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Adsorptive behavior of acrylic acid-grafted bacterial cellulose to remove cadmium for a membrane-adsorbent hybrid process

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ABSTRACT

An adsorbent for Cd ions was prepared through the modification of bacterial cellulose (BC) with acrylic acid (AAc) using electron beam-induced grafting polymerization. The modification of BC was confirmed by FTIR/ATR and scanning electron microscope (SEM). Batch adsorption test was performed to investigate adsorptive behavior of the adsorbent in aqueous solution. Adsorption was analyzed using the Benaissa, Kurniawan, Langmuir, and Freundlich models. In the kinetic behavior, it was confirmed that it was pseudo-second-order rather than pseudo-first-order kinetic rate expression. Adsorption isotherm behavior followed the Langmuir model rather than Freundlich model, indicating that AAc-grafted BC was monolayer covered with Cd ions. The adsorption capacity (Q_m) calculated from Langmuir isotherm was 68.97 mg g^{-1}. AAc-g-BC shows potential as a useful Cd-adsorbent made of an environmentally friendly material.

Keywords: Acrylic acid; Adsorbent; Bacterial cellulose; Cd adsorption; Environmentally friendly material

1. Introduction

Conventional adsorbents, such as synthetic exchange resins, have been widely applied for removing and recovering heavy metals (e.g. Cd, Cu, Cr, Pb, etc.) in the wastewater, because of their excellent adsorptive ability. Unfortunately, due to their complex manufacturing processes, they are expensive, and in addition, they become pollutants when their adsorptive ability is lost, as conventional adsorbents are often non-renewable and non-biodegradable [1].

For these reasons, biomaterials have recently attracted interest as an abundant provider of raw material and a renewable chemical feedstock in adsorbent industry. Biomaterials such as cellulose and chitosan are renewable, biodegradable, cheap and available in large amounts [2–5]. In particular, cellulose is regarded as the most abundant and renewable biopolymer in nature. It is also one of the promising raw materials for modern industry, because it is prepared at low cost to introduce various functions [6,7]. Yet despite such advantages, industrial applications of cellulose have been limited due to its weak

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mechanical properties. In this regard, the cellulose produced by microorganisms may be more useful for the preparation of multifunctional materials and the improvement of mechanical properties [8,9].

Bacterial cellulose (BC) is known to have high tensile strength due to its high degree of crystallinity. It has been used for diverse applications (e.g. high fidelity acoustic material, high-quality paper, diet and desert food, artificial skin, cover-membrane for glucose biosensor, binder for powders, thickener for paint, etc.) [7]. It was recently used to prepare an environmentally friendly ion-exchange membrane by modifying the ion-exchangeable site [10,11]. BC modified with negatively charged functional groups is expected to have high potential as an adsorbent to remove heavy metal in wastewater because it can attract heavy metals through electrostatic attraction. In this regard, the objectives of this study were to modify BC to remove heavy metal, and to characterize the modified BC. BC was modified with cation exchangeable polymer through electron beam-induced grafting polymerization [12], and then, its adsorptive behavior was investigated for Cd.

2. Materials and methods

2.1. Chemicals and bacterial strain

Cadmium standard solution (1,000 $mg\,l^{-1}$) was purchased from Kanto Chemical Co. Inc. (Tokyo, Japan) to prepare different concentrations of Cd solutions used for adsorption study. Both aqueous solutions and Cd solutions were prepared using deionized distilled water. Other chemicals used were analytical grade.

A BC-producing strain *Acetobacter* sp strain JH232 was originally isolated from vinegar produced from fermented persimmon juice [13]. The strain was used to produce the BC used in this study.

2.2. BC production

For BC production, strain JH232 was cultured in fed-batch mode as described previously [10,13]. BC pellicles were harvested at the end of fed-batch fermentation and rinsed with distilled water. The BC was then washed with 0.1 M NaOH and neutralized by rinsing with distilled water. Neutralized BC was dried using a gel dryer at 80˚C (Model 583, Bio-Rad; Richmond, CA) [11]. The dried BC was used for adsorbent preparation.

2.3. Preparation of acrylic acid-grafted BC (AAc-g-BC) adsorbent

The acrylic acid (AAc; Kanto Chemical Co., Inc.) was purified with an inhibitor-removal column to remove the inhibitors and then 30 wt.% of AAc aqueous solution was prepared. It was used as a functional monomer to adsorb heavy metal to BC. The energy source to modify AAc onto the BC was electron beams that was generated from a high-voltage accelerator (ELV-0.5, BINP) with maximum power of 25 kW and beam current of 40 mA, respectively. At that time, the energy of electron beam was the 0.7 MeV and the electron beam current was applied at 10 mA (100 kGy). Irradiated dose was controlled by varying both conveyor speed and beam current. BC for irradiation was mounted on an aluminum plate and was transported by the conveyor at a speed of 2 $m\,min^{-1}$. CTA film with 15% triphenylphosphate as additive and UV spectrophotometer (UV-1,201, Shimadzu Co., Ltd.) were used for dose measurement according to ISO/ASTM 51,650. To modify AAc onto BC, the 100 kGy EB-irradiated BC was immersed to 30 wt.% of AAc aqueous solution for a half day at 25˚C, after which it dried after cleaning several times in distilled water and then immersed in 0.1 M NaOH to transform H^+ form to Na^+ form. After it was fully dried and cleaned, it was used in the adsorptive experiment.

2.4. Batch adsorption study

Batch test was performed to monitor the removal of Cd ions by the BC adsorbent and obtain the equilibrium data. Four different concentrations (20, 50, 100, and 200 $mg\,l^{-1}$) of Cd solutions were employed in the test. The solutions were prepared by diluting Cd standard solution (1,000 $mg\,l^{-1}$) with deionized distilled water. The solutions were adjusted to pH 6 with 1 M NaOH.

Fixed volume (40 ml) of each Cd-solution was transferred into a glass bottle containing the adsorbent (0.07 g of BC). BC was cut into small pieces (approximately 1.5 × 1.5 mm) before being used for the batch test. The bottle was sealed with butyl rubber stoppers and aluminum crimps and then agitated for 10 h on a mechanical shaker (100 rpm) at 25˚C. The batch experiment was performed in triplicate. Control for the batch experiment was also performed, without adding adsorbents. The solution in the bottle was sampled with a syringe at various times and then was centrifuged at 10,000 rpm for 5 min. The supernatant was filtered (pore size, 0.45 μm) and the filtrate was analyzed for Cd ion concentration using ICP-OES

Spectrometer (Model, Activa S; HORIBA Scientific, Kyoto, Japan). The amount of Cd adsorbed, q (mg g^{-1}) was calculated according to Eq. (1):

$$q = (C_0 - C_f)V/M \tag{1}$$

where C_0 and C_f are initial and final Cd concentrations (mg l^{-1}), respectively, V is the volume (l) of Cd solution used and M is the mass (g) of the adsorbent.

3. Results and discussion

3.1. Confirmation of AAc-g-BC

AAc-grafted BC was analyzed through FTIR spectroscopy to examine chemical change of the BC structure.

Fig. 1 shows the infrared spectra of un-grafted BC and grafted BC. The spectrum of AAc-g-BC showed that the adsorption band assigned to the carboxyl group (-C=O) was observed at around 1,740 cm^{-1}, indicating that acrylate residues were bound to the BC. In addition, the morphological difference of BC and AAc-g-BC was evaluated using scanning electron microscope (SEM).

Fig. 2 shows SEM images of pristine BC and AAc-g-BC. While there were many pores in pristine BC, there were few pores in AAc-g-BC, indicating that AAc polymer was attached to the BC surface. Two results supported the premise that AAc was successfully grafted to BC.

3.2. Effects of contact time and initial Cd concentration

The adsorption behavior of adsorbent as a function of time at various initial-concentrations of Cd was shown in Fig. 3.

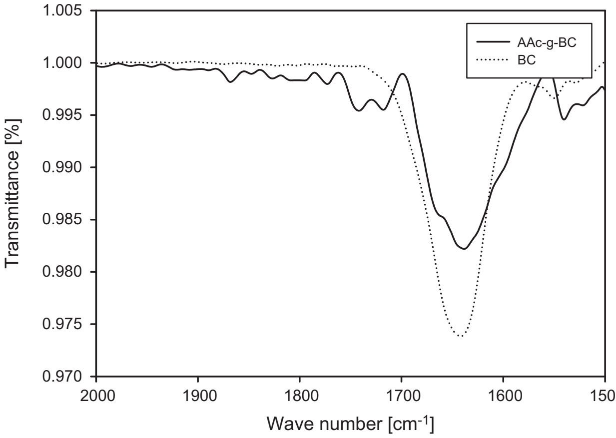

Fig. 1. FTIR/ATR spectra of BC and AAc-g-BC.

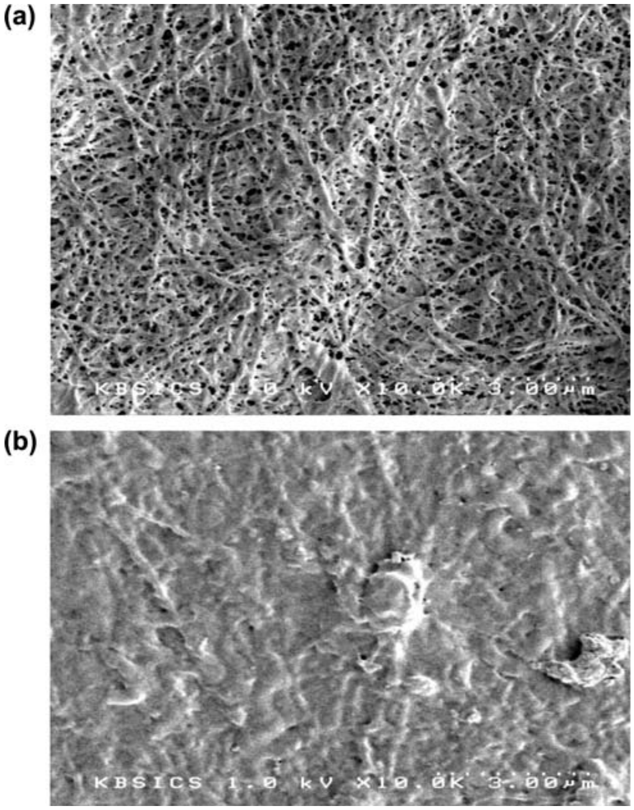

Fig. 2. SEM photographs of BC (a) and AAc-g-BC (b).

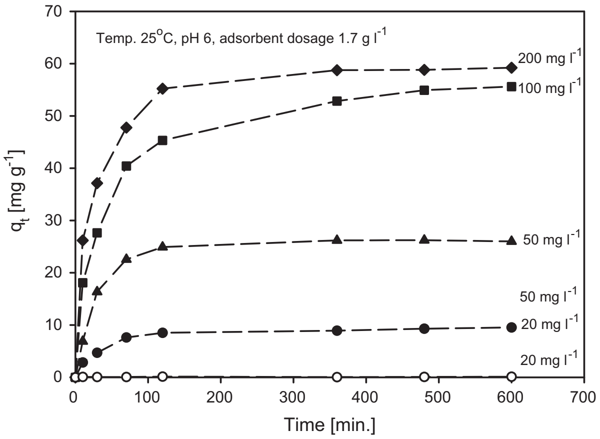

Fig. 3. Cd uptake of adsorbent as a function of time at various initial concentrations of Cd. Open symbols indicate pristine BC, while solid symbols indicate AAc-g-BC.

In the test, AAc-g-BC adsorbed Cd ions, while pristine BC did not, indicating that AAc-g-BC was a more excellent adsorbent than pristine BC in terms of Cd adsorption. This can be explained as follows: the grafted carboxylate ion (–COO^{-}) acted strongly as Cd uptake site in AAc-g-BC, while hydroxyl (OH) group acted weakly for Cd uptake in pristine BC. As shown in Fig. 3, the adsorption of Cd increased rapidly until about 80 min and reached a plateau at about 120 min. The rapid uptake shown for the first 80 min. implied that the availability of many adsorption sites on the adsorbent surface led to much adsorption of Cd. As the metal ions get attached to the sites with contact time, the amount of adsorbed metal ions gradually reaches a maximum, establishing equilibrium. This result of rapid and following gradual uptake was also described in a previous study [14]. As shown in Fig. 3, that is, the adsorption of Cd increased from 5 to 38 $\mathrm{mg\,g^{-1}}$ as initial concentration of Cd increased from 20 to 200 $\mathrm{mg\,l^{-1}}$, implying that the driving force depending on the concentration gradient increases with an increasing initial concentration of Cd [15].

3.3. Adsorption kinetic studies

Adsorption kinetics refers to the relationships between the uptake rate of solute and adsorption time. Applying the data of Fig. 3 to the first-order rate Eq. (2) and the pseudo-second-order rate Eq. (3), adsorption kinetics of Cd for AAc-g-BC adsorbent can be described according to Benaissa model [16] and Kurniawan model [17]. Each equation is described as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{2}$$

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \tag{3}$$

where q_e and q_t are the amounts of metal ion adsorbed (mg $\mathrm{g^{-1}}$) at equilibrium and time t, respectively. K_1 ($\mathrm{min^{-1}}$) is the Lagergren rate constant of adsorption, K_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$) is the pseudo-second-order rate constant of adsorption. Kinetic parameters of these models for different concentrations were calculated from the slope and intercepts of the linear plots of $\ln(q_e - q_t)$ vs. t in Fig. 4 and t/q_t vs. t in Fig. 5.

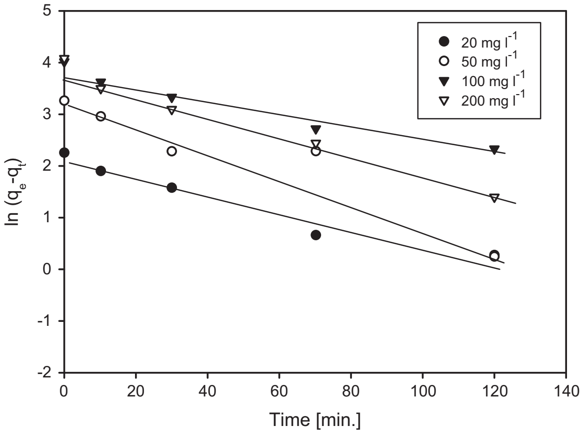

Fig. 4. Pseudo-first-order plots of Cd adsorption of AAc-g-BC adsorbent.

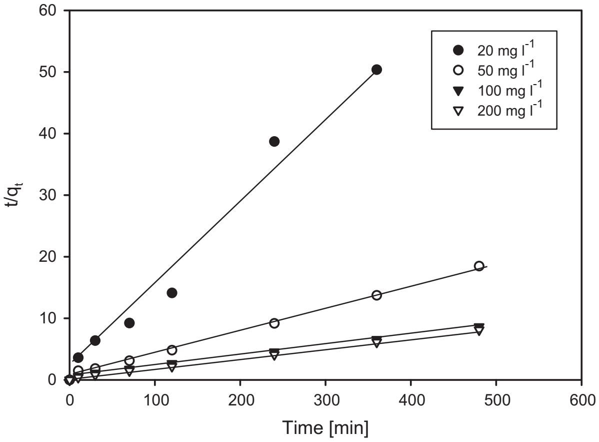

Fig. 5. Pseudo-second-order plots of Cd adsorption of AAc-g-BC adsorbent.

Their results are summarized in Table 1. The constant K_2 is used in Eq. (4) to calculate the initial sorption rate h_0 ($\mathrm{mg\,g^{-1}\,min^{-1}}$), at $t \to 0$ as follows:

$$h_0 = K_2 q_e^2 \tag{4}$$

Table 1
Kinetic parameters for the Cd adsorption of AAc-g-BC adsorbent

Conc.	q_e (exp.)	Pseudo-first-order			Pseudo-second-order		
(mg $\mathrm{l^{-1}}$)	(mg $\mathrm{g^{-1}}$)	K_1 ($\mathrm{min^{-1}}$)	q_e (cal.)	R^2	K_2 ($\mathrm{g\ mg^{-1}\,min^{-1}}$)	q_e (cal.)	R^2
20	9.52	1.66×10^{-2}	8.17	0.9541	3.10×10^{-2}	7.04	0.9835
50	26.18	2.26×10^{-2}	25.72	0.8992	3.54×10^{-2}	27.02	0.9975
100	54.82	1.35×10^{-2}	45.65	0.9518	1.72×10^{-2}	58.10	0.9964
200	58.85	2.00×10^{-2}	47.01	0.9780	1.37×10^{-3}	60.60	0.9988

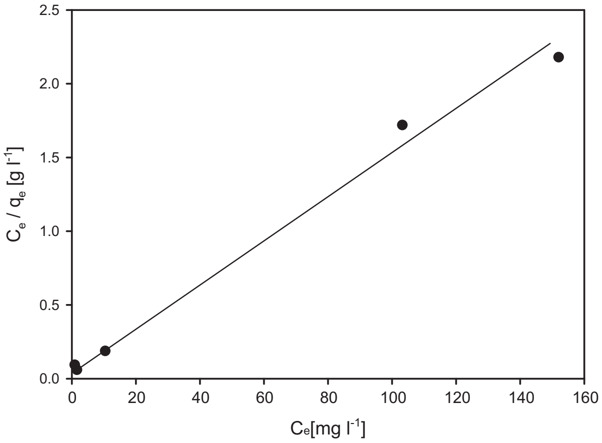

Fig. 6. Langmuir isotherm for the Cd adsorption of AAc-g-BC adsorbent.

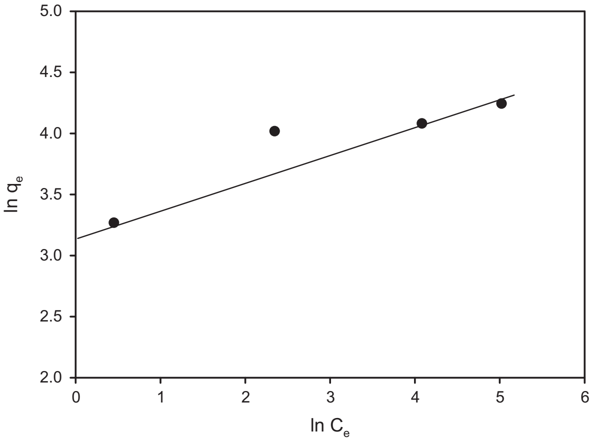

Fig. 7. Freundlich isotherm for the Cd adsorption of AAc-g-BC adsorbent.

The obtained R^2 (value of correlation coefficient) for the pseudo-second-order kinetic model was above 0.983 at different concentrations, and thus, the pseudo-second-order kinetic model provided the best correlation coefficients with the experimental data for the adsorption of Cd ion. The calculated q_e values from the pseudo-second-order kinetic model were much closer to the experimental values of q_e than that of pseudo-first-order model, suggesting that the experimental data for Cd adsorption agrees better with the pseudo-second-order kinetic model.

3.4. Adsorption isotherms

By applying adsorption isotherm models such as Langmuir [18,19] and Freundlich [20], the distribution of metal ions between liquid and solid phases can be generally described. The Langmuir and Freundlich sorption models were applied in the study to analyze and fit experimental data, when the solute uptake was caused by monolayer and multilayer sorption on an adsorbent. The Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent [19], while the Freundlich isotherm is based on multilayer adsorption and is applicable to highly heterogeneous surfaces. The two models can be expressed by the following equations:

$$\text{Langmuir isotherm}\, C_e/q_e = 1/Q_m b + C_e/Q_m \tag{5}$$

$$\text{Freundlich isotherm}\, \ln q_e = \ln K_F + (1/n) \ln C_e \tag{6}$$

where q_e (mg g^{-1}) is the adsorption amount of adsorbent at equilibrium, C_e (mg l^{-1}) is the equilibrium concentration of adsorbate, and Q_m (mg g^{-1}) and b (l mg^{-1}) are the Langmuir constants related to the maximum sorption capacity of metal ions and energy of adsorption. K_F and n are adsorption capacity and adsorption intensity constants, respectively.

Table 2
Isotherm constants for the Cd adsorption of AAc-g-BC adsorbent

Langmuir isotherm			Freundlich isotherm		
Q_m (mg g $^{-1}$)	b (l mg^{-1})	R^2	K_F (mg g^{-1})	n	R^2
68.97	0.21	0.9916	27.41	5.02	0.8559

The parameters of Langmuir and Freundlich isotherm were calculated from slop of linear plots of C_e/q_e vs. C_e in Fig. 6 and ln q_e vs. ln C_e in Fig. 7, respectively.

The calculated values are summarized in Table 2. As described in Table 2, the value of correlation coefficient R^2 in Langmuir is 0.992, while in Freundlich, it is 0.856. The result of R^2 shows that the Langmuir model is better fitted than the Freundlich isotherm. Meanwhile, the adsorption capacity (Q_m) calculated from Langmuir isotherm is 68.97 mg g^{-1} and K_F is 27.41 mg g^{-1}. This result also shows that Langmuir adsorption isotherm model is much closer to the experimental values (q_e) than the Freundlich adsorption isotherm model. It was implied that the AAc-g-BC was monolayer covered with Cd ions.

4. Conclusions

BC was modified with AAc by irradiating electron beam to remove Cd metal in aqueous solution. The

AAc-g-BC as adsorbent for the removal of Cd showed the following behavior:

(1) In the kinetic behavior, it was confirmed that it was pseudo-second-order rather than pseudo-first-order kinetic rate expression.
(2) In adsorption isotherm behavior, it was followed by the expression of the Langmuir model rather than that of the Freundlich model, indicating that AAc-grafted BC was monolayer covered with Cd ions.
(3) The adsorption capacity (Q_m) calculated from Langmuir isotherm was 68.97 $\mathrm{mg\,g^{-1}}$.
(4) AAc-g-BC shows potential as a useful Cd-adsorbent made of an environmentally-friendly material.

Symbols

q — the amount of Cd adsorbed, $\mathrm{mg\,g^{-1}}$
C_0 — initial Cd concentration, $\mathrm{mg\,l^{-1}}$
C_f — final Cd concentration, $\mathrm{mg\,l^{-1}}$
V — volume of Cd solution used, l
M — mass of the adsorbent, g
q_e — amounts of metal ion adsorbed at equilibrium, $\mathrm{mg\,g^{-1}}$
q_t — amounts of metal ion adsorbed at time t, $\mathrm{mg\,g^{-1}}$
K_1 — Lagergren rate constant of adsorption, $\mathrm{min^{-1}}$
K_2 — pseudo-second-order rate constant of adsorption, $\mathrm{g\,mg^{-1}\,min^{-1}}$
h_0 — initial sorption rate at $t \to 0$, $\mathrm{mg\,g^{-1}\,min^{-1}}$
C_e — equilibrium concentration of adsorbate, $\mathrm{mg\,l^{-1}}$
Q_m — Langmuir constants related to the maximum sorption capacity, $\mathrm{mg\,g^{-1}}$
b — energy of adsorption, $\mathrm{l\,mg^{-1}}$
K_F — Freundlich constants related to the maximum sorption capacity, $\mathrm{mg\,g^{-1}}$
n — adsorption intensity constants
R^2 — value of correlation coefficient

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