Synthesis of new adsorbents and removal of chromium from aqueous solution

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Contents

Chapter 1 General Introduction

1.1 Background

With the rapid growth of mankind, society, science and technology, the environmental disorder with a big pollution problem has become one of the most important issues in the past half century [1]. One of the intractable environmental problems is water pollution by heavy metals [2], and has become a challenge for life on earth because of the anthropogenic activities. Heavy metals in environmental water have been a major preoccupation of their toxicity towards aquatic life, human beings and the environment [3].

Due to serious hazardous effects of heavy metal ions on human health and toxicity in the environment [4], it is important to develop a simple and highly effective removal method as well as sensitive analytical method for environmental pollutants to improve the quality of environment and human life.

The environmental conservation is of increasing social and economic importance. Various treatment technologies such as ion exchange, precipitation, ultrafiltration, reverseosmosis and electro dialysis have been used for the removal of heavy metal ions from aqueous solution [5]. However, these processes have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost.

Many works for the removal of heavy metals by adsorption has been reported [6, 7]. Particularly, the development of high efficiency and low cost adsorbents has been aroused general interest in recent years. Biological materials as adsorbent for water purification have become a hot research topic [8, 9]. Biological adsorbent has the advantages of recyclable, low cost, easy operation and little possibility of secondary pollution [10, 11].

1.2 Heavy Metals

Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe), and the platinum group elements [12].

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [13]. they enter the body system through food, air, and water and bio-accumulate over a period of time.

Although adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues and is even increasing in some areas [14], such as metal plating facilities, mining operations, and tanneries. In these heavy metals, Cr is on the top priority list of toxic pollutants defined by the US EPA.

Cr mainly consists of two stable oxidation states such as trivalent state Cr(III) and hexavalent state Cr(VI) in natural aqueous environment [15]. The typical mobile forms of Cr(VI) in natural environment are CrO_4^{2-}, $HCrO_4^-$, the relative distribution of each species depends on the solution pH, on the concentration of Cr(VI) and redox potential [16], Cr(III) tends to form $[Cr(H_2O)_6]^{3+}$, $Cr(H_2O)_5(OH)^{2+}$, $Cr(H_2O)_4(OH)_2^+$, or Cr(III) organic complexes.

The use of Cr and its compounds in several industrial processes (automobile manufacturing, production of steel and alloys, mining of chrome ore, plating and electroplating, etc.) leads to contamination of natural waters mainly due to improper disposal methods [17].

They can be taken up by plants and easily be leached out into the deeper soil layers, leading to ground and surface water pollution. It is well known that Cr(III) is essential materials for living organisms, whereas Cr(VI) is the most toxic form, it can diffuse as CrO_4^{2-} or $HCrO_4^-$ through cell membranes [18] lead to carcinogenic, mutagenic, liver damage, pulmonary congestion, and causes skin irritation resulting in ulcer formation to living organisms [19, 20, 21, 22].

From above-mentioned, Cr(VI) must be substantially removed from the wastewater before being discharged into the aquatic system. Therefore the separation and reduction of Cr in wastewater is very important for environmental protection and human health.

1.3 Adsorbents

Different technologies for the removal of heavy metal ions are available such as chemical precipitation, coagulation, ion exchange, membrane technologies, adsorption. Adsorption has been proved as one of the most efficient methods for the removal of heavy metals from aqueous media [23]. The major advantages of biosorption are its high effectiveness, easy operation, no two pollution, and the use of inexpensive biosorbents.

1. 3. 1 Yukitsubaki carbon

Yukitsubaki carbon has great potential for the removal of heavy metal ions due to properties such as large surface area, microporous structure, and high adsorption capacity. It is an evergreen shrub of the Camellia family, a plant native to the mountainous region of the multi snowy area of the Japan Sea side. Yukitsubaki grows very slowly, even if it's diameter is 4 - 5 cm when the age is over 40 years, it has a high density, hard texture and porous structure, easy to obtain and low cost . Therefore, it is expected as an adsorbent for the treatment of wastewater.

In present studies, 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. The adsorption capacity of Yukitsubaki carbon was investigated for the removal of heavy metal from aqueous solution under varying experimental conditions.

1. 3. 2 Chitosan and silicon dioxide

Chitosan has proven to be very efficient as biosorbent for the recovery of several toxic metals such as mercury (Hg), uranium (U), molybdenum (Mo), vanadium (V) and platinum (Pt) [24, 25, 26], which full chemical name is known as (1,4)-2-amino-2-deoxy-β-D-glucose, can be environmentally friendly adsorbent due to the low price and no second pollution. Chitosan is produced by the alkaline deacetylation of chitin, which is the most abundant biopolymer in nature originated from cellulose. Chitosan is a polymer that can be obtained from the shells of seafood such as prawns, crabs, and lobsters [27]. The biopolymer is characterized by its high percentage of nitrogen, existed in the form of amine groups， free amino groups and hydroxyl groups, which responsible for metal ion binding through chelation mechanisms [28].

However, chitosan had some defects such as notable swelling in aqueous media and nonporous structure resulting in a very low surface area [29]. Therefore, many types of chemical modification can be undertaken to produce some chitosan derivatives for improving the removal efficiency of the heavy metal [30]. For example, silicon dioxide can be one of the materials for offsetting the defects of chitosan because it has many characteristics such as rigid structure, porosity and high surface area.

Silica gels are low-density solids, consisting of silicon oxide. The study of silica gels has attained considerable attention due to open mesoporic structure, high surface area, large pore volume and good performance as effective adsorbents [31]. Silicon dioxide is a synthetic amorphous polymer with silanol groups on the surface allowing metal adsorption [32, 33]. In case of silicon dioxide, the modified silicon dioxide through the graft between silanol groups and ligands has been developed [34, 35, 36]. At present, an interest has grown in the field of organic and in organic hybrid materials. The silica gels doped with some organic or inorganic material possess a number of novel properties [37].

Due to above-mentioned reason, novel materials were designed to combine the beneficial properties of silica gel and chitosan. The hybrid membrane of chitosan and silicon dioxide was synthesized in this work to enhance the adsorption potential of heavy metal ions. In present studies, the adsorption capacity of the hybrid membrane was investigated for the removal of heavy metal ions from aqueous solution under varying experimental conditions.

The another hand, carboxymethyl chitosan has been prepared by using chloroacetic acid (and chitosan) under alkaline conditions to improve the removal efficiency, the hybrid membrane of carboxymethyl chitosan and silicon dioxide was synthesized, and use to removal heavy metal ions from aqueous solution by the hybrid membrane of carboxymethyl chitosan and silicon dioxide under varying experimental conditions.

Moreover, the novel adsorbent can be recycled for adsorption heavy metal ions compared with the disposable adsorbent.

1.4 Theory

1. 4. 1 Langmuir and Freundlich Isotherm Models

Langmuir and Freundlich isotherms were modeled in order to evaluate the performance of adsorbents in adsorption processes by the relationship between the metal uptake (q_e) and the concentration of heavy metal ion (C_e) at equilibrium. Langmuir and Freundlich adsorption isotherms can be expressed, respectively.

The Langmuir isotherm equation is defined as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \qquad (1\text{-}1)$$

where C_e is the concentration of *heavy metal ion* at equilibrium ($\mathrm{mg \cdot dm^{-3}}$), q_e and q_{max} are the amount of adsorption of *heavy metal ion* at equilibrium ($\mathrm{mg \cdot g^{-1}}$) and the maximum adsorption capacity by the adsorbents ($\mathrm{mg \cdot g^{-1}}$) respectively, K_L ($\mathrm{dm^{-3} \cdot mg^{-1}}$) is the adsorption constant of Langmuir isotherm.

The linearized Freundlich isotherm equation is defined as follows:

$$\log_{10} q_e = \log_{10} K_F + (1/n) \log_{10} C_e \qquad (1\text{-}2)$$

In this equation, K_F is the adsorption capacity ($(\mathrm{mg \cdot g^{-1}}) \cdot (\mathrm{dm^{-3} \cdot mg^{-1}})^{1/n}$), $1/n$ is the adsorption intensity. The values of $1/n$ and K_F were determined on the basis of the plots of q_e versus C_e in log scale.

1. 4. 2 Kinetic Models

Kinetic models have been proposed to determine the rate of adsorption of the adsorbent. In addition, the process of kinetic study is very important for understanding the reaction process and the rate of adsorption reactions.

The pseudo first-order model is given by the following equation:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (1\text{-}3)$$

where q_e and q_t are the adsorption capacity of heavy metal ion using the adsorbents at equilibrium and time t, respectively ($\mathrm{mg \cdot g^{-1}}$), and k_1 is the rate constant of the pseudo-first-order adsorption ($\mathrm{h^{-1}}$).

The pseudo-second order rate equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \qquad (1\text{-}4)$$

where k ($\mathrm{g \cdot mg^{-1} \cdot h^{-1}}$) is the rate constant of the second-order model, and q_e and q_t are the adsorption capacities of heavy metal ion using the adsorbents at equilibrium and time t, respectively ($\mathrm{mg \cdot g^{-1}}$).

The adsorption capacity of adsorbents for heavy metal ion was calculated using the mass balance equation:

$$q_\mathrm{e} = \frac{(C_i - C_e)}{m} \cdot V \qquad (1\text{-}5)$$

where q_e is the adsorption capacity ($\mathrm{mg \cdot g^{-1}}$) of heavy metal ion by the adsorbents at equilibrium, C_i and C_e are the concentrations of heavy metal ion at initial and equilibrium in a batch system respectively ($\mathrm{mg \cdot dm^{-3}}$), V ($\mathrm{dm^{-3}}$) is the volume of the heavy metal solution, and m (g) is the mass of the adsorbents.

1.5 The Purpose and Outline of the Thesis

The environmental conservation is of increasing social and economic importance. One of the intractable environmental problems is water pollution by heavy metals. Heavy metals in environmental water have been a major preoccupation for many years because of their toxicity towards aquatic life, human beings and the environment.

Due to serious hazardous effects of heavy metal ions on human health and toxicity in the environment, it is important to develop a simple and highly effective removal method as well as sensitive analytical method for environmental pollutants to improve the quality of environment and human life.

In this thesis, Yukitsubaki carbon and the hybrid membrane as biosorbent has been investigated in a batch system for removal chromium from aqueous solution.

In this paper, there are 4 chapters.

In Chapter 1, the general introduction was stated.

In Chapter 2，removal of chromium from aqueous solution using 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).

The adsorption of Cr on Yukitsubaki carbon conformed to the Langmuir isothermal adsorption equation. The rates of adsorption were found to conform to pseudo-second order kinetics. Overall the modified Yukitsubaki carbon exhibited a higher adsorption capacity and stronger chemical affinity of Cr than that of pristine carbon.

In Chapter 3, the hybrid membrane of chitosan-silicon dioxide and the hybrid membrane of carboxymethyl chitosan-silicon dioxide were synthesized respectively as new adsorbent material for the removal of Cr(VI) from aqueous solutions. The adsorption potential of Cr(VI) by the hybrid materials was investigated by varying experimental conditions such as pH, contact time and the dosage of the hybrid membrane. Adsorption isotherms of Cr(VI) onto the hybrid membrane were studied with varying initial concentrations under optimum experiment conditions. The surface property of the hybrid membrane was characterized by SEM (scanning electron microscope) and Fourier transform infrared spectrometer (FT-IR). The concentrations of Cr(VI) in solution are determined by ICP-AES (inductively coupled plasma atomic emission spectrometry). The present study investigates the adsorption mechanisms of Cr(VI) onto the hybrid membrane.

The following conclusions can be drawn considering the results of this work.

(1) The hybrid membrane exhibited high adsorption capacity for Cr(VI). The removal of Cr(VI) was more than 80% under the optimal experimental conditions (at

pH 5, contact time of 60 min, dosage of 0.25 g.dm^{-3} and initial Cr(VI) concentration of 40 mg·dm^{-3}). (2) The adsorption isotherm of Cr(VI) by the hybrid membrane of carboxymethyl chitosan and silicon dioxide was more suitably described by Langmuir model, and the correlation coefficients were more than 0.998. It suggests that monolayer chemical adsorption of Cr(VI) on the hybrid membrane is more dominant. The maximum adsorption capacity was estimated as 80.7 mg·g^{-1} for Cr(VI) under the optimum conditions. The adsorption capacity of the hybrid membrane for Cr(VI) in this work is on a level with that of another adsorbents in previous works. (3) The best fit was obtained with a pseudo-second order kinetic model while investigating the adsorption kinetics of Cr(VI) adsorption on the hybrid membrane, and the correlation coefficients was more than 0.9. The rate constant (k) are 3.4×10^{-2} g·mg^{-1}·h^{-1}.

From this work, it was quantitatively found that the hybrid membrane of carboxymethyl chitosan and silicon dioxide could be an efficient adsorbent for Cr(VI). It is very significant information from the viewpoint of environmental protection, and can be used for treating industrial wastewaters including pollutants.

In Chapter 4, according to chapter 2 and 3, the conclusions were clarified.

Chapter 2 Removal of Chromium from Aqueous Solution Using Yukitsubaki Carbon

2. 1 Introduction

Water pollution due to heavy metal has become one of the largest problems in recent years [38,39]. In particular, releasing wastewater containing heavy metal poses a threat to both human health and environment [40, 41]. The water that we drink may contain industrial wastewater with chromium [42].

Cr mainly consists of two stable oxidation states such as trivalent state Cr(III) and hexavalent state Cr(VI) in natural aqueous environment. Cr(VI) may be present in the form of CrO_4^{2-} or $HCrO_4^-$, whereas Cr(III) tends to form $[Cr(H_2O)_6]^{3+}$, $Cr(H_2O)_5(OH)^{2+}$, $Cr(H_2O)_4(OH)_2^+$, 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 [43, 44].

Therefore the separation and reduction of chromium in waste water is very important for environmental protection and human health. 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. 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 [45].

From above-mentioned, sorption experiment of Cr using chitosan was performed in previous paper [46]. 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.

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. 2 Experimental Sections

2. 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% HNO_3 and 30% HNO_3 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 $mg \cdot dm^{-3}$ $Cr(NO_3)_3$ solution), and Cr(VI) standard solutions were prepared by diluting a standard solution (1,000 $mg \cdot dm^{-3}$ $K_2Cr_2O_7$ 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. 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 N_2 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-AES (inductively coupled plasma mass spectrometry) instrument (ThermoFisher Scientific X2) was used to determine the concentration of Cr.

2. 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 cm^3 of containing known amount of Cr (Cr(III) or Cr(VI)) in a 200 cm^3 conical flask, and the suspensions was 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 $g\cdot dm^{-3}$)). The pH of each solution was adjusted by using 0.1 $mol\cdot dm^{-3}$ NaOH and 0.1 $mol\cdot dm^{-3}$ HNO_3.

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-AES.

2. 3 Results and Discussion

2. 3. 1 Characteristics of Yukitsubaki Carbon

The morphologies of pristine Yukitsubaki carbon and modified carbon characterized by SEM are shown in Fig. 2-1. Moreover, the surface properties including specific surface areas of pristine and modified Yukitsubaki carbon determined by N_2-BET method are shown in Table 2-1. The pore structures of all the samples are similar to each other. However, judging from the SEM images in Fig. 2-1, the surface area of modified Yukitsubaki carbon (HNO_3 30%) (Fig. 2-1c) seems to be slightly changed with the acid treatment, whereas that of modified Yukitsubaki carbon (HNO_3 10%) (Fig. 2-1b) seems to be hardly varied. This is consistent with the data of the specific surface area in Table 2-1. 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. 2-2. From it, a characteristic broad band, which may be due to graphite structure in carbon, is observed at around 1,610 cm^{-1}. The peak at 3,300 cm^{-1} is related to hydroxyl groups (-OH), and 1,120 cm^{-1} is related to carbonyl groups (-C=O), and then the peaks at 2,920 and 2,850 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 have been carried out at the present work.

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

2. 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 [47]. 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 °C, while the concentration of Cr(III) or Cr(VI) was kept constant at 100 ppb, and Yukitsubaki carbon dosage was 1.0 $g{\cdot}dm^{-3}$. The contact time was 4 h.

The results for Cr(III) are shown in Fig 2-3a. 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 $4 \leq pH \leq 6$. 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 2-3b. 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 $4 \leq pH \leq 7$. Thus pH 3 was selected as the optimal pH for further work.

Species distribution of Cr at different pH based on theoretical calculation [48] is shown in Fig 2-4. From Fig 2-4a, Cr(III) exists predominantly as Cr^{3+} at pH 1-3, whereas exists predominantly as $CrOH^{2+}$ at pH 4-6. Furthermore, from the results of FTIR spectra in Fig 2-2, 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 ($HCrO_4^-$) between pH 2 and 6.5, and it exists as chromate ions (CrO_4^{2-}) at pH above 6.5 (Fig 2-4b). It is considered that this anion species has a tendency to bind to the protonated active sites of the Yukitsubaki carbon at optimum pH.

2. 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 Cr(VI) using 1.0 g·dm^{-3} Yukitsubaki carbon (100 μg·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 2-5a). 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 2-5b). 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.

2. 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 g·dm^{-3} have been studied in

100 ppb (μg·dm^{-3}) of Cr solution. The removal of Cr(III) more than 98% was observed for 1.0 g·dm^{-3} dosage (Fig 2-6a). The removal of Cr(VI) more than 93% was observed for 0.5 g·dm^{-3} dosage (Fig 2-6b), but no remarkable increase is observed at a dosage more than 0.5 g·dm^{-3}. Therefore, 1.0 g·dm^{-3} was considered as optimum dosage for Cr(III), and 0.5 g·dm^{-3} was considered for Cr(VI), respectively for the rest of the study.

2. 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 results for Langmuir and Freundlich are shown in Fig 2-7 and 2-8. 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 2-2, 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.

2. 3. 6 Kinetic Studies

The results for kinetic studies are shown in Fig 2-9. From Fig 2-9, 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 2-9, the pseudo second-order kinetic coefficients for Cr(III) and Cr(VI) by Yukitubaki carbon are estimated (Table 2-3). The rate constant of second-order equation (*k*) diffusion are 2.94 × 10^{-2} g·mol^{-1}·h^{-1} for Cr(III) and 3.40 × 10^{-2} g·mol^{-1}·h^{-1} for Cr(VI). The correlation coefficients were more than 0.99 for both Cr(III) and Cr(VI) adsorption on Yukitubaki carbon.

2. 3. 7 Effect of Competitive Ions on the Sorption of Cr

2. 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 dosage (1 g·dm^{-3}) under the presence of common ions (Na^+, K^+, Ca^{2+} and Mg^{2+}) at different concentrations 0, 50, 100 and 200 ppm (Fig. 2-10a). 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.

2. 3. 7. 2 Effect of Competitive Anions (Cl^-, NO_3^- and SO_4^{2-}) 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^-, NO_3^- and SO_4^{2-}) at different concentrations 0, 50, 100 and 200 ppm (Fig 2-10b). 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 Fig 2-10a 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.

2. 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 9.96×10^{-2} $mg \cdot g^{-1}$, 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.

Tables

Table 2-1 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

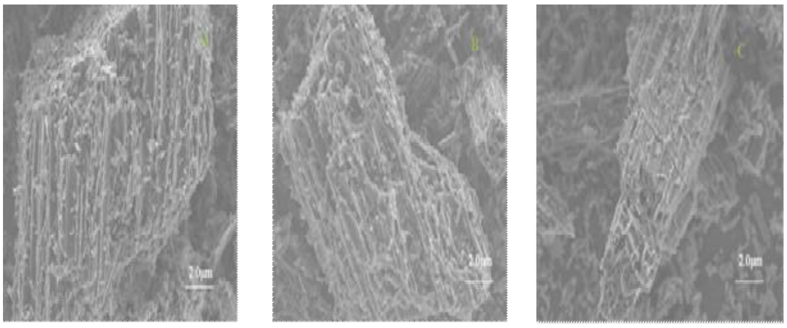
Table 2-2 Coefficient of Langmuir and Freundlich isotherms for Cr (Cr(III)and Cr(VI)) using Yukitubaki.

	Langmuir isotherm			Freundlich isotherm		
	q_{max} ($mg \cdot g^{-1}$)	K_L ($dm^3 \cdot g^{-1}$)	R^2	K_F ($(\mu g \cdot g^{-1}) \cdot (dm^{-3} \cdot \mu g^{-1})^{1/n}$)	$1/n$	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

Table 2-3 The pseudo second-order kinetic coefficient for Cr(III) and Cr(VI) using Yukitubaki carbon.

	q_{e} ($mg \cdot g^{-1}$)	k ($g \cdot mol^{-1} \cdot h^{-1}$)	R
Cr(III)	0.117	2.94×10^{-2}	0.994
Cr(VI)	0.114	3.40×10^{-2}	0.999

Figures



(a) (b) (c)

Fig. 2-1 The SEM images of pristine and modified Yukitsubaki carbon (a) pristine; (b) HNO$_3$ 10%; (c) HNO$_3$ 30%.

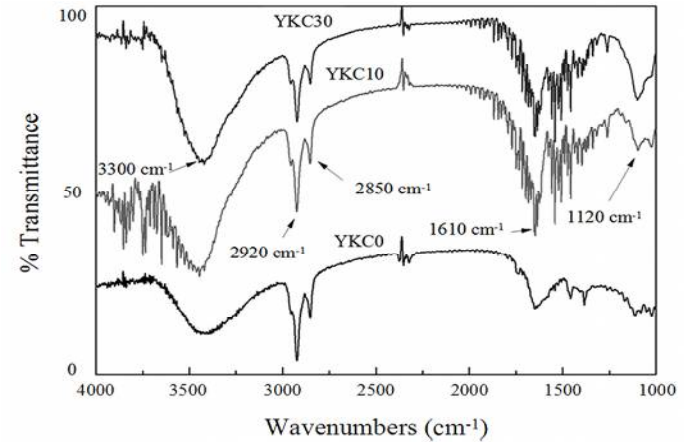
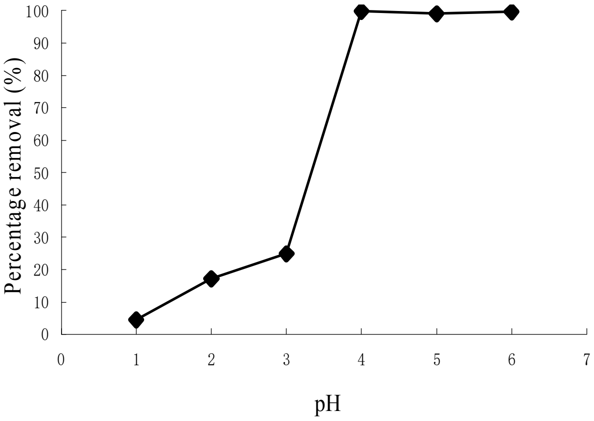
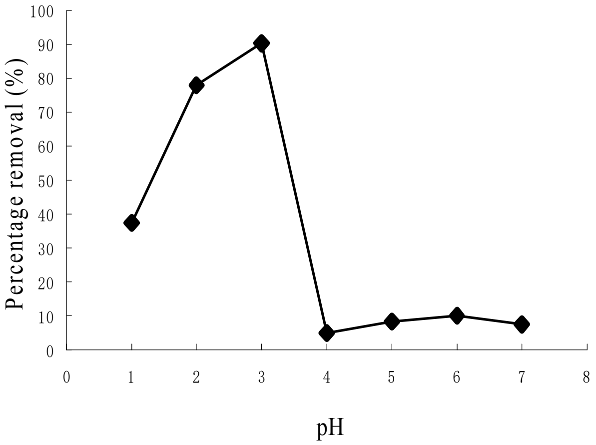


Fig. 2-2 The FTIR spectra of pristine and modified Yukitsubaki carbon.

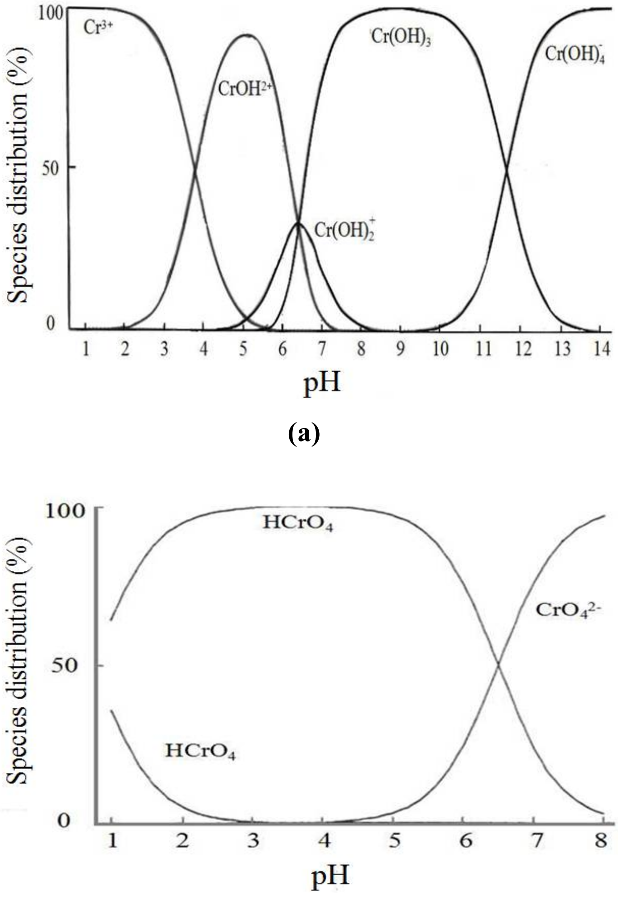


(a)



(b)

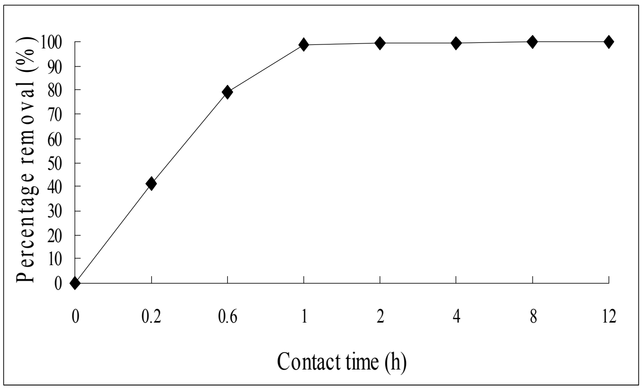
Fig. 2-3 Effect of pH on percent removal of Cr using Yukitubaki, (a): Cr(III); (b): Cr(VI).



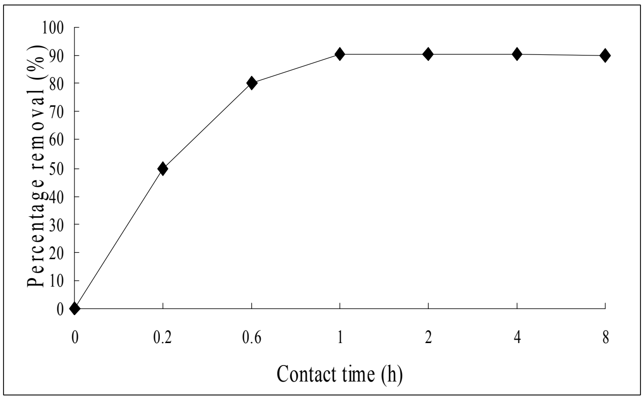
(a)

(b)

Fig. 2-4 Species distribution curves of Cr in environmental water, (a): Cr(III); (b): Cr(VI).



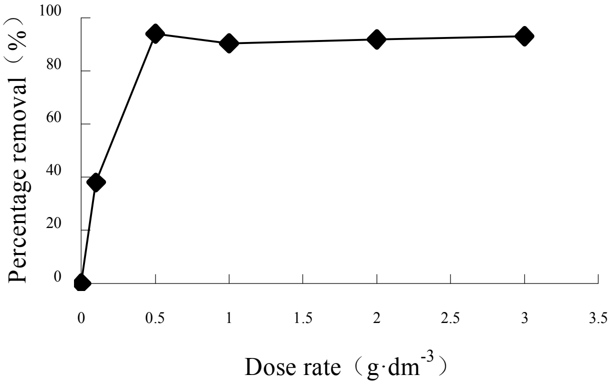
(a)



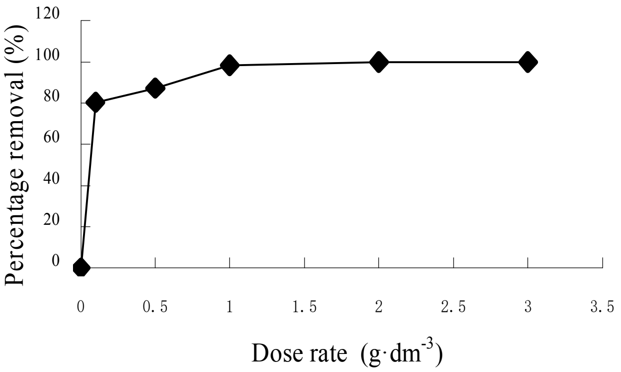
(b)

Fig. 2-5 Effect of contact time on percent removal of Cr using Yukitubaki

(a): Cr(III); (b): Cr(VI).

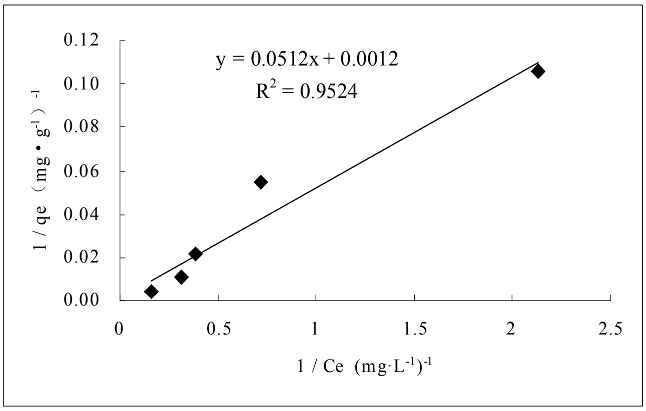


(a)

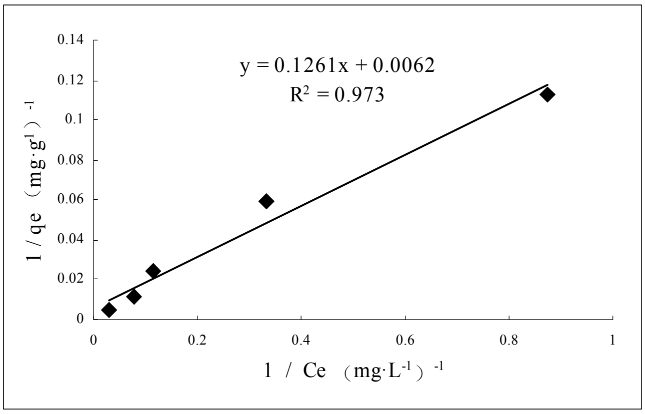


(b)

Fig. 2-6 Effect of dose rate on percent removal of Cr using Yukituba, (a): Cr(III); (b): Cr(VI).

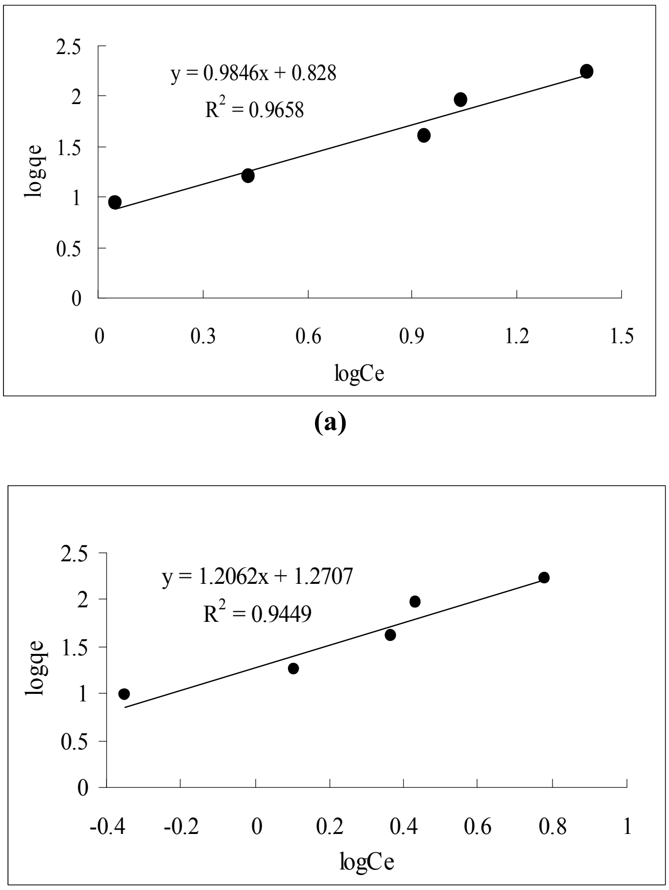


(a)



(b)

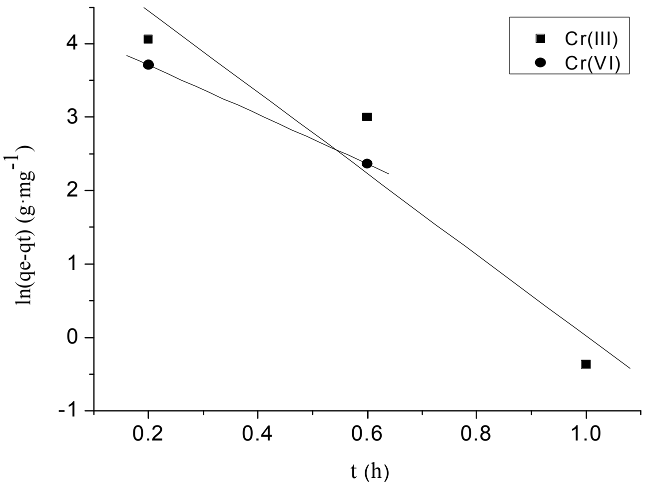
Fig. 2-7 Langmuir liner fit of batch sorption data for Yukitubaki, (a): Cr(III); (b):Cr(VI).



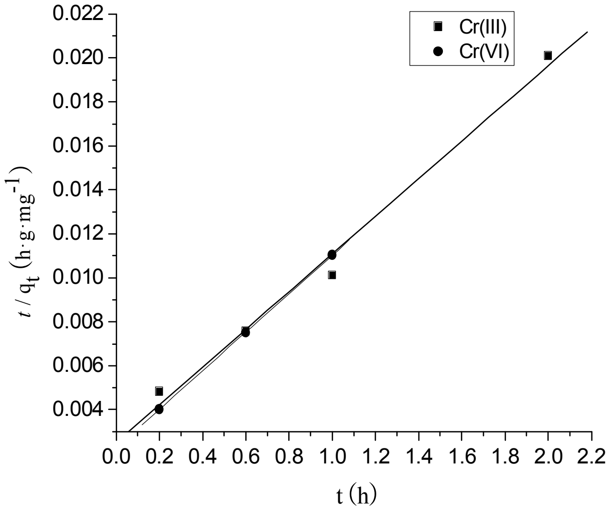
(a)

(b)

Fig. 2-8 Freundlich liner fit of batch sorption data for Yukitubaki, a: Cr(III); b:Cr(VI).

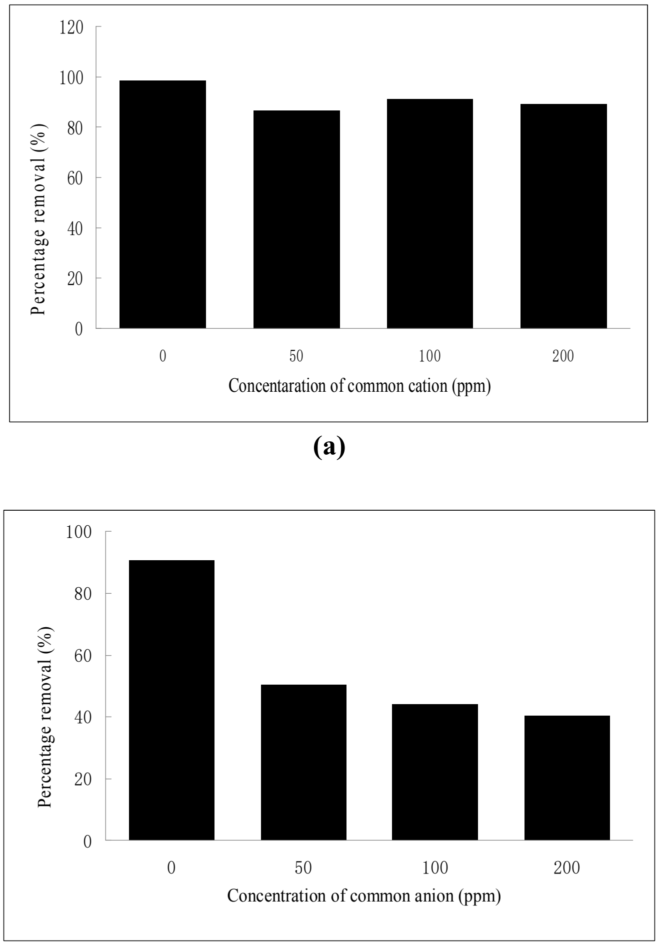


(a)



(b)

Fig. 2-9 The kinetic model on Yukitubaki, (a): The pseudo first -order kinetic model; (b): The pseudo second-order kinetic model.



(a)

(b)

Fig. 2-10 Effect of common ion on percent removal of Cr using Yukitubaki carbon (a): Cr(III); (b): Cr(VI).

Chapter 3 Removal of Cr(VI) Using the Hybrid Membrane

3. 1 Introduction

The heavy metal contamination is a serious problem to the environment [49], and has become a challenge for life on earth because of the anthropogenic activities. Among the toxic metals, chromium has been reported to be toxic to animals and humans, and it is known to be carcinogenic [50, 51]. Chromium consists of two stable oxidation states such as trivalent state Cr(III) and hexavalent state Cr(VI) in natural environment. Cr(VI) is more toxic, carcinogenic and mutagenic.

They can be taken up by plants and easily be leached out into the deeper soil layers, leading to ground and surface water pollution. Because of its high toxicity and its water solubility in the full pH range. The effluents are discharged onto the open land or into the sewage system. These industries are major sources of chromium pollution in the environment [52]. Cr(VI) must be substantially removed from the wastewater before being discharged into the aquatic system.

Many works for the removal of heavy metals by adsorption has been reported [6, 7, 29]. Particularly, the development of high efficiency and low cost adsorbents has been aroused general interest in recent years.

Chitosan, which full chemical name is known as (1,4)-2-amino-2-deoxy-β-D-glucose, can be environmentally friendly adsorbent due to the low price and no second pollution. Chitosan has free amino groups and hydroxyl groups, which can remove the heavy metal ions by forming stable metal chelates.

However, chitosan had some defects such as notable swelling in aqueous media and nonporous structure resulting in a very low surface area [29]. Therefore, many types of chemical modification can be undertaken to produce some chitosan derivatives for improving the removal efficiency of the heavy metal [30]. For example, silicon dioxide can be one of the materials for offsetting the defects of chitosan because it has many characteristics such as rigid structure, porosity and high surface area.

Silicon dioxide is a synthetic amorphous polymer with silanol groups on the surface allowing metal adsorption [32, 33]. In case of silicon dioxide, the modified silicon dioxide through the graft between silanol groups and ligands has been developed [34, 35, 36].

Therefore, we have investigated the efficiency of the hybrid membrane of chitosan and silicon dioxide as sorbent for Cr(VI) [53]. In this study, carboxymethyl chitosan has been prepared by using chloroacetic acid (and chitosan) under alkaline conditions to improve the removal efficiency of Cr(VI) by the hybrid membrane.

Then, novel adsorption materials were designed to combine the beneficial properties of carboxymethyl chitosan and silicon dioxide. Moreover, the novel adsorbent can be recycled for adsorption heavy metal ions compared with the disposable adsorbent.

From above-mentioned, the hybrid membrane of carboxymethyl chitosan and silicon dioxide was synthesized in this work to enhance the adsorption potential of Cr(VI). The adsorption capacity of the hybrid membrane was investigated for the removal of Cr(VI) from aqueous solution under varying experimental conditions.

3. 2 Experimental Sections

3. 2. 1 Materials, Reagent and Apparatus

3-Aminopropyltriethoxysilane was purchased from Nacalal Tesque., Inc (Tokyo, Japan), and chitosan was from Tokyo Chemical Industry Co. (Tokyo, Japan). Cr(VI) standard solutions were prepared by diluting a standard solution (1,005 mg·dm^{-3} $K_2Cr_2O_7$ solution) purchased from Kanto Chemical Co., Inc. All other chemical reagents were also bought 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.

The pH of Cr(VI) aqueous solution were measured by the pH meter (HORIBA UJXT 06T8, Japan). The surface property of hybrid membrane of carboxymethyl chitosan and silicon dioxide was characterized by SEM (JEOL, JSM-5800, Japan) and Fourier transform infrared spectroscopy in pressed KBr pellets (FTIR-4200, Jasco, Japan). The concentrations of Cr(VI) in solution were determined by ICP-AES (inductively coupled plasma atomic emission spectrometry).

3. 2. 2 Prepared Hybrid Membrane of Chitosan and Silicon Dioxide

The solution of chitosan (3%, w/v) was prepared by dissolving 3 g of chitosan in 100 ml of 0.2 mol·dm^{-3} acetic acid solution. Silica sols (which was prepared by dissolving 2 ml of 3-Aminopropyltriethoxysilane in 100 ml ethanol) was added into the solution of chitosan (3%, w/v) at 25 °C and was stirred for 24 h. The hybrid membrane of chitosan and silicon dioxide was dried at 25 °C.

3. 2. 3 Prepared Hybrid Membrane of Carboxymethyl Chitosan and Silicon Dioxide

Under alkaline conditions, chitosan can reaction with chloroacetic acid to obtain the carboxymethyl chitosan. Chitosan was accurately weighed 5g into a round-bottomed flask containing 75 ml isopropanol and 25 ml ultrapure water, and then 6.75 g of sodium hydroxide was added for alkalization. The mixed solution was stirred in a water bath at 50°C for 2 h, and was cooled to room temperature after continued stirring for 4h. In addition, chloroacetic acid solution was prepared by dissolving 6 g of chloroacetic acid in 25 ml isopropanol solution, and slowly dropped into the round-bottomed flask under stirring for 4h. The solution was adjusted to neutral using hydrochloric acid, and washed three times with 70% isopropanol, and then filtered. After washing completely with 90% isopropanol again, the solution was filtered. Then, carboxymethyl chitosan was dried at 50°C and used for preparation of hybrid membrane.

The reaction process of hybrid membrane synthesized from carboxymethyl chitosan and silicon dioxide is shown in Fig 3-1. The solution of carboxymethyl chitosan (3%, w/v) was prepared by dissolving 3 g of carboxymethyl chitosan in 100 ml ultrapure water. Silica sols (prepared by dissolving 5 ml of 3-Aminopropyltriethoxysilane in 100 ml ethanol) was added into the solution of carboxymethyl chitosan (3%, w/v) at 25 °C, and the solution was stirred for 24 h. The hybrid membrane of carboxymethyl chitosan and silicon dioxide was dried at 25 °C.

3. 2. 4 Sorption Experiment of Cr(VI) Using Hybrid Membrane

The adsorption capacities of Cr(VI) from aqueous solution using the hybrid membrane of chitosan and silicon dioxide were investigated by a batch method. hybrid membrane of chitosan and silicon dioxide was thoroughly mixed with 50 ml of containing known concentrations of Cr(VI) in a 200 ml conical flask. According to the above-mentioned procedure, Cr(VI) were adsorbed at different pH values (1-7), contact time (20-120min) and sorbent dosage (0.05-0.3 g.dm^{-3}). The pH of each solution was adjusted by using 0.1 mol dm-3 NaOH and 0.1 mol dm-3 HCl. Adsorption isotherms of Cr(VI) onto hybrid membrane of chitosan and silicon dioxide were measured at varying initial Cr(VI) concentrations (10-50 ppm) under optimized conditions.

3. 3 Results and Discussion (Part I: Removal of Cr(VI) Using the Hybrid Membrane of Chitosan and Silicon Dioxide)

3. 3. 1 Characteristics of Chitosan and Silicon Dioxide

The SEM pictures of hybrid membrane of chitosan and silicon dioxide are shown in Fig 3-2. It can be observed that hybrid adsorbents exist in the form of particles. Rashidova et al. (2004) prepared the hybrid adsorbents of chitosan and silica, and proposed the theory of chitosan and silica network where chitosan moieties were combined through silica groups via both ionic and covalent bonds [54]. The hybrid adsorbents synthesized in this work also may contain free amino groups that are responsible for metal ion binding through chelation mechanisms.

3. 3. 2 Effect of pH

For obtaining the optimum conditions regarding the adsorption of Cr(VI) onto the hybrid membrane of chitosan and silicon dioxide, the effects of pH on the removal of Cr(VI) were investigated under the fixed condition of initial Cr(VI) concentration (50 ppm), the contact time (100 min) and the dosage of the adsorbent (0.2 $g.dm^{-3}$).

The results for pH dependency are shown in Fig 3-3. The removal of Cr(VI) more than 76% was observed at pH3. It is well known that pH influences significantly in the adsorption processes by affecting both the protonation of the surface groups and the degree of the ionization of the adsorbates [55]. The surface of the adsorbent will be positively charged at lower pH, and it will not favor the adsorption of positively charged ions. Then it will favor the adsorption of Cr(VI) in the anionic form as $HCrO_4^-$ [56].

As shown in Fig 3-4 taken from Irgolic et al. [48], the dominant form of Cr(VI) exists as hydrogen chromate anions ($HCrO_4^-$) between pH 2 and 6.5. With the increase of pH, the dominant species will change from $HCrO_4^-$ to other form CrO_4^{2-} [57]. Then, pH 3 was selected as the optimal pH for further work.

3. 3. 3 Effect of Contact Time

The effect of contact time on the adsorption capacity of Cr(VI) using hybrid membrane of chitosan and silicon dioxide is studied at optimal pH under the initial Cr(VI) concentration of 50 ppm and the hybrid membrane dosage of 0.2 $g.dm^{-3}$. The removal rate reached 76.4% as shown in Fig 3-5. The adsorption capacity of hybrid membrane for Cr(VI) reached adsorption equilibrium at 80min, and after that there are a slight decrease due to the swelling properties of hybrid membrane absorbent. Therefore, the optimized contact time was selected for 80 min.

3. 3. 4 Effect of Hybrid Membrane Dosage

Under optimized condition of pH and contact time, sorption behavior of the hybrid membrane at different dosages from 0.1 $g{\cdot}dm^{-3}$ to 0.3 $g{\cdot}dm^{-3}$ have been studied in 50 ppm of Cr(VI) solution. The results are shown in Fig 3-6. The adsorption capacity of hybrid membrane for Cr(VI) reached adsorption equilibrium at 0.2 $g.dm^{-3}$, and the removal rate reached 78.6%. However, remarkable decrease is observed at a dosage more than 0.2 $g{\cdot}dm^{-3}$. Thus, 0.2 $g.dm^{-3}$was considered as optimized dose.

3. 3. 5 Effect of Initial Concentration

Study was carried out by varying initial concentrations from 10 ppm to 50 ppm under optimized conditions of pH 3, contact time (i.e., 80 min) and sorbent dosage (i.e., 0.2 g·dm^{-3}). There was a continuous increase in the uptake of Cr per gram of adsorbent up to the concentration of 40 μg·dm^{-3}, but the uptake is almost constant at further higher concentrations (Fig 3-7). The removal rate reached 78.7%. Then, 40ppm was considered as optimum initial concentration for Cr(VI).

3. 3. 6 Adsorption Isotherms

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes [58]. Langmuir and Freundlich isotherms were used in this work to evaluate the performance of adsorbents by the relationship between the metal uptake (q_e) and the concentration of metal ion (C_e) at equilibrium. The adsorption data obtained for Cr(VI) using hybrid membrane of chitosan and silicon dioxide were analyzed by Langmuir (Fig 3-8) and Freundlich equations (Fig 3-9). The correlation coefficient (R^2) of these isotherms for Cr(VI) on the hybrid membrane is shown in Table 3-1 along with other relevant parameters. From Table 3-1, it is found that R^2 value for Cr(VI) is comparatively large, and favorable adsorption of Cr(VI) on the hybrid membrane was presented. Particularly, R^2 values in Langmuir isotherm are larger than that in Freundlich isotherm.

This result suggests that the adsorption of Cr on hybrid membrane of chitosan and silicon dioxide mainly occurred by monolayer reaction.

3. 3. 7 Kinetic Studies

Kinetic model were tested in this study for the sorption of Cr(VI) onto the hybrid membrane of chitosan and silicon dioxide under the optimized experimental conditions. It is observed that the rates of adsorption were found to conform to pseudo-second order equation than pseudo first-order equation in this work. The results for kinetic studies are shown in Fig 3-10. Based on the data in Fig 3-10, the pseudo second-order kinetic coefficients for Cr(VI) by the hybrid membrane are estimated (Table 3-2). The rate constant of second-order equation (*k*) diffusion are 1.17 × 10^{-2} $g \cdot mol^{-1} \cdot h^{-1}$ for Cr(VI). The correlation coefficients (R^2) were 0.996 for Cr(VI) adsorption on the hybrid membrane.

3. 4 Results and Discussion (Part II: Removal of Cr(VI) Using the Hybrid Membrane of Carboxymethyl Chitosan and Silicon Dioxide)

3. 4. 1 Characteristics of the Hybrid Membrane of Carboxymethyl Chitosan and Silicon Dioxide

The FT-IR spectroscopy is an important technique of characterization used to explain the changes in chemical structures (i.e., the functional group on the surface of the samples).

FTIR spectra of the hybrid membrane of carboxymethyl chitosan and silicon dioxide are presented in Fig 3-11. The strong broad band at the wave number region of 3300-3500 cm^{-1} is the characteristic of $–NH_2$ stretching vibration, and the band at 3400 cm^{-1} are related to symmetrical valent vibration of free NH_2 and –OH groups [60]. The –CH stretching vibration in –CH and $–CH_2$ were observed at 2916 cm^{-1} and 1376 cm^{-1}. The $–NH_2$ bending vibration was observed at 1652 cm^{-1} shifted to lower frequencies (The lower frequencies observed in the hybrid membrane may be explained by the presence of primary amine salt $-NH_3^+$ [59]). A strong C=O stretching band at 1655 cm^{-1} may be related to the carboxymethyl group. Others bands at 1090 cm^{-1} are related to Si-O-Si valent vibrations [29]. The results of FTIR analysis show that the hybrid membrane of carboxymethyl chitosan and silicon dioxide were prepared successfully in this study.

The surface property of the hybrid membrane of carboxymethyl chitosan and silicon dioxide was investigated by SEM, and SEM images are shown in Fig 3-12.

The surface morphology of the hybrid membrane showed the form of grain coalescence, which may be due to the crosslinking among adjacent carboxymethyl chitosan groups. Moreover, there was the porous structure in the surface of hybrid membrane. It indicates that silicon dioxide was incorporated into the carboxymethyl chitosan definitely, and thereby the porous structure increased.

Carboxymethyl has a high chelating ability for metal ions to form stable metal chelates. The lone pair electrons on the nitrogen atom can also constitute coordination bonds with the metal ions to form the complex precipitation. The molecule also may contain free amino groups and hydroxyl groups, which can remove the heavy metal ions by chelation mechanisms.

3. 4. 2 Effect of pH

The effects of pH on the removal of Cr(VI) were investigated under the following condition: initial concentration of Cr(VI) for 50 mg·dm^{-3}, the contact time of 120 min, and the dosage of the adsorbent for 0.2 g·dm^{-3}.

The effect of pH on the removal of Cr(VI) using the hybrid membrane is shown in Fig 3-13. It is well known that pH influences significantly the adsorption processes by affecting both the protonation of the surface groups and the chemical form of Cr(VI). Cr(VI) exist in variety of form with different pH, Cr(VI) exist in the form of H_2CrO_4 at pH 1 [60], and different forms such as $Cr_2O_7^{-}$, $HCrO_4^{-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$, while $HCrO_4^{-}$ predominates at the pH range from 2.0 to 6.0. Furthermore, this form shifts to CrO_4^{2-} and $Cr_2O_7^{2-}$ when pH increases [61, 62]. The process of shifts is given by the following Eq (6-8):

$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^-$ (3-1)

$HCrO_4^{2-} \leftrightarrow H^+ + CrO_4^{2-}$ (3-2)

$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O$ (3-3)

It is found that the adsorption capacity was relatively low at pH 1. It may attributable to the strong competition between H_2CrO_4 and protons for adsorption sites. The adsorption efficiency of Cr(VI) increased with the increase of pH, and reached maximum at pH 5 (80%). It is considered that the ($-NH_2$) in the adsorbent may be protonated to form ($-NH_3^+$) at pH 2-6. The surface of hybrid membrane become positively-charged due to strong protonation at these pH range, which leads to a stronger attraction between the positively-charged surface and the negatively-charged $Cr_2O_7^{2-}$and $HCrO_4^-$. Then protonation will enhance the Cr(VI) adsorption at pH 5-6. However, at higher pH, Cr may precipitate from the solution as its hydroxides. Hence, pH5 was considered as optimum pH for further work.

3. 4. 3 Effect of Contact Time

Adsorption experiments were performed in order to determine the optimum contact time at pH5 under the condition of the concentration of Cr(VI) for 50 $mg \cdot dm^{-3}$, and the dosage of the adsorbent for 0.2 $g \cdot dm^{-3}$. The experimental results are shown in Fig 3-14. It can be observed that the adsorption capacity of Cr(VI) increases with increasing time within 60 min. The removal rate for Cr(VI) reached approximately 80% at 60 min, and after that there is no appreciable increase Then, 60 min was selected as the optimized contact time.

3. 4. 4 Effect of Hybrid Membrane Dosage

In order to estimate the optimal dosage of the hybrid membrane, the adsorption experiments were carried out with the range of 0.05- 0.3g·dm^{-3} for the adsorbent under the optimum conditions of pH (pH 5) and contact time (60 min), and the concentration of Cr(VI) for 50 mg·dm^{-3}. The results are shown in Fig 3-15. The results indicate that the adsorption capacity of hybrid membrane for Cr(VI) reached adsorption equilibrium at the dosage of 0.25 g·dm^{-3}, and that no significant change is observed at a dosage from 0.2 to 0.3 g·dm^{-3}. The removal rate reached about 80% at 0.25 g·dm^{-3}, and 0.25 g·dm^{-3} was selected as the optimal dosage.

3. 4. 5 Effect of Initial Concentration

The experiments were performed by varying concentrations from 10 to 50 mg·dm^{-3} under optimized condition of pH (pH 5) and contact time (60 min) with adsorbent dosage (0.25 g·dm^{-3}). The results are shown in Fig 3-16. There was a slight increase from 20 to 50 mg·dm^{-3} except at the concentrations of 30 mg·dm^{-3}. The initial concentrations was taken as 40 mg·dm^{-3}. Data from these studies were fitted to the Langmuir and Freundlich isotherm equations.

3. 4. 6 Adsorption Isotherms

In this work, Langmuir and Freundlich isotherms were investigated in order to evaluate the performance of adsorbents in adsorption processes.

The adsorption data obtained for Cr(VI) using the hybrid membrane were analyzed by Langmuir (Fig 3-17) and Freundlich equations (Fig 3-18). The correlation coefficient (R^2) of Langmuir and Freundlich isotherms for Cr(VI) using the hybrid membrane is shown in Table 3-3 along with other relevant parameters.

The maximum adsorption capacity (q_{max}) calculated from Langmuir model was 80.7 mg·g^{-1}. Based on Table 3-3, it is found that R^2 value of Langmuir isotherm is larger than that of Freundlich isotherm. This result suggests that the adsorption of Cr(VI) on the hybrid membrane of carboxymethyl chitosan and silicon dioxide mainly occurred by monolayer reaction.

The comparison of maximum adsorption capacity of the hybrid membrane of carboxymethyl chitosan and silicon dioxide for Cr(VI) in present study with that of another adsorbents in literatures are presented in Table 3-4. As seen in Table 3-4, the adsorption capacity of the hybrid membrane for Cr(VI) in this work is on a level with that of another adsorbents in previous works.

3. 4. 7 Kinetic Studies

Kinetic models were tested in this study for the adsorption of Cr(VI) onto the hybrid membrane under the optimized experimental conditions. Adsorption time is one of the important factors which help us to predict kinetics as well as the mechanism of the uptake of heavy metals on material surface [63].

The results for rate constant (k) and the amount of adsorbed Cr(VI) (q_e) are shown in Table 3-5 along with the regression coefficients (R^2). From Table 3-5, it is found that R^2 value of the pseudo second-order is larger than that of pseudo first-order, therefore, the pseudo second-order kinetic model provided more comparable than the pseudo first-order model.

Then, the linear plot of t/qt versus t for Cr(VI) adsorption system is shown in Fig

3-19. It implies that the adsorption kinetics based on the experimental values is in good agreement with the pseudo second-order kinetic model, and that the rate constant of second-order equation (*k*) are 3.4×10^{-2} $g \cdot mg^{-1} \cdot h^{-1}$ in this work.

3. 4. 8 Adsorption Mechanism of Cr(VI) by the hybrid membrane

Novel adsorbent for Cr(VI) was synthesized by carboxymethyl chitosan and silicon dioxide. The hybrid membrane has carboxymethyl, free amino group and hydroxyl groups on its surface as the adsorption site. It can remove Cr(VI) by forming stable metal chelates, and the porous structure of hybrid membrane enhance the adsorption capacity of Cr(VI).

From the kinetic studies, it is found that the pseudo second-order model provided more comparable, the pseudo second-order model implies that the adsorption process for Cr(VI) was mainly chemical, and that the adsorption process involves the valency forces through sharing electrons between the metal ions and adsorbent.

Moreover, the adsorption isotherm of Cr(VI) by the hybrid membrane was more suitably described by Langmuir model, indicating that monolayer adsorption of Cr(VI) on the hybrid membrane is more dominant.

3. 4. 9 Regeneration Studies

From industrial and technological point of view, it is desirable to recover and reuse the adsorbed material. Then, regeneration experiments were conducted using the hybrid membrane after adsorption of Cr(VI) at pH 13.5. In each desorption experiment, 75 mg of the spent adsorbent after adsorption was treated with 200ml of 0.5 $mol \cdot dm^{-3}$ NaOH and 2 $mol \cdot dm^{-3}$ NaCl solution as desorption agent, and then filtered. Cr(VI) content in the filtrate was determined by ICP-AES. Adsorption and desorption studies have been continued during five cycles at room temperature for 4 hours as eluent. The adsorption capacity after desorption using the above leaching agents are shown in Fig 3-20. From this figure, it is found that the hybrid membrane still present the high adsorption capacity (74.6%) towards Cr(VI) within 3 cycles.

3. 5 Conclusions

The efficiency of hybrid membrane of chitosan and silicon dioxide as an adsorbent for Cr(VI) was investigated. According to these studies, the following conclusions were clarified:

(1) The optimal conditions of adsorption Cr(VI) using hybrid membrane of chitosan and silicon dioxide are determined. The optimal pH is pH 3; the optimal contact time is 80 min; the optimal dosage is 2.0g.dm^{-3} and 40ppm was considered as optimum initial concentration.

(2) The hybrid membrane exhibited high adsorption capacity for Cr(VI). The removal of Cr(VI) was 78.7% under this optimal experimental conditions.

(3) Cr(VI) adsorption using hybrid membrane of chitosan and silicon dioxide conforms to the Langmuir isotherm adsorption equation, and the correlation coefficients are more than 0.98. The maximum adsorption capacity of Cr(VI) calculated by Langmuir model was 2.1×10^{-2} mg·g^{-1}.

(4) The best fit was obtained with a pseudo-second order kinetic model while investigating the adsorption kinetics.

The present study investigated the efficiency of the hybrid membrane synthesized from carboxymethyl chitosan and silicon dioxide as an adsorbent for Cr(VI) by batch techniques. The following conclusions can be drawn considering the results of this work.

(5) The hybrid membrane exhibited high adsorption capacity for Cr(VI). The removal of Cr(VI) was more than 80% under the optimal experimental conditions (at

pH 5, contact time of 60 min, dosage of 0.25 g.dm^{-3} and initial Cr(VI) concentration of 40 mg·dm^{-3}).

(6) The adsorption isotherm of Cr(VI) by the hybrid membrane of carboxymethyl chitosan and silicon dioxide was more suitably described by Langmuir model, and the correlation coefficients were more than 0.998. It suggests that monolayer chemical adsorption of Cr(VI) on the hybrid membrane is more dominant. The maximum adsorption capacity was estimated as 80.7 mg·g^{-1} for Cr(VI) under the optimum conditions. The adsorption capacity of the hybrid membrane for Cr(VI) in this work is on a level with that of another adsorbents in previous works.

(7) The best fit was obtained with a pseudo-second order kinetic model while investigating the adsorption kinetics of Cr(VI) adsorption on the hybrid membrane, and the correlation coefficients was more than 0.9. The rate constant (*k*) are 3.4×10^{-2} g·mg^{-1}·h^{-1}.

According to the above conclusions, the results show that it was quantitatively clarified to some extent that hybrid membrane of chitosan - silicon dioxide and carboxymethyl chitosan - silicon dioxide can be an efficient adsorbent for Cr(VI), It is very significant information from the viewpoint of environmental protection, and can be used for treating industrial wastewaters including pollutants.

Tables

Table 3-1 Coefficient of Langmuir and Freundlich isotherms for Cr(VI) using hybrid membrane of chitosan and silicon dioxide

	Langmuir isotherm			Freundlich isotherm		
	q_{max} [mg·g^{-1}]	K_L [dm^{-3}·mg^{-1}]	R^2	K_F [(mg·g^{-1})·(dm^{-3}·µg^{-1})$^{1/n}$]	$1/n$	R^2
Hybrid membrane	21.2	1.32-01	0.985	3.21	0.78	0.912

Table 3-2 The pseudo second-order kinetic coefficient for Cr(VI) using hybrid membrane of chitosan and silicon dioxide

	q_e (mg·g^{-1})	k (g·mol^{-1}·h^{-1})	R
Cr(VI)	0.106	1.17×10^{-3}	0.996

Table 3-3 Coefficient of Langmuir and Freundlich isotherms for Cr(VI) using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

	Langmuir isotherm			Freundlich isotherm		
Hybrid membrane	q_{max} [mg·g^{-1}]	K_L [dm^{-3}·mg^{-1}]	R^2	K_F [(mg·g^{-1})·(dm^{-3}·mg^{-1})$^{1/n}$]	$1/n$	R^2
	80.7	0.531	0.998	56.7	0.0834	0.867

Table 3-4: Comparison of adsorption capacity for Cr(VI) by different adsorbents.

Adsorbent	Adsorption capacity (mg·g^{-1})	References
Cross-linked chitosan bentonite composite	89.1	[64]
Chitosan/polyvinyl alcohol/containing cerium(III)	52.9	[5]
STAC-modified rectorite	21.0	[65]
Ethylenediamine-modified cross-linked magnetic chitosan	51.8	[60]
Clarified sludge	26.3	[66]
A novel modified graphene oxide/chitosan	86.2	[67]
Chitosan-g-poly/silicagel nanocomposite	55.7	[68]
Hybrid membrane of carboxymethyl chitosan and silicon dioxide	80.7	This study

Table 3-5 The kinetic coefficient for Cr(VI) using hybrid membrane of carboxymethyl chitosan and silicon dioxid

Cr(VI)	pseudo-first-order			pseudo-second-order		
	q_e (mg·g^{-1})	K_1 (h^{-1})	R^2	q_e (mg·g^{-1})	K_2	R^2
	79.7	8.91	0.924	94.4	3.42×10^{-2}	0.990

Figures

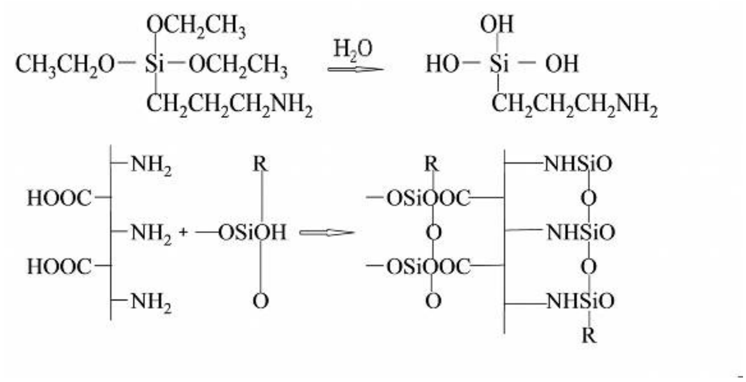


Fig 3-1 The reaction principle of the carboxymethyl chitosan crosslinking with 3-Aminopropyltriethoxysilane.

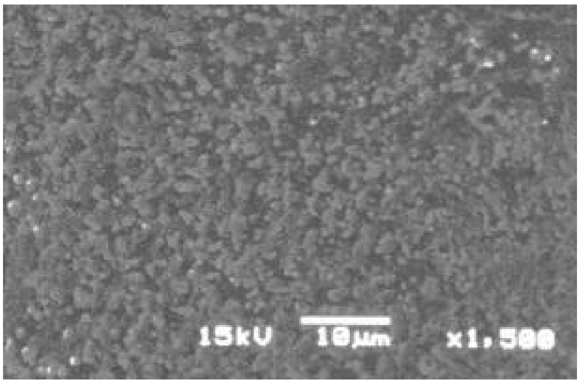


Fig. 3-2 SEM pictures of hybrid membrane of chitosan and silicon dioxide

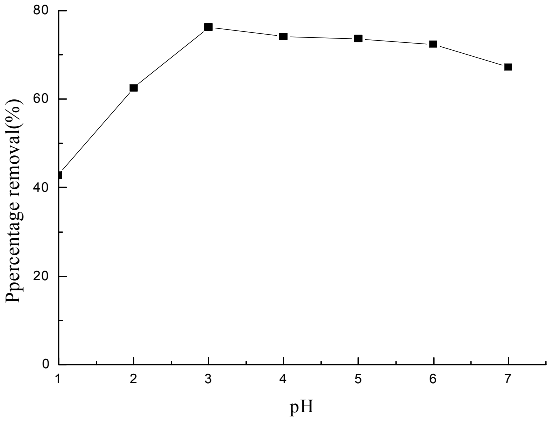


Fig. 3-3 Effect of pH on percent removal of Cr(VI) using hybrid membrane of chitosan and silicon dioxide

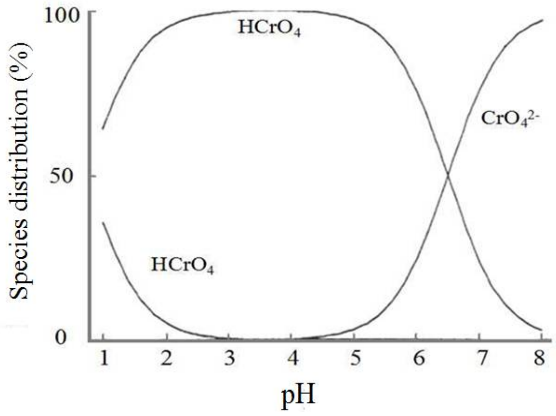


Fig. 3-4 Species distribution curves of Cr(VI) in environmental water

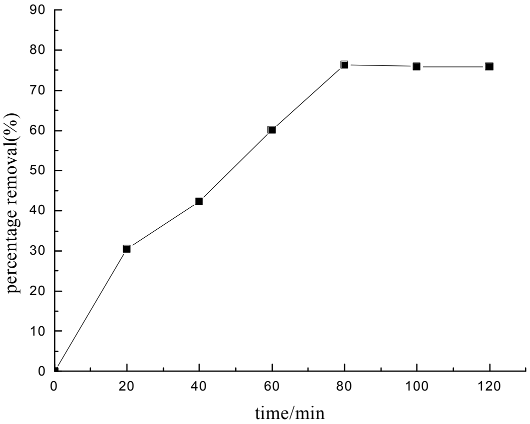


Fig. 3-5 Effect of contact time on percent removal of Cr(VI) using hybrid membrane of chitosan and silicon dioxide

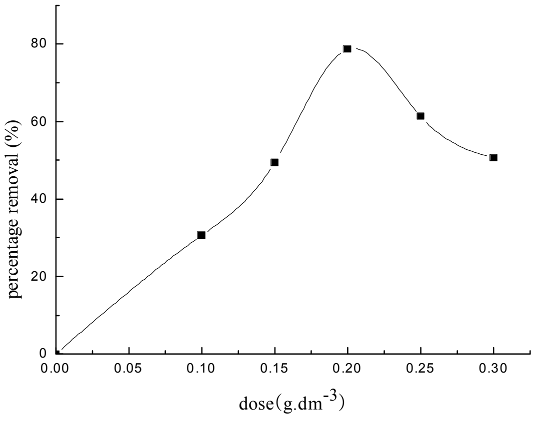


Fig. 3-6 Effect of dose on percent removal of Cr(VI) using hybrid membrane of chitosan and silicon dioxide

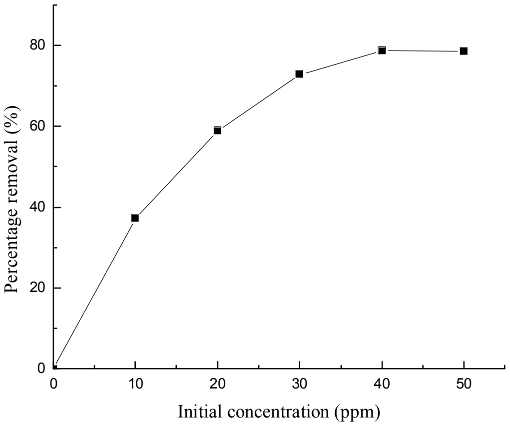


Fig. 3-7 Effect of initial concentration on percent removal of Cr(VI) using hybrid membrane of chitosan and silicon dioxide

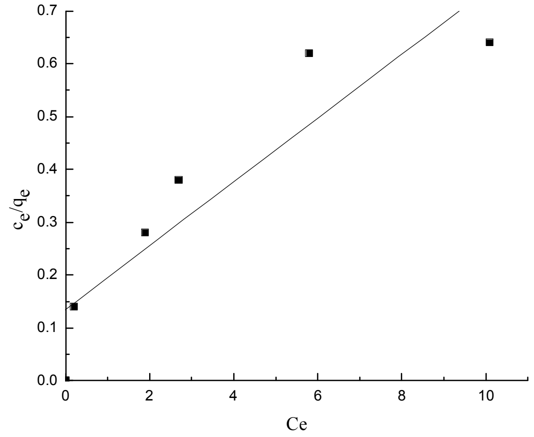


Fig. 3-8 Langmiur isotherm of Cr(VI) adsorption onto hybrid membrane of chitosan and Silicon dioxide

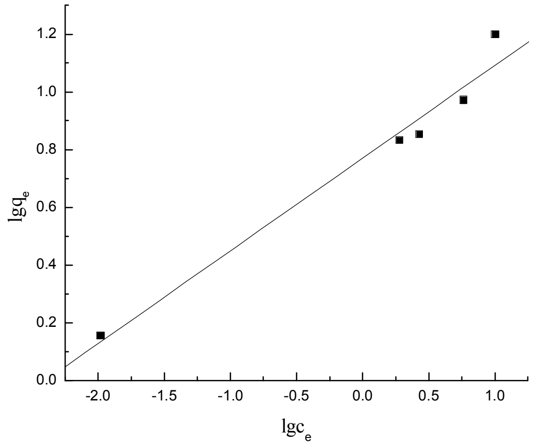


Fig. 3-9 Freundlich isotherm of Cr(VI) adsorption onto hybrid membrane of chitosan and Silicon dioxide

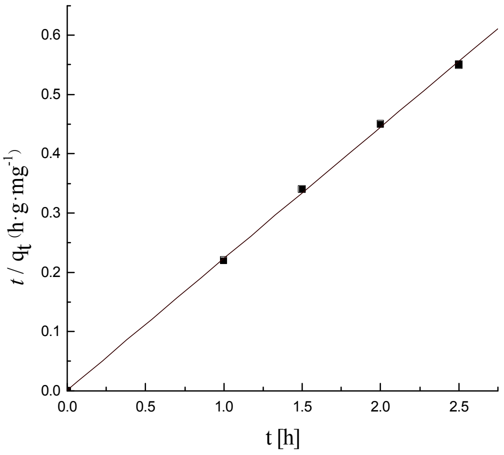


Fig. 3-10 The pseudo second-order kinetic model on hybrid membrane of chitosan and silicon dioxide

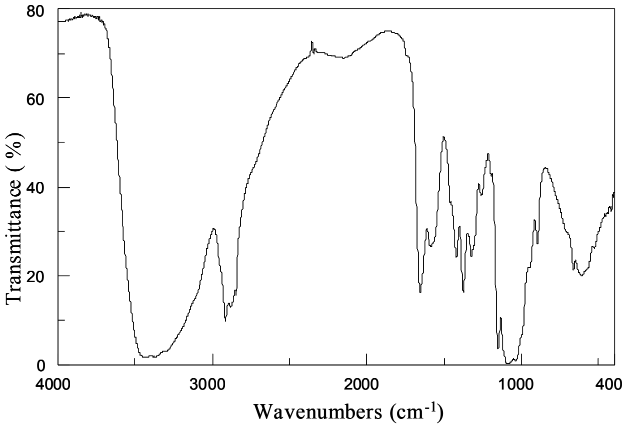


Fig. 3-11 FTIR spectra of hybrid membrane of carboxymethyl chitosan and silicon dioxide.

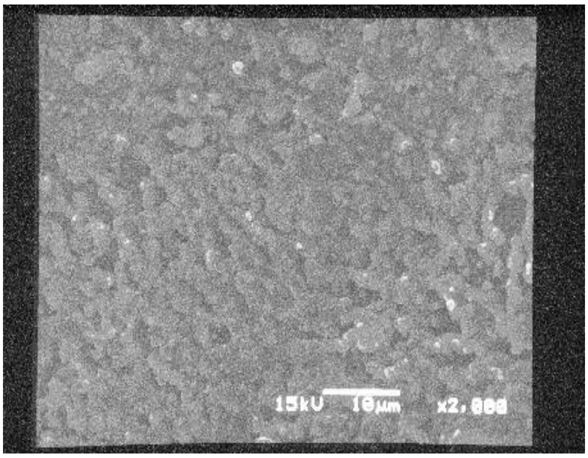


Fig. 3-12 SEM pictures of hybrid membrane of carboxymethyl chitosan and silicon dioxide.

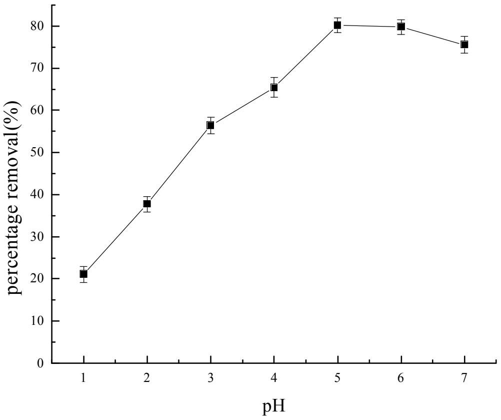


Fig. 3-13 Effect of pH for Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

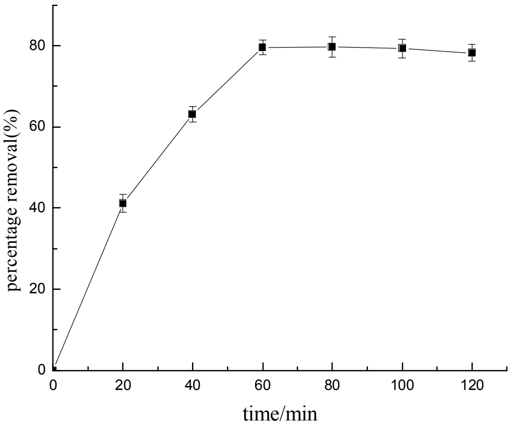


Fig. 3-14 Effect of contact time for Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

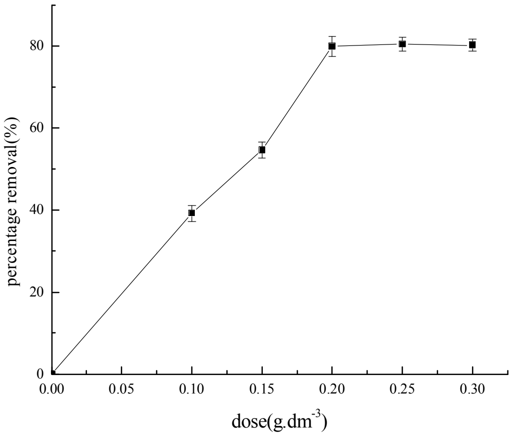


Fig. 3-15 Effect of dosage of adsorbent for Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

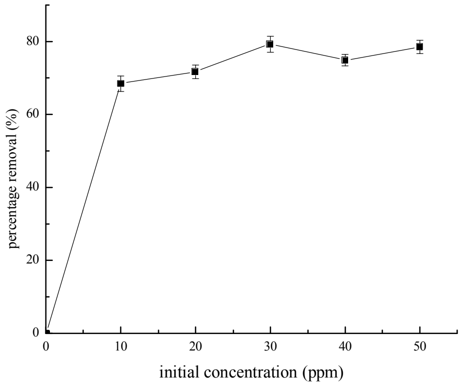


Fig. 3-16 Effect of initial concentration for Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

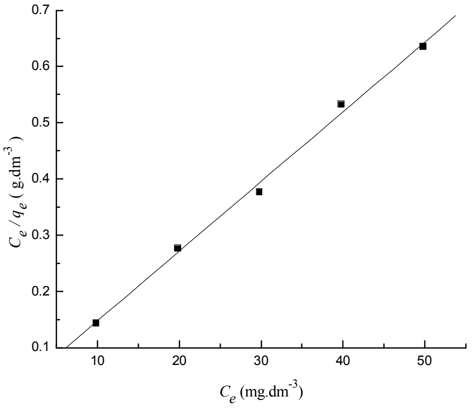


Fig. 3-17 Langmiur isotherm of Cr (VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

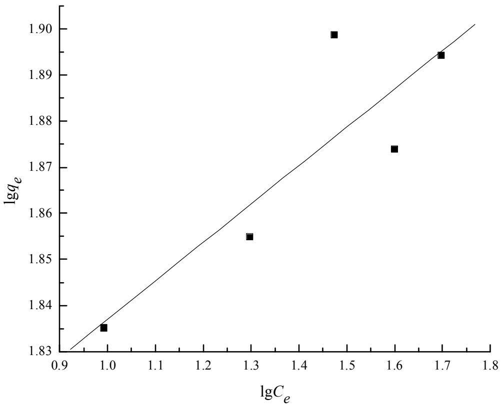


Fig. 3-18 Freundlich isotherm of Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxid

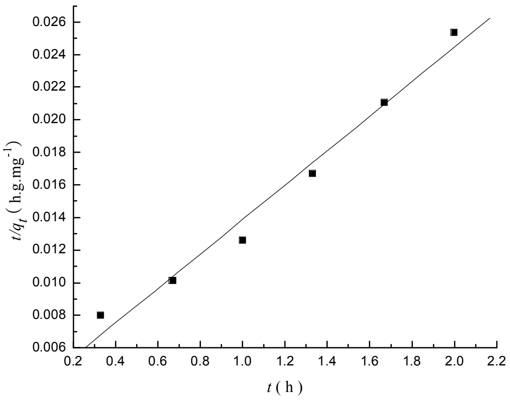


Fig. 3-19 The pseudo second-order kinetic model of Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

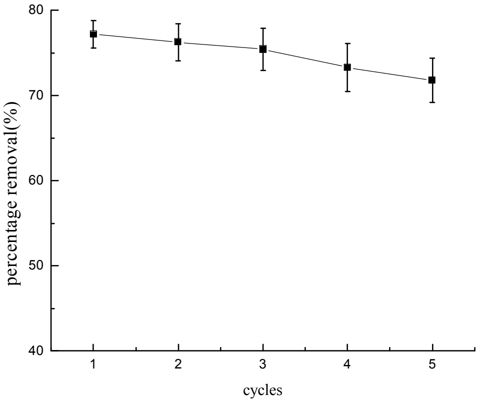


Fig. 3-20 The adsorption capacity after desorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide for Cr (VI).

Chapter 4 Conclusions

The various materials have been synthesized for removal Cr from aqueous solutions. The efficiency of Yukitsubaki carbon, hybrid membrane of chitosan - silicon dioxide and hybrid membrane of carboxymethyl chitosan - silicon dioxide as adsorbent for Cr by batch techniques were investigated. To understand the adsorption process, adsorption isotherms of Langmuir and Freundlich were investigated under the optimal conditions.In addition, the process of kinetic study is very important for understanding the reaction process and the rate of adsorption reactions. According to these studies, the following conclusions 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 9.96×10^{-2} $mg \cdot g^{-1}$, respectively.

(4) The hybrid membrane exhibited high adsorption capacity for Cr(VI). The removal of Cr(VI) was 78.7% under this optimal experimental conditions.

(5) Cr(VI) adsorption using hybrid membrane of chitosan and silicon dioxide conforms to the Langmuir isotherm adsorption equation, and the correlation coefficients are more than 0.98. The maximum adsorption capacity of Cr(VI) calculated by Langmuir model was 2.1×10^{-2} $mg \cdot g^{-1}$.

(6) The hybrid membrane exhibited high adsorption capacity for Cr(VI). The removal of Cr(VI) was more than 80% under the optimal experimental conditions.

(7) The adsorption isotherm of Cr(VI) by the hybrid membrane of chitosan - silicon dioxide and hybrid membrane of carboxymethyl chitosan - silicon dioxide were more suitably described by Langmuir model. It suggests that monolayer chemical adsorption of Cr.

(8) All the best fit were obtained with a pseudo-second order kinetic model while investigating the adsorption kinetics of Cr(VI) adsorption on the Yukitsubaki carbon, hybrid membrane of chitosan - silicon dioxide and carboxymethyl chitosan - silicon dioxide.

According to the above conclusions, the results show that it was quantitatively clarified to some extent that Yukitsubaki carbon, hybrid membrane of chitosan - silicon dioxide and carboxymethyl chitosan - silicon dioxide can be an efficient adsorbent for Cr(VI), it is very significant information from the viewpoint of environmental protection, and can be used for treating industrial wastewaters including pollutants.

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