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Carboxymethyl-Chitosan Cross-Linked 3-Aminopropyltriethoxysilane Membrane for Speciation of Toxic Chromium from Water

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Additional information is available at the end of the chapter

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Abstract

Adsorption of Cr(VI) from aqueous solution onto the nanomaterials prepared by modified chitosan was investigated in a batch system to evaluate the efficiency of biomass as an adsorbent. The crosslinking materials of chitosan & silicon dioxide and carboxymethyl chitosan & silicon dioxide were synthesized, respectively, as new adsorbent materials for the removal of Cr(VI) from aqueous solutions. The adsorption potential of Cr(VI) by the nanomaterials for desalination was investigated by varying experimental conditions such as pH, contact time and the dosage of the nanomaterials. Adsorption isotherms of Cr(VI) onto the membrane were studied with varying initial concentrations under optimum experiment conditions. The surface property of the 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 membrane of carboxymethyl chitosan & silicon dioxide exhibited higher adsorption capacity than the membrane of chitosan & silicon dioxide for Cr(VI). The adsorption sites and specific surface area may be increased by changing from chitosan to carboxymethyl chitosan. The maximum adsorption capacity was estimated as $80.7 \text{ mg} \cdot \text{g}^{-1}$ for Cr(VI) under the optimum conditions.

Keywords: nanomaterials, carboxymethyl chitosan, silicon dioxide, adsorption isotherms, kinetic model

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]. 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, reverse osmosis 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].

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 bioaccumulate 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. Among these heavy metals, Cr is one of the top priority list of toxic pollutants defined by the U.S. Environmental Protection Agency.

Cr mainly consists of two stable oxidation states such as trivalent state Cr(III) and hexavalent state Cr(VI) in natural aqueous environment [15]. Cr(VI) is more toxic, carcinogenic and mutagenic. The typical mobile forms of Cr(VI) in natural environment are CrO_4^{2-} , HCrO_4^- ; and 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 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2^+$, or Cr(III) organic complexes. 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. Cr(VI) can diffuse as CrO_4^{2-} or HCrO_4^- through cell membranes [18] leading to carcinogenic, mutagenic, liver damage, pulmonary congestion, and causes skin irritation resulting in ulcer formation to living organisms [19–22].

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

Different technologies for the removal of heavy metal ions are available such as chemical precipitation, coagulation, ion exchange, membrane technologies, and 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 biomaterials.

Chitosan has proven to be very efficient biosorbent for the removal of several toxic metals such as mercury (Hg), uranium (U), molybdenum (Mo), vanadium (V) and platinum (Pt) [24–26]. 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 is produced by the alkaline deacetylation of chitin, and the preparation process of chitosan is shown in **Figure 1**. Chitosan is the most abundant biopolymer in nature originated from cellulose that can be obtained from the shells of seafood such as prawns, crabs, and lobsters [27]. The biopolymer is characterized by its high content of nitrogen, and is existed in the form of amine groups, free amino groups and hydroxyl groups, which are 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 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 mesoporous 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 [34–36]. At present, an interest has grown in the field of organic and inorganic 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 adsorption materials were designed to combine the beneficial properties of silica gel and chitosan. The membrane of cross-linked chitosan with

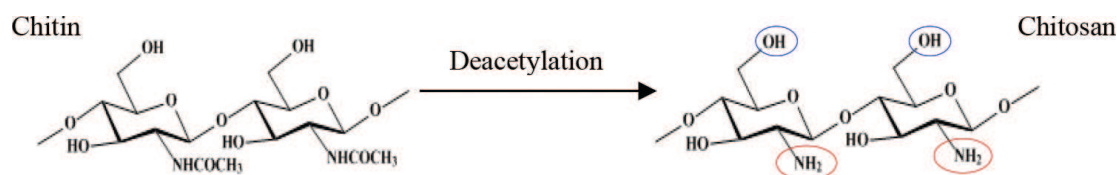


Figure 1. The preparation process of chitosan using chitin.

silicon dioxide was synthesized in this work to enhance the adsorption potential of heavy metal ions. Furthermore, carboxymethyl chitosan has been prepared by using chloroacetic acid (and chitosan) under alkaline conditions to improve the removal efficiency. Using the carboxymethyl chitosan, the membrane of carboxymethyl chitosan & silicon dioxide was also synthesized, and was employed to remove heavy metal ions from aqueous solution. In present study, the adsorption capacity of the membrane was investigated for the removal of toxic chromium ions from aqueous solution under varying experimental conditions.

Moreover, the surface morphology of the cross-linked membrane was determined to characterize these nanomaterials for desalination, and regeneration experiments were also conducted using the membrane.

2. Experimental sections

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 were measured by the pH meter (HORIBA UJXT 06 T8, Japan). The surface property of the membrane of carboxymethyl chitosan & 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).

2.2. Prepared the membrane of chitosan & silicon dioxide

The solution of chitosan (3%, w/v) was prepared by dissolving 3 g of chitosan in 100 ml of $0.2 \text{ mol} \cdot \text{dm}^{-3}$ 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 membrane of cross-linked chitosan with silicon dioxide was dried at 25°C .

2.3. Prepared the membrane of carboxymethyl chitosan & silicon dioxide

Under alkaline conditions, chitosan can react with chloroacetic acid to obtain the carboxymethyl chitosan. Chitosan (5 g) was accurately weighed 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 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, 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 membrane.

The reaction process of membrane synthesized from carboxymethyl chitosan & silicon dioxide is shown in **Figure 2**. 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 membrane of carboxymethyl chitosan & silicon dioxide was dried at 25°C.

2.4. Adsorption experiment of Cr(VI) using the membrane

The adsorption capacities of Cr(VI) from aqueous solution using the membrane were investigated by a batch method. The membrane 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 the membrane of chitosan & silicon dioxide were measured at varying initial Cr(VI) concentrations (10–50 ppm) under optimized conditions.

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

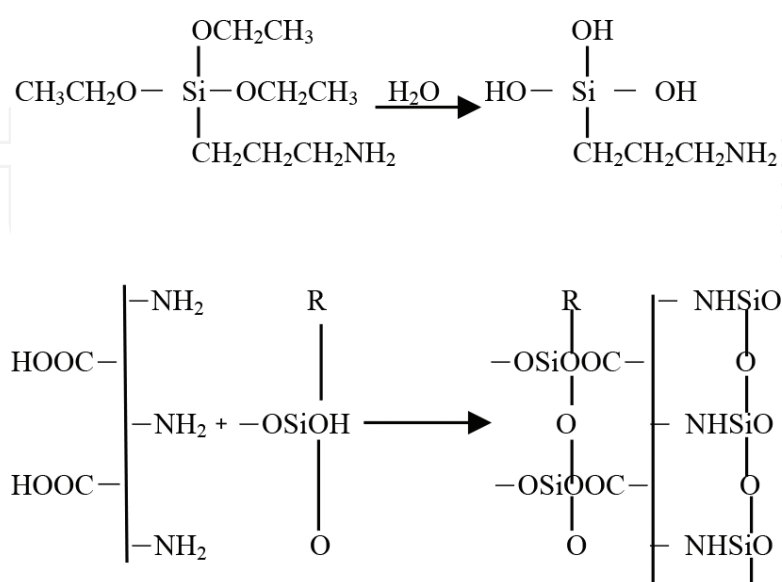


Figure 2. The reaction principle of the carboxymethyl chitosan crosslinked with 3-aminopropyltriethoxysilane.

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

where q_e is the adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$) of 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 ($\text{mg} \cdot \text{dm}^{-3}$), V (dm^{-3}) is the volume of the heavy metal solution, and m (g) is the mass of the adsorbents.

2.5. 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.

The 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 heavy metal ion at equilibrium ($\text{mg} \cdot \text{dm}^{-3}$), q_e and q_{\max} are the amount of adsorption of heavy metal ion at equilibrium ($\text{mg} \cdot \text{g}^{-1}$) and the maximum adsorption capacity by the adsorbents ($\text{mg} \cdot \text{g}^{-1}$) 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:

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

In this equation, K_F is the adsorption capacity [$(\text{mg} \cdot \text{g}^{-1}) \cdot (\text{dm}^{-3} \cdot \text{mg}^{-1})^{1/n}$], $1/n$ 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 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 heavy metal ion using the adsorbents 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:

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

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 heavy metal ion using the adsorbents at equilibrium and time t , respectively ($\text{mg} \cdot \text{g}^{-1}$).

3. Results and discussion

3.1. Characteristics of the cross-linked membrane

The SEM pictures of the membrane of cross-linked chitosan with silicon dioxide are shown in **Figure 3**. It can be observed that the nanomaterial exists in the form of particles. The theory of chitosan and silica network where chitosan moieties were combined through silica groups via both ionic and covalent bonds was proposed [38]. The adsorbents synthesized in this work also may contain free amino groups that are responsible for metal ion binding through chelation mechanisms.

The surface property of the membrane of carboxymethyl chitosan & silicon dioxide was also investigated by SEM, and SEM images are shown in **Figure 4**. The surface morphology of the 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 the 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

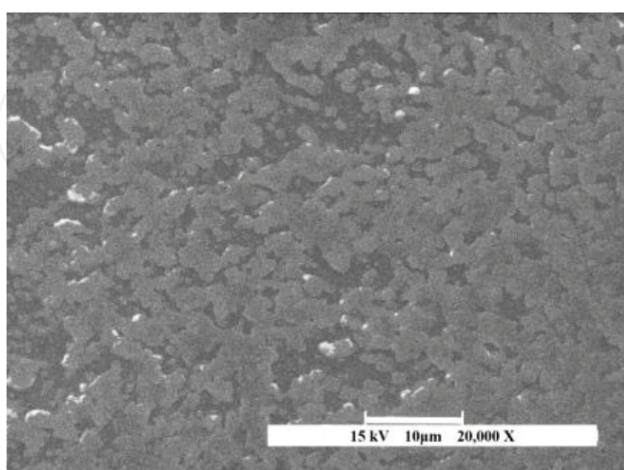


Figure 3. SEM pictures of the membrane of chitosan and silicon dioxide.

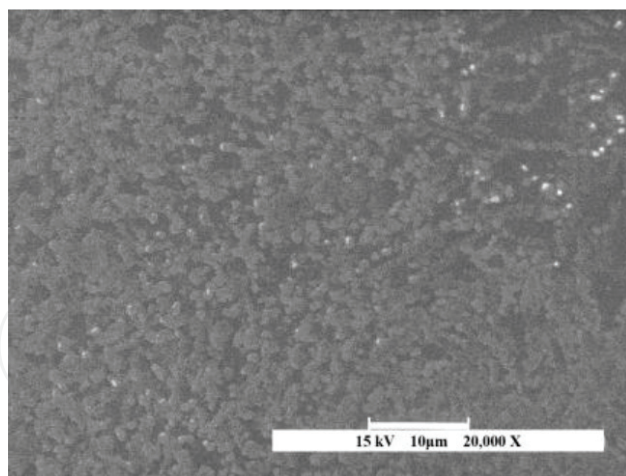


Figure 4. SEM pictures of the membrane of carboxymethyl chitosan and silicon dioxide.

complex precipitation. The molecule also may contain free amino groups and hydroxyl groups, which can remove the heavy metal ions by chelation mechanisms.

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 membrane of carboxymethyl chitosan & silicon dioxide are presented in **Figure 5**. The strong broad band at the wave number region of $3300\text{--}3500\text{ cm}^{-1}$ 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. The --CH stretching vibration in --CH and --CH_2 were observed at 2916 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 membrane may be explained by the presence of primary amine salt --NH_3^+ [39]). A strong C=O stretching band at 1655 cm^{-1} may be related to the carboxymethyl group. Others bands at 1090 cm^{-1} are

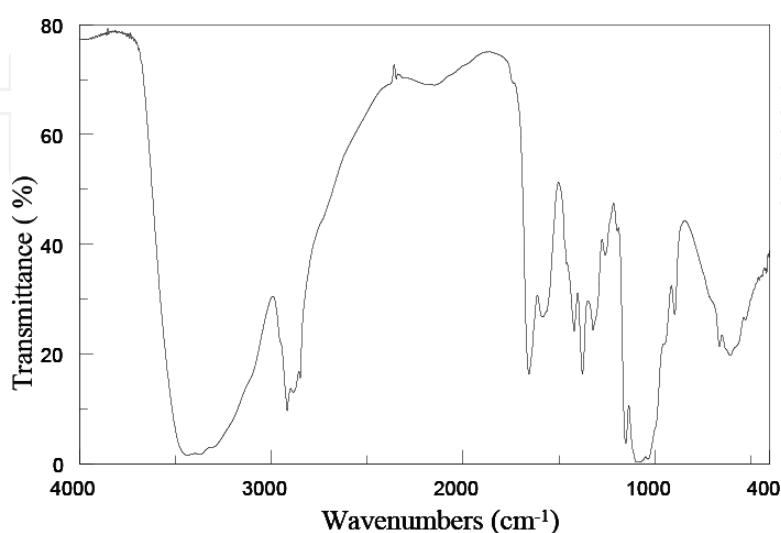


Figure 5. FTIR spectra of membrane of carboxymethyl chitosan & silicon dioxide.

related to Si-O-Si valent vibrations. The results of FTIR analysis show that the membrane of carboxymethyl chitosan & silicon dioxide were prepared successfully in this study.

3.2. Effect of parameters on adsorption

3.2.1. Effect of pH

For obtaining the optimum conditions regarding the adsorption of Cr(VI) onto the membrane, 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 100 or 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 these membranes are shown in **Figures 6 and 7** (**Figure 6**: chitosan & silicon dioxide, **Figure 7**: carboxymethyl chitosan & silicon dioxide).

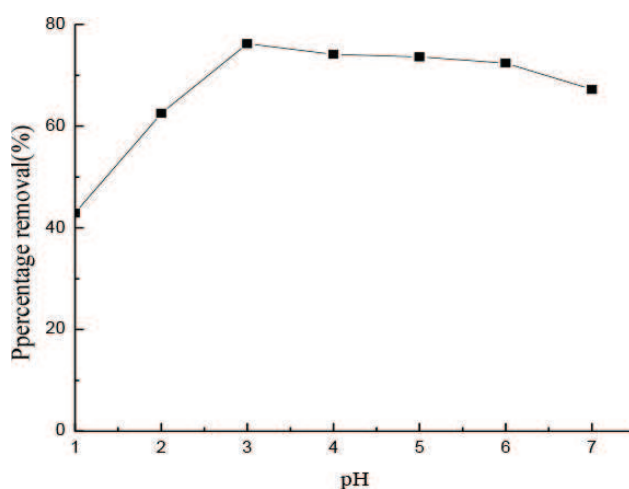


Figure 6. Effect of pH on the removal of Cr(VI) using the membrane of chitosan & silicon dioxide.

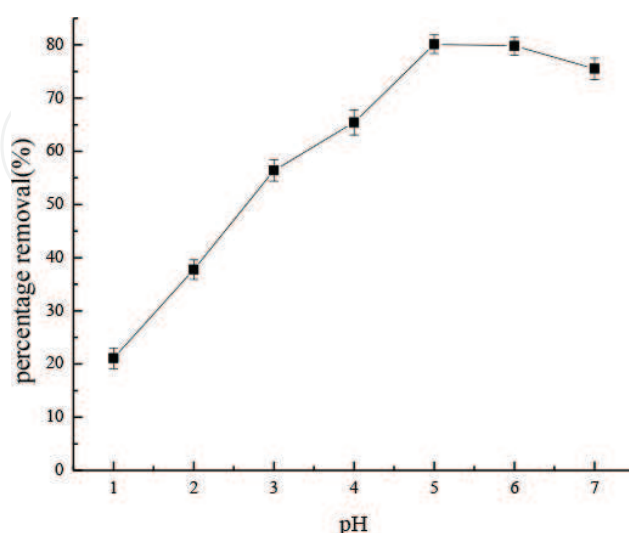


Figure 7. Effect of pH on the removal of Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide.

In case of cross-linking membrane of chitosan & silicon dioxide, the removal of Cr(VI) more than 76% was observed at pH 3 (**Figure 6**). 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 [40]. 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^- [41]. As shown in **Figure 8** taken from Irgolic et al. [42], the dominant form of Cr(VI) exists as hydrogen chromate anions (HCrO_4^-) between pH 2 and 6. With the increase of pH, the dominant species will change from HCrO_4^- to other form CrO_4^{2-} [43].

Then, pH 3 was selected as the optimal pH in case of the membrane of chitosan & silicon dioxide for further work. 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 [44], and different forms such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$, 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 [45, 46]. The process of shifts is given Eqs. (6)–(8):



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. In case of carboxymethyl chitosan & silicon dioxide, the adsorption efficiency of Cr(VI) increased with the increase of pH, and reached 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 membrane become positively-charged due to strong protonation at these pH range, which leads to a

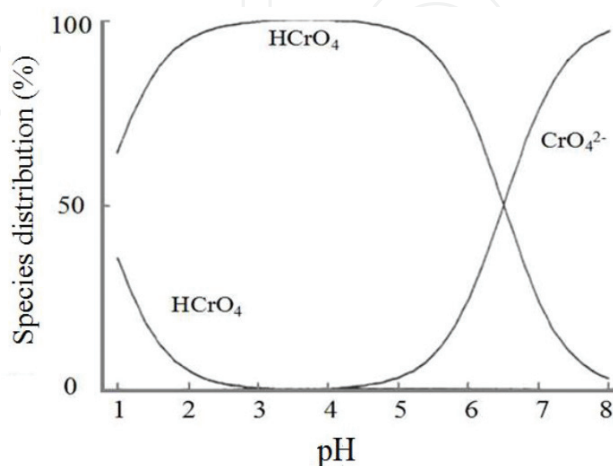


Figure 8. Species distribution curves of Cr(VI) in environmental water.

stronger attraction between the positively-charged surface and the negatively-charged $\text{Cr}_2\text{O}_7^{2-}$ 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, pH 5 was considered as optimum pH for further work.

3.2.2. Effect of contact time

Adsorption experiments were performed in order to determine the optimum contact time at optimal pH 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 effect of contact time on the removal of Cr(VI) using the membrane of chitosan & silicon dioxide in **Figure 9**, the adsorption capacity of the membrane for Cr(VI) reached adsorption equilibrium at 80 min, and after that there are a slight decrease due to the swelling properties of the membrane absorbent. Therefore, the optimized contact time was selected for 80 min.

The effect of contact time on the removal of Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide is shown in **Figure 10**. 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.

3.2.3. Effect of the membrane dosage

In order to estimate the optimal dosage of the 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, contact time, and the concentration of Cr(VI) for $50 \text{ mg} \cdot \text{dm}^{-3}$.

The effect of dosage on the removal of Cr(VI) using the membrane of the membrane of chitosan & silicon dioxide are shown in **Figure 11**. The adsorption capacity of membrane for Cr(VI) reached adsorption equilibrium at $0.2 \text{ g} \cdot \text{dm}^{-3}$, and the removal rate reached 78.6%.

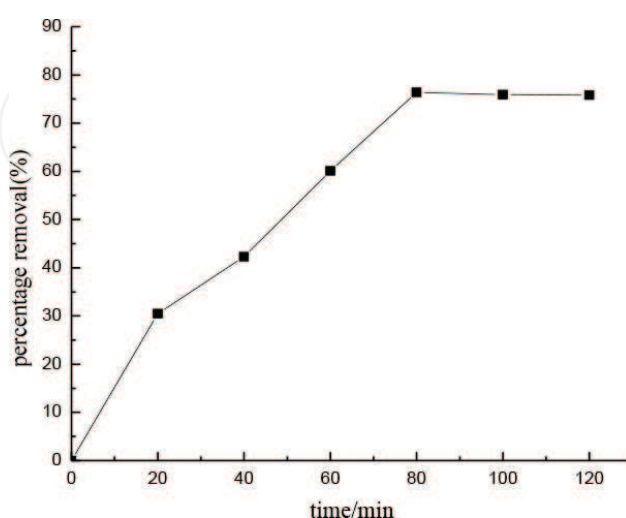


Figure 9. Effect of contact time for Cr(VI) adsorption using the membrane of chitosan & silicon dioxide.

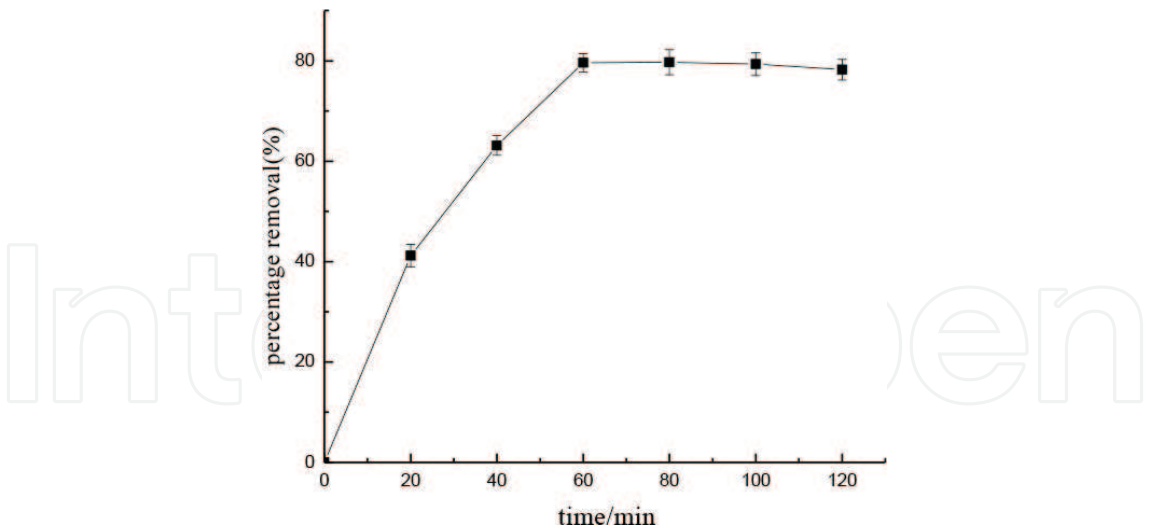


Figure 10. Effect of contact time for Cr(VI) adsorption using the membrane of carboxymethyl chitosan & silicon dioxide.

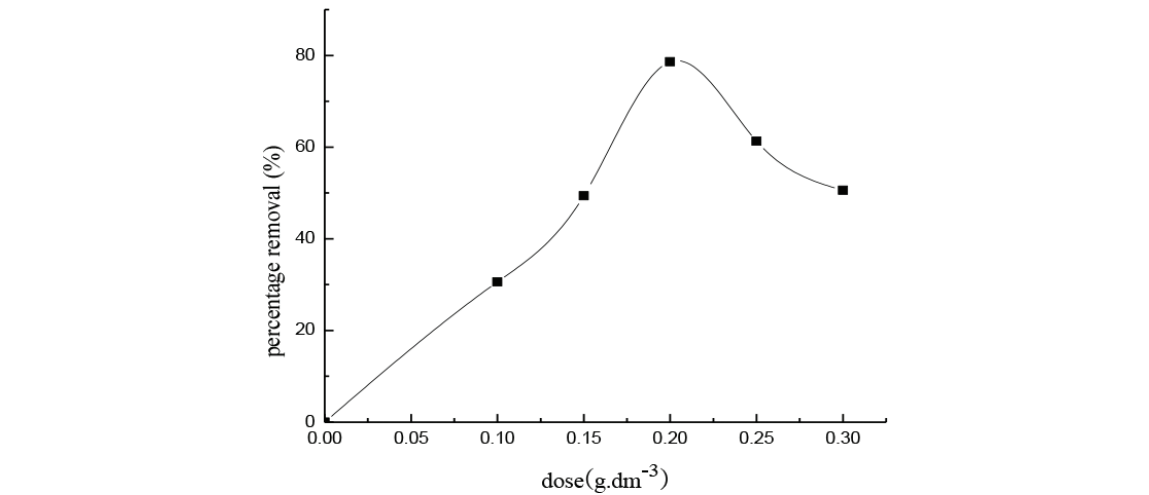


Figure 11. Effect of dose on percent removal of Cr(VI) using the membrane of chitosan & silicon dioxide.

However, remarkable decrease is observed at a dosage more than $0.2 \text{ g} \cdot \text{dm}^{-3}$. Thus, $0.2 \text{ g} \cdot \text{dm}^{-3}$ was considered as optimized dose.

The effect of dosage on the removal of Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide is shown in **Figure 12**. The results indicate that the adsorption capacity of the membrane for Cr(VI) reached 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 0.2 to $0.3 \text{ g} \cdot \text{dm}^{-3}$. The removal rate reached about 80% at $0.25 \text{ g} \cdot \text{dm}^{-3}$, and $0.25 \text{ g} \cdot \text{dm}^{-3}$ was selected as the optimal dosage.

3.2.4. Effect of initial concentration

The experiments were performed by varying concentrations from 10 to $50 \text{ mg} \cdot \text{dm}^{-3}$ under optimized condition of pH, contact time and adsorbent dosage.

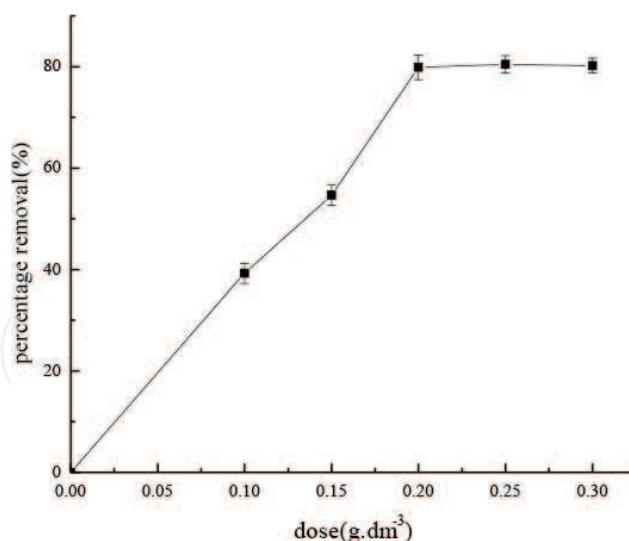


Figure 12. Effect of dosage of adsorbent for Cr(VI) adsorption using the membrane of carboxymethyl chitosan & silicon dioxide.

The effect of initial concentration on the removal of Cr(VI) using the membrane of chitosan & silicon dioxide is shown in **Figure 13**. There was a continuous increase in the uptake of Cr(VI) per gram of adsorbent up to the concentration of $40 \text{ mg} \cdot \text{dm}^{-3}$, but the uptake is almost constant at further higher concentrations. The removal rate reached 78.7%. Then, $40 \text{ mg} \cdot \text{dm}^{-3}$ was considered as optimum initial concentration for Cr(VI).

The effect of initial concentration on the removal of Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide is shown in **Figure 14**. There was a slight increase from 20 to $50 \text{ mg} \cdot \text{dm}^{-3}$ except at the concentrations of $30 \text{ mg} \cdot \text{dm}^{-3}$. The initial concentration was taken as $40 \text{ mg} \cdot \text{dm}^{-3}$.

Data from these studies were fitted to the Langmuir and Freundlich isotherm equations.

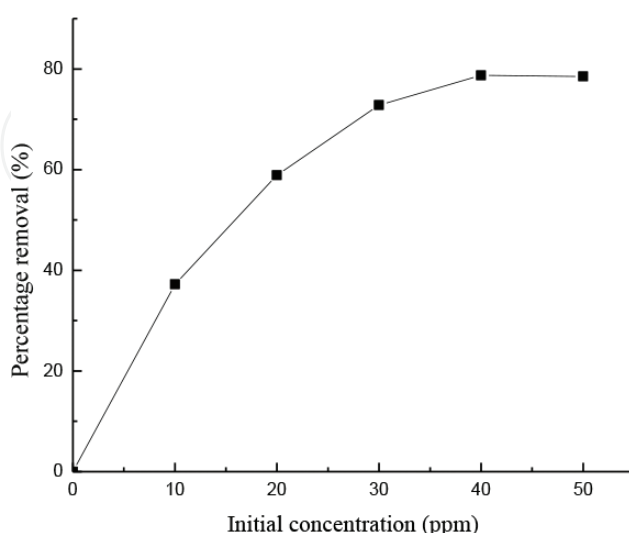


Figure 13. Effect of initial concentration for Cr(VI) adsorption using the membrane of chitosan & silicon dioxide.

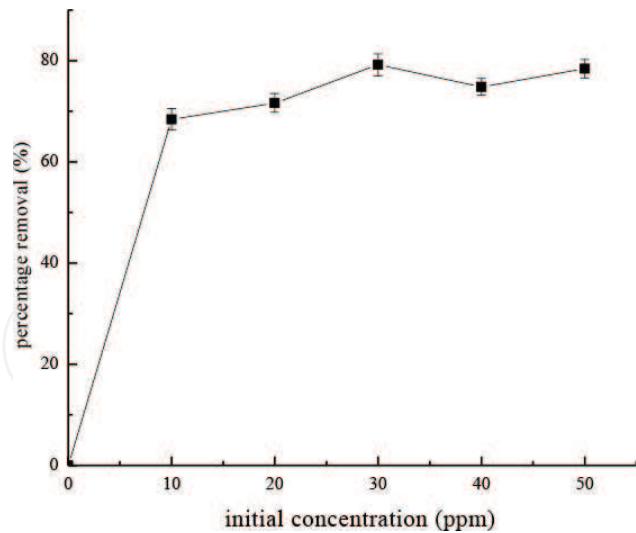


Figure 14. Effect of initial concentration for Cr(VI) adsorption using the membrane of carboxymethyl chitosan & silicon dioxide.

3.3. Adsorption isotherms

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes [47]. To understand the adsorption process of Cr(VI) using the membrane, adsorption isotherms of Langmuir and Freundlich were investigated under the optimal conditions.

The adsorption data obtained for Cr(VI) using the membrane of chitosan & silicon dioxide were analyzed by Langmuir (**Figure 15**) and Freundlich equations (**Figure 16**). The correlation coefficient (R^2) of these isotherms for Cr(VI) on the 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 membrane was presented. Particularly, R^2 values in Langmuir isotherm are larger than that in Freundlich isotherm. The maximum adsorption capacity (q_{max}) calculated from Langmuir model was $21.2 \text{ mg}\cdot\text{g}^{-1}$. This result

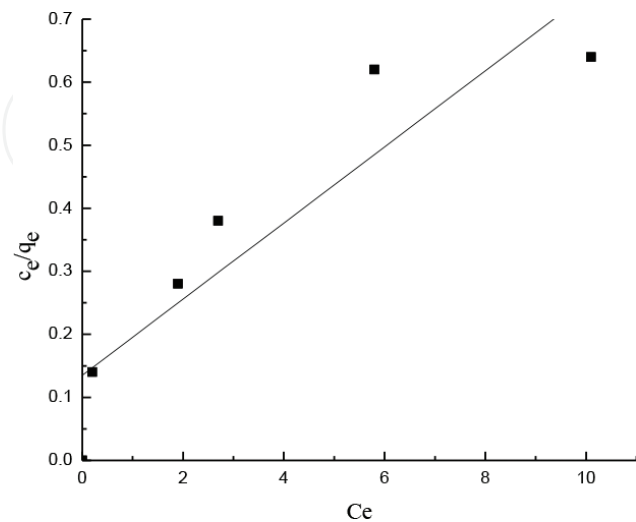


Figure 15. Langmuir isotherm of Cr(VI) adsorption onto the membrane of chitosan & silicon dioxide.

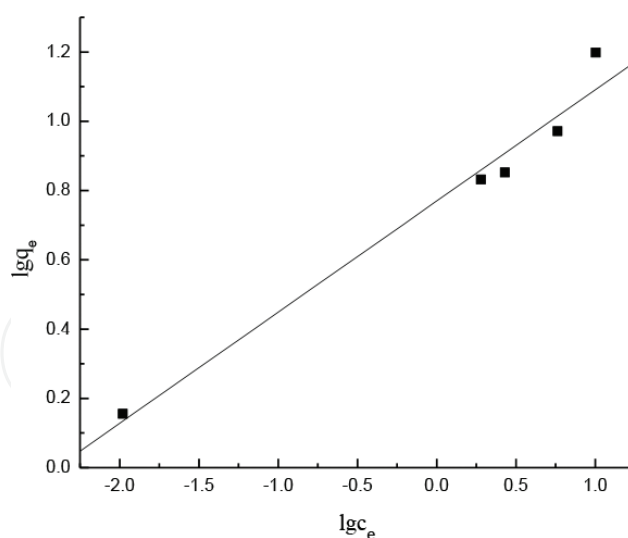


Figure 16. Freundlich isotherm of Cr(VI) adsorption onto the membrane of chitosan & silicon dioxide.

	Langmuir isotherm		Freundlich isotherm			
	q_{max} [mg·g ⁻¹]	K_L [dm ⁻³ ·mg ⁻¹]	R^2	K_F [(mg·g ⁻¹)·(dm ⁻³ ·mg ⁻¹) ^{1/n}]	1/n	R^2
Membrane (chitosan & silicon dioxide)	21.2	1.32·10 ⁻¹	0.985	3.21	0.78	0.912

Table 1. Coefficient of Langmuir and Freundlich isotherms for Cr(VI) using the membrane of chitosan & silicon dioxide.

suggests that the adsorption of Cr(VI) on the membrane of chitosan & silicon dioxide mainly occurred by monolayer reaction.

The adsorption data obtained for Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide were analyzed by Langmuir (**Figure 17**) and Freundlich equations (**Figure 18**). The correlation coefficient (R^2) of Langmuir and Freundlich isotherms for Cr(VI) using the membrane is shown in **Table 2** along with other relevant parameters.

The maximum adsorption capacity (q_{max}) calculated from Langmuir model was 80.7 mg·g⁻¹. Based on **Table 2**, 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 membrane of carboxymethyl chitosan & silicon dioxide mainly occurred by monolayer reaction.

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

3.4. Kinetic studies

Kinetic models were tested in this study for the adsorption of Cr(VI) onto the membrane under the optimized experimental conditions. Adsorption time is one of the important factors which

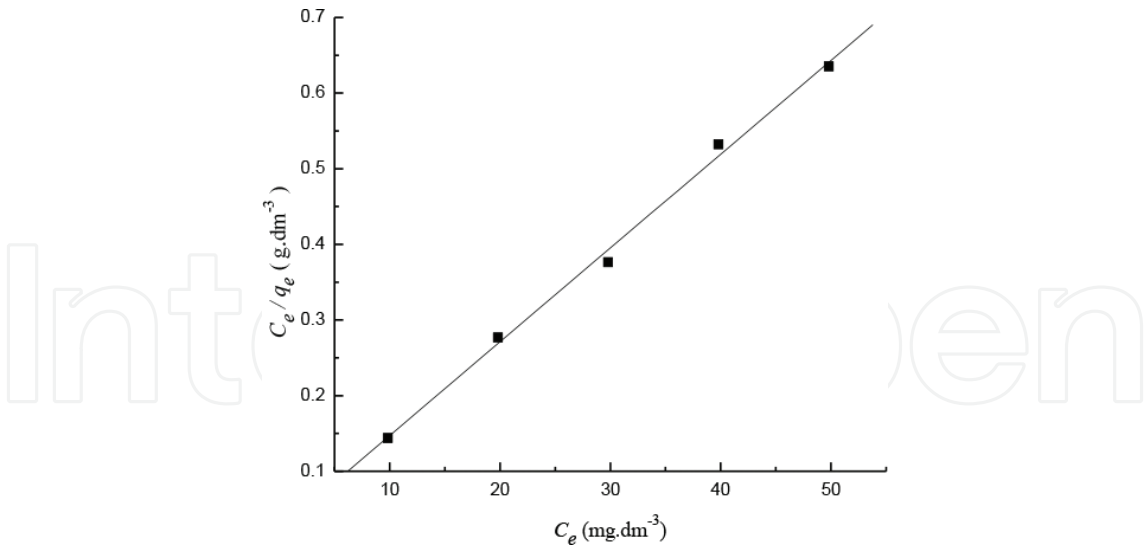


Figure 17. Langmuir isotherm of Cr(VI) adsorption using the membrane of carboxymethyl chitosan & silicon dioxide.

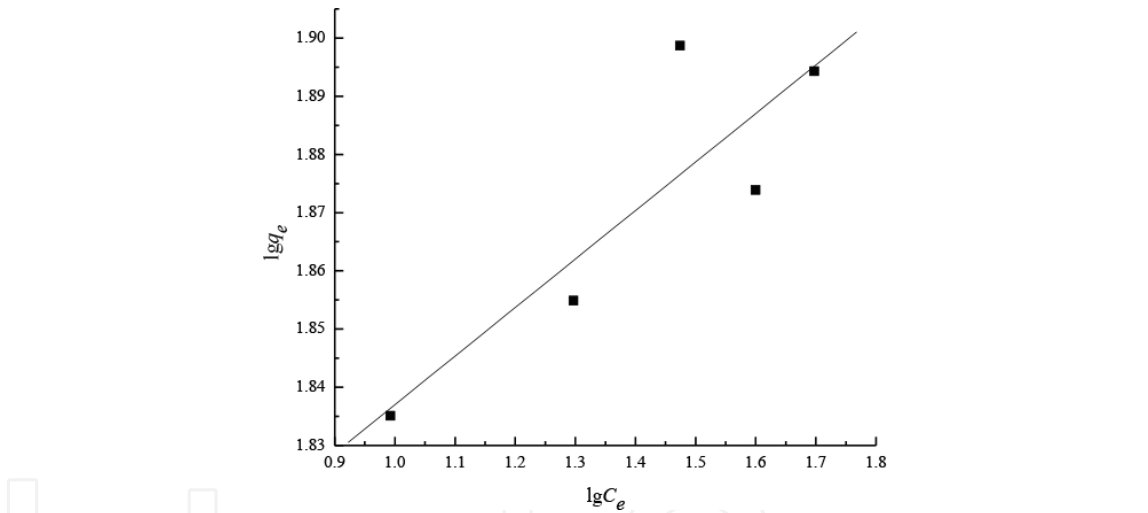


Figure 18. Freundlich isotherm of Cr(VI) adsorption using the membrane of carboxymethyl chitosan & silicon dioxide.

	Langmuir isotherm			Freundlich isotherm		
	q_{max} [mg.g ⁻¹]	K_L [dm ⁻³ .mg ⁻¹]	R^2	K_F [(mg.g ⁻¹). (dm ⁻³ .mg ⁻¹) ^{1/n}]	1/n	R^2
Membrane (carboxymethyl chitosan & silicon dioxide)	80.7	0.531	0.998	56.7	0.0834	0.867

Table 2. Coefficient of Langmuir and Freundlich isotherms for Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide.

help us to predict kinetics as well as the mechanism of the uptake of heavy metals on material surface [47].

The adsorption data obtained for Cr(VI) using the membrane of chitosan & silicon dioxide were analyzed by kinetic studies are shown in **Figure 19**. Based on the data in **Figure 18**, the pseudo second-order kinetic coefficients for Cr(VI) by the membrane are estimated (**Table 3**). The rate constant of second-order equation (k) diffusion are $1.17 \times 10^{-2} \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ for Cr(VI). The correlation coefficients (R^2) were 0.996 for Cr(VI) adsorption on the membrane.

The results for rate constant (k) and the amount of adsorbed Cr(VI) (q_e) are shown in **Table 4** along with the regression coefficients (R^2). From **Table 4**, 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.

Then, the pseudo first-order and pseudo second-order kinetic model of Cr(VI) adsorption using the membrane of carboxymethyl chitosan & silicon dioxide are shown in **Figures 20** and **21**. 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 $3.4 \times 10^{-2} \text{ g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$ in this work.

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)

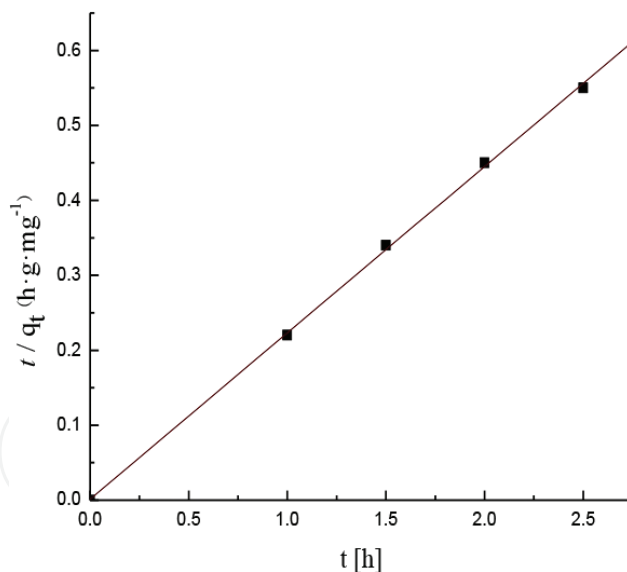


Figure 19. The pseudo second-order kinetic model on the membrane of chitosan & silicon dioxide.

	$q_e \text{ (mg}\cdot\text{g}^{-1}\text{)}$	$K_2 \text{ (g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}\text{)}$	R^2
Cr(VI)	0.106	1.17×10^{-3}	0.996

Table 3. The pseudo second-order kinetic coefficient for Cr(VI) using the membrane of chitosan & silicon dioxide.

	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
Cr(VI)	79.7	8.91	0.924	94.4	3.42×10^{-2}	0.990

Table 4. The kinetic coefficient for Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide.

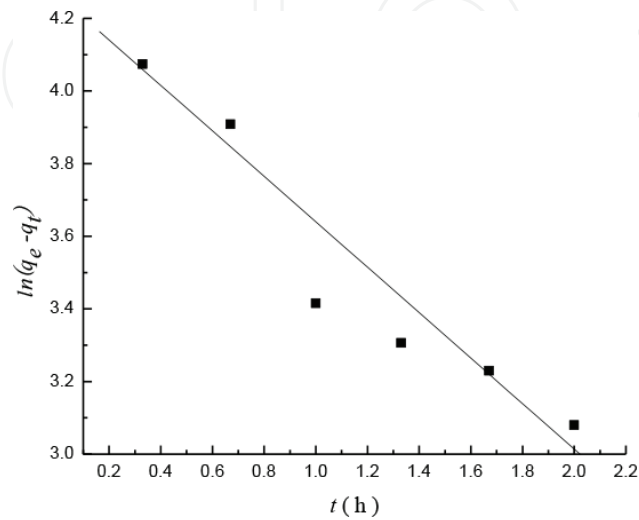


Figure 20. The pseudo first-order kinetic model of Cr(VI) adsorption using the membrane of carboxymethyl chitosan & silicon dioxide.

was mainly chemical, and that the adsorption process involves the valency forces through sharing electrons between the metal ions and adsorbent.

It is obvious that the adsorption capacity of Cr(VI) by the membrane of carboxymethyl chitosan & silicon dioxide is higher than that by the membrane of chitosan & silicon dioxide from the comparison of each maximum adsorption capacity.

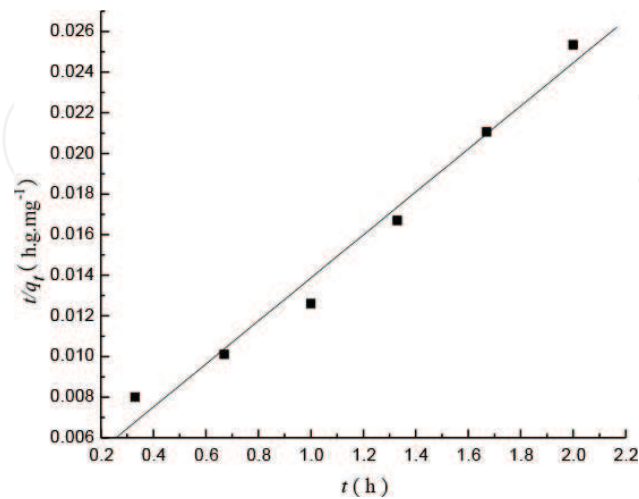


Figure 21. The pseudo second-order kinetic model of Cr(VI) adsorption using the membrane of carboxymethyl chitosan & silicon dioxide.

Adsorbent	Adsorption capacity (mg·g ⁻¹)	References
Cross-linked chitosan bentonite composite	89.1	[48]
Chitosan/polyvinyl alcohol/containing cerium(III)	52.9	[49]
STAC-modified rectorite	21.0	[50]
Ethylenediamine-modified cross-linked magnetic chitosan	51.8	[44]
Clarified sludge	26.3	[51]
A novel modified graphene oxide/chitosan	86.2	[52]
Chitosan-g-poly/silica gel nanocomposite	55.7	[53]
Membrane of chitosan & silicon dioxide	21.2	This study
Membrane of carboxymethyl chitosan & silicon dioxide	80.7	This study

Table 5. Comparison of adsorption capacity for Cr(VI) by different adsorbents.

The comparison of maximum adsorption capacity of Cr(VI) by these membranes in present study with that of another adsorbents in literatures are presented in **Table 5**. As seen in **Table 5**, the adsorption capacity of the membrane for Cr(VI) in this work is on a level with that of another adsorbents in previous works.

3.5. Effect of competitive ions on the adsorption of Cr(VI)

Competitive experiment for Cr(VI) was performed at optimized pH (pH 5), contact time (60 min) and sorbent dosage (0.25 g·dm⁻³) under the presence of competitive ions (Cu²⁺, Ni²⁺, Zn²⁺, Pb²⁺) at different concentrations 0, 10, 20, 30 and 40 ppm (**Figure 22**), and the presence of common ions (Cl⁻, NO₃⁻ and SO₄²⁻) at different concentrations 0, 10, 20 and 40 ppm (**Figure 23**). From **Figures 22** and **23**, it is suggested that adsorption capacity of Cr(VI) by the

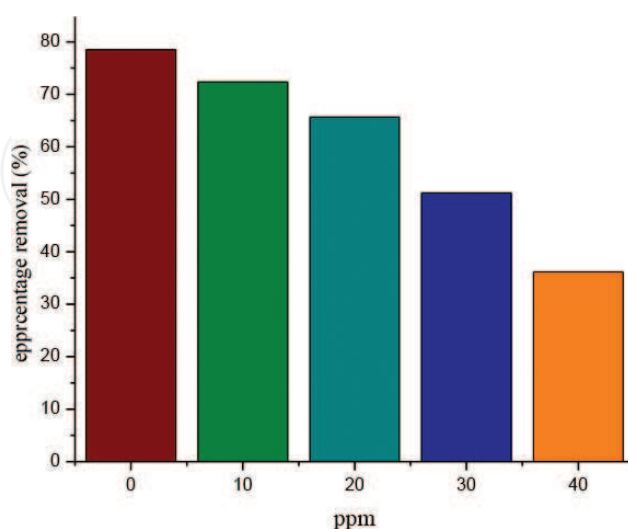


Figure 22. Effect of competitive ions (Cu²⁺, Ni²⁺, Zn²⁺, Pb²⁺) on the adsorption of Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide.

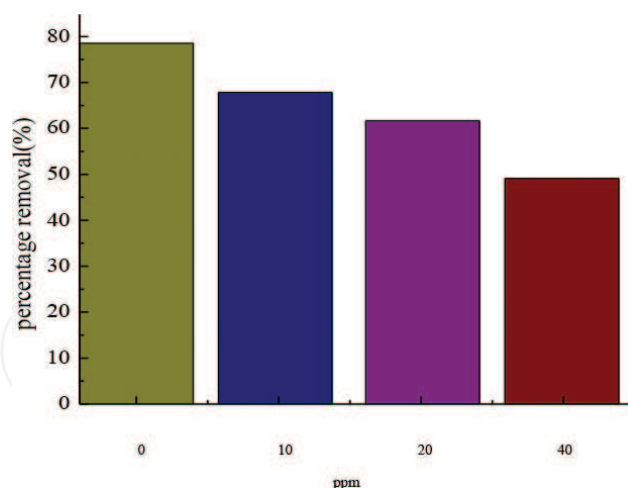


Figure 23. Effect of competitive ions (Cl^- , NO_3^- and SO_4^{2-}) on the adsorption of Cr(VI) using the membrane of carboxymethyl chitosan & silicon dioxide.

membrane decreases as the concentration of competitive ion increases. However, it can be effective adsorbent for Cr(VI) even under the presence of low concentration competition ions.

3.6. Adsorption mechanism

Novel adsorbent for Cr(VI) was synthesized by chitosan & silicon dioxide. Adsorption mechanism chromium onto the membrane is shown in **Figure 24**.

The 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 membrane enhance the adsorption capacity of Cr(VI). Silanol groups (Si-OH) on the silica surface cross-linked with amino groups and carboxyl groups on the carboxymethyl chitosan were reacted to prepare the membrane. The main role of silicon dioxide is as follows: (1) the specific surface area of the membrane is increased by the porous structure of silicon dioxide, (2) the hydroxyl groups in silicon dioxide may enhance the adsorption capacity of the membrane for the removal of Cr(VI). Carboxymethyl chitosan as well as chitosan was used to enhance the adsorption capacity in this work, and the adsorption sites and specific surface area will increase by changing from chitosan to carboxymethyl chitosan.

3.7. 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 membrane of carboxymethyl chitosan & silicon dioxide 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 $0.5 \text{ mol} \cdot \text{dm}^{-3}$ NaOH and $2 \text{ mol} \cdot \text{dm}^{-3}$ 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 h as eluent. The

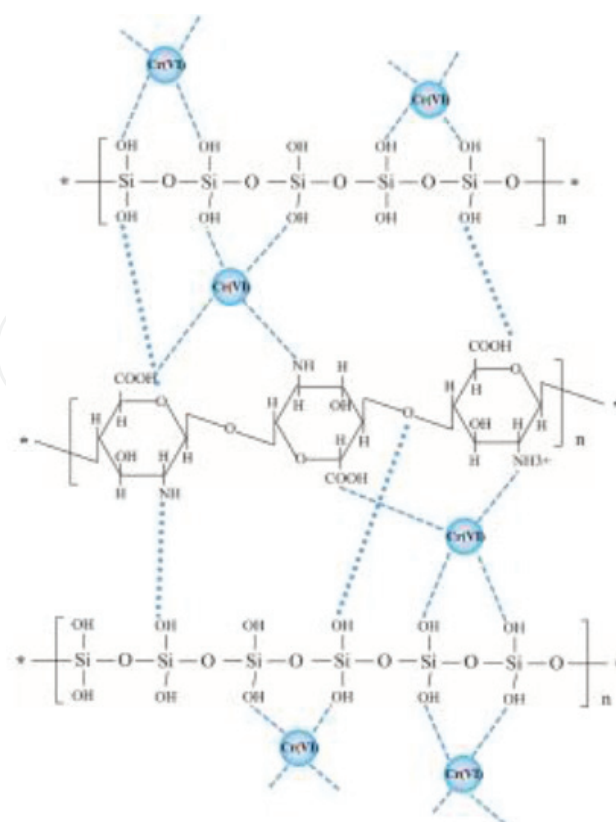


Figure 24. Adsorption mechanism for the removal chromium onto the membrane of carboxymethyl chitosan & silicon dioxide.

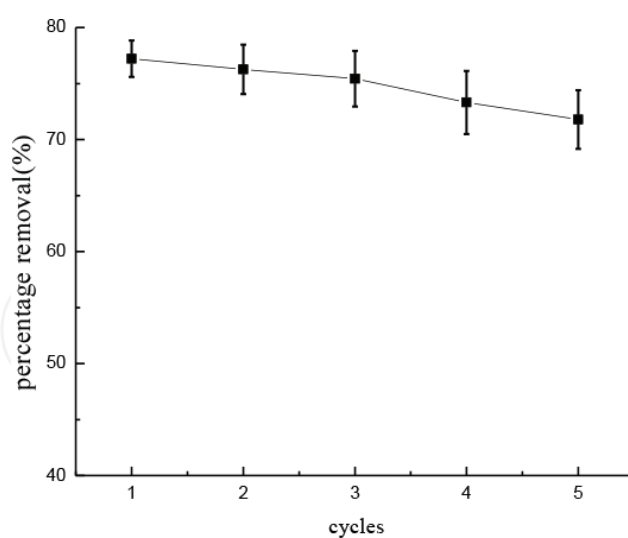


Figure 25. Adsorption capacity after desorption using the membrane of carboxymethyl chitosan & silicon dioxide.

adsorption capacity after desorption using the above leaching agent is shown in **Figure 25**. From this **Figure 25**, it is found that the membrane still present the high adsorption capacity (74.6%) towards Cr(VI) within three cycles.

4. Conclusions

The efficiency of the membrane synthesized as an adsorbent for Cr(VI) was investigated by batch techniques. The following conclusions can be drawn considering the results of this work:

1. The optimal conditions of adsorption Cr(VI) using the membrane of chitosan & 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 $40 \text{ mg} \cdot \text{dm}^{-3}$ was considered as optimum initial concentration. The removal of Cr(VI) by the membrane 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 $40 \text{ mg} \cdot \text{dm}^{-3}$). The adsorption of Cr(VI) using the membrane conforms to the Langmuir isotherm adsorption equation, and the correlation coefficients was 0.985. The maximum adsorption capacity of Cr(VI) calculated by Langmuir model was $21.2 \text{ mg} \cdot \text{g}^{-1}$.
2. The adsorption isotherm of Cr(VI) by the membrane of carboxymethyl chitosan & silicon dioxide was also more suitably described by Langmuir model, and the correlation coefficients was 0.998. It suggests that monolayer chemical adsorption of Cr(VI) on the membrane is more dominant. The maximum adsorption capacity was estimated as $80.7 \text{ mg} \cdot \text{g}^{-1}$ for Cr(VI) under the optimum conditions. The adsorption capacity of the membrane for Cr(VI) in this work is on a level with that of another adsorbents in previous works. The best fit was obtained with a pseudo-second order kinetic model while investigating the adsorption kinetics of Cr(VI) adsorption on the membrane, and the correlation coefficients was 0.990. The rate constant (k) are $3.4 \times 10^{-2} \text{ g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$.
3. From regeneration experiments (repetition of adsorption and desorption experiment), it is found that the membrane of chitosan & silicon dioxide still presents the high adsorption capacity (74.6%) towards Cr(VI) within three cycles.

From this work, it was quantitatively found that nanomaterials for desalination synthesized in this study 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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References

- [1] Huang CH, Chang KP, Ou HD, Chiang YC, Wang CF. Adsorption of cationic dyes onto mesoporous silica. *Microporous and Mesoporous Materials*. 2011;**141**(1):102-109
- [2] Sağ Y, Aktay Y. Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and *Rhizopus arrhizus*. *Biochemical Engineering Journal*. 2002;**12**(2):143-153
- [3] Chiron N, Guilet R, Deydier E. Adsorption of Cu(II) and Pb(II) onto a grafted silica: isotherms and kinetic models. *Water Research*. 2003;**37**(13):3079-3086
- [4] Guo Z, Li DD, Luo XK, Ya H, Li QN, Zhao M, Li M. 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*. 2017;**490**(5):11-22
- [5] Fu F, Wang Q. Removal of heavy metal ions from wastewater: A review. *Journal of Environmental Management*. 2011;**92**:407-418
- [6] Ali RM, Hamad HA, Hussein MM, Malash GF. Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecological Engineering*. 2016;**91**:317-332
- [7] Park JH, Ok YS, Kim SH, Cho JS, Heo JS, Delaune RD, Seo DC. Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. *Chemosphere*. 2016;**142**:77-83
- [8] El-Enany AE, Issa AA. Cyanobacteria as a biosorbent of heavy metals in sewage water. *Environmental Toxicology and Pharmacology*. 2000;**8**(2):95-101
- [9] Nourbakhsh MN, Kiliçarslan S, İlhan S, Özdağ H. Biosorption of Cr⁶⁺, Pb²⁺ and Cu²⁺ ions in industrial waste water on *Bacillus*. *Chemical Engineering Journal*. 2002;**85**(2):351-355
- [10] Albadarin AB, Mangwandi C, Walker GM, Allen SJ. Influence of solution chemistry on Cr (VI) reduction and complexation onto date-pits/tea-waste biomaterials. *Journal of Environmental Management*. 2012;**114**:190-201
- [11] Kobya M. Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: Kinetic and equilibrium studies. *Bioresource Technology*. 2004;**91**(3):317-321

- [12] Duruibe JO, Ogwuegbu MOC, Egwurugwu JN. Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*. 2007;**2**(5):112-118
- [13] Bailey SE, Olin TJ, Bricka RM, Adrian DD. A review of potentially low-cost sorbents for heavy metals. *Water Research*. 1999;**33**(11):2469-2479
- [14] Järup L. Hazards of heavy metal contamination. *British Medical Bulletin*. 2003;**68**(1):167-182
- [15] Zhao H, Liao X, Zhou ZQ. Study on the adsorption of modified peanut shell for Cr⁶⁺ in Wastewater. *Applied Chemical Industry*. 2011;**40**:78-84
- [16] Fendorf SE. Surface reactions of chromium in soils and waters. *Geoderma*. 1995;**67**:55-71
- [17] Sarin V, Sarvinder ST, Pant KK. Thermodynamic and breakthrough column studies for the selective sorption of chromium from industrial effluent on activated eucalyptus bark. *Bioresource Technology*. 2006;**97**:1986-1993
- [18] Sankararamakrishnan N, Dixit A, Iyengar L, Sanghi R. Removal of hexavalent chromium using a novel cross linked xanthated chitosan. *Bioresource Technology*. 2006;**97**(18):2377-2382
- [19] Partensky DB, Wilbourn CJ, Rice JM. An IARC evaluation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans as risk factors in human carcinogenesis. *Environmental Health Perspectives*. 1998;**106**:755-760
- [20] Cieslak GM. Toxic and mutagenic effects of chromium (VI). *Polyhedron*. 1996;**15**:3667-3918
- [21] Donais MK, Henry R, Rettberg T. Chromium speciation using an automated liquid handling system with inductively coupled plasma-mass spectrometric detection. *Talanta*. 1999;**49**:1045-1050
- [22] Acosta RI, Rodriguez X, Gutierrez C, Guadalupe MM. Biosorption of chromium (VI) from aqueous solutions onto fungal biomass. *Bioinorganic Chemistry and Application*. 2004;**2**:1-7
- [23] Kotas J, Stasicka Z. Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution*. 2000;**107**:263-283
- [24] Inoue K, Fingerman M, Nagabhushanam R, Thompson M. Application of chitosan in separation and purification of metals. *Recent Advances in Marine Biotechnology, Environmental Marine Biotechnology*. 1998;**2**:63-97
- [25] Guibal E, Larkin A, Vincent T, Tobin JM. Chitosan sorbents for platinum sorption from dilute solutions. *Industrial and Engineering Chemistry Research*. 1999;**38**(10):4011-4022
- [26] Guzman J, Saucedo I, Revilla J, Navarro R, Guibal E. Vanadium interactions with chitosan: Influence of polymer protonation and metal speciation. *Langmuir*. 2002;**18**(5):1567-1573
- [27] Ng JCY, Cheung WH, McKay G. Equilibrium studies of the sorption of Cu(II) ions onto chitosan. *Journal of Colloid and Interface Science*. 2002;**255**(1):64-74
- [28] Arrascue ML, Garcia HM, Horna O, Guibal E. Gold sorption on chitosan derivatives. *Hydrometallurgy*. 2003;**71**:191-200

- [29] Repoa E, Warchoń JK, Bhatnagar A, Sillanpää M. Heavy metals adsorption by novel EDTA-modified chitosan–silica hybrid materials. *Journal of Colloid and Interface Science*. 2011;**358**(1):261-267
- [30] Varma AJ, Deshpande SV, Kennedy JF. Metal complexation by chitosan and its derivatives: A review. *Carbohydrate Polymers*. 2004;**55**(1):77-93
- [31] Fricke J. *Aerogels an Fascinating Class of High-Performance Porous Solids*. Berlin, Heidelberg: Springer; 1986. pp. 2-19
- [32] Michard P, Guibal E, Vincent T, Cloirec PL. Sorption and desorption of uranyl ions by silica gel: pH, particle size and porosity effects. *Microporous Materials*. 1996;**5**(5):309-324
- [33] Tran HH, Roddick FA, Donnell JA. Comparison of chromatography and desiccant silica gels for the adsorption of metal ions—I. Adsorption and kinetics. *Water Research*. 1999; **33**(13):2992-3000
- [34] Bois L, Bonhommé A, Ribes A, Pais B, Raffin G, Tessier F. Functionalized silica for heavy metal ions adsorption. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2003;**221**(1-3):221-230
- [35] Jal PK, Patel S, Mishra BK. Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. *Talanta*. 2004;**62**(5):1005-1028
- [36] Gandhi MR, Meenakshi S. Preparation and characterization of silica gel/chitosan composite for the removal of Cu(II) and Pb(II). *International Journal of Biological Macromolecules*. 2012;**50**(3):650-657
- [37] Smirnova I, Mamic J, Arlt W. Adsorption of drugs on silica aerogels. *Langmuir*. 2003;**19**: 8521-8525
- [38] Rashidova SS, Shakarova DS, Ruzimuradov ON. Bionanocompositional chitosan-silica sorbent for liquid chromatography. *Journal of Chromatography*. 2004;**800**:49-53
- [39] Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*. Amsterdam: Elsevier; 1991
- [40] Eveliina R, Jolanta KW, Amit B, Mika S. Heavy metals adsorption by novel EDTA-modified chitosan–silica hybrid materials. *Journal of Colloid and Interface Science*. 2011;**358**:261-267
- [41] Huang CP, Bowers AR. The use of activated carbon for chromium(VI) removal. *Water Technology*. 1978;**10**:45-47
- [42] Irgolic KJ, Greschonig H, Howard AG. *Encyclopedia of Analytical Science*. Vol. 1. New York: Academic Press; 1999. p. 729
- [43] Erhan D, Mehmet K, Elif S. Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water SA*. 2004;**30**:533-540

- [44] Hu XJ, Wang JS, Liu YG, Li X, Zeng GM, Bao ZL, Long F. Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics. *Journal of Hazardous Materials*. 2011;**185**(1):306-314
- [45] Karthikeyan T, Rajgopal S, Miranda LR. Chromium(VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. *Journal of Hazardous Materials*. 2005; **124**(1):192-199
- [46] Akram M, Bhatti HN, Iqbal M, Noreen S, Sadaf S. Biocomposite efficiency for Cr (VI) adsorption: Kinetic, equilibrium and thermodynamics studies. *Journal of Environmental Chemical Engineering*. 2017;**5**(1):400-411
- [47] Copello GJ, Varela F, Martinez R. Immobilized chitosan as biosorbent for the removal of Cd (II), Cr(III) and Cr(VI) from aqueous solutions. *Bioresource Technology*. 2008;**99**:6538-6544
- [48] Liu Q, Yang BC, Zhang LZ, Huang RH. Adsorptive removal of Cr (VI) from aqueous solutions by cross-linked chitosan/bentonite composite Korean. *Journal of Chemical Engineering*. 2015;**32**(7):1314-1322
- [49] Wang FF, Ge MQ. Fibrous mat of chitosan/polyvinyl alcohol/containing cerium (III) for the removal of chromium (VI) from aqueous solution. *Textile Research Journal*. 2013;**83**(6): 628-637
- [50] Hong H, Jiang WT, Zhang X, Tie L, Li Z. Adsorption of Cr (VI) on STAC-modified rectorite. *Applied Clay Science*. 2008;**42**(1):292-299
- [51] Bhattacharya AK, Naiya TK, Mandal SN, Das SK. Adsorption, kinetics and equilibrium studies on removal of Cr (VI) from aqueous solutions using different low-cost adsorbents. *Chemical Engineering Journal*. 2008;**137**(3):529-541
- [52] Zhang L, Luo H, Liu P, Fang W, Geng J. A novel modified graphene oxide/chitosan composite used as an adsorbent for Cr (VI) in aqueous solutions. *International Journal of Biological Macromolecules*. 2016;**87**:586-596
- [53] Nithya R, Gomathi T, Sudha PN, Anil S, Venkatesan J, Kim SK. Removal of Cr (VI) from aqueous solution using chitosan-g-poly (butyl acrylate)/silica gel nanocomposite. *International Journal of Biological Macromolecules*. 2016;**87**:545-554