

Research Article

Adsorption of Cr(VI) onto Hybrid Membrane of Carboxymethyl Chitosan and Silicon Dioxide

Yanling Deng,¹ Naoki Kano,² and Hiroshi Imaizumi²

¹Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan

²Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Niigata 950-2181, Japan

Correspondence should be addressed to Naoki Kano; kano@eng.niigata-u.ac.jp

Received 24 December 2016; Revised 23 February 2017; Accepted 22 March 2017; Published 12 April 2017

Academic Editor: Khalid Z. Elwakeel

Copyright © 2017 Yanling Deng et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this study, a new adsorbent material was synthesized by using carboxymethyl chitosan and silicon dioxide. The hybrid membrane was used as an adsorbent 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 (FTIR). 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 results provide new insight, demonstrating that the modified hybrid membrane can be an efficient adsorbent for Cr(VI) from the aqueous solution.

1. Introduction

The environmental conservation is of increasing social and economic importance. One of the intractable environmental problems is water pollution by heavy metals [1]. Heavy metals in the environmental water have been a major preoccupation for many years because of their toxicity towards aquatic life, human beings, and the environment [2].

Among the toxic metals, chromium has been reported to be toxic to animals and humans, and it is known to be carcinogenic [3, 4]. 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. It is highly toxic as it can diffuse as CrO_4^{2-} or HCrO_4^- through cell membranes [5]. The effluents are discharged onto the open land or into the sewage system. These industries are major sources of chromium pollution in the environment [6].

Due to serious hazardous effects of heavy metal ions on human health and toxicity in the environment [7], 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 the environment and the human life.

Various treatment technologies such as ion exchange, precipitation, ultrafiltration, reverse osmosis, and electrodialysis have been used for the removal of heavy metal ions from aqueous solution [8]. However, these processes have some disadvantages, such as high consumption of reagent and energy, low selectivity, and high operational cost [9].

Many works for the removal of heavy metals by adsorption have been reported [10–12]. Particularly, the development of high efficiency and low cost adsorbents has aroused general interest in recent years.

Chitosan, whose 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 [10]. Therefore, many types of chemical modification can be undertaken to produce some chitosan derivatives for improving the removal efficiency of the heavy metal [13]. 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 [14, 15]. In case of silicon dioxide, the modified silicon dioxide through the graft between silanol groups and ligands has been developed [16–18].

Therefore, we have investigated the efficiency of the hybrid membrane of chitosan and silicon dioxide as sorbent for Cr(VI) [19]. 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 of heavy metal ions compared with the disposable adsorbent.

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

2. Experimental

2.1. Materials, Reagent, and Apparatus. 3-Aminopropyltriethoxysilane was purchased from Nacal 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 ($1,005 \text{ mg}\cdot\text{dm}^{-3} \text{ K}_2\text{Cr}_2\text{O}_7$ 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 ($>18.2 \text{ M}\Omega$ 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 was measured by the pH meter (HORIBA UJXT 06T8, Japan). The surface property of the hybrid membrane of carboxymethyl chitosan and silicon dioxide was characterized by a SEM (JEOL, JSM-5800, Japan) and Fourier transform infrared spectroscopy in pressed KBr pellets (FTIR-4200, Jasco, Japan). The concentrations of Cr(VI) in the solution were determined by ICP-AES (inductively coupled plasma atomic emission spectrometry).

2.2. Prepared Carboxymethyl Chitosan. Under alkaline conditions, chitosan can react with chloroacetic acid to obtain the carboxymethyl chitosan. 5 g of chitosan was accurately weighed into a round-bottomed flask containing 75 ml isopropanol and 25 ml ultrapure water, and then 6.75 g of

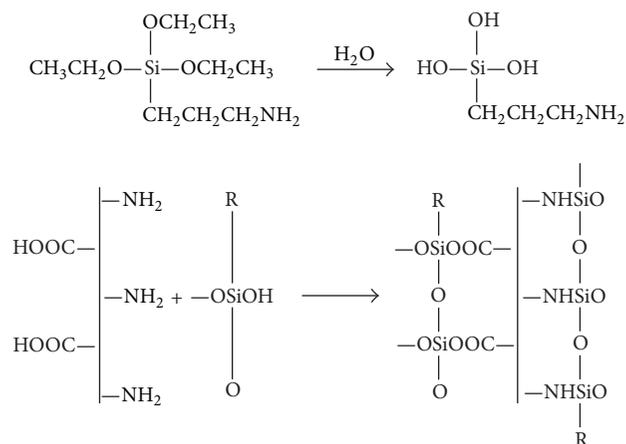


FIGURE 1: The reaction principle of the carboxymethyl chitosan crosslinking with 3-Aminopropyltriethoxysilane.

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 continuing stirring for 4 h. 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 4 h. The solution was adjusted to neutral using hydrochloric acid, 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 the preparation of hybrid membrane.

2.3. The Prepared Hybrid Membrane of Carboxymethyl Chitosan and Silicon Dioxide. The reaction process of hybrid membrane synthesized from carboxymethyl chitosan and silicon dioxide is shown in Figure 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 to the solution of carboxymethyl chitosan (3%, w/v) at 25°C , and the solution was stirred for 24 h. The hybrid membrane was dried at 25°C .

2.4. Adsorption Experiment of Cr(VI) Using Hybrid Membrane of Carboxymethyl Chitosan and Silicon Dioxide. The adsorption of Cr(VI) using hybrid membrane was studied by a batch method with various pH range of 1–7, contact time range of 20–120 min, sorbent dosage range from 0.05 to $0.3 \text{ g}\cdot\text{dm}^{-3}$, and initial concentrations range of 10 – $50 \text{ mg}\cdot\text{dm}^{-3}$.

Firstly, 50 ml solution of Cr(VI) was placed into a 200 ml conical flask. During the uptake experiment, the pH of the Cr(VI) solution was adjusted using $0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaOH}$ or $0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ HCl}$. The concentration of Cr(VI) was determined by ICP-AES. Adsorption isotherms of Cr(VI) using the hybrid membrane were studied with varying initial concentrations under optimum experiment conditions.

The adsorption capacity of hybrid membrane for Cr(VI) was calculated using the mass balance equation:

$$q_e = \frac{(C_i - C_e)}{m} \cdot V, \quad (1)$$

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

2.5. Langmuir and Freundlich Isotherm Model. To understand the adsorption process of Cr(VI) using the hybrid membrane, adsorption isotherms of Langmuir and Freundlich were investigated under the optimal conditions.

Langmuir isotherm equation is defined as follows:

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

where C_e is the concentration of Cr(VI) at equilibrium ($\text{mg}\cdot\text{dm}^{-3}$), q_e and q_{\max} are the amount of adsorption of Cr(VI) at equilibrium ($\text{mg}\cdot\text{g}^{-1}$) and the maximum adsorption capacity by the hybrid membrane ($\text{mg}\cdot\text{g}^{-1}$), respectively, K_L ($\text{dm}^{-3}\cdot\text{mg}^{-1}$) is the adsorption constant of Langmuir isotherm.

The linearized Freundlich isotherm equation is defined as follows:

$$\log_{10} q_e = \log_{10} K_F + \left(\frac{1}{n}\right) \log_{10} C_e. \quad (3)$$

In this equation, K_F is the adsorption capacity ($(\text{mg}\cdot\text{g}^{-1})\cdot(\text{dm}^{-3}\cdot\text{mg}^{-1})^{1/n}$) and $1/n$ 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.

2.6. 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 the adsorption reactions.

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

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t, \quad (4)$$

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

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

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{t}{q_e}, \quad (5)$$

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

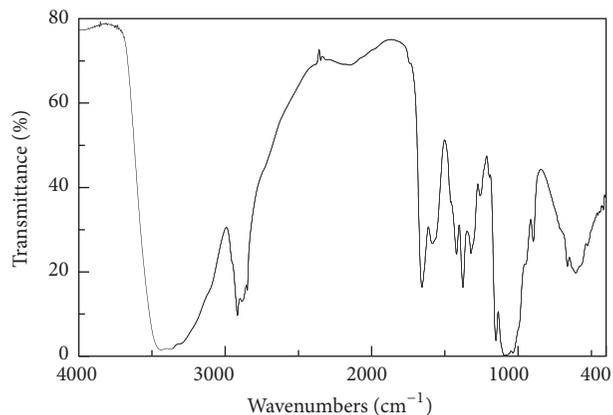


FIGURE 2: FTIR spectra of hybrid membrane of carboxymethyl chitosan and silicon dioxide.

3. Results and Discussion

3.1. Characteristics of the Hybrid Membrane of Carboxymethyl Chitosan and Silicon Dioxide. The FTIR spectroscopy is an important technique of characterization used to explain the changes in the 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 Figure 2. The strong broadband at the wave number region of $3300\text{--}3500\text{ cm}^{-1}$ is the characteristic of -NH_2 stretching vibration, and the bands at 3400 cm^{-1} are related to the symmetrical valent vibration of free NH_2 and -OH groups [27]. The -CH stretching vibration in -CH and -CH_2 was 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^+ [28]). A strong C=O stretching band at 1655 cm^{-1} may be related to the carboxymethyl group. Other bands at 1090 cm^{-1} are related to Si-O-Si valent vibrations [10]. The results of FTIR analysis show that the hybrid membrane of carboxymethyl chitosan and silicon dioxide was 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 Figure 3. 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.

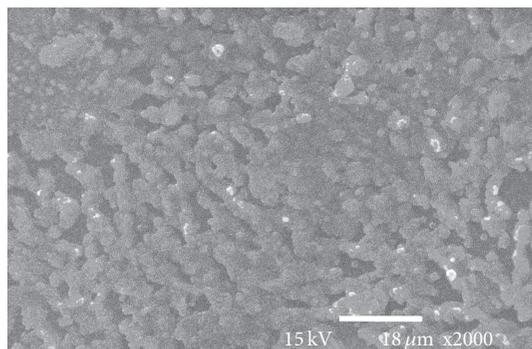


FIGURE 3: SEM pictures of hybrid membrane of carboxymethyl chitosan and silicon dioxide.

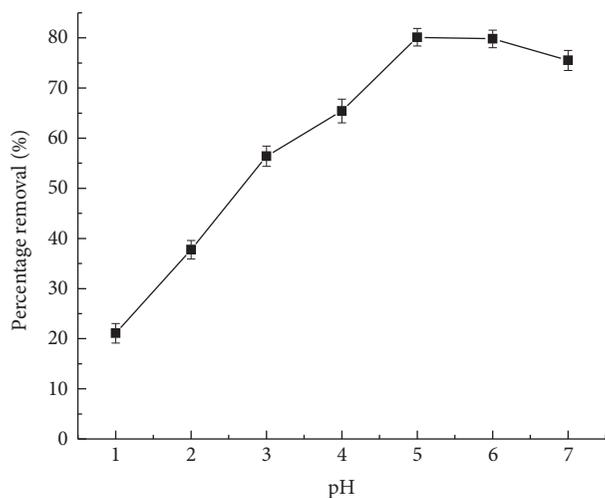


FIGURE 4: Effect of pH for Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

3.2. 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 $50 \text{ mg}\cdot\text{dm}^{-3}$, the contact time of 120 min, and the dosage of the adsorbent for $0.2 \text{ g}\cdot\text{dm}^{-3}$.

The effect of pH on the removal of Cr(VI) using the hybrid membrane is shown in Figure 4.

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) exists in a variety of forms with different pH, and it exists in the form of H_2CrO_4 at pH 1.0 [23] and different forms such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, and $\text{Cr}_4\text{O}_{13}^{2-}$, while HCrO_4^- predominates at the pH range from 2.0 to 6.0. Furthermore, this form shifts to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ when pH increases [29, 30]. The process of shifts is given by the following equations:

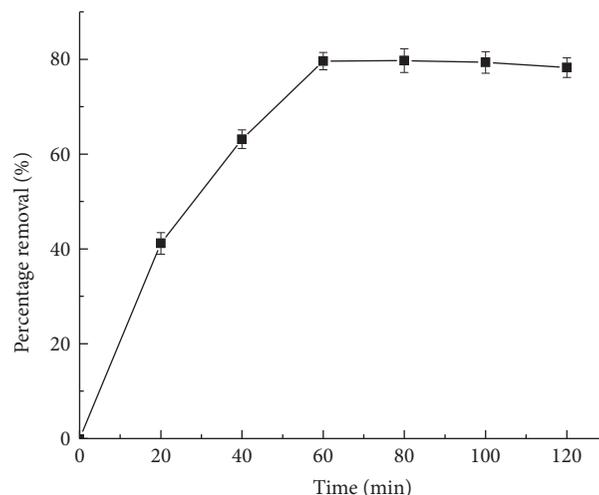
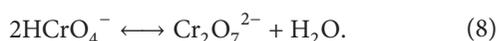


FIGURE 5: Effect of contact time for Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

It is found that the adsorption capacity was relatively low at pH 1. It may be 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 the maximum at pH 5 (80%). It is considered that the $(-\text{NH}_2)$ in the adsorbent may be protonated to form $(-\text{NH}_3^+)$ at pH 2–6. The surface of the hybrid membrane became positively charged due to the strong protonation at these pH ranges, which leads to a stronger attraction between the positively charged surface and the negatively charged $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- . Then, the 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, pH 5 was considered as the optimum pH for further work.

3.3. Effect of Contact Time. Adsorption experiments were performed in order to determine the optimum contact time at pH 5 under the condition of the concentration of Cr(VI) for $50 \text{ mg}\cdot\text{dm}^{-3}$ and the dosage of the adsorbent for $0.2 \text{ g}\cdot\text{dm}^{-3}$. The experimental results are shown in Figure 5. 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. 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 $0.05\text{--}0.3 \text{ g}\cdot\text{dm}^{-3}$ for the adsorbent under the optimum conditions of pH (pH 5) and contact time (60 min) and the concentration of Cr(VI) for $50 \text{ mg}\cdot\text{dm}^{-3}$. The results are shown in Figure 6. The results indicate that the adsorption capacity of hybrid membrane for Cr(VI) reached the adsorption equilibrium at the dosage of $0.25 \text{ g}\cdot\text{dm}^{-3}$ and that no significant change is observed at a dosage from

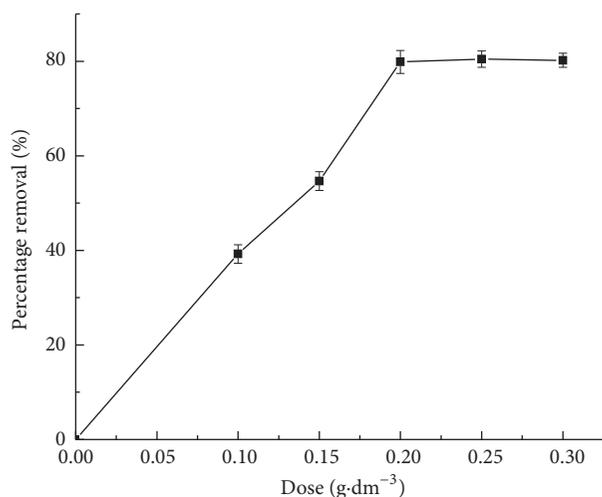


FIGURE 6: Effect of dosage of adsorbent for Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

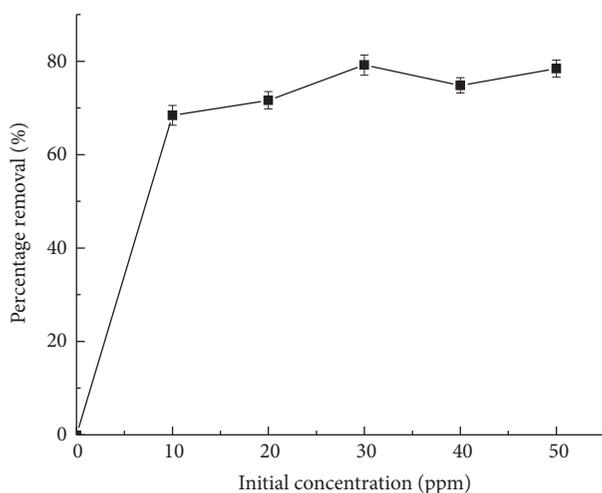


FIGURE 7: Effect of initial concentration for Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

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.

3.5. 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 Figure 7. There was a slight increase from 20 to 50 mg·dm⁻³ except at the concentrations of 30 mg·dm⁻³. The initial concentrations were taken as 40 mg·dm⁻³. The data from these studies were fitted to the Langmuir and Freundlich isotherm equations.

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

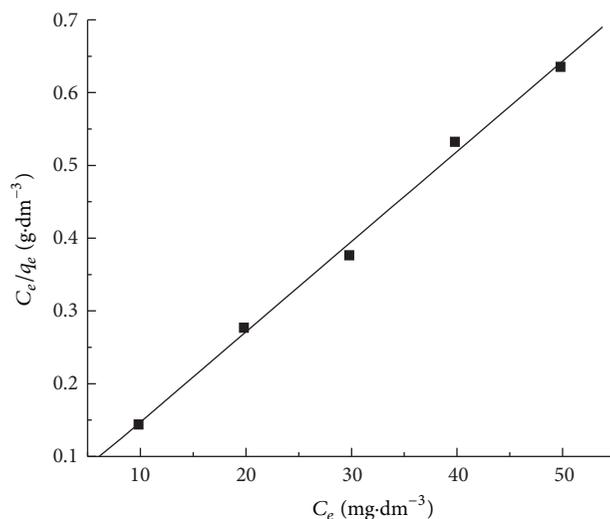


FIGURE 8: Langmuir isotherm of Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

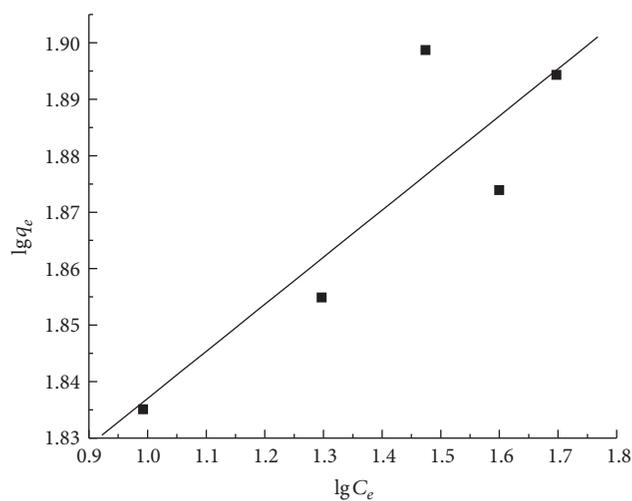


FIGURE 9: Freundlich isotherm of Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

The adsorption data obtained for Cr(VI) using the hybrid membrane were analyzed by Langmuir (Figure 8) and Freundlich (Figure 9) equations. The correlation coefficient (R^2) of Langmuir and Freundlich isotherms for Cr(VI) using the hybrid membrane is shown in Table 1 along with other relevant parameters.

The maximum adsorption capacity (q_{\max}) calculated from Langmuir model was 80.7 mg·g⁻¹. Based on Table 1, 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 the maximum adsorption capacity of the hybrid membrane of carboxymethyl chitosan and silicon dioxide for Cr(VI) in the present study with that of other

TABLE 1: Coefficient of Langmuir and Freundlich isotherms for Cr(VI) using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

q_{\max} [mg·g ⁻¹]	Hybrid membrane				
	Langmuir isotherm		Freundlich isotherm		
	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 2: Comparison of adsorption capacities for Cr(VI) by different adsorbents.

Adsorbent	Adsorption capacity (mg·g ⁻¹)	References
Crosslinked chitosan bentonite composite	89.1	[20]
Chitosan/polyvinyl alcohol/containing cerium(III)	52.9	[21]
STAC-modified rectorite	21.0	[22]
Ethylenediamine-modified crosslinked magnetic chitosan	51.8	[23]
Clarified sludge	26.3	[24]
A novel modified graphene oxide/chitosan	86.2	[25]
Chitosan-g-poly/silica gel nanocomposite	55.7	[26]
Hybrid membrane of carboxymethyl chitosan and silicon dioxide	80.7	This study

adsorbents in literatures [20–26] is presented in Table 2. As seen in Table 2, 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.

3.7. 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 the kinetics as well as the mechanism of the uptake of heavy metals on material surface [31].

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

Then, the linear plot of t/qt versus t for Cr(VI) adsorption system is shown in Figure 10. 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 the second-order equation (k) is 3.4×10^{-2} g·mg⁻¹·h⁻¹ in this work.

3.8. Adsorption Mechanism of Cr(VI) by the Hybrid Membrane. The novel adsorbent for Cr(VI) was synthesized by using 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 the hybrid membrane enhances the adsorption capacity of Cr(VI).

From the kinetic studies, the adsorption reaction was found to conform to the pseudo-second-order kinetics, suggesting the importance of porous structure. This implies that the adsorption process for Cr(VI) was mainly chemical

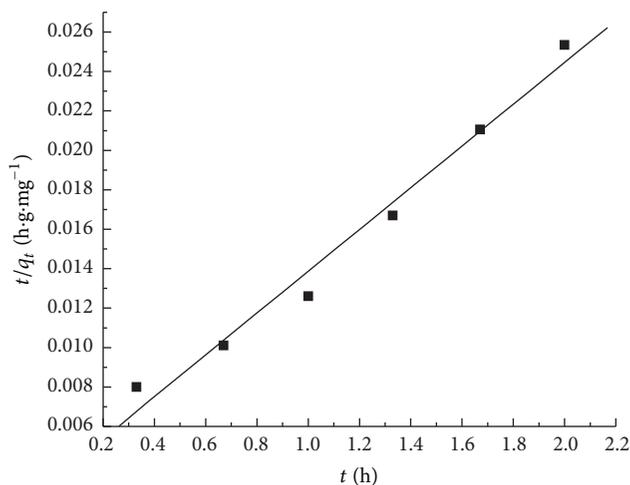


FIGURE 10: The pseudo-second-order kinetic model of Cr(VI) adsorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

and that the adsorption process involves the valency forces through sharing electrons between the metal ions and the 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.

3.9. 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 200 ml of 0.5 mol·dm⁻³ NaOH and 2 mol·dm⁻³ NaCl solution as desorption agent

TABLE 3: The kinetic coefficient for Cr(VI) using hybrid membrane of carboxymethyl chitosan and silicon dioxide.

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

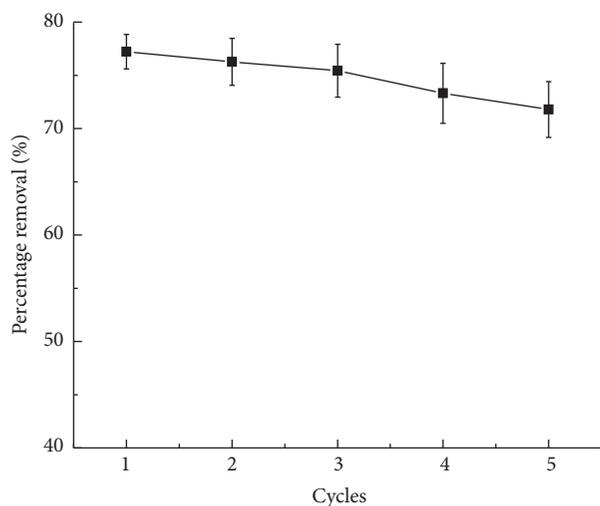


FIGURE 11: The adsorption capacity after desorption using hybrid membrane of carboxymethyl chitosan and silicon dioxide for Cr(VI).

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 is shown in Figure 11. From this figure, it is found that the hybrid membrane still presents the high adsorption capacity (74.6%) towards Cr(VI) within 3 cycles.

4. Conclusions

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:

- (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. This 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 other 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 coefficient was more than 0.9. The rate constant (k) is 3.4×10^{-2} g·mg⁻¹·h⁻¹.
- (4) 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.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

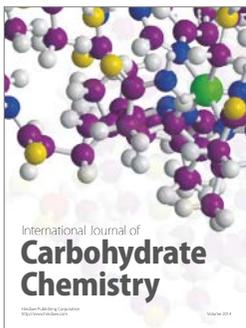
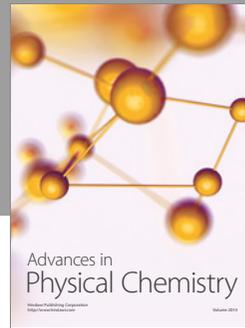
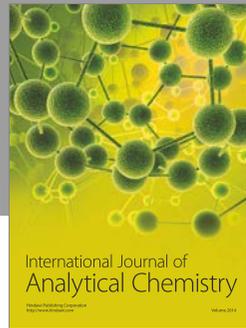
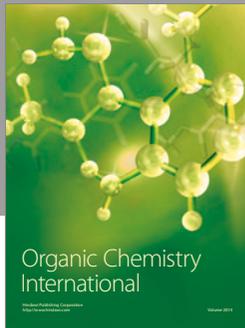
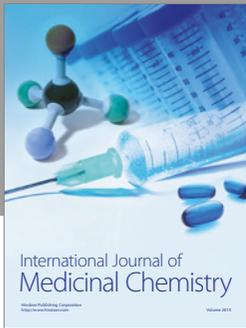
Acknowledgments

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (Research Program (C), no. 16K00599) and a fund for the promotion of Niigata University KAAB Projects from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors are also grateful to Mr. M. Ohizumi of Office for Environment and Safety in Niigata University and to Dr. M. Teraguchi, Mr. T. Nomoto, and Professor T. Tanaka of Faculty of Engineering in Niigata University for permitting the use of ICP-AES, FTIR, and SEM and for giving helpful advice in measurement.

References

- [1] Y. Sağ and Y. Aktay, "Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and *Rhizopus arrhizus*," *Biochemical Engineering Journal*, vol. 12, no. 2, pp. 143–153, 2002.
- [2] N. Chiron, R. Guilet, and E. Deydier, "Adsorption of Cu(II) and Pb(II) onto a grafted silica: isotherms and kinetic models," *Water Research*, vol. 37, no. 13, pp. 3079–3086, 2003.
- [3] C. Raji and T. S. Anirudhan, "Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics," *Water Research*, vol. 32, no. 12, pp. 3772–3780, 1998.
- [4] E. Demirbas, M. Kobya, E. Senturk, and T. Ozkan, "Adsorption kinetics for the removal of chromium (VI) from aqueous

- solutions on the activated carbons prepared from agricultural wastes," *Water SA*, vol. 30, no. 4, pp. 533–539, 2004.
- [5] N. Sankaramakrishnan, A. Dixit, L. Iyengar, and R. Sanghi, "Removal of hexavalent chromium using a novel cross linked xanthated chitosan," *Bioresource Technology*, vol. 97, no. 18, pp. 2377–2382, 2006.
- [6] S. A. Khan, Riaz-ur-Rehman, and M. A. Khan, "Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite," *Waste Management*, vol. 15, no. 4, pp. 271–282, 1995.
- [7] Z. Guo, D. Li, X. Luo et al., "Simultaneous determination of trace Cd(II), Pb(II) and Cu(II) by differential pulse anodic stripping voltammetry using a reduced graphene oxide-chitosan/poly-L-lysine nanocomposite modified glassy carbon electrode," *Journal of Colloid and Interface Science*, vol. 490, no. 5, pp. 11–22, 2017.
- [8] F. Fu and Q. Wang, "Removal of heavy metal ions from wastewaters: a review," *Journal of Environmental Management*, vol. 92, no. 3, pp. 407–418, 2011.
- [9] M. M. Montazer-Rahmati, P. Rabbani, A. Abdolali, and A. R. Keshtkar, "Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae," *Journal of Hazardous Materials*, vol. 185, no. 1, pp. 401–407, 2011.
- [10] E. Repo, J. K. Warchoř, A. Bhatnagar, and M. Sillanpää, "Heavy metals adsorption by novel EDTA-modified chitosan-silica hybrid materials," *Journal of Colloid and Interface Science*, vol. 358, no. 1, pp. 261–267, 2011.
- [11] R. M. Ali, H. A. Hamad, M. M. Hussein, and G. F. Malash, "Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis," *Ecological Engineering*, vol. 91, pp. 317–332, 2016.
- [12] J.-H. Park, Y. S. Ok, S.-H. Kim et al., "Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions," *Chemosphere*, vol. 142, pp. 77–83, 2016.
- [13] A. J. Varma, S. V. Deshpande, and J. F. Kennedy, "Metal complexation by chitosan and its derivatives: a review," *Carbohydrate Polymers*, vol. 55, no. 1, pp. 77–93, 2004.
- [14] P. Michard, E. Guibal, T. Vincent, and P. Le Cloirec, "Sorption and desorption of uranyl ions by silica gel: pH, particle size and porosity effects," *Microporous Materials*, vol. 5, no. 5, pp. 309–324, 1996.
- [15] H. H. Tran, F. A. Roddick, and J. A. O'Donnell, "Comparison of chromatography and desiccant silica gels for the adsorption of metal ions—I. Adsorption and kinetics," *Water Research*, vol. 33, no. 13, pp. 2992–3000, 1999.
- [16] L. Bois, A. Bonhommé, A. Ribes, B. Pais, G. Raffin, and F. Tessier, "Functionalized silica for heavy metal ions adsorption," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 221, no. 1–3, pp. 221–230, 2003.
- [17] P. K. Jal, S. Patel, and B. K. Mishra, "Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions," *Talanta*, vol. 62, no. 5, pp. 1005–1028, 2004.
- [18] M. Rajiv Gandhi and S. Meenakshi, "Preparation and characterization of silica gel/chitosan composite for the removal of Cu(II) and Pb(II)," *International Journal of Biological Macromolecules*, vol. 50, no. 3, pp. 650–657, 2012.
- [19] Y. Deng, N. Kano, and H. Imaizumi, "Removal of chromium from aqueous solution using hybrid membrane of chitosan and silicon dioxide," *Journal of Chemistry and Chemical Engineering*, vol. 10, no. 5, pp. 199–206, 2016.
- [20] Q. Liu, B. Yang, L. Zhang, and R. Huang, "Adsorptive removal of Cr(VI) from aqueous solutions by cross-linked chitosan/bentonite composite," *Korean Journal of Chemical Engineering*, vol. 32, no. 7, pp. 1314–1322, 2015.
- [21] F. F. Wang and M. Q. Ge, "Fibrous mat of chitosan/polyvinyl alcohol/containing cerium(III) for the removal of chromium(VI) from aqueous solution," *Textile Research Journal*, vol. 83, no. 6, pp. 628–637, 2013.
- [22] H. Hong, W.-T. Jiang, X. Zhang, L. Tie, and Z. Li, "Adsorption of Cr(VI) on STAC-modified rectorite," *Applied Clay Science*, vol. 42, no. 1–2, pp. 292–299, 2008.
- [23] X.-J. Hu, J.-S. Wang, Y.-G. Liu et al., "Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics," *Journal of Hazardous Materials*, vol. 185, no. 1, pp. 306–314, 2011.
- [24] A. K. Bhattacharya, T. K. Naiya, S. N. Mandal, and S. K. Das, "Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents," *Chemical Engineering Journal*, vol. 137, no. 3, pp. 529–541, 2008.
- [25] L. Zhang, H. Luo, P. Liu, W. Fang, and J. Geng, "A novel modified graphene oxide/chitosan composite used as an adsorbent for Cr(VI) in aqueous solutions," *International Journal of Biological Macromolecules*, vol. 87, pp. 586–596, 2016.
- [26] R. Nithya, T. Gomathi, P. N. Sudha, J. Venkatesan, S. Anil, and S.-K. Kim, "Removal of Cr(VI) from aqueous solution using chitosan-g-poly(butyl acrylate)/silica gel nanocomposite," *International Journal of Biological Macromolecules*, vol. 87, pp. 545–554, 2016.
- [27] G. N. Kousalya, M. Rajiv Gandhi, and S. Meenakshi, "Sorption of chromium(VI) using modified forms of chitosan beads," *International Journal of Biological Macromolecules*, vol. 47, no. 2, pp. 308–315, 2010.
- [28] D. Lin-Vien, N. B. Colthup, W. G. Fateley, and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Elsevier, Amsterdam, Netherlands, 1991.
- [29] T. Karthikeyan, S. Rajgopal, and L. R. Miranda, "Chromium(VI) adsorption from aqueous solution by Hevea Brasiliensis sawdust activated carbon," *Journal of Hazardous Materials*, vol. 124, no. 1–3, pp. 192–199, 2005.
- [30] M. Akram, H. N. Bhatti, M. Iqbal, S. Noreen, and S. Sadaf, "Biocomposite efficiency for Cr(VI) adsorption: kinetic, equilibrium and thermodynamics studies," *Journal of Environmental Chemical Engineering*, vol. 5, no. 1, pp. 400–411, 2017.
- [31] V.-P. Dinh, N.-C. Le, T.-P. Nguyen, and N.-T. Nguyen, "Synthesis of α -MnO₂ nanomaterial from a precursor γ -MnO₂: characterization and comparative adsorption of Pb(II) and Fe(III)," *Journal of Chemistry*, vol. 2016, Article ID 8285717, 9 pages, 2016.



Hindawi

Submit your manuscripts at
<https://www.hindawi.com>

