

Adsorption of Chromium (VI) from Aqueous Solution Using Zeolite/Chitosan Hybrid Composite

Meiling Pang¹, Naoki Kano^{2*} and Hiroshi Imaizumi²

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

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

Abstract: This study investigated the adsorption ability of ZCHC (zeolite/chitosan hybrid composite) as adsorbent for chromium (Cr(VI)), ZCHC was prepared with sol-gel method by mixing zeolite and chitosan. Adsorption experiment from aqueous solutions containing known amount of Cr(VI) using zeolite, chitosan and ZCHC was explored to evaluate the efficiency of ZCHC as adsorbent for Cr in a batch system. The amount of Cr(VI) adsorbed at different pH values, initial concentrations, adsorbent dosages, and contact times were determined by ICP-AES (inductively coupled plasma-atomic emission spectrometry) in order to determine the optimum conditions for Cr(VI) adsorption. Furthermore, the adsorption mechanism of Cr(VI) by zeolite, chitosan and ZCHC was investigated by applying Langmuir and Freundlich isotherm equations to the data obtained. In addition, the rates of adsorption were found to conform to pseudo-second order kinetics.

Key words: Adsorption, chromium, zeolite, chitosan, hybrid composite, adsorption isotherms, kinetics.

1. Introduction

Contamination of toxic metals in the aquatic environment is one of the most debatable problems in the world with industrial development [1, 2]. Heavy metals are considered to be potentially hazardous and can cause physiological and neurological disorders [3-5].

Cr consists of two stable oxidation states such as trivalent state Cr(III) and hexavalent state Cr(VI) in natural aqueous environment. It is well known that, Cr(III) is essential materials for living organisms, whereas, Cr(VI) is more toxic, carcinogenic and mutagenic, is considered as severe pollutant due to high water-solubility and toxicity [6-10]. The maximum levels permitted in wastewater are $5 \text{ mg}\cdot\text{dm}^{-3}$ for trivalent and $0.05 \text{ mg}\cdot\text{dm}^{-3}$ for hexavalent chromium [11].

Natural zeolites have been used as cationic exchange materials for the remediation of heavy metals and other contaminants due to their excellent properties as adsorbents. They also have the

advantages of being very abundant in nature and possessing high chemical stability.

During the last decade, alternative and novel modifications have been exploited to give zeolites new properties that can increase their applications. In fact, modifications with cationic surfactants, such as high molecular-weight quaternary ammonium salts, have rapidly become important because they provide zeolites with the potential to behave as anionic exchangers [12, 13].

Among environmentally friendly technologies for the removal of heavy metals from aquatic effluent, biosorption has attracted increasing research interest recently [14-17]. The major advantages of biosorption are its high effectiveness in reducing the heavy metals and the use of inexpensive biosorbents [9, 17].

Among many biosorbents, chitosan can be an excellent biosorbent for metals because its amine ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups may serve as coordination sites to form complexes with various heavy metal ions [12, 13, 18]. Uses of chitosan on the removal of various pollutants have been adequately reviewed [5, 18-24].

*Corresponding author: Naoki Kano, associate professor, research fields: environmental chemistry and environmental preservation.

The scientific literature gives no previous data of removal of Cr(VI) by ZCHC (zeolite/chitosan hybrid composite). There are only some articles reporting materials based on chitosan modified with different types of zeolites for removal of nitrates, humic acid, copper ion [12, 17]. In this paper, the results of adsorption experiment for Cr(VI) from aqueous solution using ZCHC was presented to investigate the efficiency of ZCHC as adsorbent for Cr for more practical use in future.

2. Experimental Sections

2.1 Materials and Reagents

Chitosan (M.W. (molecular weight) 100,000-300,000) was purchased from ACROS ORGANICS Co. (New Jersey, USA). Zeolite was purchased from Kanto Chemical Corporation, Inc. Zeolite was heated at 700 °C for 3 h to activate the surface in a muffle furnace and then washed with hydrochloric acid (5%, volume) and deionized water (at 80 °C) to remove fine powders and contaminants and was then dried at 110 °C for 2 h before use.

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

2.2 Preparation and Characterization of ZCHC

ZCHC was prepared by mixing solutions of chitosan and dispersions of zeolite in water. First, 1 g chitosan was dissolved in 20 cm³ of 0.2 M acetic acid with constant stirring at temperature of 50 °C. Then, 10 cm³ of deionized water was added into 10 cm³ chitosan sol solution, and was heated and stirred for 1 h. These solutions were mixed, while zeolite was

dispersed in the chitosan solution with constant stirring for 5 h at a temperature of 50 °C. Then, the solution was transferred into five centrifuge tubes (10 cm³), which were centrifuged at 9,000 rpm for 5 min, and then washed with deionized water to remove contaminants. The mixed solutions were put on Petri dishes, and were left to dry at room temperature for 24 h. The obtained films with a thickness of 0.1 mm were used for the following adsorption experiments.

The structure of the zeolite, chitosan and ZCHC were carried out by N₂ adsorption/desorption tests (Micromeritics TriStar 3020). The BET (Brunauer, Emmet and Teller) method was applied to determine the surface area. The surface morphology of zeolite, chitosan and ZCHC were surveyed using SEM (scanning electron microscopy, JCM-6000, JEOL).

2.3 Adsorption Experiment for Cr Using Chitosan and ZCHC

For investigating the effects of pH, contact time, adsorbent dose and initial concentration on the adsorption of Cr(VI), the following experiments were performed using zeolite, chitosan and ZCHC. Adsorbent was thoroughly mixed with 50 cm³ of containing known amount of Cr(VI) in a 200 cm³ conical flask, and the suspensions was shaken in a water bath at room temperature (25 ± 2 °C). Adsorption experiments were conducted in the pH range of 2-8, contact time from 1 h to 24 h, adsorbent dosage 0.1-2.0 g·dm⁻³, and initial concentration from 20 to 200 µg·dm⁻³. The pH of each solution was adjusted by using 0.1 mol·dm⁻³ NH₃ aq (aqueous solution)/0.1 mol·dm⁻³ HNO₃.

Following each adsorption experiment, the suspension containing adsorbent and the above standard solution was filtered through a 0.1 µm membrane filter (Advantec Mixed Cellulose Ester, 47 mm) to remove Cr(VI) that have been adsorbed into the adsorbent, and the concentration of this metal in the filtrate was determined with an ICP-AES (inductively coupled plasma-atomic emission spectroscopy).

The metal uptake by the adsorbent was calculated using the Eq. (1):

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

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

2.4 Langmuir and Freundlich Isotherm Model

Adsorption isotherms of adsorption data were studied at varying initial concentration from $20 \mu\text{g} \cdot \text{dm}^{-3}$ to $200 \mu\text{g} \cdot \text{dm}^{-3}$ under optimized conditions. Two common adsorption models, Langmuir and Freundlich isotherm models were applied to evaluate the adsorption data obtained for Cr(VI) based on Dahiya et al. [2, 17].

Langmuir model assumes monolayer adsorption onto a surface and is given by:

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

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

On the other hand, the linearized Freundlich model isotherm is represented by the Eq. (3):

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

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

2.5 Kinetic Studies

Kinetic models have been proposed to determine the mechanism of the adsorption process, which

provide useful data to improve the efficiency of the adsorption and feasibility of process scale-up [3, 14]. In the present investigation, the mechanism of the adsorption process was studied by fitting pseudo first-order and second-order reactions to the experimental data.

The pseudo first-order model is given by the 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) at equilibrium and time t , respectively ($\text{mol} \cdot \text{g}^{-1}$), and k_1 is the rate constant of the pseudo-first-order adsorption (h^{-1}).

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

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

where, k is the rate constant of the pseudo-second-order adsorption ($\text{g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$).

3. Results and Discussions

3.1 Characteristics of ZCHC

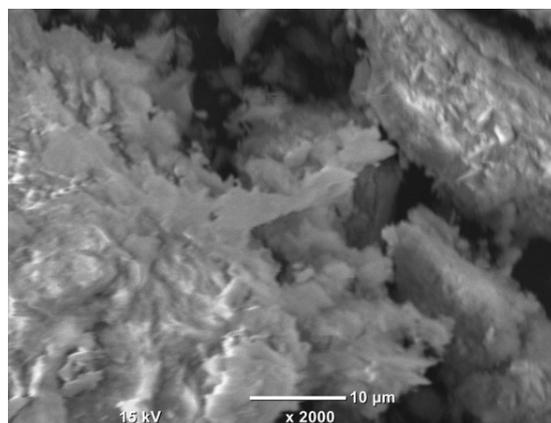
The surface property of zeolite, chitosan and ZCHC were investigated by N_2 adsorption, and the analytical results for the adsorption/desorption isotherms are shown in Table 1. The pore volume was calculated from the amount of N_2 adsorbed at the relative pressure of 0.99. The pore size was calculated from the adsorption average pore width ($4 V/A$ by BET) in this work. The SEM pictures of the chitosan and ZCHC are shown in Fig. 1. By comparing the surface structure chitosan and ZCHC, the zeolite treatment leads to a remarkable increase in the surface area and mesoporous volume of ZCHC sample. Then ZCHC can be a good adsorbent for Cr.

3.2 Adsorption of Cr(VI) on ZCHC

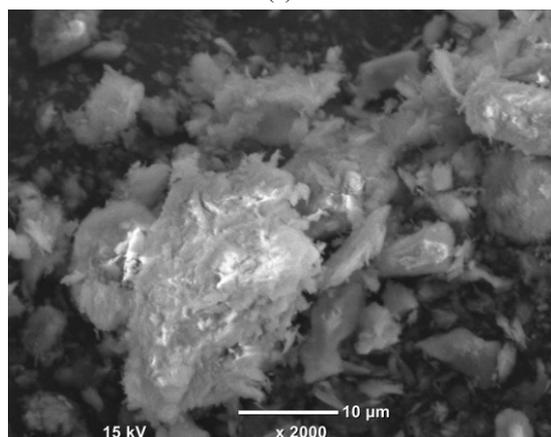
For obtaining the optimum conditions regarding the adsorption of Cr(VI), the effects of pH, contact time and dosage of adsorbents (i.e., zeolite, chitosan and

Table 1 Texturals characteristics of adsorbents.

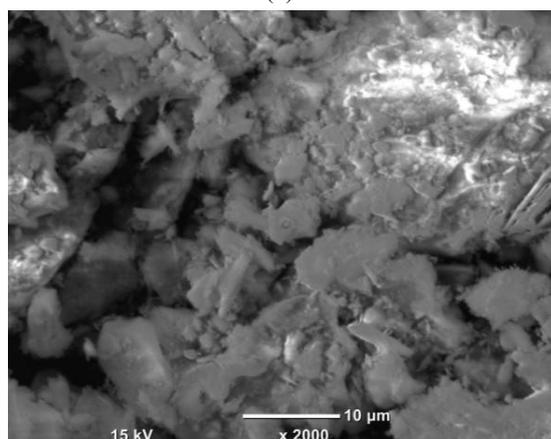
Adsorbent	BET surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Pore size (nm)
Zeolite	5.63	0.0474	26.8
Chitosan	0.612	0.00385	25.2
ZCHC	9.25	0.0485	21.0



(a)



(b)



(c)

Fig. 1 SEM images of chitosan and ZCHC (a: Zeolite; b: Chitosan; c: ZCHC).

ZCHC) on the removal of Cr(VI) from the aqueous solution were investigated.

3.2.1 Effect of pH

Solution pH is one of the most important parameters affecting adsorption characteristics. In many cases, the dominant chemical species alter as pH varies. To investigate the effect of solution pH on Cr(VI) removal efficiency by ZCHC, the pH of the solution was varied from 2-8 (in 100 μg·dm⁻³ of solution using 1.0 g·dm⁻³ ZCHC dosage for contact time of 6 h). The experimental results using ZCHC are shown in Fig. 2 along with that by chitosan.

Cr(VI) exists as hydrogen chromate anions (HCrO₄⁻) between pH 2.0 and pH 6.5, and it exists as chromate ions (CrO₄²⁻) at pH 8 according to the following Eqs. (6-8) [25-27]:



The adsorption capacity of Cr(VI) reached maximum at pH 3 in case of using ZCHC (whereas at pH 4 for zeolite and chitosan), where Cr(VI) may exist as HCrO₄⁻ or (Cr₂O₇²⁻). This anion species has a tendency to bind to the protonated active sites of the chitosan in solution at optimum pH [23]. Cr(VI) exists as chromate ion (CrO₄²⁻) at pH above 6.5. At pH 8, the uptake capacities are very low. This could be explained as competitiveness between chromate and hydroxyl ions. Then, pH 3 was taken for the removal of Cr(VI) by ZCHC (and pH 4 was used for zeolite and chitosan) for further experiments.

3.2.2 Effect of Contact Time

The effect of contact time on the adsorption capacity of Cr(VI) using 1.0 g·dm⁻³ adsorbent (100 μg·dm⁻³ of solution) is investigated.

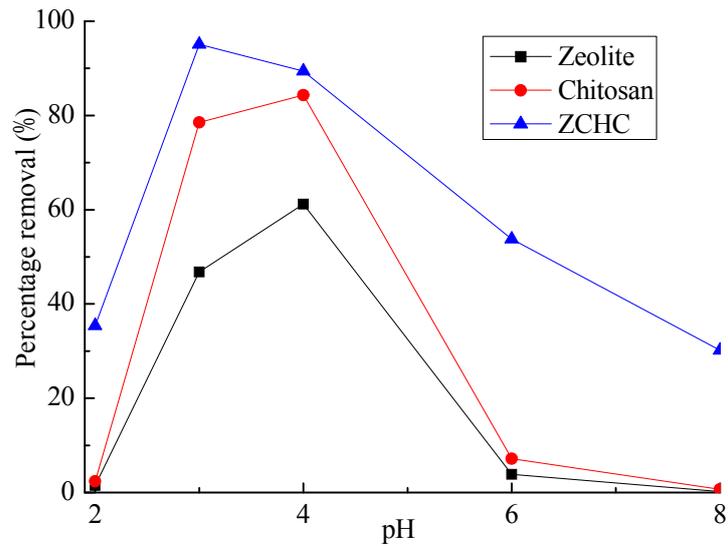


Fig. 2 Effect of pH on percent removal of Cr(VI) using adsorbents.

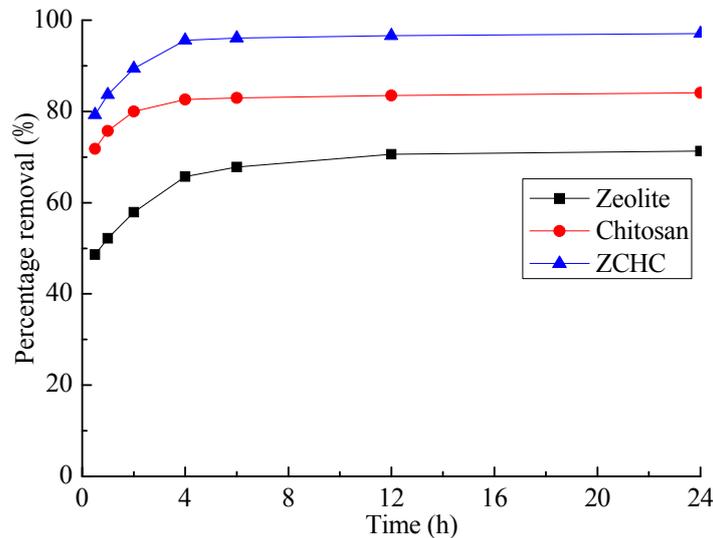


Fig. 3 Effect of contact time on percent removal of Cr(VI) using chitosan and adsorbents.

The adsorption capacity of adsorbents for Cr(VI) are shown in Fig. 3. More than 50% (in case of zeolite), 60% (in case of chitosan) and 80% (in case of ZCHC) adsorption was observed within first 30 min, and approximately 80% (in case of zeolite and chitosan) and 95% (in case of ZCHC) was obtained at 240 min (i.e., 4 h) and after that there is no appreciable increase. Hence, the optimized contact time was taken 4 h for the removal of Cr(VI) in our experimental work.

3.2.3 Effect of Adsorbent Dosage

Under optimized condition of pH and contact time,

adsorption behaviors onto adsorbents at different dosages from $0.1 \text{ g}\cdot\text{dm}^{-3}$ to $2.0 \text{ g}\cdot\text{dm}^{-3}$ have been studied in $100 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$ of Cr solution. The removal of Cr(VI) more than 90% was observed for $1.0 \text{ g}\cdot\text{dm}^{-3}$ dosage, but no remarkable increase is observed at a dosage more than $1.0 \text{ g}\cdot\text{dm}^{-3}$. Therefore, $1.0 \text{ g}\cdot\text{dm}^{-3}$ was considered as optimum dosage for the removal of Cr(VI) in the study.

3.3 Effect of Initial Concentration

Study was carried out by varying initial concentrations from $20 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$ to $200 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$ under

optimized conditions of pH 4, contact time (i.e., time 4 h) and adsorbent dosage (i.e., 1.0 g·dm⁻³). There was a continuous increase in the uptake of Cr(VI) per gram of adsorbent up to the concentration of 100 µg·dm⁻³, but the uptake is almost constant at further higher concentration for Cr(VI). Data obtained from the variation of initial concentrations were fitted for adsorption isotherms [9] to estimate the relevant parameters mentioned in Section 2.4.

3.4 Adsorption Isotherms

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes. The adsorption data obtained for Cr(VI) using zeolite, chitosan and ZCHC were analyzed by Langmuir (Fig. 4) and Freundlich equations. The correlation coefficients (R^2) of these isotherms for Cr(VI) on each adsorbent are shown in Table 2 along with other relevant parameters.

From Table 2, it is found that R^2 value for Cr(VI) on each adsorbent is comparatively large, and

favorable adsorption of Cr by adsorbents were presented. Particularly, R^2 values in Langmuir isotherm are large for any Cr(VI). This result suggests that the adsorption of Cr(VI) on chitosan or ZCHC mainly occurred by monolayer reaction.

3.5 Kinetic Studies

The linear plot of t/q_t versus time t for Cr(VI) adsorption under the optimized experimental conditions is shown in Fig. 5. The pseudo-second-order rate constant (k) and the amount of adsorbed lead (q_e), obtained from the intercept and slope of the plot of t/q_t vs. t are listed in Table 3 along with the regression coefficients (R^2). It implies that the adsorption kinetics based on the experimental values are in good agreement with the pseudo second-order kinetic model. The intraparticle diffusion model indicated that the relationship between the concentration of Cr(VI) and the square root of time are linear. This suggests that the adsorption process could be controlled by intraparticle diffusion.

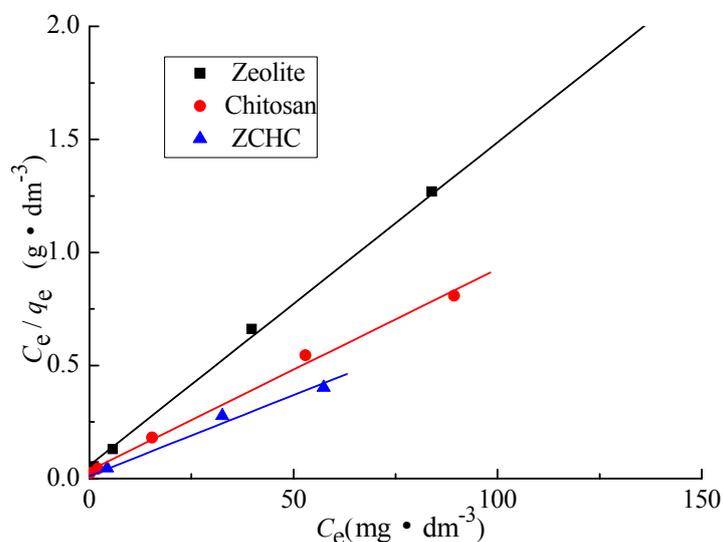


Fig. 4 Langmuir isotherm of Cr(VI) adsorption onto adsorbents.

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

	Langmuir isotherm			Freundlich isotherm		
	q_{\max} (µg·g ⁻¹)	K_L (dm ⁻³ ·µg ⁻¹)	R^2	K_F ((µg·g ⁻¹)·(dm ⁻³ ·µg ⁻¹) ^{1/n})	1/n	R^2
Zeolite	70.0	0.245	0.999	17.4	0.526	0.957
Chitosan	92.2	0.253	0.998	30.6	0.311	0.964
ZCHC	109	0.645	0.994	57.7	0.237	0.955

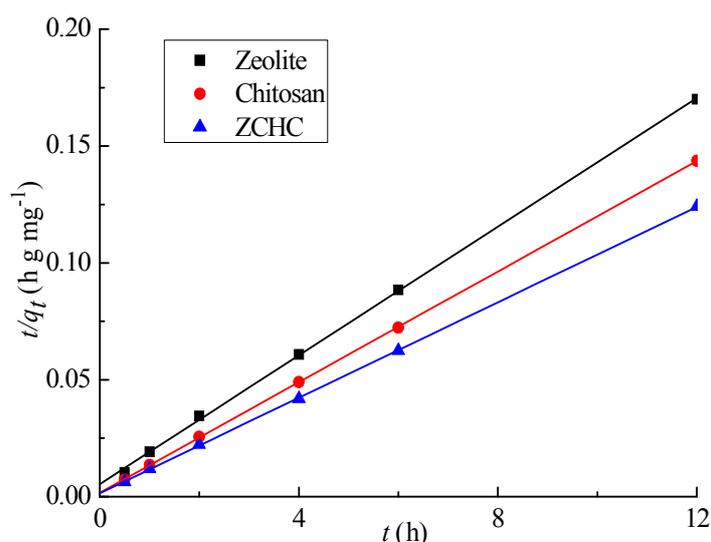


Fig. 5 The pseudo-second-order kinetic model for adsorbents.

Table 3 Kinetic coefficient for Cr(VI) adsorption on adsorbents.

Adsorbents	q_e ($\mu\text{g}\cdot\text{g}^{-1}$)	k ($\text{g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$)	R
Zeolite	72.6	0.0351	0.999
Chitosan	84.5	0.0724	0.999
ZCHC	97.9	0.0869	0.999

4. Conclusions

The aim of this investigation was to prepare and characterize a ZCHC, and investigate the ability of this hybrid composite to be used for Cr(VI) removal. The hybrid composite exhibits higher adsorption capacity and stronger chemical affinity than pristine zeolite and chitosan.

The isotherm models such as Langmuir and Freundlich were used to analyze the adsorption data. The adsorption of Cr(VI) by the ZCHC was well fitted to Langmuir isotherms, which suggests that the adsorption of Cr(VI) on ZCHC mainly occurred by monolayer reaction. The kinetic studies of Cr(VI) adsorption by the ZCHC was analyzed using the pseudo-first order and pseudo-second order kinetic models, and it shows better fitting for the pseudo-second order of Cr(VI) adsorption.

From the above results, ZCHC (which was prepared with sol-gel method by mixing zeolite and chitosan) can be an effective adsorbent for Cr(VI) from aqueous solution. This provides very significant information

from the viewpoint of environmental protection.

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