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Removal of Chromium from Aqueous Solution Using Hybrid Membrane of Chitosan and Silicon Dioxide

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Abstract: Adsorption experiment from aqueous solutions containing known amount of chromium (Cr) using hybrid membrane of chitosan and silicon dioxide was explored to evaluate the efficiency of the membrane as sorbent for Cr(VI). Some variable parameters such as pH, contact time and the dosage of the membrane were optimized. Adsorption isotherms of Cr(VI) onto the hybrid membrane were measured with varying initial concentrations under optimized condition. Furthermore, the sorption mechanism of Cr by the membrane was investigated by applying Langmuir and Freundlich isotherm equations to the data obtained. The surface morphology of the membrane was determined by SEM (scanning electron microscope) for material characterization. The concentrations of Cr in solution are determined by ICP-MS (inductively coupled plasma mass spectrometry). Hybrid membrane of chitosan and silicon dioxide can be an efficient sorbent for Cr(VI).

Key words: Hybrid membrane, chitosan, silicon dioxide, adsorption isotherms, kinetics.

1. Introduction

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]. The heavy metal contamination is a serious problem to the environment [2], and has become a challenge for life on earth because of the anthropogenic activities. The use of chromium 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 [3].

Particularly, Cr(VI) is the most toxic form, being carcinogenic and mutagenic to living organisms [4]. It leads to liver damage or pulmonary congestion, and causes skin irritation resulting in ulcer formation [5].

The typical mobile forms of Cr(VI) in natural environment are CrO_4^{2-}, $HCrO_4^-$ and H_2CrO_4. The relative distribution of each species depends on the solution pH, on the Cr(VI) concentration and on the redox potential [6]. 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. Cr(VI) must be substantially removed from the wastewater before being discharged into the aquatic system.

Different technologies for the removal of Cr(VI) 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 [7]. The major advantages of biosorption are its high effectiveness, easy operation, no two pollutions, and the use of inexpensive biosorbents.

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) [8-10].

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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 [11]. The biopolymer is characterized by its high percentage of nitrogen, existed in the form of amine groups that are responsible for metal ion binding through chelation mechanisms [12].

Silica gels are low-density solids, consisting of silicon oxide. The study of silica gels has attained considerable attention due to open mesoporous structure, high surface area, large pore volume and good performance as effective adsorbents [13]. 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 [14, 15].

Due to above-mentioned reason, novel materials were designed to combine the beneficial properties of silica gel and chitosan. In this paper, the adsorption potential of the hybrid material for Cr(VI) from aqueous solution was investigated under varying experimental conditions. Moreover, the surface morphology of the hybrid adsorbents was determined by SEM (scanning electron microscope) to characterize these materials.

2. Experimental Sections

2.1 Materials and Reagents

Chitosan was purchased 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), which was 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. The pH meter (HORIBA UJXT 06T8, Japan) was used for the measurement of pH.

The hybrid membrane of chitosan and silicon dioxide were characterized by a SEM (JEOL, JSM-5800, Japan). The samples were placed on a microgrid of silicon, and transferred to the analytical chamber in the equipment, an ICP-MS (inductively coupled plasma mass spectrometry) instrument (Thermo Fisher Scientific X2, Japan) was used to determine the concentration of Cr(VI).

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.

2.3 Sorption Experiment of Cr(VI) Using Hybrid Membrane of Chitosan and Silicon Dioxide

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 (20-120 min) 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.

The adsorption capacities of Cr(VI) using hybrid membrane of chitosan and silicon dioxide was calculated using the Eq. (1):

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

where q_e is the adsorption capacities of Cr(VI) using hybrid membrane of chitosan and silicon dioxide at equilibrium ($mg \cdot g^{-1}$), C_i and C_e are the initial and equilibrium concentrations of Cr(VI) in a batch system respectively ($mg \cdot dm^{-3}$), V is the volume of the solution (dm^3), and m is the dry weight of hybrid membrane of chitosan and silicon dioxide (g).

2.4 Langmuir and Freundlich Isotherm Model

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 metal ion (C_e) at equilibrium. Langmuir and Freundlich adsorption isotherms can be expressed, respectively, the Langmuir equation is defined as Eq. (2):

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

where, C_e and q_e are the concentration of Cr(VI) at equilibrium ($mg \cdot L^{-1}$) and the amount of adsorption of Cr(VI) at equilibrium ($mg \cdot g^{-1}$) respectively, q_{max} is the maximum adsorption capacity on the surface of hybrid membrane ($mg \cdot g^{-1}$), and K_L is the equilibrium adsorption constant ($L \cdot mg^{-1}$). A plot of C_e/q_e versus C_e gives a straight line with slope of $1/q_{max}$, and intercept is $1/(K_L q_{max})$.

The Freundlich isotherms equation is defined as Eq. (3):

$$\log_{10} q_e = \log_{10} K_F + (1/n) \log_{10} C_e \quad (3)$$

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

2.5 Kinetic Studies

The study of sorption kinetics in aqueous solution is important because it provides deep understanding of the reaction pathways and the mechanism of sorption reactions [16]. In the present study, the mechanism of the adsorption process was investigated by fitting pseudo first-order and second-order reactions to the experimental data.

The pseudo-first order rate equation is generally expressed as follows Eq. (4):

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

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

The pseudo-second order rate equation is expressed as Eq. (5):

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

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

3. Results and Discussion

3.1 Characteristics of Chitosan and Silicon Dioxide

The SEM pictures of hybrid membrane of chitosan and silicon dioxide are shown in Fig. 1. It can be observed that hybrid adsorbents exist in the form of particles. Rashidova et al. [17] 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. The hybrid adsorbents synthesized in this work also may contain free amino groups that are responsible for metal ion binding through chelation mechanisms.

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

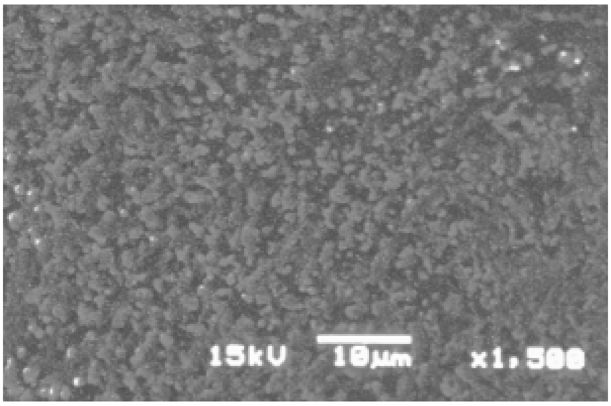

Fig. 1 SEM pictures of hybrid membrane of chitosan and silicon dioxide.

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. 2. The removal of Cr(VI) more than 76% was observed at pH 3. 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 [18]. 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 $HCrO_4^-$ [19, 20].

As shown in Fig. 3 taken from Irgolic et al. [21], 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-} [22]. Then, pH 3 was selected as the optimal pH for further work.

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. 4. The adsorption capacity of hybrid membrane for Cr(VI) reached adsorption equilibrium at 80 min, and after that there

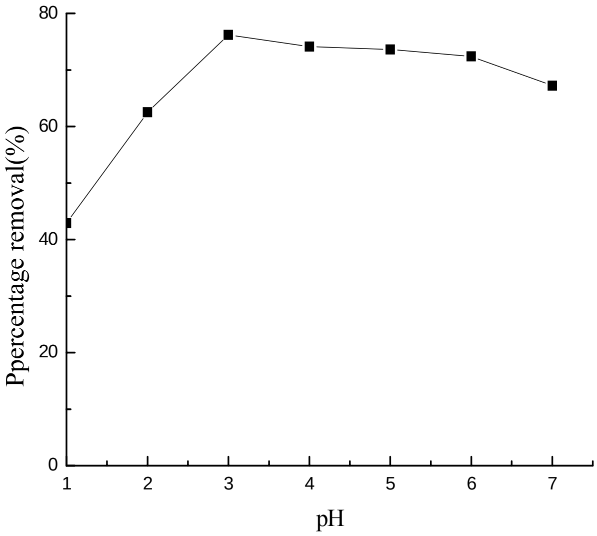

Fig. 2 Effect of pH on percent removal of Cr(VI) using hybrid membrane of chitosan and silicon dioxide.

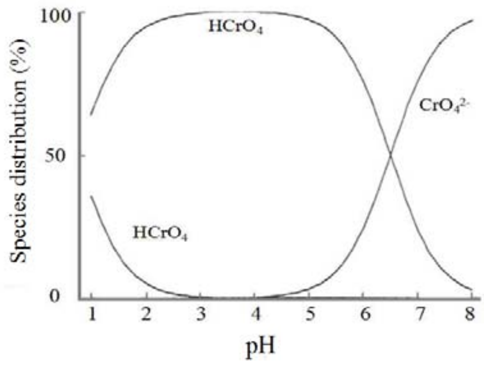

Fig. 3 Species distribution curves of Cr(VI) in environmental water.

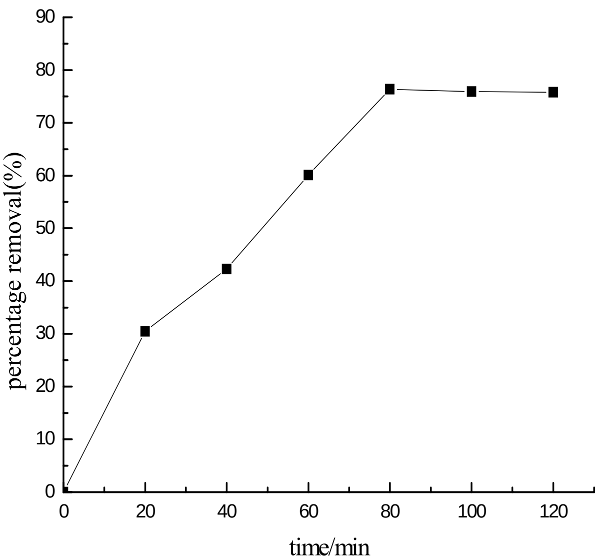

Fig. 4 Effect of contact time on percent removal of Cr(VI) using hybrid membrane of chitosan and silicon dioxide.

are a slight decrease due to the swelling properties of hybrid membrane absorbent. Therefore, the optimized contact time was selected for 80 min.

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·dm^{-3} to 0.3 g·dm^{-3} have been studied in 50 ppm of Cr(VI) solution.

The results are shown in Fig. 5. 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·dm^{-3}. Thus, 0.2 g·dm^{-3} was considered as optimized dose.

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 (i.e., 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. 6). The removal rate reached 78.7%. Then, 40 ppm was considered as optimum initial concentration for Cr(VI).

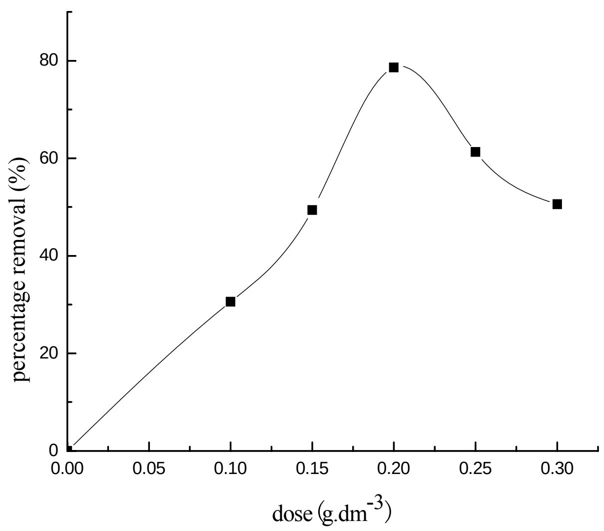

Fig. 5 Effect of dose on percent removal of Cr(VI) using hybrid membrane of chitosan and silicon dioxide.

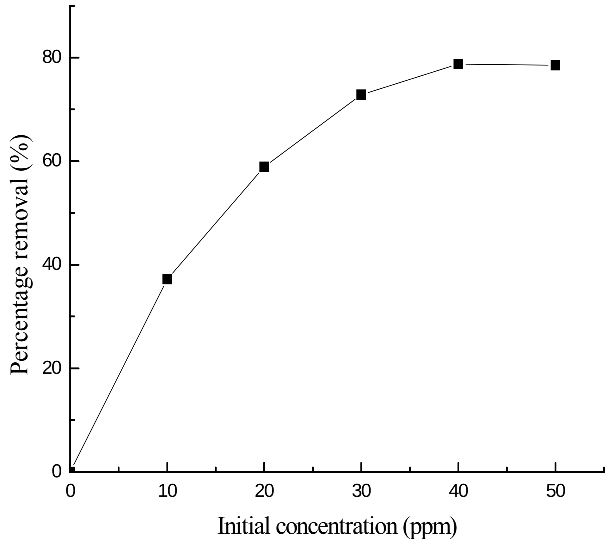

Fig. 6 Effect of initial concentration on percent removal of Cr(VI) using hybrid membrane of chitosan and silicon dioxide.

3.6 Adsorption Isotherms

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes [23]. 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. 7) and Freundlich equations (Fig. 8). The correlation coefficient (R^2) of these isotherms for Cr(VI) on the hybrid membrane is shown in Table 1 along with other relevant parameters. From Table 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.

3.7 Kinetic Studies

Kinetic models were tested in this study for the sorption of Cr(VI) onto the hybrid membrane of

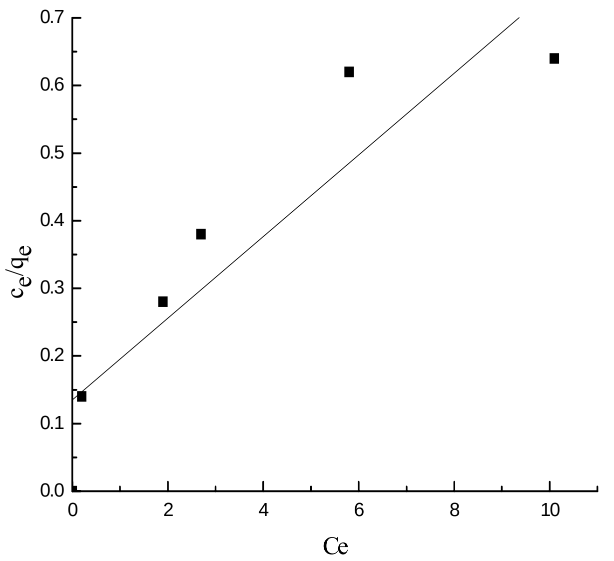

Fig. 7 Langmuir isotherm of Cr(VI) adsorption onto hybrid membrane of chitosan and Silicon dioxide.

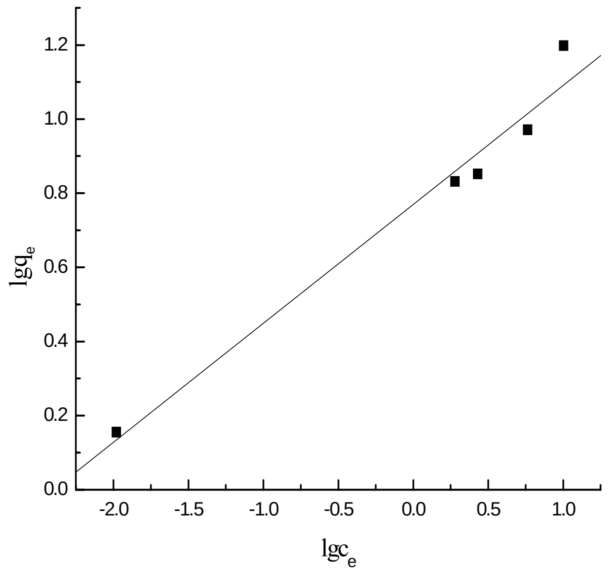

Fig. 8 Freundlich isotherm of Cr(VI) adsorption onto hybrid membrane of chitosan and Silicon dioxide.

Table 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	2.1E+02	1.32-01	0.985	3.21	0.78	0.912

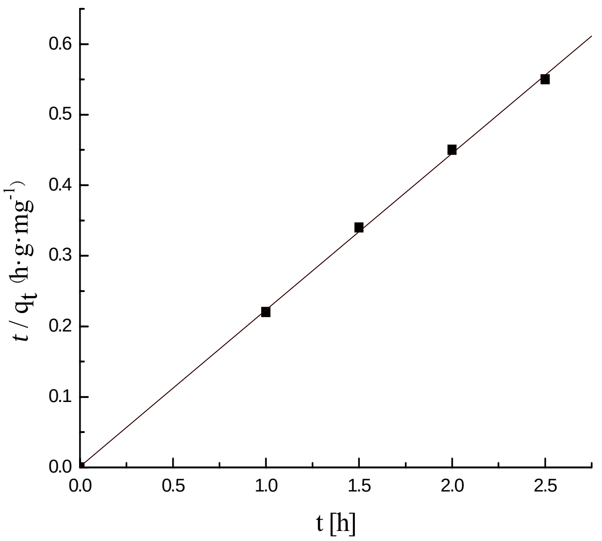

Fig. 9 The pseudo second-order kinetic model on hybrid membrane of chitosan and silicon dioxide.

Table 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

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. 9. Based on the data in Fig. 9, the pseudo second-order kinetic coefficients for Cr(VI) by the hybrid membrane are estimated (Table 2). The rate constant of second-order equation (k) diffusion is 1.17 × 10^{-2} g·mol^{-1}·h^{-1} for Cr(VI). The correlation coefficients (R^2) were 0.996 for Cr(VI) adsorption on the hybrid membrane.

4. 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 2.0 g·dm^{-3} and 40 ppm 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.

According to the above conclusions, the results show that it was quantitatively clarified to some extent that hybrid membrane of chitosan and silicon dioxide can be an efficient sorbent for Cr(VI), which provides important information for the management of water pollution problems.

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