



Characteristics of biochar derived from marine macroalgae and fabrication of granular biochar by entrapment in calcium-alginate beads for phosphate removal from aqueous solution



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HIGHLIGHTS

- Granular biochar (LB-CAB) was prepared by entrapment in calcium-alginate beads.
- Pyrolysis temperature has a strong effect on properties of biochars.
- Adsorption tests show the endothermic nature of adsorption process.
- Phosphate adsorption capacity of LB-CAB was higher than other powdered biochars.

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ABSTRACT

In this work, granular biochar, *Laminaria japonica*-derived biochar (LB)-calcium alginate beads (LB-CAB), was successfully prepared by dropping a mixture of powder biochar and alginate solution into a calcium chloride solution for phosphate adsorption. Among different marine macroalgae derived biochars, LB exhibited the best performance, showing a phosphate removal rate of 97.02%, which was attributed to its high Ca/P and Mg/P ratios. With increasing pyrolysis temperature up to 600 °C, the physicochemical properties of LB became suitable for adsorbing phosphate. Experimental results of kinetics and equilibrium isotherms at different temperatures (10–30 °C) showed that the phosphate adsorption process is endothermic and is mainly controlled by external mass transfer and the intraparticle diffusion rate. The maximum adsorption capacity was found to be 157.7 mg g⁻¹ at 30 °C, as fitted by the Langmuir-Freundlich model, which is higher than capacities of other powder form of biochars.

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1. Introduction

Fresh water is the most fundamental and important resource to all creatures for living and ecosystem maintenance. Of the around 2.7% of total global water resources such as groundwater, lake, rivers, and glaciers, only 0.6% of fresh water is usable as drinking water (Shrimali and Singh, 2001). However, even that portion is being harmed significantly by the release of pollutants into aquatic ecosystems through human activities. In particular, considering the correlation between the nitrogen/phosphorous ratio and eutrophication, consistently sustaining phosphorous concentrations at low levels is considered vital in preventing eutrophication (Chris and William, 2002). Furthermore, phosphorous, a necessary

mineral for most creatures, is a finite resource on earth, and thus phosphorous recovery is should also be considered (Loganathan et al., 2014).

In this regard, largely on the basis of environmentally friendly and financially viable aspects, considerable attention has been devoted to the application of biochar as a practical approach because of its low-cost and effectiveness for adsorbing phosphate from aqueous solutions and strong potential for application in many fields (Zhou et al., 2013). Biochar is a predominantly stable black carbon materials derived from pyrolyzing low-cost biomass under oxygen-limited conditions. To date, various biochars have been converted from terrestrial biomass including wood, agricultural residues, dairy manure, sewage sludge, and organic waste (Mohan et al., 2014). Biochar has a large surface area, porous structure, and abundant functional groups, and thus may be effective for the removal of various pollutants from aqueous solutions.

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More recently, biochar derived from marine macroalgae has been garnering considerable attention as a relatively more promising and alternative low-cost adsorbent because marine macroalgae is massively abundant and biochar converted from this source has a high binding affinity to pollutants (Kim et al., 2016). Jung et al. (2016) also demonstrated that biochar derived from marine macroalgae can be applied as a fertilizer after phosphate adsorption. Thus, it is expected that converting marine macroalgae into biochar followed by phosphate removal can be an ideal way of producing added value. However, even though the powder form of biochar provides effective performance for contaminant adsorption, the beneficial uses of biochar may be hampered by the difficulty of recovering and collecting biochar in powder form after the adsorption process. Furthermore, powder form is not suitable for column-type filtration due to low hydraulic conductivity, making it even less attractive as an adsorbents.

Alginates (alginic acid) are natural polysaccharides that are produced by brown algae, and can produce an insoluble hydrogel in the presence of metallic divalent cations according to complex ionic interaction via ionotropic gelation. Owing to their simplicity, biocompatibility, and cost effectiveness, Ca^{2+} have been widely applied as gelling agent to immobilize activated carbon (Kim et al., 2008), bentonite-activated carbon (Benhouria et al., 2015), and biochar derived from chicken manure (Do and Lee, 2013) in calcium-alginate beads to remove dyes and metals (e.g., Cu^{2+} and Pb^{2+}) from aqueous solutions. However, there have been no reports focusing on the immobilization of biochar derived from marine macroalgae as a particulate form and its application to phosphate removal. Upon this research background, the aim of this work is to prepare particulate biochar by entrapping powder form of biochar into porous structured calcium-alginate beads for phosphate adsorption from an aqueous solution. Three different marine macroalgae, brown (*Laminaria japonica* and *Undaria pinnatifida*) and red (*Porphyra tenera*) macroalgae, which are intensively cultivated in the world as well as South Korea in particular, were selected for the study. It was found that *L. japonica*-derived biochar (LB) possessed the highest phosphate adsorption capability, and thus, in subsequent batch tests, LB and LB-calcium alginate beads (LB-CAB) were applied to determine the characteristics of them and estimate phosphate adsorption properties including kinetics and equilibrium isotherms.

2. Materials and methods

2.1. Preparation of biochar derived from marine macroalgae

Prior to the pyrolysis process, three different marine macroalgae were washed using fresh water to remove preexisting salt, sand, etc., and then oven-dried at 60 °C for 24 h. Subsequently, they were ground and sieved to a size of below 1.0 mm. After that, in order to convert them to biochar, a slow pyrolysis process was conducted in a horizontal electric furnace (TF-80-6, Woori Science Instrument Co., South Korea) with a quartz tubular reactor. A suitable amount of the marine macroalgae powder was placed in a porcelain boat in the middle of the quartz tubular reactor. For selection of a suitable biochar derived from three different marine macroalgae, the pyrolysis conditions were fixed at 600 °C at a rate of 7 °C min⁻¹ under a N₂ environment (a N₂ flow rate of 25 ml min⁻¹) for 1 h. The obtained biochars from *L. japonica*, *U. pinnatifida*, and *P. tenera*, were denoted as LB, UB, and PB, respectively, according to different species. On the other hand, the pyrolysis temperature was varied from 200 to 800 °C to determine the optimal pyrolysis temperature for production of *L. japonica* derived biochar. The various LBs obtained under different pyrolysis temperature were denoted as LB200, LB400, LB600, and LB800, respec-

tively, according to the pyrolysis temperature. After cleaning several times of prepared LBs with distilled deionized water (Milli Q plus, Merck Millipore Co., Germany), the prepared biochars were oven-dried at 60 °C for 24 h, and then sealed in a container before use.

2.2. Fabrication of granular LB by entrapping calcium-alginate beads

Granular biochar was prepared according to the procedure described by Benhouria research group (Benhouria et al., 2015). In detail, 2% (w/v) sodium alginate solution was prepared by mixing sodium alginate in 500 mL of distilled deionized water with stirring for 1 h. Subsequently, 2% (w/v) of LB was added to the alginate solution, and the mixture was then stirred for 10 h. After the mixture became homogeneous, it was dropped through a burette into 2% (w/v) calcium chloride to form granules with gentle stirring. The excess unbounded calcium chloride from the beads surface was removed by washing several times with distilled deionized water, and then oven-dried at 45 °C for 24 h. The prepared granular LB by entrapping calcium-alginate beads was denoted as LB-CAB. As shown in the following Supplementary data (Fig. S3), the average diameters of LB-CAB before and after dry was 3.31 and 1.17 mm, respectively.

2.3. Phosphate adsorption test: powdered biochar

As a preliminary assessment, in order to determine the most suitable marine macroalgae, the comparison study of LB, UB, and PB in terms of the potential for phosphate adsorption from an aqueous solution was performed. For the test, a stock solution containing phosphate of 20 mg L⁻¹ was prepared by using KH₂PO₄ in distilled deionized water. The phosphate removal rates were then determined by mixing 0.05 g of each biochar with reaction vessels containing 50 ml of phosphate solution. The solution pH condition was adjusted to 6.0 with 0.1 M of HCl and NaOH using a LabQuest2 portable meter (LQ2-LE, Vernier, USA); the reaction vessels were then homogeneously shaken in an orbit shaking incubator at 200 rpm with controlled temperature at 20 °C for 48 h (WIS02011, WiseCube®, Germany). The samples were immediately filtered using a syringe filter with an opening of 0.45 μm; the phosphate concentrations in the filtrates were then analyzed using an ion chromatographer (DX-120, Dionex, USA). The phosphate removal rate was calculated by using the following equation:

$$\text{Phosphate removal rate (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the phosphate concentration (mg/L) of the initial and final solution, respectively.

Furthermore, in order to determine the effect of the pyrolysis temperature on phosphate adsorption of various LBs under different pyrolysis temperature (LB200–LB800), the phosphate removal rate also monitored. In this test, the experimental instruments and procedures were the same as those used for the preceding test.

Based on the result of preliminary tests, in order to evaluate the adsorption property of LB600, phosphate adsorption kinetics were investigated. The adsorption kinetics of phosphate were investigated by mixing 1.0 g of LB600 with 1.0 L of 1000 mg L⁻¹ phosphate solutions in digestion vessels. The instruments and experimental procedures were the same as those used for the preceding tests, while the solution temperatures were controlled at 10, 20, and 30 °C. At appropriate time intervals, the mixture was taken periodically from the reaction vessels. After checking the initial and final phosphate concentrations, the amount of phosphate adsorbed onto LB600 was then calculated by the following equation:

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