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Removal characteristics of copper by marine macro-algae-derived chars

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HIGHLIGHTS

- ▶ Biochars derived from *Undaria pinnatifida* proved to be useful for the removal of copper.
- ▶ Physical activation with steam enhanced the adsorption of Cu.
- ▶ The pseudo-second order kinetic model explained well the adsorption kinetic data.

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ABSTRACT

The char derived from the fast pyrolysis of macro-algae biomass, a brown alga *Undaria pinnatifida*, proved to be useful for the removal or recovery of copper from aqueous solutions. Even at a low dose of 0.1 g char/L, a high adsorption capacity was obtained. Physical activation with steam enhanced the adsorption of Cu, but chemical activation with a KOH solution decreased the adsorption capacity. A pseudo-second order kinetic model was used to explain the adsorption kinetics. The physically-activated char showed a Langmuir type of isotherm, and had a maximum adsorption capacity of 125.85 mg Cu/g. Based on the adsorption capacity, even at a low copper concentration, the char derived from the fast pyrolysis of *U. pinnatifida* is a valuable adsorbent for recovering copper from aqueous solutions.

1. Introduction

Copper (Cu) is one of most common heavy metals found in the environment and industrial wastewater because of its widespread use [1–5]. Generally, Cu could be removed by chemical precipitation as a form of $Cu(OH)_2$; however, the process produces large volume of sludge to be disposed. The chemical precipitation is not effective to treat low concentration of metal [6]. Recently, adsorption technology has been investigated to remove metals from water and wastewater because of the cost-effectiveness and easy operation [6,7]. Many researchers reported that various materials including biomass and industrial by-products could be applied to remove toxic metals or metalloids as adsorbents [1–5,7–9]. Additionally, biomass, such as wood, organic waste including sludge from wastewater/water treatment facilities and agricultural residue, has been used for oil production by fast pyrolysis [10–12]. More recently, seaweeds and marine/fresh micro-algae have attracted attention because of the huge amounts in marine environments. In addition, in Korea, macro-algae, such as brown algae, tangles, laver and sea lettuce, have been used as food for a long time. Recently, application of macro-algae to synthesis of bio-oil was also reported [13]. A by-product is generated by the pyrolysis of biomass; the most common by-products are gases and char. Pyrolytic gases can provide heat for the pyrolysis reactor, and char can be used for the production of activated carbon [14–16].

Activated carbon and/or char can remove a range of pollutants from an aqueous stream and air including volatile organic compounds, formaldehyde, polyaromatic hydrocarbons, halogenated compounds, heavy metals and oxyanionic compounds [17–19].

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Several studies have reported the biosorption ability of seaweed or micro-algae for various heavy metals. In particular, the potential use of seaweed for the recovery of heavy metal ions from aqueous effluents has been studied [20] but the adsorption characteristics of char derived from macro-algae have not been reported. To prepare activated carbon from char, chemical and/or physical activation is a common choice to enhance the surface area and improve the surface functionality for specific purposes [14–16,21,22]. Physical activation is known as gas activation, which is activated at temperatures >600 °C by gases, such as O_3, CO_2, and steam. Chemical activation produces micropores by activating a carbon material with a chemical dose such as KOH. The resulting chemically activated char has high surface area.

This study examined the characteristics of char obtained from pyrolysis of macro-algae to remove copper from a water system. In addition, the char was activated using physical and chemical methods. The effects of activation and other process parameters were investigated to determine the adsorption characteristics of the char produced.

2. Experimental

2.1. Macro-algae

A common natural macro-alga, a brown alga *Undaria pinnatifida* (U. *pinnatifida*), was collected from the southern coastal areas in Korea. The alga was dried, cut and pulverized by a grinding mill, and sieved through 5.7-mm and 1.0-mm meshes. To prepare macro-algae-based char which was labeled U, 8.0 g of *U. pinnatifida* was pyrolyzed in a batch reactor for 1 h at 500 °C with a N_2 gas flow of 50 mL min^{-1}.

To prepare physically activated char, the char (U) produced from the seaweed was modified in a reactor with 40 vol.% water vapor. The reactor temperature was increased from room temperature to 700 °C at a rate of 5 °C min^{-1}, and maintained at that temperature for 1 h. The physically activated char was labeled UW.

The chemically activated char was prepared using an alkaline solution, KOH. The char was mixed with 1.0 M KOH at a mass ratio of 1:1 on hot plates for 4 h to evaporate water, and then dried in an oven at 100 °C for 24 h. The dried sample was washed with 5.0 M HCl and H_2O to remove the residual potassium. The chemically activated char was labeled UK. All samples were stored in desiccators to prevent the absorption of moisture.

2.2. Adsorption

Copper solutions were prepared by dissolving analytical grade $Cu(NO_3)_2 \cdot 3H_2O$ (Junsei, Japan) in deionized water. The initial cupric concentration ranged from 5 to 50 mg L^{-1}. Batch adsorption tests were performed in a 200-mL Erlenmeyer flasks at 20 °C. Typically, 10 mg of seaweed char was placed in a flask containing 100 mL of a copper solution with its pH adjusted to 5.0 ± 0.5, and the mixture was stirred at 150 rpm in a shaking incubator. After 48 h, the suspension was filtered (#42, Whatman, USA), and the filtrate was analyzed by ICP (Inductively Coupled Plasma, ICPE-9000 SHIMADZU, JP). The effects of the experimental parameters, such as the initial metal ion concentration 5–50 mg L^{-1}, pH 2.5–6.5, sorbents dosage 0.03–0.3 g L^{-1} and temperature 20 °C on the removal of Cu(II) ions were studied in a batch type reactor for a specific contact time of 0.25–96 h.

2.3. Characterization of char

A Pyris Series (Perkin Elmer) was used to analyze the thermal characteristics of char under the following conditions: heating rate of 10 °C min^{-1}, temperature range from room temperature to 900 °C in a 50-mL min^{-1} N_2 gas flow. Vario Micro Cube (Elementar Analysensysteme GmbH) was used to analyze the C, H, N and S contents, and the oxygen content was calculated by the difference. Metal contents of char were analyzed by ICP–OES (ACTIVA, JY HORIVA). A N_2 adsorption–desorption analyzer (Micromeritics, Tristar 3000) was used to evaluate the surface area and pore size of the char. Fourier Transform Infra-Red spectroscopy (FTIR, thermo Nicolet 380) was used to identify the functional groups of char. The cations on the surface of char were extracted with NH_4OAc (1.0 N CH_3COONH_4) to determine the exchangeable cations. NH_4OAc was adjusted to pH 7 using CH_3COOH and NH_4OH and mixed with the char. The cations were analyzed by ICP (ICPE-9000, Shimadzu, JP).

3. Results and discussion

3.1. Characterization of adsorbents

Table 1 lists the results of the proximate (moisture, ash, and combustibles) and ultimate (C, H, O, N, and S) analyses of the seaweed char. Physical activation with water vapor increased the ash content and decreased the combustible content but chemical activation reduced the ash content significantly. It is probable that the alkaline solution increased the solubility of the non-combustible fraction causing the ash to be washed out during activation. Resultantly, chemical activation increased the carbon content dramatically.

Activation influenced the specific surface area of the char as well. As is shown in Table 2, the specific surface area of the char before the activation was not detectable. Physical activation increased the surface area significantly, while chemical activation enhanced the surface area to an even larger extent (Table 2). The

Table 2
Physical characteristics of seaweed char.

	BET surface Area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})	Ave. pore Diameter (nm)
U	N.D.	N.D.	N.D.
UW	57.9	0.02	1.25
UK	1287.0	0.64	2.00

N.D. – Not detected.

Table 1
Elemental analysis of seaweed char.

	Proximate (wt.%)			Ultimate[a] (wt.%)				
	Moisture (%)	Ash (%)	Combustibles (%)	C	H	N	S	O[b]
U	4.3	47.7	48.0	56.6	2.7	4.8	3.0	33.0
UW	3.6	68.5	27.9	77.5	1.5	3.9	8.0	9.0
UK	3.7	5.5	90.8	93.6	0.7	2.1	2.9	0.7

[a] Values without ash and moisture.
[b] By difference.