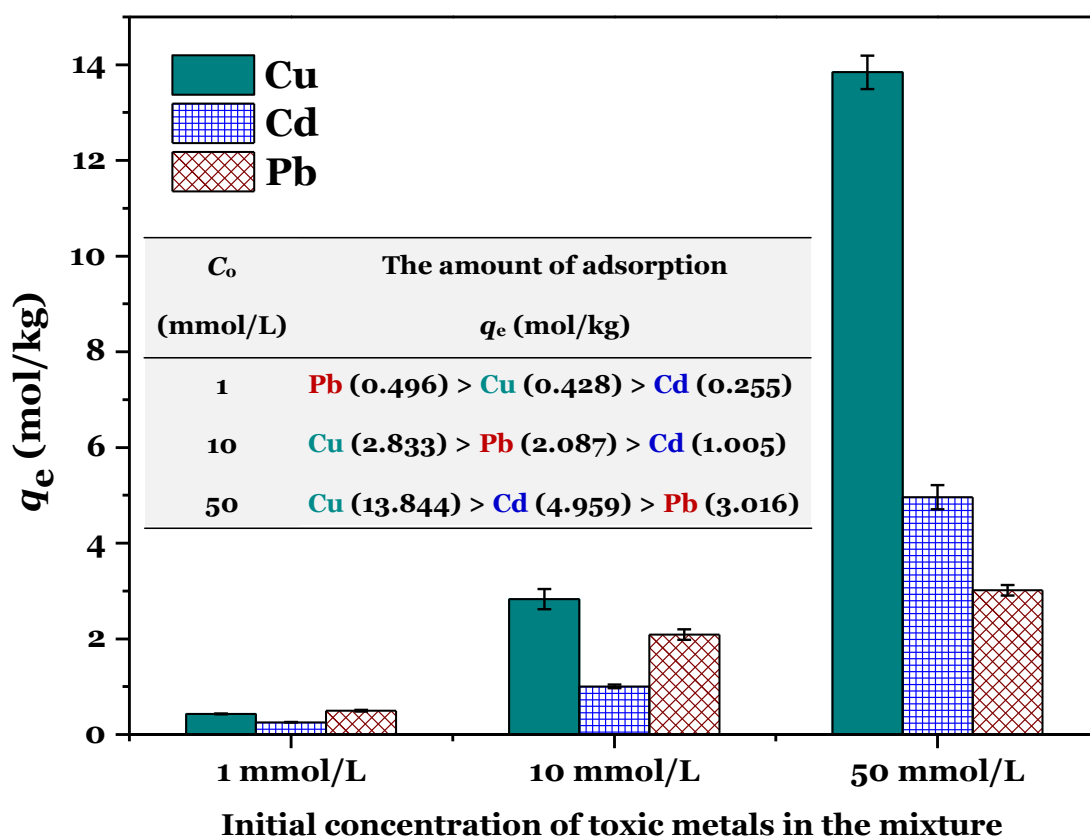
**Figure 5.** Zeta potential of (a) hydrochar (b) biochar, and (c) AC before and after grafting process



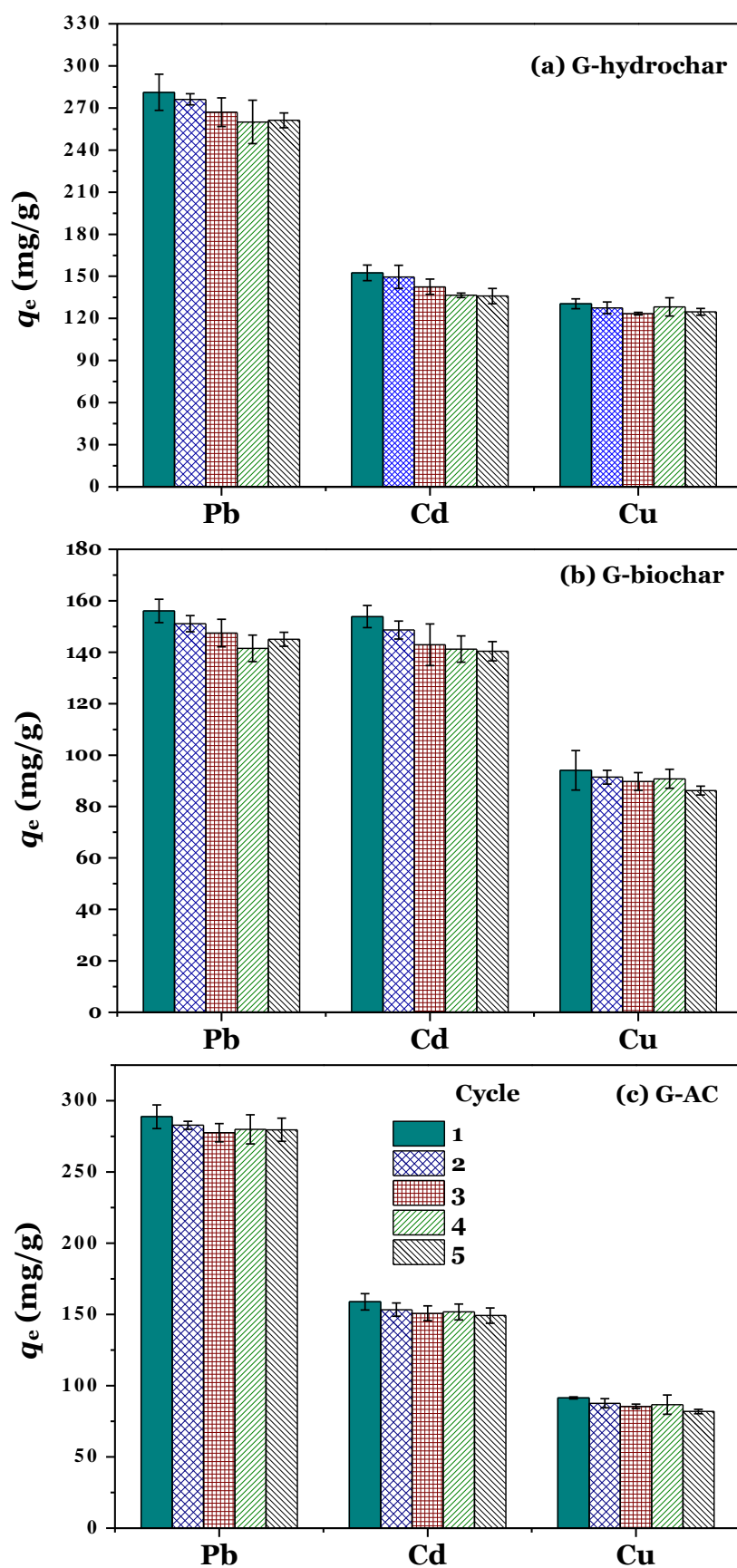
**Figure 6.** Adsorption isotherm of various potential toxic metals onto (a–b) pristine and (c–d) grafted carbonaceous materials (the linear indicating the fitting the Langmuir model; the linear for fitting the Freundlich model provided in Figure S2)



**Figure 7.** Comparison of the maximum capacities of the three metal ions on the un-grafted and grafted carbonaceous materials and commercial activated carbon (the bars indicating standard errors)



**Figure 8.** Comparison of the maximum capacities of the three metal ions on the un-grafted carbonaceous materials (the bars indicating standard error)



**Figure 9.** Adsorption/desorption cycle (the bars indicating standard deviation). Experimental conditions: adsorption ( $\sim 0.4$  g/L,  $C_0 \sim 1000$  mg/L, pH 5.0, 30 °C, and 24 h) and desorption ( $\sim 0.4$  g/L, 0.1 N HCl, 30 °C, and 1h)

**Table 1.** Textural characteristics of carbonaceous materials un-grafted (hydrochar, biochar, and AC) and grafted (G-hydrochar, G-biochar, and G-AC)

	Surface area (m <sup>2</sup> /g)				Pore volume (cm <sup>3</sup> /g)			<i>L</i> <sub>o</sub> (nm)
	<i>S</i> <sub>BET</sub>	<i>S</i> <sub>Lang</sub>	<i>S</i> <sub>micro</sub>	<i>S</i> <sub>Ext</sub>	<i>V</i> <sub>Total</sub>	<i>V</i> <sub>micro</sub>	<i>V</i> <sub>Ultra-micro</sub>	
1. Un-grafted materials								
Hydrochar	3.078	3.490	—	—	0.022	0.003	—	28.5
Biochar	533.3	618.9	349.4	183.9	0.223	0.119	0.091	1.68
AC	991.9	1250	770	221.9	0.485	0.302	0.327	1.96
2. Grafted materials								
G-hydrochar	3.796	6.125	—	—	0.005	0.003	—	5.47
G-biochar	487.6	495.1	331.9	155.7	0.218	0.108	0.080	1.79
G-AC	927.4	1035	828.3	99.1	0.402	0.320	0.306	1.73

**Note:** *S*<sub>BET</sub> (BET surface area), *S*<sub>Lang</sub> (Langmuir surface area), *S*<sub>ext</sub> (external surface area), *S*<sub>micro</sub> (micropore surface area), *V*<sub>total</sub> (total pore volume), *V*<sub>micro</sub> (micropore volume), *V*<sub>Ultra-micro</sub> (ultra-micropore volume), *L*<sub>o</sub> (average pore width).



**Table 2.** Elemental compositions of the carbonaceous materials (determined by XPS) and their zeta potentials

	Atomic percentage					Zeta potential (mV) at pH 5.0
	%C	%O	%Ce	%Na	%K	
1. Un-grafted (pristine) materials						
Hydrochar	80.5	19.5	—	—	—	−36.2
Biochar	81.2	18.8	—	—	—	−31.3
AC	76.6	23.2	—	—	0.14	−21.2
2. Grafted materials						
G-hydrochar	77.4	21.0	0.02	1.59	—	−40.1
G-biochar	73.4	22.5	0.35	3.72	—	−38.2
G-AC	74.4	24.1	0.44	1.10	—	−25.5

**Table 3.** Relevant parameters of the Langmuir model for adsorption of potential toxic metals by un-grafted (or pristine), grafted materials, and commercial activated carbon (CAC) at pH 5

	Unit	Pristine materials			Grafted materials			CAC
		Hydrochar	Biochar	AC	G-hydrochar	G-biochar	G-AC	
1. Pb adsorption								
$Q_{\max}$	mg/g	109.3	53.9	101.8	271.4	153.6	259.1	25.15
$Q_{\max}$	mol/kg	0.528	0.260	0.491	1.310	0.742	1.250	0.121
$K_L$	L/mol	2702	783	1884	25,502	14,557	34,872	11,470
adj- $R^2$	—	0.9599	0.9973	0.9409	0.9709	0.9989	0.9841	0.9928
red- $\chi^2$	—	1.5E-03	1.8E-05	1.7E-03	8.9E-03	1.0E-04	4.5E-03	1.2E-05
2. Cd adsorption								
$Q_{\max}$	mg/g	74.7	69.1	73.1	146.0	143.6	146.1	22.13
$Q_{\max}$	mol/kg	0.664	0.614	0.651	1.299	1.278	1.300	0.197
$K_L$	L/mol	623.1	501.2	480.1	15,840	13,334	6035	8645
adj- $R^2$	—	0.9738	0.9964	0.9946	0.9087	0.9412	0.9322	0.9826
red- $\chi^2$	—	1.2E-03	1.5E-04	2.5E-04	2.7E-02	1.7E-02	1.9E-02	8.2E-05
3. Cu adsorption								
$Q_{\max}$	mg/g	72.8	53.6	54.4	130.9	92.6	96.3	21.83
$Q_{\max}$	mol/kg	1.146	0.844	0.856	2.059	1.457	1.516	0.343
$K_L$	L/mol	2985	316	917	1749	3166	2645	3992
adj- $R^2$	—	0.9015	0.9804	0.9758	0.9540	0.9414	0.9111	0.9930
red- $\chi^2$	—	1.7E-02	1.6E-03	2.7E-03	2.8E-02	1.9E-02	2.9E-02	9.5E-05

**Note:** Adsorption isotherm of CAC was provided in Figure S3.

**Table 4.** The enhanced ratio for the adsorptive amounts of tested metal ions

	Potential toxic metals		
	Cu <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>
Hydrochar	1.797	1.956	2.483
Biochar	1.727	2.080	2.850
Activated carbon	1.772	1.998	2.545

**Declaration of interests**

☒ **The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.**

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

## **Author statement**

On behalf of the authors of this paper (Jin-Wei Zhang, Sarah Mariska, Sabolc Pap, Hai Nguyen Tran, Huan-Ping Chao), I disclose that we do not use AI and AI-assisted technologies in preparing this manuscript. I also declared that all authors have agreed to the submission of this manuscript. We also declared that this work is original and has not been submitted or considered elsewhere. The authors declare no competing financial interest.



**Enhanced separation capacity of carbonaceous materials (hydrochar, biochar, and activated carbon) towards potential toxic metals through grafting copolymerization**

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## ABSTRACT

Oxygen-containing groups in the surface of materials (i.e.,  $-\text{COOH}$  and  $-\text{OH}$ ) often play a key role in adsorbing toxic metals. Acrylic acid ( $\text{CH}_2 = \text{CHCOOH}$ ) is used as a green grafter for enhancing the density of those groups in carbonaceous materials, and ammonium cerium nitrate is used as an initiator. Hydrochar (prepared through hydrothermal carbonization at  $190\text{ }^\circ\text{C}$ ), biochar (generated via pyrolyse at  $800\text{ }^\circ\text{C}$ , and activated carbon (AC; produced through chemical activation with  $\text{K}_2\text{CO}_3$  at  $800\text{ }^\circ\text{C}$ ) derived from ginger residues were used as feedstock materials for the grafting process. The carbonaceous materials were characterized using scanning electron microscopy, X-ray photoelectron spectrometry, Brunauer–Emmett–Teller (BET) analyzer, Fourier transform infrared spectroscopy, and zeta potential.  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  were selected as adsorbates. Equilibrium adsorption experiments for the three metal ions on the un-grafted and grafted carbonaceous materials were conducted at  $25\text{ }^\circ\text{C}$  and  $\text{pH } 5.0$ . Results indicated that the oxygen content in the grafted materials was higher than that of un-grafted ones. The grafting process could increase the  $\text{OH}$  and  $\text{COOH}$  functional groups on the carbonaceous materials, which leads to increasing the adsorptive amounts of metal ions. The Langmuir maximum adsorption capacity ( $Q_{\text{max}}$ ) of carbonaceous materials for toxic metal ions ( $\text{mol/kg}$ ) followed  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ . The adsorptive amounts of potentially toxic metal ions on the un-grafted and grafted (abbreviated as G) materials followed hydrochar  $>$  AC  $>$  biochar. The  $Q_{\text{max}}$  value of hydrochar (72.8, 74.7, and  $109.3\text{ mg/g}$ ), biochar ( $53.6$ ,  $69.1$ ,  $53.9\text{ mg/g}$ ), AC ( $54.4$ ,  $73.1$ ,  $101.8\text{ mg/g}$ ), G-hydrochar ( $130.9$ ,  $146.0$ ,  $271.4\text{ mg/g}$ ), G-biochar ( $92.6$ ,  $143.6$ ,  $153.6\text{ mg/g}$ ), G-AC ( $96.3$ ,  $146.1$ ,  $259.1\text{ mg/g}$ ) for adsorbing metals ( $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ ) was higher than that of commercial activated carbon ( $21.83$ ,  $22.13$ ,  $25.15\text{ mg/g}$ , respectively). The adsorption capacity of the grafted hydrochar was restored after five adsorption/desorption cycles. The primary adsorption mechanisms were complexation and ion exchange.

**Keywords:** Acrylic acid; Agricultural Waste; Adsorption; Desorption; Ion exchange; Heavy metal; Water treatment

## 58 **1. Introduction**

59 Wastewater discharged into rivers or irrigation ditches contains heavy metal ions that can lead  
60 to soil contamination or adverse effects on organisms. Although heavy metal ions can be removed  
61 through chemical precipitation, a small quantity is discharged into water bodies. For this reason, strict  
62 regulations have been set to limit the concentration of heavy metals in effluents. When effluent  
63 standards for heavy metals cannot be achieved using chemical precipitation, new methods are  
64 required to effectively remove heavy metals from the effluent. Various advanced treatment methods  
65 for heavy metal removal have been developed in the past [1, 2] and of these, using adsorbents is a  
66 low-cost and highly efficient treatment method. Minerals, biosorbents, and carbonaceous materials  
67 have been used to adsorb heavy metal ions [3-5]. Generally, carbonaceous materials (including  
68 activated carbon, biochar, hydrochar, carbon nanotubes, carbon spheres, and graphene oxide) are used  
69 as adsorbents in water or wastewater treatment procedures to adsorb heavy metal ions. Activated  
70 carbon with a high specific surface area is commonly used to remove contaminants [3, 4, 6, 7].

71 Activated carbon can be derived from agricultural waste rich in cellulose. The synthesis process  
72 for activated carbon is divided into two stages: carbonization and activation. Carbonization can be  
73 carried out through a hydrothermal method or calcination under oxygen-deficient conditions [8, 9].  
74 Subsequently, acid, base, and other salts were frequently used as activators to increase the surface  
75 area of activated carbon specifically [4, 9]. When agricultural waste is carbonized using the  
76 hydrothermal method, the byproduct can also be called hydrochar [10]. Hydrochar possesses rich  
77 functional groups on its surface that can effectively adsorb heavy metals [9]. The agricultural waste  
78 was calcined under oxygen-deficient conditions to generate biochar [5]. Biochar has also been used  
79 to adsorb heavy metal ions [11]. Moreover, biochar has been mixed with soil, which can reduce the  
80 uptake of heavy metal ions by plants [5].

81 In this study, ginger wastes were selected as the raw material, and three-stage processes were

82 performed to synthesize activated carbon. First, hydrochar was produced using a hydrothermal  
83 method. Second, the hydrochar was calcined at 800 °C under oxygen-deficient conditions to obtain  
84 the biochar. Third, biochar mixed with  $K_2CO_3$  was calcined to increase the specific surface area to  
85 obtain activated carbon. The synthesized hydrochar, biochar, and activated carbon were used to  
86 adsorb the heavy metal ions  $Cu^{2+}$ ,  $Cd^{2+}$ , and  $Pb^{2+}$ .

87 To further increase the adsorptive amounts of metal ions, the three carbonaceous materials were  
88 modified by a polymerization reaction, which effectively increased the OH or COOH functional  
89 groups on the surface of the carbonaceous materials [4, 12]. Acrylic acid was used to provide OH or  
90 COOH functional groups, and ammonium cerium (IV) nitrate was used as an initiator to complete  
91 the graft copolymerization reaction. Few studies have used grafted carbonaceous materials for the  
92 removal of potentially toxic metal ions. It is expected that the grafting process can effectively enhance  
93 the adsorption of potentially toxic metals on carbonaceous materials. Thus, the adsorptive amounts  
94 of the test metals on the modified carbonaceous materials were compared with those on unmodified  
95 carbonaceous materials in this study. Potential adsorption mechanisms were elucidated.

96 The authors emphasized that one raw material (ginger) produces three carbonaceous materials  
97 (hydrochar, biochar, and AC) to carry out the grafting process. Then, the authors compared the  
98 difference among the hydrochar, biochar, and AC. The increase in adsorptive amounts of three  
99 potentially toxic metals was discussed after the grafting process. The cost of biochar and hydrochar  
100 synthesis is far lower than that of activated carbon. The study can provide the best choice for  
101 wastewater treatment.

## 102 **2. Materials and methods**

### 103 **2.1. Materials**

104 All chemicals in the experiments were purchased from Merck or Sigma Aldrich (purity > 95 %)

105 and used without further purification. Ginger residues were used as the raw material in this study and  
106 purchased from a local market in Taiwan. Copper nitrate [Cu(NO<sub>3</sub>)<sub>2</sub>], cadmium nitrate [Cd(NO<sub>3</sub>)<sub>2</sub>],  
107 and lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] were used to prepare solutions for adsorption experiments. Acrylic acid  
108 (C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>) and ammonium cerium (IV) nitrate (H<sub>8</sub>CeN<sub>8</sub>O<sub>18</sub>) were selected for grafting, and potassium  
109 carbonate (K<sub>2</sub>CO<sub>3</sub>) was used as the activator to reduce secondary pollution. Sodium hydroxide  
110 (NaOH) and hydrochloric acid (HCl) were used to adjust solutions pH.

## 111 **2.2. Preparation of carbonaceous materials**

112 The ginger wastes that were collected from local markets were washed with deionized distilled  
113 water and dried in an oven at 90 °C for 4 h. The dried raw material was then ground and sieved through  
114 a 100-mesh screen. After the pre-treatment process, 15 g of raw materials mixed with 100 mL of  
115 deionized distilled water was added to a 100 mL Teflon vessel, sealed in a stainless-steel vessel, and  
116 heated at 190 °C for 24 h. When the reaction was complete, the sample was collected and washed with  
117 deionized distilled water to remove impurities. The sample was then oven-dried overnight at 60 °C,  
118 and the product was called hydrochar.

119 The 50-g hydrochar sample was placed in a crucible and covered. After calcination at 800 °C  
120 for 4 h under oxygen-deficient conditions, the sample was collected and washed with 0.1 N HCl and  
121 deionized distilled water until a near-neutral pH value was reached. The samples were oven-dried  
122 overnight at 60 °C and the product was called biochar.

123 The 50-g biochar was mixed with K<sub>2</sub>CO<sub>3</sub> at a weight ratio of 1:1 and then placed in a crucible  
124 and covered. The sample was calcined in an oven at 800 °C under oxygen-deficient conditions and  
125 then washed with 0.1 N hydrochloric acid and deionized distilled water until a near-neutral pH value  
126 was reached. After that, the sample was dried and called activated carbon (AC).

127 The three carbonaceous materials were modified using the same grafting copolymerization  
128 procedure at a room temperature 25 °C. A primary experiment was carried out to explore the optimal

129 conditions for the grafting copolymerization (data not shown). After the optimal experiment, the  
130 experimental procedure was obtained and reported in this study. Briefly, one gram of carbonaceous  
131 material was added to 200 mL of deionized distilled water, and the solution was heated to 90 °C.  
132 Twenty milliliters of acrylic acid and 20 mL of ammonium ceric nitrate (0.225 M) were added to the  
133 solution and allowed to react for 90 min. When the solution cooled to room temperature, the solid  
134 and solution were separated by centrifugation at 7000 rpm for 15 min. The samples were then oven-  
135 dried overnight at 60 °C. After the grafting copolymer reaction, the carbonaceous material samples  
136 were immersed in a 200 mL solution containing NaOH (0.2M) for 70 min. The samples were collected  
137 and rinsed with DD water until near-neutral pH values. Subsequently, the samples were dried  
138 overnight at 60 °C to generate grafted carbonaceous materials. The carbonaceous materials (hydrochar,  
139 biochar, and AC) after grafting were called G-hydrochar, G-biochar, and G-AC, respectively.

140 In summary, the procedure for the preparation of un-grafted and grafted carbonaceous materials  
141 is summarized in **Figure 1**.

142 **Figure 1**

### 143 **2.3. Properties of carbonaceous materials**

144 A field-emission scanning electron microscope (SEM, Hitachi S-4800, Japan) observed the  
145 surface morphologies of the synthesized adsorbents. An X-ray photoelectron spectrometer (XPS)  
146 device (ESCALAB 250, Thermo Scientific, USA) measured the elemental composition of the  
147 carbonaceous materials and chemical bonding on the surface of the carbonaceous materials. The  
148 functional groups on the surfaces of the adsorbents were analyzed using Fourier transform infrared  
149 spectroscopy (FTIR, FT/IR-6600, JASCO). Carbonaceous materials were mixed with potassium  
150 bromide (KBr) to obtain the FTIR spectra in the wavenumber range 400–4000  $\text{cm}^{-1}$ . The increased  
151 number of COOH groups on the grafted adsorbents can be observed in the FTIR spectra. Zeta  
152 potentials of the material were detected by a Zetasizer 3000HS (Malvern Co.)

153 Textural properties of the materials were calculated based on nitrogen adsorption/desorption  
154 isotherm at 77 K using an ASAP 2020 analyzer (Micromeritics, USA). The BET specific surface area  
155 ( $S_{\text{BET}}$ ) and Langmuir surface area ( $S_{\text{Lang}}$ ) of the materials were calculated from the Brunauer-Emmett-  
156 Teller (BET) equation and Langmuir equation, respectively. Their total pore volume ( $V_{\text{Total}} = Q_{0.99}/647$ )  
157 was computed based on the single point adsorption (quantity adsorbed  $Q_{0.99}$ ; cm<sup>3</sup>/g STP) at the highest  
158  $p/p^\circ$  value ( $\sim 0.99$ ) [13]. The  $t$ -plot method was applied for determining the micropore volume ( $V_{\text{Micro}}$ ;  
159 pore width <2 nm), micropore area ( $S_{\text{Micro}}$ ), external surface area ( $S_{\text{Ext}}$ ) of the materials [13]. Their  
160 ultra-micropore volume ( $V_{\text{Ultra-micro}}$ ) or narrow microporosity (pore width <0.8 nm) was determined  
161 by the Horvath–Kawazoe method [14].

## 162 **2.4. Adsorption experiments**

### 163 **2.4.1. Adsorption isotherm of each metal**

164 Adsorption isotherms for the potentially toxic metals on the un-grafted and grafted  
165 carbonaceous materials at 25 °C were obtained to evaluate the adsorption characteristics and estimate  
166 the maximum adsorption capacities. The concentrations of metal ions ranged from approximately 10  
167 to 1000 mg/L. To avoid precipitation, the pH values of the solutions were adjusted to 5.0 ( $\text{pH}_{\text{eq}}$ ) before  
168 and during the adsorption processes.

169 A dried mass of 0.02 g of each adsorbent was added to the solutions containing various  
170 concentrations of potentially toxic metal ions. The solutions were then placed on a reciprocal shaker  
171 at 120 rpm for 24 h. Following this, the solutions were passed through a 0.45- $\mu\text{m}$  filter. The filtrate  
172 was collected, and the potentially toxic metal concentration was measured using a flame atomic  
173 absorption spectrometer (Avanta/AAS, GBC). To avoid competitive adsorption, only one potentially  
174 toxic metal was tested in the adsorption experiment. Each experiment was performed in duplicate,  
175 and the resulting data were averaged. If the bias of a repeated experiment exceeded 15%, a triplicate  
176 run was performed. Finally, the Langmuir equation estimated the maximum adsorption capacity of

177 the adsorbents.

178 The amount of contaminants adsorbed by carbonaceous materials at a given concentration at  
179 equilibrium is represented as  $q_e$ . The  $q_e$  (mg/g) was calculated using the mass balance equation.

$$q_e = \frac{(C_o - C_e)}{m} V \quad (1)$$

180 where  $C_o$  (mg/L) and  $C_e$  (mg/L) are the initial and equilibrium concentrations of the adsorbates,  
181 respectively;  $m$  (g) is the mass of the adsorbent; and  $V$  (L) is the volume of each adsorbate solution.

182 The Langmuir and Freundlich models are shown in Equations 2 and 3 to describe the  
183 characteristics of the selected adsorbates on the composite material. Those models are often applied  
184 for modeling the experimental data of adsorption equilibrium [3, 4, 9, 12, 15]. The nonlinear  
185 regression approach correlated adsorption equilibrium data using the Origin software.

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

186 where  $Q_{\max}$  (mg/g) is the maximum adsorption capacity of the adsorbate on the adsorbent;  $K_L$  (L/mg)  
187 is the Langmuir constant; and  $K_F$  [(mg/g)/(mg/L) <sup>$n$</sup> ] and  $n$  (dimensionless) are the Freundlich  
188 constants.

189 For comparison, a commercial activated carbon (CAC) purchased from Merck Company  
190 (SAFC, 102555) was utilized. Its BET specific surface area is higher than 1000 m<sup>2</sup>/g. The maximum  
191 adsorption capacity of CAC to each target metal was estimated through the adsorption isotherm.

## 192 2.4.2. Competitive adsorption

193 The adsorption capacity of the materials under mixture solutions was studied by competitive  
194 adsorption. The initial concentrations of metal ions in the mixture were prepared at 1, 10, and 50  
195 mmol/L. Around 0.02 g of the material was added to the solution (50 mL) containing three metals  
196 ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ ) at different initial metal concentrations. The  $\text{pH}_{\text{eq}}$  of solution was maintained  
197 at 5.0 during the adsorption process. The competitive adsorption was fixed at a contact time of 24 h  
198 and 30 °C.

## 199 2.4.3. Study of adsorption–desorption cycle

200 The reusability of the metal-laden materials was evaluated through an adsorption–desorption  
201 cycle study. The selection of adsorption conditions (especially initial metal concentration) is very  
202 important these experiments. If the initial metal concentration is too low, the adsorption sites in the  
203 material might not be saturated by the metal ions. Therefore, the adsorption study was conducted at  
204 ~1000 mg/L of each toxic metal and under conditions: 0.4 g/L, pH 5.0, 24 h, and 30 °C. Because the  
205 adsorbates ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ ) are cations, an acid was used as a target desorbing agent. The  
206 experimental conditions for desorption study were 0.1 N HCl, 0.4 g/L, 30 °C, and 1 h. Desorption  
207 efficiency was calculated based on Equation 4.

$$\% \text{Desorption} = \frac{q_{e(2)}}{q_{e(1)}} \quad (4)$$

208 where  $q_{e(1)}$  and  $q_{e(2)}$  are the adsorption capacity of the material at the 1<sup>st</sup> and the 2<sup>nd</sup> cycles of  
209 adsorption and desorption, respectively.

## 210 3. Results and discussion

### 211 3.1. Characteristics of adsorbents

212 The textural characteristics of the six carbonaceous materials are presented in **Table 1**. The



hydrochar with its low  $S_{\text{BET}}$  and  $V_{\text{Total}}$  ( $3.078 \text{ m}^2/\text{g}$  and  $0.022 \text{ cm}^3/\text{g}$ ) was a typical non-porous material. The agricultural waste was produced by a hydrothermal process, which might generate a similar structure [9, 16]. In addition, the external surfaces of the hydrochar (**Figure 2a**) did not exhibit obvious pore structures because this carbonaceous material was not chemically activated or thermally treated. Activated carbon and biochar were expected to possess a higher  $S_{\text{BET}}$  value.

## Table 1

## Figure 2

In contrast to the hydrochar, the biochar ( $533.3 \text{ m}^2/\text{g}$  and  $0.223 \text{ cm}^3/\text{g}$ ) and AC ( $991.9 \text{ m}^2/\text{g}$  and  $0.485 \text{ cm}^3/\text{g}$ ) were porous materials with their high  $S_{\text{BET}}$  and  $V_{\text{Total}}$ . This is consistent with the observation of their surface morphology in **Figure 2b–2c**. Similarly, the other authors [9] reported that the  $S_{\text{BET}}$  values of activated carbons developed from hydrochar (derived from *Crocus sativus* petals) through a chemical activation (using KOH) ranged from  $788$  to  $1497 \text{ m}^2/\text{g}$ . The  $S_{\text{BET}}$  and  $V_{\text{Total}}$  value of the AC ( $991.9 \text{ m}^2/\text{g}$  and  $0.485 \text{ cm}^3/\text{g}$ ) were close to that of commercial activated carbon (CAC;  $1241 \text{ m}^2/\text{g}$  and  $0.445$ ) [4].

Notably, although the surface morphology of the grafted materials (**Figure 2d–f**) did not indicate a remarkable change compared to their pristine materials (**Figure 2a–c**), their  $S_{\text{BET}}$  and  $V_{\text{Total}}$  (especially for biochar and AC) decreased after the grafting process (**Table 1**). However, the change of textural properties of three materials after grafting was less important than others (i.e., surface chemistry and functionality) in determining the adsorption amounts of toxic metals. In essence, toxic metal ions adsorbed on carbonaceous materials are mainly correlated with the functional groups on their surface rather than their textural properties [12, 17]. Thus, the  $S_{\text{BET}}$  value was less relative to the adsorption amount. However, a high  $S_{\text{BET}}$  may increase the adsorption of other contaminants, such as organic contaminants [3]. In contrast, the adsorbent with a high  $S_{\text{BET}}$  value could provide more active sites to increase the grafting efficiency. In addition, it provides information to understand the

237 characteristics of carbonaceous materials.

238 For carbonaceous materials, the oxygen content is a critical factor in determining the adsorptive  
239 amounts of potentially toxic metal ions. The oxygen content correlates with the COOH or OH groups  
240 that might generate ion exchange or complexation reactions with metal ions [5, 9]. The carbon content  
241 can determine whether the synthesized material is carbonaceous. The main elements of the six  
242 carbonaceous materials that were measured by the XPS technique (**Figure S1**; full scan XPS survey)  
243 are listed in **Table 2**. All the carbonaceous materials in this study were mainly composed of C and O,  
244 and the other elements (i.e., Na and Ce) were present after grafting. The carbon contents of all samples  
245 exceeded 70%, demonstrating the successful production of carbonaceous materials. The oxygen  
246 content ranged from 18% to 25%, indicating that the adsorbents can uptake potentially toxic metal  
247 ions through feasible complexation mechanisms [5, 9, 12]. Since the grafting process requires the use  
248 of NaOH and H<sub>8</sub>CeN<sub>8</sub>O<sub>18</sub>, sodium, and cerium were present in the grafted carbonaceous materials.  
249 In addition, K<sub>2</sub>CO<sub>3</sub> was used as the activator, causing AC to possess a small amount of potassium.

250 **Table 2**

251 The main objective of the grafting process was to increase the number of oxygen-containing  
252 groups (–COOH or –OH) on the surface of carbonaceous materials. The oxygen content of the grafted  
253 material increased after grafting. The results exhibited that the oxygen on acrylic acid was transferred  
254 onto the carbonaceous materials to form the –COOH or –OH groups and that grafting was  
255 successfully performed. Because bivalent metals were used as adsorbates, the Na (I) and Ce (IV)  
256 contents affected the adsorptive amounts. The high Na content favored the adsorption of the tested  
257 metal ions on the adsorbents. In contrast, the high Ce content did not favor the adsorption of the  
258 potentially toxic metal ions on the adsorbents.

259 The main functional groups on the adsorbent surface are critical in determining the adsorption  
260 amounts of the tested contaminants. Although the high oxygen content of carbonaceous materials

could lead to high adsorptive amounts of potentially toxic metal ions, the functional groups on the un-grafted and grafted carbonaceous materials needed to be analyzed through the narrowed scan O 1s XPS and FTIR. Although the narrowed scan C 1s XPS (**Figure 3 a–c**) provides the information on the O–C=O group at around 288 eV, the majority is helpful for identifying the C–H/C–C and C=C group (at around 284 eV) in the aromatic structure of the materials [10, 15, 18]. In contrast, **Figure 3 d–e** provides the O 1s XPS spectrum of the un-grafted and grafted materials. In general, the peaks at approximately 531, 532, and 533 eV can be designed for the carbonyl, carboxylic, and hydroxyl groups, respectively [15, 18, 19]. For the hydrochar, the main peak was shifted from 532.6 eV to 531.5 eV after the grafting process. In contrast, negligible change was observed in the relevant peak in the O 1s spectrum of the biochar before (531.7 eV) and after (531.4 eV) the grafting process. Meanwhile, the peak at 531.6 eV in the AC was deconvoluted into two peaks at 563.4 eV and 529.4 eV. The results suggest that the presence of the oxygen-containing groups in the grafted materials was different in nature.

### Figure 3

The FTIR data showed that the functional groups of the grafted carbonaceous materials were similar to those of the un-grafted carbonaceous materials (**Figure 4**). The results indicate that the grafting process did not destroy the functional groups on the adsorbent. The bands at approximately 3450  $\text{cm}^{-1}$  are attributed to the OH group stretching vibrations [9, 18]. Alcoholic phenols and carboxylic acids can provide functional groups. The bands at nearly 1640  $\text{cm}^{-1}$  are potentially provided by C=O groups, such as carboxylic acids [3, 9, 18]. Meanwhile, the identified bands at 1080  $\text{cm}^{-1}$  are attributed to C–O groups [3, 4, 10, 15]. Moreover, the bands observed at 1650  $\text{cm}^{-1}$  and 650  $\text{cm}^{-1}$  are ascribed to the vibration of aromatic C=C and C–H [10, 15, 18]. As the main components of ginger contain lignin or cellulose, carbonaceous materials derived from ginger wastes were rich in the C=O and OH groups.

## Figure 4

In addition, the intensities of the C=O and OH functional groups on the surface of the grafted materials were higher than those of the un-grafted material (**Figure 4**). The other functional groups on the surface showed no significant changes. The intensities of the C=O and OH functional groups increased in the following order: hydrochar > AC > biochar. When adsorbents had more OH and COOH functional groups on their surfaces, they yielded more cation exchange sites to adsorb the tested metal ions. In contrast, oxygen in the OH and COOH functional groups could generate a complexation reaction with  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  [5, 9]. The results indicate that grafted materials can generate higher adsorptive capacities than un-grafted materials.

The zeta potentials the carbonaceous materials (**Figure 5**) provided information on the charge state (positive or negative) on their external surface within solutions pH. In general, the external surface charge of three materials indicated remarkable changes after the grafting process. However, the tendency of such change are different among hydrochar, biochar, and AC, which results from fundamental difference on their properties (i.e., their surface chemistry in **Figure 3**). For example, the pH at the isoelectric point ( $\text{pH}_{\text{IEP}}$ ) of AC decreased from 4.21 to 2.28 after the grafting process (**Figure 5c**). A similar decrease in this point was found in the case of hydrochar. In essence, a material (i.e., G-hydrochar) with its lower  $\text{pH}_{\text{IEP}}$  value often possesses higher actively functional groups and higher negatively charged surface than others (i.e., hydrochar).

## Figure 5

### 3.2. Adsorption isotherms of potentially toxic metal ions on carbonaceous materials

The adsorption isotherms of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  on the carbonaceous materials are illustrated in **Figure 6**. The curves were concave downward, indicating that the metal ions favor adsorption on the tested carbonaceous materials. Both the un-grafted and grafted adsorbents could be used to remove the three metal ions from the solution. The curves were denoted as an L-type isotherm for the

un-grafted materials (**Figures 6a–c**) and the grafted materials (**Figures 6d–f**). The classification for the shape of adsorption isotherm has been reported in the document [20]. In essence, this shaped isotherm indicates that adsorbent has a great adsorption affinity to adsorbate in solution (even at low initial adsorbate concentration). The result suggests that the grafted materials exhibited a higher adsorption affinity to the potentially toxic metals in the solution than the un-grafted materials.

### Figure 6

As expected, the adsorption capacities of the three metal ions on the grafted materials were higher than those on the un-grafted materials. The grafting process increased the amounts of metal ions adsorbed on the carbonaceous material. According to the surface characteristics, grafted materials with the high density of the OH and COOH groups generate higher adsorption capacities for potentially toxic metal ions. The un-grafted and grafted materials exhibited a negatively charged surface (**Table 1**) because their zeta potentials were negative and ranged from  $-21.2$  to  $-40.1$  mV (**Figure 5**). In the literature, the zeta potentials of CAC and tire wastes-derived AC reported were  $-36.1$  mV and  $-34.5$  mV [4]. Therefore, the adsorption of cation metals ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ ) through electrostatic attraction was highly feasible. Generally, the primary adsorption mechanism of  $\text{Pb}^{2+}$  on carbonaceous materials was ion exchange. The primary adsorption mechanisms of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  are ion exchange and complexation reactions, respectively. The ion exchange ability depends on the ion radius. Among the three metal ions, the ion exchange ability followed the order  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . In contrast, the ability of the complex reaction for the three metal ions follows the order  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$  based on the literature [21]. The amounts of the three metal ions adsorbed can be used to evaluate the potential adsorption mechanisms.

### 3.3. Adsorptive amounts of potentially toxic metal ions on carbonaceous materials

When comparing the values of the adjusted coefficient of determination ( $\text{adj-}R^2$ ) and the reduced chi-square statistics ( $\text{red-}\chi^2$ ) for the two models, the Langmuir model ( $\text{adj-}R^2 = 0.9015$ –

0.9987 and  $\text{red-}\chi^2 = 1.2\text{E-}05\text{--}2.9\text{E-}03$ ; **Figure 6** and **Table 3**) fits well with the adsorption of the three metal ions on carbonaceous materials compared to the Freundlich model ( $\text{adj-}R^2 = 0.883\text{--}0.9939$  and  $\text{red-}\chi^2 = 66\text{E-}05\text{--}24\text{E-}03$ ; **Figure S2** and **Table S1**).

### Table 3

All  $\text{adj-}R^2$  values in the Langmuir model were greater than 0.90, indicating that the maximum adsorptive capacities of the metal ions could be estimated using the Langmuir model. In addition, all  $n$  values in the Freundlich model ( $n = 2.082\text{--}7.736$ ) were greater than 1.0, demonstrating that the test metal ions adsorbed on the synthesized materials were favorable. Generally,  $n$  values lie within the range of 1.0–10. This result is consistent with that of other studies [3, 4, 12, 15].

The maximum capacities of the three metal ions on the un-grafted carbonaceous materials followed the order of the hydrochar > AC > biochar (**Figure 7**). Similarly, the grafted carbonaceous materials exhibited the following order: G-hydrochar > G-AC > G-biochar (**Figure 7**). Functional groups, such as  $\text{--OH}$  and  $\text{--COOH}$ , are critical factors in determining the adsorptive amount of potentially toxic metal ions. The hydrochar derived from agricultural waste containing cellulose can maintain functional groups on the surface. It possessed the highest adsorptive amounts toward metal ions. The biochar was synthesized at 800 °C under oxygen-deficient conditions. The binding of the  $\text{--OH}$  and  $\text{--COOH}$  groups could be broken to form other functional groups. The results can be demonstrated by the intensities of the  $\text{--COOH}$  and  $\text{--OH}$  groups in the FTIR spectra and XPS data. The activator potassium carbonate mixed with the carbonaceous material under high-temperature and oxygen-deficient conditions can react with the functional groups on the surface of carbonaceous materials. Potassium may bond to the surface of carbonaceous materials. These results can be demonstrated through the potassium content measured by XPS. This can increase the cation exchange capacity of the adsorbent, leading to a higher adsorptive amount of metal ions.

### Figure 7

For the tested metal ions on all carbonaceous materials, the adsorptive amounts, based on the mol/kg ratio, were in the order of  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$  (**Figure 7** and **Table 3**). As mentioned before, the primary  $\text{Pb}^{2+}$  adsorption mechanism in carbonaceous materials is ion exchange. Therefore,  $\text{Pb}^{2+}$  generated the lowest amount of adsorption on the synthesized adsorbents. In addition to ion exchange,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  might generate a complexation reaction with the OH and COOH groups on the surface of the carbonaceous materials. However,  $\text{Cu}^{2+}$  possesses better complexation ability for the OH and COOH groups because it is a transition metal. The adsorptive amounts followed the order  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ . These results demonstrate that both ion exchange and complexation reactions are the primary mechanisms in this study.

### 3.4. Effects of the grafting process on the adsorptive amounts

Although the grafting process can increase the –OH and –COOH groups on carbonaceous materials, the effects of the grafting process on different carbonaceous materials could generate a discrepancy in the results. **Table 4** indicates the enhanced ratio of the adsorptive amounts of the three carbonaceous materials after the grafting process.

**Table 4**

The enhanced ratios for the adsorptive amounts of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  on the three adsorbents ranged from 1.727–1.797, 1.956–2.080, and 2.483–2.850, respectively. Although the  $S_{\text{BET}}$  values (**Table 2**) indicate the order  $\text{AC} > \text{biochar} > \text{hydrochar}$ , the enhanced ratios exhibit an approximate result for the specific metal ions in the three carbonaceous materials. The results showed that the  $S_{\text{BET}}$  values are less important parameters for the increase in the –COOH and –OH groups during the grafting process. In addition, the high enhanced ratio for the adsorptive amounts of the three potentially toxic metal ions indicated that the grafting process is effective for increasing the removal of metal ions.

For the three carbonaceous materials, the enhanced ratios of the adsorptive amounts exhibited

the order  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$ . As  $\text{Pb}^{2+}$  barely undergoes a complexation reaction with oxygen-containing functional groups, the primary adsorption mechanism was regarded as ion exchange. In contrast, complexation is an important adsorption mechanism for  $\text{Cu}^{2+}$  on carbonaceous materials. The enhanced ratios of the adsorptive amounts for  $\text{Pb}^{2+}$  were higher than those for  $\text{Cu}^{2+}$ . These results indicated that ion exchange was the primary adsorption mechanism, and the complexation reaction was the secondary mechanism.

The results reveal that the grafting process can effectively increase the amounts of potentially toxic metal ions adsorbed on carbonaceous materials. The grafted hydrochar ( $Q_{\max} = 271.4, 146.0, 130.9 \text{ mg/g}$ ) could generate the highest adsorptive amounts of metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$ ); and its values  $Q_{\max}$  were overwhelmingly higher than those of CAC (25.15, 22.13, 21.83 mg/g; **Table 3**) in this study and others reported the literature, such as powdered CAC (24.8, 1.12, and 3.18 mg/g) and granular CAC (6.21, 1.12, and 2.54 mg/g, respectively) [22].

Other researchers [4] reported that the values  $Q_{\max}$  of CAC for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  were 42.5 and 15.0 mg/g that was remarkably lower than the grafted hydrochar ( $Q_{\max} = 298.1$  and 136.3 mg/g). However, the hydrochar was seldom applied in real water or water treatment. The use of the grafted hydrochar may be more widely adopted in wastewater treatment in the future. Soil mixed with the biochar has been studied for its ability to reduce the uptake of potentially toxic metal ions by plants. The grafted biochar in the soil can effectively reduce harm to human beings. The AC is frequently used to remove organic compounds from wastewater or water. The grafted AC can simultaneously adsorb metal ions and organic contaminants to simplify the treatment process.

### 3.5. Competitive adsorption

The competitive adsorption was evaluated at three initial concentrations of the mixture metals (1, 10, and 50 mmol/L). **Figure 8** shows that the reference ranking of three metals onto G-hydrochar was in the following order:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$  (when  $C_0 = 1 \text{ mmol/L}$ ),  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$  at higher



405 concentration ( $C_o = 10$  mmol/L), and  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$  ( $C_o = 50$  mmol/L). The result suggests that  
406 the adsorption order of the grafted hydrochar toward three target metals was strongly dependent on  
407 the initial concentrations of metals in the mixture. The adsorption sites in G-hydrochar were more  
408 favorable to the Cu ions than the Pb and Cd ions at high initial concentrations (10 and 50 mmol/L).

## 409 **Figure 8**

### 410 **3.6. Cycle of adsorption/desorption**

411 The stability of G-hydrochar was evaluated through studying adsorption/desorption cycles.  
412 Because the toxic metals ( $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$ ) are cations, hydrochloric acid ( $\text{H}^+$  ions) is selected  
413 as a target desorbing agent for removing them from G-hydrochar. The adsorption study was conducted  
414 at a high metal concentration ( $\sim 1000$  mg/L) to ensure that the adsorption sites in G-hydrochar were  
415 saturated or occupied by metal ions. **Figure 9** shows the desorption efficiency was higher than 98%.  
416 The adsorption capacity of G-hydrochar slightly decreased after each cycle. The result suggest that  
417 the grafting process of the co-polymers was successful and the active adsorption sites in G-hydrochar  
418 were highly stable.

## 419 **Figure 9**

### 420 **4. Conclusions**

421 Notably, an increase in the oxygen content along with the presence of Na and Ce on the surface  
422 of grafted materials (G-hydrochar, G-biochar, and G-AC) confirm success in grafting  
423 copolymerization into the surface of the carbonaceous materials.

424 In this study, ginger waste was used as a raw material to synthesize hydrochar, biochar, and

425 activated carbon. The grafting process was performed on the three materials to increase the density  
426 of –OH and –COOH functional groups. The grafted carbonaceous materials possessed more –OH and  
427 –COOH functional groups to increase the adsorptive amounts of the tested metal ions through  
428 complexation reactions and ion exchange. The adsorptive amounts of the tested metal ions were in  
429 the order of hydrochar > AC > biochar and G-hydrochar > G-AC > G-biochar. For the tested metal  
430 ions, the adsorptive amounts followed the order  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ . The grafting process enhanced  
431 the adsorptive amounts of metal ions by approximately 1.7–2.8 times. The grafted carbonaceous  
432 hydrochar was the best adsorbent where the contaminants were potentially toxic metal ions. This  
433 material can be applied for five adsorption /desorption cycles without significant change in its  
434 adsorption capacity. When organic contaminants and potentially toxic metal ions exist in water bodies,  
435 G-AC can be used to remove them.

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