

Removal of Chromium from Aqueous Solution Using Yukitsubaki Carbon

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Abstract: Adsorption of chromium (Cr) from aqueous solution onto Yukitsubaki carbon has been investigated in a batch system. The effect of pH, contact time and carbon dosage on the adsorption of Cr by Yukitsubaki carbon have been evaluated with ICP-AES (inductively coupled plasma atomic emission spectrometer) in order to obtain the optimum conditions for the Cr adsorption process. Adsorption isotherms of Cr onto the carbon were measured at varying initial concentrations under optimized condition. The surface properties of the carbon were characterized using N₂-BET, SEM (scanning electron microscope) and FT-IR (Fourier transform infrared spectroscopy). Consequently, the following matters have been mainly clarified. (1) Yukitsubaki carbon can be an efficient sorbent for Cr, particularly for cation species Cr(III); (2) The effect of common ions on the adsorption of Cr was not significant, although the adsorption of Cr(VI) was inhibited under high concentrations of common ions; (3) Adsorption isotherms using the Yukitsubaki carbon can be generally described by Langmuir isotherm more satisfactorily for Cr. The adsorption may have occurred mainly by monolayer reaction; (4) The rates of adsorption were found to conform to pseudo-second order kinetics.

Key words: Yukitsubaki carbon, chromium, adsorption isotherms, kinetics.

1. Introduction

Water pollution due to heavy metal has become one of the largest problems in recent years [1, 2]. In particular, releasing wastewater containing heavy metal poses a threat to both human health and environment [3, 4]. The water that we drink may contain industrial wastewater with chromium [5].

Cr mainly consists of two stable oxidation states such as trivalent state Cr(III) and hexavalent state Cr(VI) in natural aqueous environment [6]. Cr(VI) may be present in the form of CrO_4^{2-} or HCrO_4^- , whereas Cr(III) tends to form $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2^+$, or Cr(III) organic complexes. It is well known that Cr(III) is essential materials for living organisms, whereas Cr(VI) is more toxic, carcinogenic, and mutagenic [7-10].

Therefore the separation and reduction of chromium in waste water is very important for environmental

protection and human health [11]. Various treatment technologies such as ion exchange, precipitation, ultrafiltration, reverse osmosis and electro dialysis have been used for the removal of heavy metal ions from aqueous solution [12]. However, these processes have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost, and difficult further treatment due to generation of toxic sludge [13].

In recent years, biological materials as adsorbent for water purification have become a hot research topic [14, 15]. Biological adsorbent has the advantages of recyclable, low cost, easy operation and little possibility of secondary pollution [16, 17].

From above-mentioned, sorption experiment of Cr using chitosan was performed in previous paper [18]. In this paper, the adsorption experiments for Cr using “Yukitsubaki” carbon (special product for Aga Town in Niigata Prefecture) have been presented as part of the adsorption study of metals using relatively low cost biomass.

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The aim of this paper is to investigate the adsorption efficiency of Yukitsubaki carbon for more practical use in the future.

Adsorption isotherms of Cr (Cr(VI) and Cr(III)) were studied and analyzed using Langmuir and Freundlich equations, and kinetics analyses were also carried out. In addition, to evaluate the characteristics of the sample used in this work, the surface morphology of the carbon was determined by SEM (scanning electron microscope) and FT-IR (Fourier transform infrared spectroscopy).

2. Experimental Sections

2.1 Materials and Reagents

Yukitsubaki carbon was made from the trunk of *Camellia japonica* L. which grows in the northeast of Japan, a particularly special product of Aga Town in Niigata Prefecture.

Yukitsubaki carbon was pestled and sieved with 60 mesh. For the removal of ash in the carbon, deashing was carried out with boiled ultrapure water, then, it was dried at 110 °C in an oven. In addition to the pristine carbon, the carbon was oxidized in 10% HNO₃ and 30% HNO₃ at 90 °C for 4 h, respectively, and washed with ultrapure water in order to completely remove residue. Subsequently the sample was heated at 300 °C for 2 h to remove the residual nitrate ions on Yukitsubaki carbon.

Cr(III) standard solutions were prepared by diluting a standard solution (1,000 mg·dm⁻³ Cr(NO₃)₃ solution), and Cr(VI) standard solutions were prepared by diluting a standard solution (1,000 mg·dm⁻³ K₂Cr₂O₇ solution), which was both purchased from Kanto Chemical Co. Inc. All other chemical reagents were also purchased from Kanto Chemical Co., Inc. All reagents used were of analytical grade, and water (> 18.2 MΩ in electrical resistance) which was treated by an ultrapure water system (Advantec aquarius: RFU 424TA, Advantec Toyo, Japan) was employed throughout the work.

2.2 Experiment of Apparatus

The morphology of Yukitsubaki carbon was characterized by a SEM (JSM-5800, JEOL, Ltd.). The material was placed on a microgrid of silicon, and transferred to the analysis chamber in the SEM equipment.

The carbon was also investigated using FTIR spectroscopy (FTIR-4200, Jasco, Corporation) to identify the functional groups. For FTIR in pressed KBr pellets, the sample was washed three times with ethanol for 5 min, filtered, and dried at 110 °C for 24 h. The spectral resolution was set to 1 cm⁻¹, and 150 scans were collected for each spectrum.

The specific surface areas and pore volumes of Yukitsubaki carbon were measured by N₂ adsorption/desorption using a surface area and pore size analyzer (TriStar II 3020, Micromeritics, Instrument Corporation) after vacuum degassing of the sample in the tube at 200 °C for 12 h.

An ICP-MS (inductively coupled plasma mass spectrometry) instrument (ThermoFisher Scientific X2) was used to determine the concentration of Cr.

2.3 Sorption Experiment of Cr Using Yukitsubaki Carbon

The adsorption capacities of Cr from aqueous solution of the Yukitsubaki carbon were investigated by a batch method. Yukitsubaki carbon was thoroughly mixed with 50 cm³ of containing known amount of Cr (Cr(III) or Cr(VI)) in a 200 cm³ conical flask, and the suspensions were shaken by an automatic shaker (PLUS SHAKER EP-1, TAITEC, Corporation) in a water bath at room temperature (25 ± 2 °C). Sorption experiments were conducted by varying the pH (1-6 or 1-7), contact time (12 min to 8 h or 12 h), sorbent dosage (0.1-3.0 g·dm⁻³). The pH of each solution was adjusted by using 0.1 mol·dm⁻³ NaOH and 0.1 mol·dm⁻³ HNO₃.

Adsorption isotherms of Cr (Cr(III) and Cr(VI)) onto Yukitsubaki carbon were measured at varying initial Cr concentrations (10-200 ppb) under

optimized conditions.

Following each sorption experiment, the suspension containing Yukitsubaki carbon and the above standard solution was filtered through a 0.45 μm membrane filter (Advantec Mixed Cellulose Ester, 47 mm) to remove Cr(III) or Cr(VI) that have been adsorbed into the Yukitsubaki carbon. Then the concentration of this metal in the filtrate was determined with an ICP-MS.

The metal uptake by the carbon was calculated using the following Eq. (1) [19]:

$$q = \frac{(C_0 - C_e)}{W} \cdot V \quad (1)$$

where, q is the adsorption capacities of Cr using Yukitsubaki carbon at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), C_0 and C_e are the initial and equilibrium concentrations of Cr(III) and Cr(VI) in a batch system respectively ($\text{mg}\cdot\text{dm}^{-3}$), V is the volume of the solution (dm^3), and W is the dry weight of each adsorbent (g).

2.4 Langmuir and Freundlich Isotherm Model

Adsorption isotherms of sorption data were studied at varying initial concentration from 10 to 200 ppb under optimized condition of pH, contact time and the dosage of Yukitsubaki carbon.

Two common adsorption models, Langmuir and Freundlich isotherm model were applied to evaluate the adsorption data [20].

Langmuir model assumes monolayer sorption onto a surface and is given by Eq. (2):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad (2)$$

where, C_e is the concentration of Cr(III) or Cr(VI) in a batch system at equilibrium ($\text{mg}\cdot\text{dm}^{-3}$), q_e is the amount of adsorption of Cr(III) or Cr(VI) at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), q_{\max} is the maximum adsorption capacity on the surface of Yukitsubaki carbon ($\text{mg}\cdot\text{g}^{-1}$), and K_L is the equilibrium adsorption constant ($\text{dm}^3\cdot\text{mg}^{-1}$). A plot of C_e/q_e versus C_e gives a straight line with slope of $1/q_{\max}$, and intercept is $1/(K_L q_{\max})$. K_L can be related to the adsorption free energy ΔG_{ads}

($\text{J}\cdot\text{mol}^{-1}$) by the following Eq. (3) [21]:

$$\Delta G_{\text{ads}} = -RT \ln K_L \quad (3)$$

where, R is the gas constant ($8.314 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature at equilibrium (K), and K_L is the equilibrium constant at temperature T .

The equilibrium constant K_L can be calculated from Eq. (4):

$$K_L = q_e/C_e \quad (4)$$

where, C_e and q_e are same as mentioned above in Eq. (2).

On the other hand, the linearized Freundlich model isotherm is represented by the following Eq. (5):

$$\log_{10} q_e = \log_{10} K_F + (1/n) \log_{10} C_e \quad (5)$$

where, K_F and $1/n$ indicate the adsorption capacity and the adsorption intensity of the system, respectively. The plots of q_e versus C_e in log scale can be plotted to determine values of $1/n$ and K_F depicting the constants of Freundlich model.

2.5 Kinetic Studies

Kinetic models have been proposed to determine the mechanism of the adsorption process, which provide useful data to improve the efficiency of the adsorption and feasibility of process scale-up [22]. In the present investigation, the mechanism of the adsorption process was studied by fitting pseudo first-order and second-order reactions to the experimental data.

The pseudo first-order model is given by the following Eq. (6):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (6)$$

where, q_e and q_t are the adsorption capacities of Cr(III) or Cr(VI) using chitosan at equilibrium and time t , respectively ($\text{mol}\cdot\text{g}^{-1}$), and k_1 is the rate constant of the pseudo-first-order adsorption (h^{-1}).

The linear form of the pseudo second-order rate equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{t}{q_e} \quad (7)$$

where, q_e and q_t are the adsorption capacities of Cr(III) or Cr(VI) using chitosan at equilibrium and time t , respectively ($\text{mol}\cdot\text{g}^{-1}$), and k is the rate constant of the pseudo-second-order adsorption ($\text{g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$).

3. Results and Discussion

3.1 Characteristics of Pristine Carbon and Modified Yukitsubaki Carbon

The morphologies of pristine Yukitsubaki carbon and modified carbon characterized by SEM are shown in Fig. 1. Moreover, the surface properties including specific surface areas of pristine and modified Yukitsubaki carbon determined by N_2 -BET method are shown in Table 1. The pore structures of all the samples are similar to each other. However, judging from the SEM images in Fig. 1, the surface area of modified Yukitsubaki carbon (HNO_3 30%) (Fig. 1c) seems to be slightly changed with the acid treatment, whereas that of modified Yukitsubaki carbon (HNO_3 10%) (Fig. 1b) seems to be hardly varied. This is consistent with the data of the specific surface area in Table 1. The decrease in the specific surface area of modified Yukitsubaki carbon (HNO_3 30%) would be attributable to the excessive oxidation with a high concentration of nitric acid.

The FTIR spectra of pristine and modified Yukitsubaki carbon are shown in Fig. 2. From it, a characteristic broad band, which may be due to graphite structure in carbon, is observed at around $1,610\text{ cm}^{-1}$. The peak at $3,300\text{ cm}^{-1}$ is related to hydroxyl groups ($-\text{OH}$), and $1,120\text{ cm}^{-1}$ is related to carbonyl groups ($-\text{C}=\text{O}$), and then the peaks at $2,920$ and $2,850\text{ cm}^{-1}$ are associated with C-H. The results of FTIR analysis show that some kinds of functional groups (such as carbonyl groups and hydroxyl groups) are introduced to pristine carbon surfaces successfully by oxidation.

Then, the first estimation concerning the adsorption of Cr (Cr(III) or Cr(VI)) on pristine Yukitsubaki carbon has been carried out at the present work.

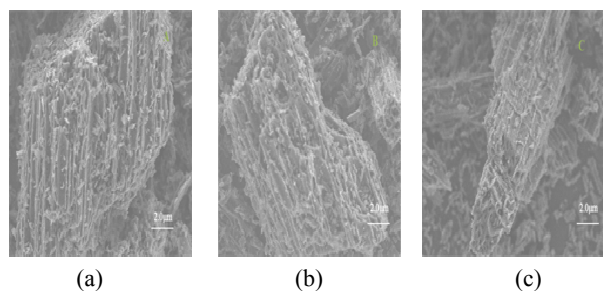


Fig. 1 The SEM images of pristine and modified Yukitsubaki carbon: (a) pristine; (b) HNO_3 10%; (c) HNO_3 30%.

Table 1 Surface properties of pristine carbon and modified Yukitsubaki carbon.

Samples	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Pristine Yukitsubaki carbon	157	0.0854	2.18
Modified carbon (HNO_3 10%)	158	0.0852	2.16
Modified carbon (HNO_3 30%)	144	0.0774	2.15

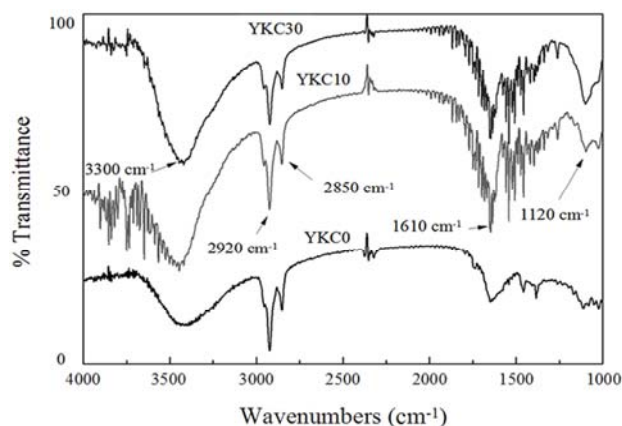


Fig. 2 The FTIR spectra of pristine and modified Yukitsubaki carbon.

In future work, the adsorption of Cr (Cr(III) or Cr(VI)) on modified Yukitsubaki carbon will be examined.

3.2 Effect of pH

Solution pH is one of the most important parameters affecting adsorption characteristics. In case of Cr, the dominant chemical species alter as pH varies [23]. In order to investigate the effects of solution pH on the uptake of Cr(III) or Cr(VI), sorption experiments were conducted at different pH values at room temperature $25\text{ }^\circ\text{C}$, while the

concentration of Cr(III) or Cr(VI) was kept constant at 100 ppb, and Yukitsubaki carbon dosage was 1.0 g·dm⁻³. The contact time was 4 h.

The results for Cr(III) are shown in Fig. 3a. The removal rate of Cr(III) is no more than 30% at pH ≤ 3, and the removal rate of Cr(III) is more than 99% at 4 ≤ pH ≤ 6. The decrease of the adsorption capacities at low pH may be attributable to the competition of protons with metal ions for active binding. Therefore, pH of 5 was taken for further experimental work.

The results for Cr(VI) are shown in Fig. 3b. The removal rate is relatively low (about 37%) at pH 1, however, the removal rate is 78% and 90% at pH 2 and 3 respectively. The removal of Cr(VI) was no more than 11% at 4 ≤ pH ≤ 7. Thus pH 3 was selected as the optimal pH for further work.

Species distribution of Cr at different pH based on theoretical calculation [24] is shown in Fig. 4. From Fig. 4a, Cr(III) exists predominantly as Cr³⁺ at pH 1-3, whereas exists predominantly as CrOH²⁺ at pH 4-6.

Furthermore, from the results of FTIR spectra in Fig. 2, hydroxyl groups (-OH) are included in Yukitsubaki carbon. Then, it can be considered that the Cr(III) adsorption occurred dominantly by the cation exchange reaction between H⁺ of hydroxyl groups on the carbon and the cationic species of Cr(III).

On the other hand, Cr(VI) exists as hydrogen chromate anions (HCrO₄⁻) between pH 2 and 6.5, and it exists as chromate ions (CrO₄²⁻) at pH above 6.5 (Fig. 4b). It is considered that this anion species has a tendency to bind to the protonated active sites of the Yukitsubaki carbon at optimum pH.

3.3 Effect of Contact Time

The effect of contact time on the adsorption capacity of Cr(III) using 1.0 g·dm⁻³ Yukitsubaki carbon (100 μg·dm⁻³ of Cr solution) is investigated at pH 5 at room temperature 25 °C. On the other hand, the effect of contact time on the adsorption capacity of

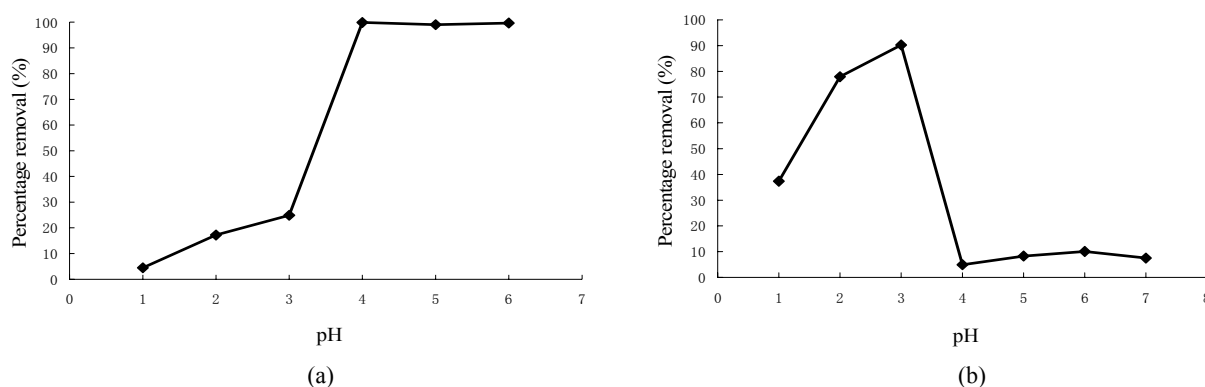


Fig. 3 Effect of pH on percent removal of Cr using Yukitubaki: (a) Cr(III); (b) Cr(VI).

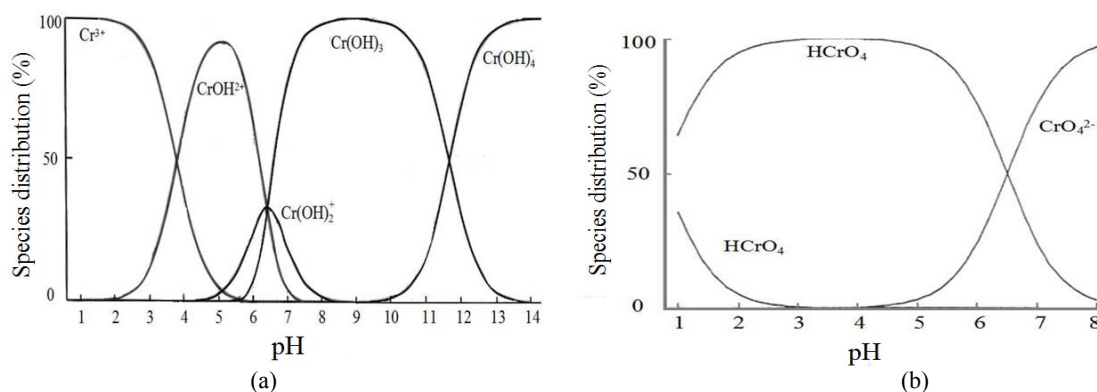


Fig. 4 Species distribution curves of Cr in environmental water: (a) Cr(III); (b) Cr(VI).

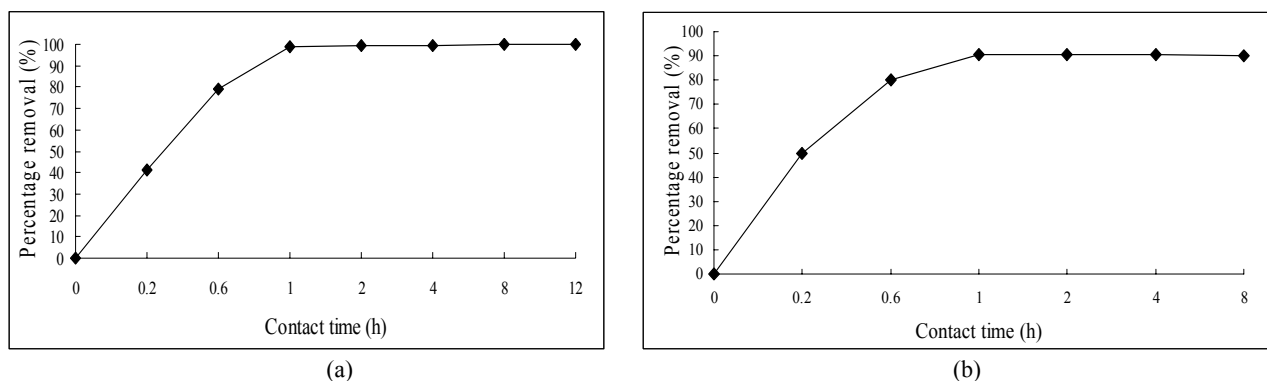


Fig. 5 Effect of contact time on percent removal of Cr using Yukitubaki: (a) Cr(III); (b) Cr(VI).

Cr(VI) using $1.0 \text{ g}\cdot\text{dm}^{-3}$ Yukitsubaki carbon ($100 \mu\text{g}\cdot\text{dm}^{-3}$ of solution) is investigated at pH 3.

The adsorption capacity of Yukitsubaki carbon for Cr(III) reached adsorption equilibrium at 1h, and after that there is no appreciable change (Fig. 5a). In case of Cr(VI) removal, more than 90% adsorption was observed within first 1 h, and after that there is no appreciable increase (Fig. 5b). Hence, the optimized contact time was chosen 2 h for Cr(III) and 1 h for Cr(VI), respectively for the rest of the experimental work.

3.4 Effect of Yukitsubaki Carbon Dosage

Under optimized condition of pH and contact time, sorption behavior of Yukitsubaki carbon at different dosages from 0.1 to $3.0 \text{ g}\cdot\text{dm}^{-3}$ have been studied in 100 ppb ($\mu\text{g}\cdot\text{dm}^{-3}$) of Cr solution. The removal of Cr(III) more than 98% was observed for $1.0 \text{ g}\cdot\text{dm}^{-3}$ dosage (Fig. 6a). The removal of Cr(VI) more than 93% was observed for $0.5 \text{ g}\cdot\text{dm}^{-3}$ dosage (Fig. 6b), but no remarkable increase is observed at a dosage more than $0.5 \text{ g}\cdot\text{dm}^{-3}$. Therefore, $1.0 \text{ g}\cdot\text{dm}^{-3}$ was considered as optimum dosage for Cr(III), and $0.5 \text{ g}\cdot\text{dm}^{-3}$ was considered for Cr(VI), respectively for the rest of the study.

3.5 Adsorption Isotherms

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes. The adsorption data obtained for Cr (Cr(III) and Cr(VI)) using Yukitsubaki carbon were analyzed by

Langmuir and Freundlich equations. The correlation coefficient (R^2) of these isotherms for Cr(III) and Cr(VI) on the carbon is shown in Table 2 along with other relevant parameters.

From Table 2, it is found that R^2 value for Cr(III) and Cr(VI) is comparatively large, and favorable adsorption of Cr by the carbon was presented. Particularly, R^2 values in Langmuir isotherm are large for both Cr(III) and Cr(VI). This result suggests that the adsorption of Cr on Yukitsubaki carbon mainly occurred by monolayer reaction.

3.6 Kinetic Studies

The results for kinetic studies are shown in Fig. 9. From Fig. 9, it is observed that the rates of adsorption were found to conform to pseudo-second order equation than pseudo first-order equation. Based on the data in Fig 9, the pseudo second-order kinetic coefficients for Cr(III) and Cr(VI) by Yukitubaki carbon are estimated (Table 3). The rate constant of second-order equation (k) diffusion are $2.94 \times 10^{-2} \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ for Cr(III) and $3.40 \times 10^{-2} \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ for Cr(VI). The correlation coefficients were more than 0.99 for both Cr(III) and Cr(VI) adsorption on Yukitubaki carbon.

3.7 Effect of Competitive Ions on the Sorption of Cr

3.7.1 Effect of Competitive Cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) on the Sorption of Cr(III).

Competitive experiment for Cr(III) was conducted at optimized pH (pH 5), contact time (2 h) and sorbent

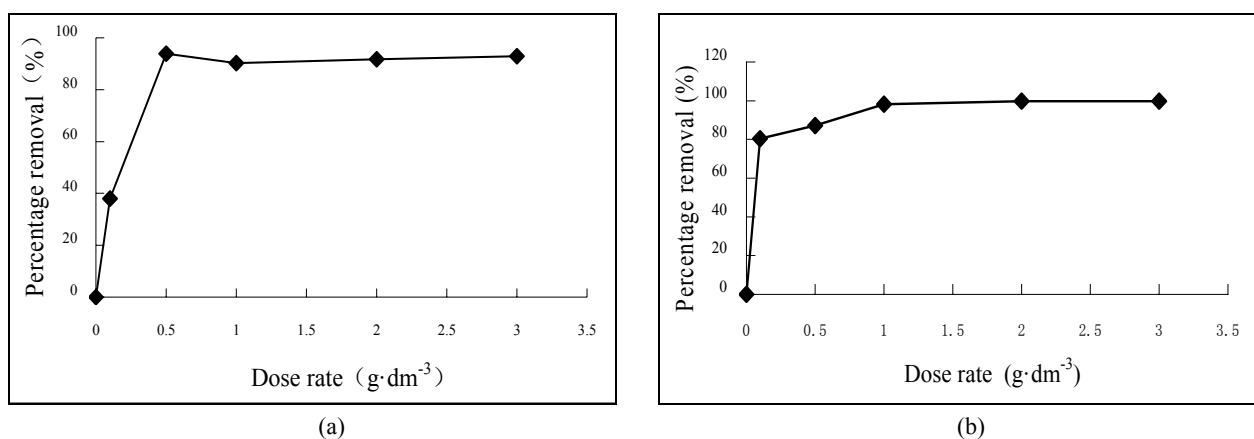


Fig. 6 Effect of dose rate on percent removal of Cr using Yukituba: (a) Cr(III); (b) Cr(VI).

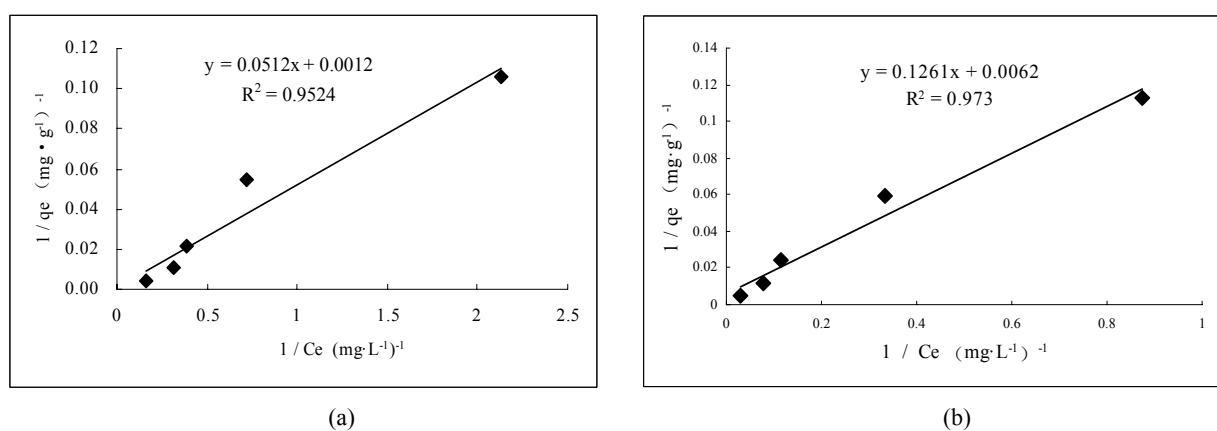


Fig. 7 Langmuir liner fit of batch sorption data for Yukitubaki: (a) Cr(III); (b) Cr(VI).

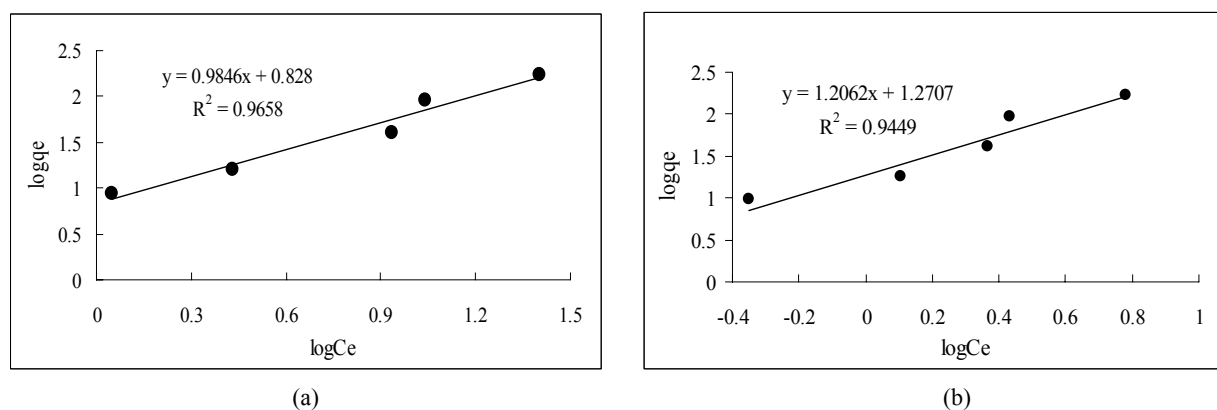


Fig. 8 Freundlich liner fit of batch sorption data for Yukitubaki: (a) Cr(III); (b) Cr(VI).

Table 2 Coefficient of Langmuir and Freundlich isotherms for Cr (Cr(III) and Cr(VI)) using Yukitubaki.

	Langmuir isotherm			Freundlich isotherm		
	q_{\max} (mg·g ⁻¹)	K_L (dm ³ ·g ⁻¹)	R^2	K_F ((μg·g ⁻¹)· (dm ⁻³ ·μg ⁻¹) ^{1/n})	1/n	R^2
Cr(III)	1.81E-01	1.94E+01	0.952	18.6	0.826	0.945
Cr(VI)	9.96E-02	2.21E+02	0.973	6.73	0.967	0.967

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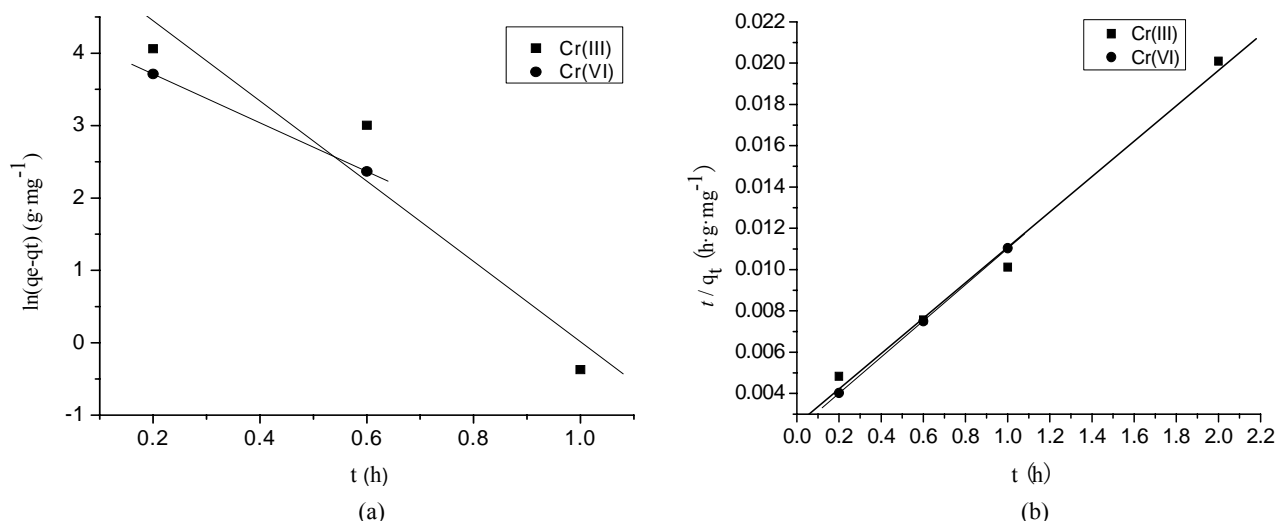
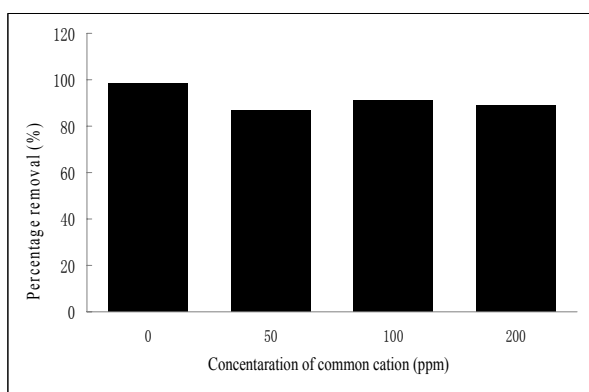


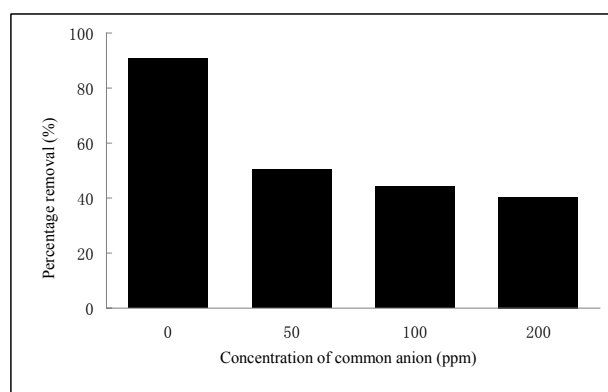
Fig. 9 The kinetic model on Yukitubaki: (a) the pseudo first -order kinetic model; (b) the pseudo second-order kinetic model.

Table 3 The pseudo second-order kinetic coefficient for Cr(III) and Cr(VI) using Yukitubaki carbon.

	q_e (mg·g ⁻¹)	k (g·mol ⁻¹ ·h ⁻¹)	R
Cr(III)	0.117	2.94×10^{-2}	0.994
Cr(VI)	0.114	3.40×10^{-2}	0.999



(a)



(b)

Fig. 10 Effect of common ion on percent removal of Cr using Yukitubaki carbon: (a) Cr(III); (b) Cr(VI).

dosage (1 g·dm⁻³) under the presence of common ions (Na⁺, K⁺, Ca²⁺ and Mg²⁺) at different concentrations 0, 50, 100 and 200 ppm (Fig. 10a). It is found that the remarkable decrease of sorption capacity of Cr(III) was not observed, even if the concentrations of common ions are 200 ppm.

3.7.2 Effect of Competitive Anions (Cl⁻, NO₃⁻ and SO₄²⁻) on the Sorption of Cr(VI)

Competitive experiment for Cr(VI) was performed at optimized pH (pH 3), contact time (1 h) and sorbent dosage (0.5 g·dm⁻³) under the presence of common

ions (Cl⁻, NO₃⁻ and SO₄²⁻) at different concentrations 0, 50, 100 and 200 ppm (Fig. 10b). In case of sorption capacity of Cr(VI), the decrease of removal (40-50%) was observed when the concentrations of common ions are 50-200 ppm.

From Figs. 10a and 10b, it is suggested that the sorption of Cr(III) on Yukitsubaki carbon was fairly good under this experimental condition. It indicates that Yukitsubaki carbon can be an efficient adsorbent for Cr(III) in aqueous environment, although it requires further investigations for applying the carbon

to use as an adsorbent for heavy metal more practically.

4. Conclusions

The efficiency of Yukitsubaki carbon as an adsorbent for Cr (Cr(III) and Cr(VI)) was investigated. From this work, the following matters were clarified:

(1) Yukitsubaki carbon exhibited high adsorption capacity for Cr. The removal of Cr(III) was more than 99%, and the removal of Cr(VI) was more than 90% under this optimal experimental conditions;

(2) The effect of common cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) on the adsorption of Cr(III) was not significant up to concentrations of 200 ppm. On the contrary, the effect of common anions (Cl^- , NO_3^- and SO_4^{2-}) on the adsorption of Cr(VI) was rather large up to the concentration of 50-200 ppm;

(3) Cr(III) and Cr(VI) adsorption on the Yukitsubaki carbon conforms to the Langmuir isotherm adsorption equation, and the correlation coefficients are more than 0.95 and 0.97, respectively. The maximum adsorption capacity of Cr(III) and Cr(VI) on chitosan calculated by the Langmuir model were 1.81×10^{-1} and $9.96 \times 10^{-2} \text{ mg} \cdot \text{g}^{-1}$, respectively;

(4) The best fit was obtained with a pseudo-second order kinetic model while investigating the adsorption kinetics, and the correlation coefficients were both more than 0.99 for Cr(III) and Cr(VI).

From these results, it was quantitatively clarified to some extent that Yukitsubaki carbon can be an efficient sorbent for Cr (particularly for Cr(III)), which provide very significant information from the viewpoint of environmental protection.

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