Synthesis of porous pig bone char as adsorbent for removal of DBP precursors from surface water
Aunnop Wongrueng, Pharkphum Rakruam, Alongorn Siri and Adisak Siyasukh

ABSTRACT
This research study aims to investigate the efficiency of synthesized porous pig bone char (PBC) for reduction of disinfection by-product (DBP) precursors from surface water. Dissolved organic matter (DOM) is commonly present in natural water and acts as a disinfection by-product precursor. Adsorption is one of the promising technologies that is commonly applied for DOM removal. Interestingly, the properties of pig bone are such that it has a surface area and pore volumes that can adsorb DOM. Pig bone was synthesized as porous bone char (PBC). The results show that synthesized PBC at 900 °C (PBC-900 °C) provides a high volume of mesoporous structure. The adsorption process was best fitted with the pseudo-second-order and Freundlich isotherm model. Thus, the mechanisms occurred on the multilayer adsorption of the surface. PBC-900 °C can remove approximately 70–80% of DOM with varying concentrations, from 0.2 g/L to 0.8 g/L. Furthermore, the results of fluorescence excitation-emission (FEEM) showed that humic acids and humic-like substances in water can be removed by using PBC at concentrations higher than 0.4 g/L. From the obtained results, it can be concluded that PBC is an alternative low-cost adsorbent which can be utilized for reduction of DBP precursors from water.

Key words | adsorption, dissolved organic matter, pig bone, porous bone char, surface water, trihalomethane formation potentials (THMFPs)

INTRODUCTION
Natural organic matter (NOM) is a major component in aquatic environments (Sillanpää 2015). NOM can cause many problems in drinking water because of processes such as oxidation, coagulation, disinfection, and adsorption (Jacangelo et al. 1995). The important compound of NOM is dissolved organic matter (DOM). DOM is generally present in several water sources (e.g. surface water, lakes, reservoirs, and ground water). High concentrations of DOM may cause severe deterioration in the water quality of drinking water because DOM is a precursor of disinfection by-products (DBPs) (Cowman & Singer 1995). Reactions between DOM and chlorine create DBPs, which include trihalomethanes (THMs) and haloacetic acids (HAAs) (Chellam & Krasner 2001). THMs include chloroform, bromodichloromethane, dibromochloromethane, and bromoform. They are classified as possible carcinogens to humans (USEPA 2004).

Several technologies, for example coagulation, ion exchange, advanced oxidation processes, membrane filtration, electrochemical methods and adsorption, have been used to remove DOM. Adsorption is one of the technologies that is widely used in drinking water purification processes due to its efficiency and convenience. Activated
carbon is commonly used as an adsorbent for the removal of DOM because it has high efficiency (Bond et al. 2011). Nevertheless, the cost of using activated carbon is still high for developing countries.

In Thailand, animals are slaughtered for meeting people’s demand for meat. Large amounts of animal bone become bone waste, which affects the environment. Although cattle farms use animal bone to feed their animals, the amount of animal bone waste still exceeds the demand for feeding. Interestingly, the properties of animal bone are such that it has a surface area and pore volumes that can adsorb various substances. Accordingly, many research studies have utilized animal bone as bone char to adsorb various substances including fluoride (Sawangjang 2016), arsenic (Chen et al. 2008), and chromium (Hyder et al. 2014). Nevertheless, there are few research studies on DOM removal by animal bone char. The commonly used adsorbents for DOM removal are granular activated carbon (GAC) (Wang et al. 2015) and powdered activated carbon (PAC) (Fabris et al. 2008). Thus, removal of DOM by animal bone char has not been well investigated.

Pig bone was selected as the adsorbent for the removal of DBP precursors from surface water. Because the properties of pig bone include high surface area (Sawangjang 2016), it can be considered a good characteristic adsorbent. The aim of this study was to synthesize and characterize porous pig bone char. The efficiency of porous pig bone char for removal of DBP precursors was investigated by using the adsorption kinetic and isotherm models.

**MATERIALS AND METHODS**

**Raw surface water**

A volume of 60 L of raw water was collected from the Ping River in the rainy season (2016) and used for all the research. The quantity and characteristics of the organic matter in the raw water were investigated by measuring various parameters including dissolved organic carbon (DOC), trihalomethane formation potentials (THMFPs), UV absorbance at wavelength 254 nm (UV254), and fluorescence excitation–emission matrix (FEEM).

**Synthesis of porous pig bone char**

The porous pig bone char (PBC) used in this study was synthesized from raw pig bone. First, raw pig bone was prepared by boiling the same at 100 °C to remove any fat that remained inside the bone. It was boiled several times until the boiling water become white and transparent, indicating that the colloid was completely released from the pig bone (Rojas-Mayorga et al. 2015). After that, it was rinsed with deionized water. Second, the clean pig bone was dried in an incubator at 100 °C for 24 h to eliminate moisture. Next, the dry bone was crushed by a hammer into fragments of 1–2 cm and crushed again by a mortar. Next, it was put into a ball mill for 2 days to produce small sizes of the bone. After that, it was filtered using a sieve at 250 μm, and any moisture was removed by drying in an incubator at 100 °C for 24 h. Finally, the bone char was synthesized by pyrolyzing in a horizontal tube for 2 hours under nitrogen ambient with varied temperature conditions, at 650 °C and 900 °C. The final particle size of pig bone char was lower than 256 μm. The morphology and elements of the synthesized porous pig bone char were investigated by using a scanning electron microscope and energy-dispersive X-ray spectroscopy (EDX). Furthermore, the physicochemical properties of the porous pig bone char were analyzed by various parameters including surface area (BET), point of zero charge (PZC), and surface charge density.

**Adsorption study**

The adsorption kinetics of the DOC by the porous PBC were studied by varying the concentrations of the PBC at 30, 60, 90, and 120 mg with 150 mL of raw surface water. It was represented at concentrations of 0.2, 0.4, 0.6, and 0.8 g/L, respectively. The experiment was conducted at room temperature and the speed of shaking was 200 revolutions per minute (rpm). Water samples were collected at various times, including 0, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 120, 180, 360, 720, and 1,440 min. In addition, the adsorption isotherm was calculated from the results obtained from the adsorption kinetics. The collected water samples were filtered through a 0.45 μm nylon syringe filter for removing the PBC. After that, the samples were analyzed for any remaining DOC.

**DBP precursors removal experiment**

The amount (concentration) of PBC used for this experiment was based on the results obtained from the study on the adsorption kinetics. PBC was mixed with 150 mL of water sample in an Erlenmeyer flask and shaken at 200 rpm with the temperature controlled at 25 °C until equilibrium time. The water sample was collected and measured for DOM concentration. The DOM concentration was
determined by measuring the DOM surrogate parameters, including DOC concentration, UV-254, and THMFPs.

**Analytical methods**

All the water samples were filtered through GF/F followed by 0.45 μm nylon prior to measurement of DOM surrogate parameters. Milli-Q water (ELGA) was used on every sample for a clean system and blank sample preparation. The DOC concentration in the water samples was measured in accordance with Standard Methods 5310 total organic carbon (TOC) (APHA/AWWA/WEF 2018), AJ-analyzer multi N/C 3100, multiWin 4.09. The UV-254 of the water samples was analyzed in accordance with the Standard Methods 5910B ultraviolet absorption method (APHA/AWWA/WEF 2018) by using Perkin-Elmer Model Lambda 365, UV/Vis spectrophotometer: Lambda 365 with matched quartz cells that provided a path length of 1 mm. The THMFPs measurements were taken according to Standard Methods 5710 A-D (APHA/AWWA/WEF 2018). Phosphate solution was used as the buffer solution before incubation at 25 ± 2 °C in amber bottles with PTFE liners. At the end of the 24 h reaction period, the free chlorine remaining in the water samples should be between 3 mg/L and 5 mg/L. The residual chlorine was measured according to the Standard Methods 4500-Cl G (APHA/AWWA/WEF 2018). The THMs were extracted with MTBE in accordance with EPA551 (USEPA 1995). Agilent 6890 Gas Chromatograph with an electron capture detector was used for measuring the THMs. The FEEM was analyzed using a spectrofluorometer with excitation wavelengths in the range of 220 nm to 600 nm.

**RESULTS AND DISCUSSION**

**Water quality**

The average pH of the Ping River was 8.4 and the average turbidity was 51.37 NTU. The concentration of the DOC was 4.492 mg/L. The THMFPs of the Ping River is 1,446.26 μg/L, which indicates that the DOM in the Ping River had greatly reacted with chlorine to form THMs. Among the THM species, chloroform was found to be at the highest concentration (1,344.09 μg/L), which corresponds well with the findings of various research studies (Rodriguez et al. 2004; Krutklom 2013). Hence, removal of DOM is necessary before it reacts with chlorine during the disinfection procedure in the drinking water purification process.

**Morphology and characteristics of porous pig bone char**

The morphology of the PBC which was pyrolyzed at 650 °C (PBC-650 °C) and the morphology of the PBC which was pyrolyzed at 900 °C (PBC-900 °C) are shown in Figure 1. The results of the morphology of both the PBC samples showed that they had smooth surfaces.

The elements of PBC including carbon (C), oxygen (O), phosphorus (P), calcium (Ca), and nitrogen (N) were analyzed, and the results are shown in Table 1. From the results, it was evident that the carbon remaining in PBC-650 °C was higher than that in PBC-900 °C. This can be taken as indicating that pyrolysis at higher temperatures can remove more carbon in pig bone. The carbon element
in the pig bone represents the organic content in the pig bone char (Leyva-Ramos et al. 2010).

Physicochemical characteristics of porous pig bone char adsorbents

The N\textsubscript{2} adsorption–desorption isotherms of both the PBC samples were investigated. Based on the IUPAC classification, both of the PBC samples were type IV and had mesoporous structures, which means large pore volumes and high surface areas, and these were defined as good properties for an adsorbent (Patel et al. 2015). The BET surface area and the volume of the mesoporous structure are summarized in Table 2. The results show that PBC-900 °C had lower BET surface area than PBC-650 °C; however, PBC-900 °C should be utilized as an alternative adsorbent as the volume of its mesoporous structure was greater than that of PBC-650 °C. The mesoporous structure provides a large pore volume and high surface area, which are defined as good properties for an adsorbent, and it exhibits good electrochemical performance (Patel et al. 2015; Tian et al. 2018). An adsorption process depends on the compatibility of molecular size and pore width of the adsorbates and the adsorbents, respectively; a small molecule prefers the micropore volume (pore width <2 nm in diameter), and a larger molecule favors the mesopore volume (2 \leq \text{pore width} \leq 50 \text{ nm}). Although the micropore is responsible for increasing the specific surface area, the absorption of large molecules in a liquid medium depends on the porosity of the mesopore range rather than the micropore (Newcombe 1997; Zimmerman et al. 2004; Aschermann et al. 2018; Siyasukh et al. 2018). Moreover, the target pollutant in this study is the DOM, for which the molecular size is normally between 1 and 7 nm on average (Kennedy & Summers 2015). For this reason, the criteria for selecting an absorbent material should be determined by the mesopore volume rather than the surface area or micropore volume. It is, therefore, more suitable to choose PBC-900 °C, whose ratio of mesopore to micropore volume is 7.7, for use as the adsorbent in this study, rather than PBC-600 °C, for which the ratio is 6.0.

The point of zero charge (PZC) expresses the pH value that affects the surface charge of the adsorbent. The PZC of the porous bone char was found to be approximately in the pH range of 6.5–8.5. If the pH of the solution was above the PZC of the porous pig bone char (>8.5), the surface of the porous pig bone char was considered to be negatively charged. On the other hand, if the pH of the solution was below the PZC of the porous pig bone char (<6.5), the surface of the porous pig bone char was considered to be positively charged. The PZC of the porous pig bone char was similar to that of PAC (poly aluminium chloride), which is generally used as the adsorbent in water treatment processes. Prarat (2011) found that the PZC and the surface charge density values of PAC were 9.5 and in the range of 8–10, respectively.

Adsorption kinetics

Based on the results regarding the morphology and the characteristics of PBC, the PBC synthesized at 900 °C (PBC-900 °C) was used as the adsorbent for the DOM experiment. The results of the adsorption kinetics of the DOC of PBC-900 °C are shown in Figure 2, where q\textsubscript{t} represents the amount of DOC adsorbed at time.
The results presented in Figure 2 show that the adsorption was fast within the short contact time. After 1 h, the adsorption of the PBC-900 °C adsorbent regularly slowed until it reached the equilibrium. The equilibrium time of adsorbent dosage at 0.2 g/L was 12 hours. For the other adsorbent dosages, the equilibrium time was 6 hours. Table 3 shows that the adsorption capacity values of DOC at equilibrium times were 19.97, 8.505, 5.589, and 4.420 mg/g at adsorbent concentrations of 0.2, 0.4, 0.6 and 0.8 g/L, respectively.

The pseudo-first-order and the pseudo-second-order were applied to examine the adsorption kinetics of the DOM onto the porous pig bone char adsorbents, as shown in Table 3. The constant (k) values of the pseudo-first-order were calculated from the slope of each regression line. Besides, the square of the slope divided by the intercept of the regression line was calculated for the constant (k) of the pseudo-second-order kinetic model. In this study, the R² (correlation coefficient) value of the pseudo-second-order kinetic model was considered for defining the kinetic model that is the best fit for the adsorbents.

Table 3 shows that the adsorption capacity values of DOC were investigated by measuring various parameters including DOC, THMFP, and FEEM. The results of DOC reduction by porous bone char are shown in Figure 3. The pseudosecond-order kinetic model (Rojas-Mayorga et al. 2013; Medellin-Castillo et al. 2014; Cazetta et al. 2016; Sawangjiang 2016).

From Table 3, it is clear that the initial adsorption rate (h) of PBC-900 °C followed the following order: PBC-0.2 g/L > PBC-0.4 g/L > PBC-0.6 g/L > PBC-0.8 g/L. The high h values indicate the fast adsorption process. Thus, the result indicates that the adsorption process involves not only the amount of adsorbent used but also the electrostatic interaction and the interparticle diffusion of adsorbent and DOM (Permrungruang 2013).

The study of the adsorption isotherm of PBC-900 °C involved investigation by varying the concentration (0.2, 0.4, 0.6, and 0.8 g/L). The R² values of the Langmuir and Freundlich models of porous bone char at 900 °C were investigated. The adsorption isotherm results of the Langmuir and the Freundlich models are shown in Table 4. The R² values of the Langmuir and the Freundlich models were 0.8802 and 0.9575, respectively. Obviously, the R² value of the Freundlich isotherm model is higher than the R² value of the Langmuir isotherm model. Hence, it can be concluded that PBC-900 °C is better fitted to the Freundlich isotherm model and that the adsorption process occurs via multilayer adsorption on the surface (Jimenez-Reyes & Solache-Rios 2010).

### Reduction of DOC, UV-254, and FEEM

The efficiency of PBC-900 °C for DOM reduction was investigated by measuring various parameters including DOC, THMFP, and FEEM. The results of DOC reduction by porous bone char are shown in Figure 3.

The results showed that the DOC concentration was strongly adsorbed on varying the concentration of PBC-900 °C adsorbent as 0.2, 0.4, 0.6, and 0.8 g/L. The increase of the PBC-900 °C provided higher DOC reduction, but it was not significantly different for the different concentrations. The DOC concentration in raw water was 4.492 mg/L. In the adsorption experiment, the DOC that remained after adsorption by PBC-900 °C at 0.2, 0.4, 0.6, and 0.8 g/L was 1.310, 1.090, 0.957, and 0.954 mg/L, respectively. The percentages of DOC reduction of PBC-900 °C at 0.2, 0.4, 0.6, and 0.8 g/L were higher than 70%. The result was compared with DOC reduction by

### Table 3 | Kinetic parameters of DOC adsorption on porous pig bone char at 900 °C

<table>
<thead>
<tr>
<th>PBC (g/L)</th>
<th>Qe, exp (mg/g)</th>
<th>Qe, cal mg/g</th>
<th>K1, min⁻¹</th>
<th>R²</th>
<th>Qe, cal mg/g</th>
<th>K2, min⁻¹</th>
<th>R²</th>
<th>h (mg/g.min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>19.97</td>
<td>2.49</td>
<td>-0.0005</td>
<td>0.1227</td>
<td>20.05</td>
<td>0.0475</td>
<td>0.9995</td>
<td>18.94</td>
</tr>
<tr>
<td>0.4</td>
<td>8.505</td>
<td>4.05</td>
<td>-0.0003</td>
<td>0.1566</td>
<td>8.64</td>
<td>0.1317</td>
<td>0.9998</td>
<td>9.55</td>
</tr>
<tr>
<td>0.6</td>
<td>5.589</td>
<td>0.58</td>
<td>0.0002</td>
<td>0.095</td>
<td>5.31</td>
<td>0.1902</td>
<td>0.9999</td>
<td>5.94</td>
</tr>
<tr>
<td>0.8</td>
<td>4.420</td>
<td>0</td>
<td>0.0006</td>
<td>0.0607</td>
<td>4.10</td>
<td>0.2443</td>
<td>0.9999</td>
<td>4.77</td>
</tr>
</tbody>
</table>
Chloroform was found in the highest concentration among the THM species. The concentration of chloroform in raw water was 1,344.09 μg/L. It was found to have decreased to 472.23, 543.84, 620.43, and 392.82 μg/L after adsorption by PBC-900 °C at 0.2, 0.4, 0.6, and 0.8 g/L, respectively. The results showed that the THMFPs greatly decreased due to the reduction in the DBPs precursor DOC. The DBPs precursor is an important factor that affects THMFPs (Hua & Reckhow 2007; Bond et al. 2009). The efficiency of porous pig bone char to reduce THMFPs was found to be in the range of 47.3% to 67.3%. When compared with the efficiency of commercial PAC, as studied by Wudthigarn (2015), it was found that the efficiency of commercial PAC for THMFPs reduction was 70%.

The characteristics of DOM in raw water and treated water by PBC-900 °C were investigated by using the FEEM technique. The result of the FEEM method using raw water from the Ping River is illustrated in Figure 5. The result showed that two peaks of DOM (A and B) were found in raw water. The results after adsorption by porous bone char at different concentrations are shown in Figure 5. The results presented in Figure 5 show that two peaks of DOM (A and B) were found when PBC-900 °C was used at 0.2 g/L. In contrast, the fluorescent peak was not detected in the other porous bone char concentrations (0.4, 0.6, and 0.8 g/L). Based on the PAC adsorption, the fluorescent peak was not detected after the adsorption process (Wudthigarn 2015).

**CONCLUSIONS**

From the results of the morphology and the characteristics of synthesizing porous pig bone char, it can be concluded that PBC-900 °C not only provides a mesoporous structure but also gives a higher volume of mesopores than PBC-650 °C. The pH of the PZC of the porous pig bone char was similar to that of the commercial PAC adsorbent. Furthermore, the adsorption process was best fitted with the pseudo-second-order and the adsorption capacity at equilibrium times (19.97 mg/g within 1 h) was found at the concentration of 0.2 g/L of porous pig bone char. In addition, the Freundlich isotherm model was observed to give the highest R² values. So, the mechanisms could be concluded as occurring in the form of multilayer adsorption on the surface.

From the DBPs precursor reduction results, the efficiency of the DBPs precursor reduction was found to be in the range of 70–80% with varying concentrations of PBC-900 °C (0.2 g/L to 0.8 g/L). Chloroform was the major
Figure 5 | FEEM of raw water and treated water at different concentrations of PBC-900°C.
species in the THMFPs, both in raw water and treated water. The THMFPs were found to have significantly decreased by PBC-900 °C adsorption, at 47.3% to 67.3%. From the results obtained from FEEM, it can be concluded that using 0.2 g/L concentration of PBC-900 °C cannot remove the humic acids and the humic-like substances in water. On the other hand, increasing the porous bone char concentrations to 0.4, 0.6, and 0.8 g/L could remove those substances. From the obtained results, it can be concluded that synthesized porous pig bone char is an alternative low-cost adsorbent which can be utilized for reduction of DBP precursors from water.

ACKNOWLEDGEMENTS

The authors would like to thank the Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Bangkok, Thailand, for the financial support.

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First received 24 July 2018; accepted in revised form 13 November 2018. Available online 21 November 2018.