Cu²⁺ ion reduction in wastewater over RDF-derived char

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Abstract

Refuse-derived fuel (RDF) produced using municipal solid waste was pyrolyzed to produce RDF char. For the first time, the RDF char was used to remove aqueous copper, a representative heavy metal water pollutant. Activation of the RDF char using steam and KOH treatments was performed to change the specific surface area, pore volume, and the metal cation quantity of the char. N_2 sorption, Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), and Fourier transform infrared spectroscopy were used to characterize the char. The optimum pH for copper removal was shown to be 5.5, and the steam-treated char displayed the best copper removal capability. Ion exchange between copper ions and alkali/alkaline metal cations was the most important mechanism of copper removal by RDF char, followed by adsorption on functional groups existing on the char surface. The copper adsorption behavior was represented well by a pseudo-second-order kinetics model and the Langmuir isotherm. The maximum copper removal capacity was determined to be 38.17 mg/g, which is larger than those of other low-cost char adsorbents reported previously.

Key words: adsorption, activation, char, pyrolysis
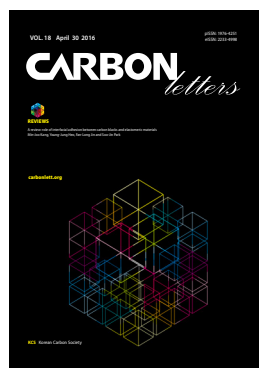
1. Introduction

Biomass has received significant attention as a renewable resource for energy and industrial feedstock. The mass cultivation of biomass, however, often has adverse effects, such as deforestation and encroachment on cropland normally reserved for food production. In this regard, the recycling of organic waste as biomass is an attractive research topic. Municipal solid waste (MSW) is a representative organic waste being produced globally at increasing rates, in concert with the rapid growth of the world's population; the global production of MSW was 1700 million tonnes in 1990, with an increase to 2300 million tonnes in 2005. In order to reduce its volume prior to transportation, MSW is often converted into a pellet-shaped solid fuel called refuse-derived fuel (RDF) [1].

RDF has several advantages: ease of handling, absence of odor, high density, resistance to decay, and a heating value 1.5–1.7 times higher than that of typical waste. RDF can be used in thermochemical conversion processes, such as combustion, pyrolysis, and gasification. Char is a by-product of pyrolysis, a process used to produce bio-oil. Having similar properties to those of activated carbon, char can be used as adsorbent media that can improve the economy of the pyrolysis process.

Water pollution due to aqueous heavy metal ions is a serious environmental problem

[2-5]. Upon being absorbed by organisms, heavy metals can accumulate and disturb the proper functioning of ecosystems. Strict regulations for the control of heavy metal emissions have promoted the development of efficient technologies for heavy metal removal [6]. Copper is a representative heavy metal emitted from an assortment of industrial activities, being utilized in mining, metal processing, and petroleum refining [7-13]. Wastewater and sludge produced from these processes contain various concentrations of copper ions, having adverse effects on the aquatic environment. Copper ions are harmful to human health even at low concentrations, and absorption of excessive copper ions can cause ailments such as Wilson disease [14].

One effective way to remove heavy metals contained in wastewater is by adsorption. The most commonly used adsorbent is activated carbon [15-21]. Among the alternative adsorbents that can replace activated carbon, biochar, a by-product of biomass pyrolysis, has recently received extensive attention because of its low cost [14,22-41].

In this study, the removal of copper using RDF-derived char was evaluated for the first time. The effects of physical activation using steam treatment and chemical activation using KOH treatment on the copper removal efficiency were examined. The effects of several process parameters (adsorbent dose, aqueous metal ion concentration, adsorption time, temperature, and pH) on the adsorption efficiency were also investigated.

2. Experimental

2.1. Preparation and characterization of RDF char samples

The RDF char (referred to as RC hereafter) used in this study was produced in a MSW treatment system located in R city, South Korea.

Physical and chemical activations were used to activate the RC [14,24]. In the physical activation, RC was treated in a fixed-bed reactor with a moisture concentration of 40 vol% and a temperature of 700°C. The temperature was increased at a rate of 5°C/min to 700°C and then maintained at this value for 1 h. The RC activated by way of this method is referred to as RDFW.

For the chemical activation, KOH was used with a mass ratio between KOH and char of 1:1. To remove moisture, the mixture of the RC and KOH solutions was dried on a hot plate for 2 h and in an oven set at 110°C for 24 h. The sample was then neutralized with a 5 M HCl solution to remove residual K^+ ions before being washed with distilled water and dried. The RC activated in this method is referred to as RDFK.

A N_2 adsorption-desorption analyzer (Tristar 3000; Micromeritics, USA) was used to determine the average pore size and surface area of the char samples. The functional groups existing on the char surface were identified using Fourier transform infrared spectroscopy (FT-IR; Thermo Nicolet 380, Thermo Nicolet Co., USA). The sample used for the analysis was prepared by mixing KBr and char at a ratio of 100:1.

The quantity of exchangeable cations (Ca, Mg, K, and Na)

contained in the char samples was measured by cation extraction using a 1.0 N CH_3COONH_4 (NH_4OAc) solution, with the pH adjusted to 7 using NH_4OH and CH_3COOH. An inductively coupled plasma (ICP) analyzer (ICPE-9000, SHIMADZU, Kyoto, Japan) was used to analyze the extracted cations.

2.2. Cu²⁺ removal experiment

The Cu^{2+} removal experiments were carried out using 200-mL Erlenmeyer flasks, which were maintained at a temperature of 20°C. In each experiment, 20 mg of char sample was added to 100 mL of aqueous Cu(II) nitrate trihydrate solution (Junsei Chemical Co., USA), with an initial concentration and pH of 10 mg/L and 5.0 ± 0.5, respectively. The flask containing this solution was stirred at a rate of 150 rpm for 48 h to assure equilibrium. After filtering the suspension, the filtrate solution was analyzed using the ICP analyzer.

The equilibrium adsorption capacity q_e (mg/g) was determined as follows:

$$q_e = (C_i - C_e) \times \frac{V}{1000w} \qquad (1)$$

where C_i and C_e are the copper concentrations (mg/L) measured at the beginning and at equilibrium, respectively, V the volume (mL) of the copper solution, and w the mass (g) of the adsorbent. In the experiments carried out to examine the effects of pH, the copper solution pH was adjusted within a range of 2.5–6.5 using HNO_3 and NaOH.

The time-dependent removal rate was interpreted using two semi-empirical adsorption kinetics models: a pseudo-first-order model [16] and a pseudo-second-order model [17]. In the pseudo-first-order adsorption kinetics model, the removal rate is assumed to be proportional to the difference between the equilibrium adsorption capacity and the amount currently adsorbed:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (2)$$

where q_t is the amount of adsorbate (mg/g) adsorbed at time t and k_1 the pseudo-first-order adsorption rate constant (min⁻¹). By integrating eq (2) and applying an initial condition of $q_t = 0$ at $t = 0$, we obtain the following:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \qquad (3)$$

The pseudo-second-order adsorption kinetics model is described by the following differential equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (4)$$

where k_2 is the pseudo-second-order adsorption rate constant (g/mg/min). By integrating eq (4) and applying an initial condition of $q_t = 0$ at $t = 0$, we obtain the following eq (5).

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (5)$$

The adsorption capacity of the RDF-derived char was evaluated using adsorption isotherms. The experimental data obtained for equilibrium states were fitted using the two most widely used

isotherms: the Langmuir and Freundlich isotherms. The Langmuir isotherm is represented by

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (6)$$

where C_e is the equilibrium concentration (mg/L), Q_0 (mg/g) represents the maximum adsorption capacity, and b (L/mg) denotes the Langmuir constant representing the degree of adsorption affinity. Q_0 and b are determined from the slope and y-intercept of the linear plot of C_e/q_e vs. C_e.

The Freundlich isotherm is expressed by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (7)$$

where K_F is a constant representing the adsorption capacity of the adsorbent (mg/g) and $1/n$ represents the adsorption strength. K_F and n are determined from the slope and y-intercept of the log q_e vs. log C_e plot. Larger values for K_F and $1/n$ indicate higher adsorption capabilities. [14]

3. Results and Discussion

3.1. Characteristics of RDF chars

Table 1 shows the properties of the RDF-derived chars used in this study. The specific surface area and pore volume of RC were 31 m²/g and 0.034 cm³/g, respectively. When it was activated physically using steam treatment (RDFW), specific surface area and pore volume increased substantially to 147 m²/g and 0.105 cm³/g, respectively. Chemical activation using KOH treatment (RDFK) increased these values even further, to 576 m²/g and 0.376 cm³/g, respectively. This increase in specific surface area and pore volume is likely due to the generation of mesopores, micropores, and macropores resulting from the treatments using steam or KOH [14,39].

Physical activation also increased the ash content, from 38.1% to 50.1%. This was attributed to the removal of amorphous carbon material contained in volatile matter and fixed carbon by steam treatment [14]. Conversely, chemical activation reduced the ash content, which was attributed to the wash-out of mineral species by the KOH solution. The order of Ca^{2+}, Mg^{2+}, Na^+, and K^+ ion content in ash, from largest to lowest values, was RDFW > RC > RDFK. Only K^+ was increased by chemical activation, owing to the residual K^+ created by the KOH treatment.
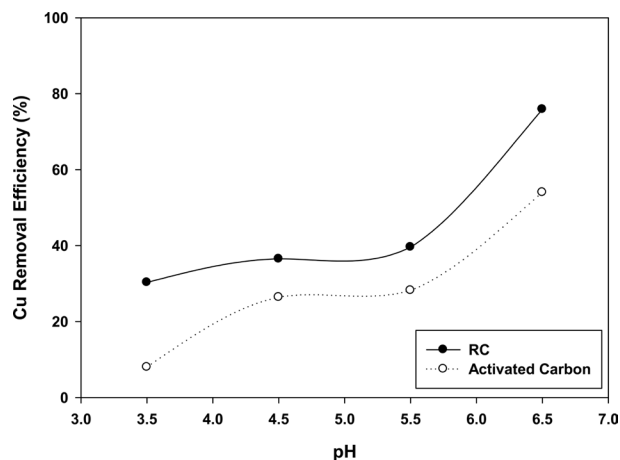

Fig. 1. Cu removal efficiency of refuse-derived fuel char and activated carbon at different pH levels.

3.2. Effect of pH on copper removal

Fig. 1 shows the copper removal efficiency, obtained using RC and activated carbon at different pH levels. The removal efficiency of RC was higher than that of activated carbon at all tested pH levels. The copper removal efficiency increased with increasing pH for both adsorbents. The increase was particularly significant when the pH was increased from 5.5 to 6.5.

In general, the effects of pH on the removal of Cu can be explained as follows: at a low pH value corresponding to high concentrations of H^+ ions, Cu ions must compete with H^+ ions for adsorption, resulting in low adsorption efficiencies. In addition, the functional groups existing on the adsorbent surface tend to have a positive charge at low pH levels, suppressing the adsorption of positive Cu ions. On the other hand, at a pH higher than 6, Cu ions form $Cu(OH)_2$ precipitates. Therefore, the main Cu removal mechanism at pH values higher than 6 is not adsorption but precipitation [14].

In this study, the high Cu removal efficiency obtained at a pH of 6.5 is also believed to be derived from precipitation. Therefore, the optimal pH for Cu adsorption by char was determined to be 5.5. Consequently, all subsequent experiments were conducted at this pH level.

| Table 1. Physical properties of RDF-derived chars									
Sample	Ash (wt%)	ICP-AES				Elemental analysis (%)			S_{BET} (m²g⁻¹)	V_{tot} (cm³g⁻¹)
		Ca	Mg	Na	K	C	H	N		
RC	38.1	62,490	6984	15,460	15,950	44.3	3.9	1.8	31	0.034
RDFW	50.1	78,570	8675	20,440	22,080	45.9	0.6	1.2	147	0.105
RDFK	33.9	13,250	2291	2278	46,920	61.9	0.8	1.8	576	0.376

RDF, refuse-derived fuel; ICP, inductively coupled plasma; AES, Atomic Emission
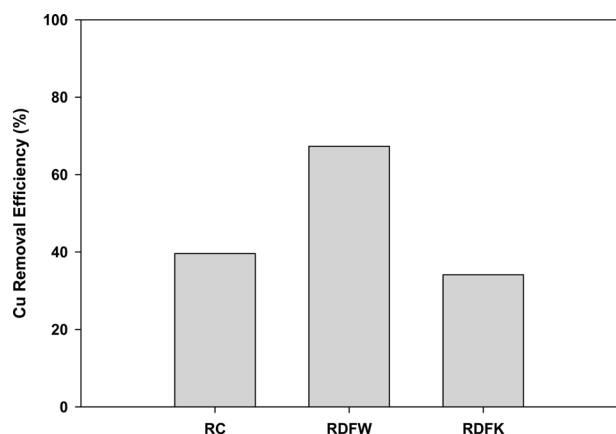
Fig. 2. Comparison of the copper removal efficiency of refuse-derived fuel-derived chars.

Table 2. Released alkali/alkaline-earth cations during the removal of copper

Char	Amount of released alkali/alkaline-earth cations (mg/L)			
	Ca^{2+}	K^+	Mg^{2+}	Na^+
Without char	0	0	0	0
RC	3.06	1.46	0.0784	3.76
RDFW	5.93	1.1	0.107	3.46
RDFK	0.455	1.35	0	2.01
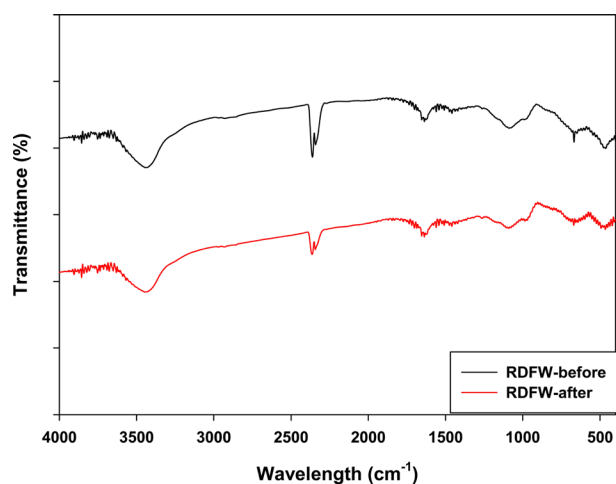
Fig. 3. FT-IR spectra of RDFW before and after Cu adsorption.

3.3. Adsorption test

Fig. 2 compares the Cu removal efficiencies obtained using different RDF-derived chars. All three chars that were tested showed higher Cu removal efficiencies than that of activated carbon, demonstrating the high potential of cheap RDF-derived char for heavy metal removal. One interesting result observed in Fig. 2 was that RDFK, with the largest specific surface area,

showed lower Cu removal efficiency than RC, while RDFW showed the highest removal efficiency. This result implies the existence of another important factor, other than specific surface area, that determines the Cu removal efficiency. The quantity of alkali and alkaline-earth ions (Table 1) is believed to be this factor.

Park et al. [14] suggested that the quantity of alkali and alkaline-earth metal ions was a more important factor than the specific surface area in determining the Cu removal efficiency of seaweed-derived chars. Machida et al. [40] reported that the adsorption of Pb^{2+} in an aqueous solution onto charcoal was negligible after an acid treatment, which removed charcoal minerals. Based on this result, they argued that the minerals in charcoal played an important role in the removal of Pb^{2+}.

To verify this hypothesis, the amounts of cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) emitted from the char to the solution during the removal of Cu ions were measured (Table 2). The largest amount of ions was emitted from RDFW, which showed the highest Cu removal efficiency. Conversely, RDFK, whose Cu removal efficiency was the lowest, emitted the smallest amount of ions. This result supports the hypothesis that the main mechanism of Cu removal by RDF char is the ion exchange between the alkali/alkaline-earth ions contained in the char and aqueous Cu ions.

To evaluate the role of the adsorption of Cu ions on the char functional groups, the change in the status of the functional groups by adsorption was determined using FT-IR. As shown in Fig. 3, the FT-IR peak intensity of RDFW decreased after copper adsorption. According to a previous study, stretching vibration bands of hydroxyl (-OH) groups appear in the wavelength range 3420–3620 cm^{-1} [41]. The peaks observed at 1200–1100 cm^{-1} and 1600 cm^{-1} can be assigned as C–O stretching vibration peaks and C=O stretching peaks, respectively [42]. An amide-derived C≡N peak is known to appear in the range of 2300–2400 cm^{-1} [14]. The decrease in the peak intensity by adsorption of Cu was the most intense for the C≡N peak, implying that the contribution of C≡N groups to Cu adsorption was the most significant. The results shown in Fig. 3 indicate that the adsorption of Cu on the char functional groups also plays an important role in the removal of aqueous copper ions.
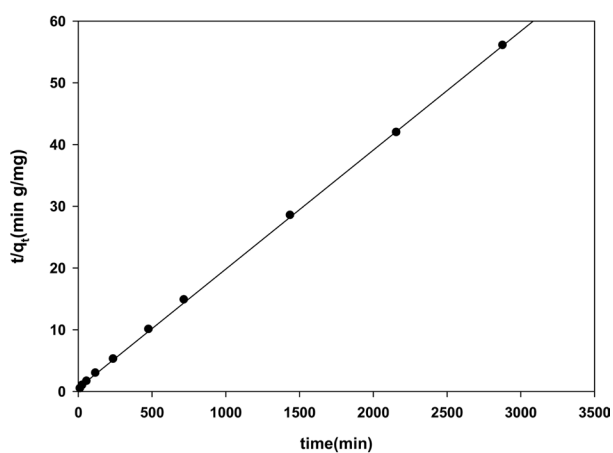
3.4. Adsorption kinetics

The kinetics of the Cu adsorption on RDFW, which showed the highest Cu removal efficiency, were analyzed using the pseudo-first-order model, eq (3), and the pseudo-second-order model, eq (5). When eq (3) was applied, $\log(q_e - q_t)$ was plotted against t and fitted linearly to obtain the rate constant k_1 and the correlation coefficient r_1^2. When eq (5) was used, on the other hand, k_2 and the correlation coefficient r_2^2 were obtained by plotting and linearly fitting $1/(q_e - q_t)$ against t.

The linear fitting results and the obtained kinetic parameter values are shown in Fig. 4 and Table 3. The pseudo-first-order model could not explain the copper removal kinetics properly; the linear fitting of $\log(q_t - q_t)$ against t was poor (Fig. 4a). On the other hand, the linear fitting using the pseudo-second-order model was excellent (Fig. 4b) and r_2^2 was much higher than r_1^2.
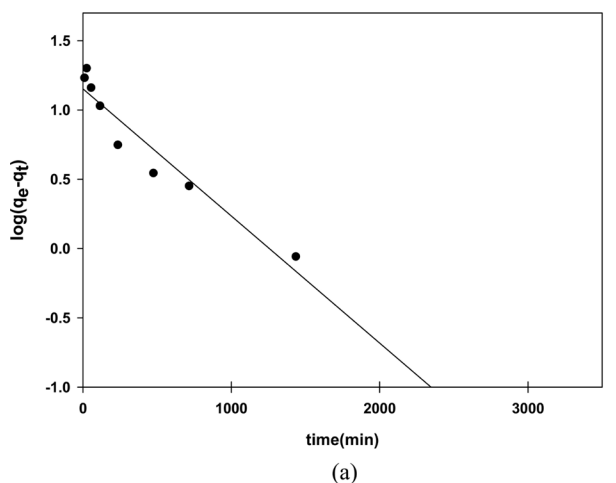
(a)

(b)

Fig. 4. Adsorption kinetic model for the removal of copper by RDFW. (a) Pseudo-first order model. (b) Pseudo-second order model.
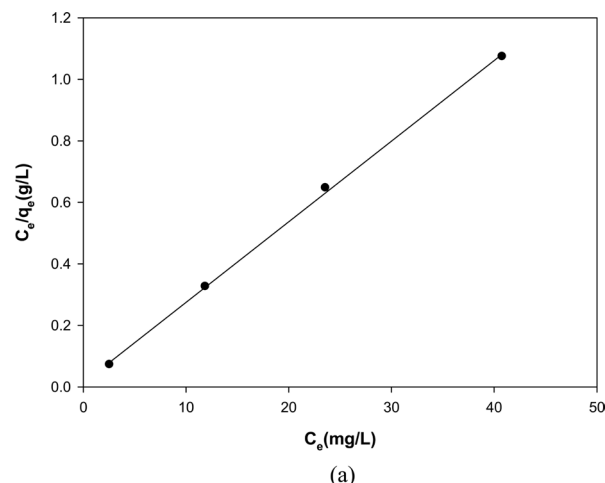

(a)

(b)

Fig. 5. Adsorption isotherms: (a) Langmuir isotherm and (b) Freundlich isotherm.

Table 3. Adsorption kinetic parameters for two different models obtained from linear regression for RDFW

Pseudo-first order		Pseudo-second order		h
r^2	k_1	r^2	k_2	
0.9224	2.11×10^{-3}	0.9998	6.85×10^{-4}	1.84

Table 4. Adsorption constants for Langmuir and Freundlich isotherm models obtained for the RDFW

Langmuir isotherm			Freundlich isotherm		
Q_0	b	R^2	K_f	1/n	R^2
38.17	2.13	0.9993	35.15	0.017	0.7013

Table 5. Maximum Cu removal capacity values of various low-cost char adsorbents

Char source[a]	Maximum Cu removal quantity (mg g⁻¹)
Hardwood	7.44
Switch grass	7.12
Corn straw	12.52
Amino-modified biochar	17.01
Composted swine manure	20.11
Sewage sludge	10.56
RDF	38.17

RDF, refuse-derived fuel.
[a]The data of other char sources except RDF were cited from Table 7 [24].
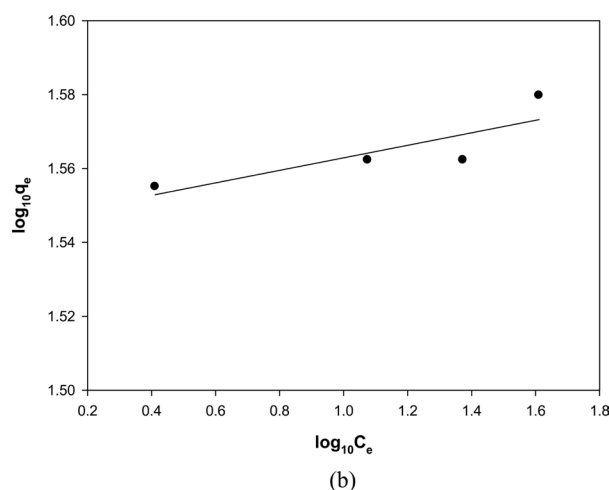
Several previous studies have also reported that metal removal using biomass-derived char could be better explained by a pseudo-do-second-order model [14,24].

3.5. Adsorption isotherms

The equilibrium adsorption characteristics of RDFW were examined using Langmuir and Freundlich isotherms (Fig. 5). Table 4 summarizes the isotherm constants obtained by linearly fitting the experimental data using the two isotherm methods. Fig. 5 clearly shows that the Langmuir isotherm could explain the adsorption behavior of Cu ions on RDFW much better than the Freundlich isotherm. This is supported by the correlation coefficient values shown in Table 4 (0.9993 for the Langmuir

isotherm vs. 0.7013 for the Freundlich isotherm). The maximum Cu removal capacity (Q_0) of RDFW was determined to be 38.17 mg/g. Compared to the maximum Cu removal capacity values of other low-cost char adsorbents found in the literature, the capability of RDFW for Cu removal is excellent (Table 5).

4. Conclusions

When RDF char was activated using steam treatment, the surface area, pore volume, and quantity of alkali and alkaline-earth metal ions increased substantially. On the other hand, activation using KOH treatment reduced the quantity of metal ions, although the surface area and pore volume increased. The steam-treated char exhibited the highest Cu removal capability among the chars tested in this study, which is attributed to the ion exchange between the Cu ions and alkali/alkaline metal ions (Ca^{2+}, Mg^{2+}, K^+ and Na^+). Adsorption of Cu ions on the char surface functional groups was another important Cu removal mechanism. The Cu removal behavior of RDF char was explained well by the Langmuir isotherm and a pseudo-second-order kinetics model. The maximum Cu removal capacity was determined to be 38.17 mg/g, which is larger than those of other low-cost char adsorbents reported previously. The results of the present study suggest that RDF char can be an effective low-cost adsorbent for removing aqueous heavy metal ions.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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