Journal of Colloid and Interface Science 525 (2018) 143–151

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

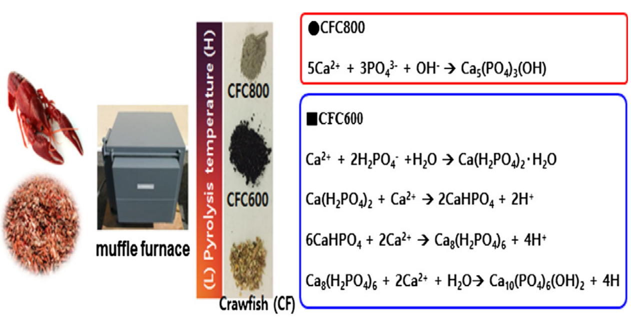
Regular Article

Effect of pyrolysis temperature on phosphate adsorption characteristics and mechanisms of crawfish char

Jong-Hwan Park [a], Jim J. Wang [a,*], Ran Xiao [a,b], Baoyue Zhou [a], Ronald D. Delaune [c], Dong-Cheol Seo [d]

[a] School of Plant, Environmental and Soil Sciences, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA
[b] College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi 712100, China
[c] Department of Oceanography and Costal Sciences, College of the Coast and Environment, Louisiana State University, Baton Rouge, LA 70803, USA
[d] Divison of Applied Life Science (BK21 Program) & Institute of Agriculture and Life Science, Gyeongsang National University, Jinju 52828, South Korea

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 February 2018
Revised 26 March 2018
Accepted 19 April 2018
Available online 21 April 2018

Keywords:
Adsorption
Crawfish waste
Char
Phosphate
Precipitation
Pyrolysis
Calcium
Element mapping

ABSTRACT

The purpose of this study was to investigate the characteristics of crawfish char (CFC) derived at different pyrolysis temperature and to evaluate its adsorption characteristics on phosphate. Phosphate adsorption by CFC occurred rapidly at the beginning of the reaction, and the time to reach equilibrium was dependent on the pyrolysis temperature. Maximum adsorption capacities of phosphate by CFC at different pyrolysis temperatures were high in order of CFC800 (70.9 mg/g) > CFC600 (56.8 mg/g) > CFC400 (47.2 mg/g) ≫ CFC200 (9.5 mg/g) ≈ uncharred crawfish feedstock (CF) (7.1 mg/g). Spectroscopic analyses using SEM-EDS and FTIR showed that the phosphate present in the CFC itself was associated with carbon, while the phosphate adsorbed on the CFC was closely related to calcium. The adsorption of phosphate by CFC is dominantly affected by pH. Phosphate adsorption of CFC600 primarily occurred at acid and neutral pH which is related to dissolved calcium from surface and phosphate hydrolysis product ($H_2PO_4^-$), while phosphate adsorption of CFC800 mainly took place at alkaline pH, with precipitation mechanism between PO_4^{3-} and calcium dissolved from free CaO and $Ca(OH)_2$. Overall, CFC derived at pyrolysis temperatures above 400 °C is effective for waste reduction and phosphate treatment in wastewater.

1. Introduction

Crawfish (CF), also known as crayfish, is a species of crustaceans living in freshwater and is taxonomically classified as *Astacoidea* and *Parastacoidea* [1]. In the U.S., CF is a typically produced in Louisiana, and its total annual yield ranged from 10,000 to

* Corresponding author.
E-mail addresses: zoqlsqkr@gmail.com (J.-H. Park), JJWang@agcenter.lsu.edu (J.J. Wang), xiaoran0012@gmail.com (R. Xiao), bzhou5@lsu.edu (B. Zhou), rdelaun@lsu.edu (R.D. Delaune), drseodc@gmail.com (D.-C. Seo).

https://doi.org/10.1016/j.jcis.2018.04.078
0021-9797/

27,000 tons during last decade [2,3]. The dishes made with CF are highly popular with people all over the United States particularly in the Southern region, and CF dishes are usually enjoyed from April to June. In general, many people eat only the tail meat, which is only 15–20% of the total crawfish weight [4]. Considering the annual yield and the percentage of consumed tail meat, the amount of CF waste generated annually is expected to be substantial. However, the remaining CF waste is discarded with general waste without any post treatment.

Despite the efforts of many researchers to recycle CF waste for decades, known useful techniques are relatively poor. Examples of successful studies include the production of chitin and chitosan from crawfish waste through acid and alkali treatments [5,6], and the extraction of carotenoids (astaxanthin) through solvent extraction [7]. However, these techniques are costly and time-consuming to utilize, and the amount of CF waste that is recycled by these technologies is extremely limited. Therefore, the development of new economical and creative technologies to effectively recycle CF is urgently required.

The pyrolysis technology of the waste has attracted attention from many researchers because the treatment process is simpler than other technologies and it can be applied to a large amount of waste [8]. In addition, pyrolysis technology to treat waste resources is effective in reducing waste, and chars derived from waste resources are known as an effective adsorbent for various pollutants [9]. Recently, it has been reported that char produced from pyrolysis of agricultural residue, sewage sludge, food waste, animal manure and bone is effective for the adsorption of various contaminants such as heavy metals, PHAs, pesticides, dyes and PO_4^{3-} [9–11]. However, since the adsorption characteristics of char for treating pollutants depend on the characteristics of raw materials and pyrolysis conditions, the optimum pyrolysis temperature and raw material selection are essential for utilizing char as an adsorbent [12]. It is also important to select an adsorbent suitable for pollutant because adsorption characteristics of adsorbents vary depending on the pollutants in the wastewater [13]. In particular, char produced from pyrolysis of crustacean waste contains a large amount of calcium, suggesting that it could be utilized as an adsorbent of phosphate in wastewater.

Phosphate is known to be discharged to nearby water systems through a variety of routes such as leaching and runoff of fertilizers used in agriculture, household detergents, and chemical treatment process of industrial facilities [14]. Phosphates are essential for the growth of aquatic organisms and plants, but excessive phosphate concentrations in waterbodies induce the growth and proliferation of phytoplankton, leading to eutrophication. It also has a negative impact on aquatic organisms and animals [15]. Since eutrophication occurs mainly when phosphate concentrations are above 0.02 mg/L in waterbodies [16], wastewater treatment plants use chemicals such as Al and Mg salts and adsorbents to treat phosphate below required standards. However, the unfavorable economics of using treatment chemicals and the post-treatment sludge produced are problematic. On the other hand, in the case of using adsorbents, low phosphate adsorption efficiency requires that the adsorbent be replaced frequently. Therefore, utilization of calcium rich-char obtained from pyrolysis of CF as a phosphate adsorbent could be a breakthrough technology that can improve waste reduction as well as phosphate treatment efficiency.

Recently, it has been reported that char produced from a crab shell is effective for phosphate adsorption [17], and some researchers emphasized the mechanism of phosphate adsorption by adsorbent containing a large amount of calcium [18,19]. However, there has been no study on phosphate adsorption by crawfish char. Furthermore, although adsorption of heavy metals and organic contaminants by crayfish char has been reported [20,21], there is still limited information on the CFC properties as influenced by pyrolysis temperature and on the mechanism of pollutants adsorption. Therefore, the purpose of this study was to determine the optimum pyrolysis temperature for CFC production and to evaluate its phosphate adsorption characteristics.

2. Material and method

2.1. Preparation and characterization of crawfish char

Crawfish waste was collected from region restaurant in Baton Rouge (LA, USA), and used to produce CFC with slow pyrolyzer. Briefly, CF waste was rinsed first for several times with deionized (DI) water to remove remained impurities such as meat and salt, oven-dried (60 °C), and ground to pass through a < 0.5 mm sieve. Dried CF waste was placed in porcelain crucibles with a cover and pyrolyzed at different temperatures (200, 400, 600 and 800 °C) for 2 h after it reached set temperature in a muffle furnace (FA 1730; Thermolyne Sybron Corporation, Dubuque, IA) under limited oxygen condition with nitrogen gas purged. The resulting CFCs were stored in an airtight container before use. For the convenience of discussion, char samples were termed as CFC200, CFC400, CFC600 and CFC800 to indicate chars made at pyrolysis temperature of 200, 400, 600 and 800 °C, respectively.

The yield and ash contents of CFC samples are calculated according to:

$$\text{Yield}(\%) = (W_{char}/W_{feedstock}) \times 100\% \quad (1)$$

$$\text{Ash content}(\%) = (W_{ash}/W_{char}) \times 100\% \quad (2)$$

where W_{char}, W_{ash} and $W_{feedstock}$ are dry weights (g) of char, ash and feedstock, respectively.

The pH values of CFCs were characterized in a 1:20 (w/v) extracts prepared by shaking samples in deionized water at 100 rpm for 2 h. The total C and N contents in CFC were analyzed with an FlashEA 1112 Elemental Analyzer (Elementar Analysen system GmbH, Germany). Total concentrations of other elements such as K, Ca, Mg, Na were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Spectro Ciros, SPECTRO, USA) after digestion followed the EPA method 3050B.

2.2. Adsorption characteristics

Adsorption experiments of phosphate were carried out with batch equilibration method and stock phosphate solutions of 1000 mg/L was prepared by dissolving KH_2PO_4 in DI water. Maximum adsorption capacities of phosphate by CFC in aqueous solution were evaluated by two adsorption isotherm models (Freundlich and Langmuir isotherm). Briefly, a series of suspension in 50 mL centrifuge tubes was prepared, each containing 0.05 g of CFC and 25 mL phosphate solutions with concentration levels from 2 to 240 mg/L. The initial pH value of the solutions was adjusted to 6 by HCl and NaOH solutions (0.1 M) with stirring. The samples were equilibrated for 24 h on a rotary shaker at constant room temperature (25.0 ± 0.2 °C). And then samples were separated by centrifugation during 10 min at 4000 rpm and the solution was filtered by filter paper (0.45 μm). The concentrations of phosphate in residual solutions were analyzed by the molybdenum blue-ascorbic acid method [22]. The amount of phosphate adsorbed per mass unit of CFC was calculated by difference between the initial and equilibrium concentrations in solution. Adsorption isotherms were fitted with both the Freundlich and Langmuir models.

To establish the reaction time, phosphate adsorption of CFC was carried out by weighing 0.05 g of CFC in centrifuge tubes followed by additions of 25 mL of solutions containing 200 mg/L phosphate. The initial pH solution value was adjusted to 6 using 0.1 M HCl or