

Study on Removal of Cr(VI) from Aqueous Solution by Cross-Linked Chitosan

Xiaoyu Du¹, Yanling Deng¹, Shunsuke Sekiguchi¹, Naoto Miyamoto², Naoki Kano² and Hiroshi Imaizumi²

1. Graduation 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: In this paper, the adsorbent for the removal of hexavalent Cr (Chromium) from aqueous solutions has been prepared by modifying chitosan composite with EP (Epichlorohydrin) or GA (Glutaraldehyde). The modified cross-linked chitosan was characterized by SEM (Scanning Electron Microscopy) and FT-IR (Fourier Transform Infrared Spectroscopy). Batch adsorption experiments were carried out to evaluate the adsorption of Cr(VI) by the cross-linked chitosan under different conditions. Furthermore, the sorption mechanism of Cr(VI) by the cross-linked chitosan was investigated by applying Langmuir and Freundlich isotherm equations to the data obtained. The concentration of Cr in solution was determined by ICP-MS (Inductively Coupled Plasma Mass Spectrometry). The cross-linked chitosan can be an efficient sorbent for Cr(VI).

Key words: Cross-linked chitosan, EP (Epichlorohydrin), GA (Glutaraldehyde), hexavalent Cr (Chromium), adsorption isotherms, kinetics.

1. Introduction

As is well known, the investigations on abundant levels of toxic heavy metal ions (e.g. hexavalent Cr (chromium), Cr(VI)) discharged to the environment (and its persistence in the environment) have now been receiving considerable attention with the development of society and the industrial economy [1]. Thus, there is need to develop novel materials having improved physicochemical properties for the removal of heavy metal ions from aqueous solution.

Chitosan is a basic polysaccharide polymer with active functional groups, and has unique physiological activity and physicochemical properties [2]. Chitosan can be easily obtained due to the widespread natural occurrence of its source which is found in the shells of crustaceans, e.g. crabs, prawns, shrimps and insects. Further, chitin is easily converted to chitosan, the desired end product, through deacetylation [3]. Therefore, chitosan has attracted increasing research

interest as a potential biosorbent for the removal of heavy metal ions since it has both amine and hydroxyl groups that may serve as coordination sites to form stable chelates with various heavy metal ions [4].

Cr mainly exists in two oxidation states such as Cr(III) and Cr(VI) in natural aqueous environment. Cr(VI) has been considered more toxicity and hazardous to public health due to its mutagenic and carcinogenic properties [5]. The environmental standard of Cr(VI) is less than 0.05 mg/L, and the drainage standard is less than 0.5 mg/L. At natural aqueous environment, it may be present form of CrO_4^{2-} or HCrO_4^- . On the hand, Cr(III) is low toxicity, essential materials for living organisms, and the environmental standard is less than 2 mg/L. Various methods of chromium removal include filtration, chemical precipitation, adsorption, electrode position and membrane systems or even ion exchange process. Among these methods, adsorption is one of the most economically favorable and a technically easy method [6, 7]. Then authors adopted the adsorption method for the removal of Cr(VI) with the materials based on chitosan because they have high potential for adsorption of Cr [8-10].

Corresponding author: Naoki Kano, associate professor, Ph.D., research fields: environmental analysis and environmental reservation.

However, chitosan has some defects such as dissolution in acid media and notable swelling in aqueous media. Therefore, many types of chemical modification can be undertaken for offsetting the defects of chitosan. In this study, chitosan was modified by cross-linking with EP (Epichlorohydrin) or GA (glutaraldehyde).

In regard to EP cross-linked chitosan, amino groups of chitosan were not damaged during the process of cross-linking because EP are mainly associated with hydroxyl groups. In the case of GA cross-linked chitosan, the reaction of Schiff base between the aldehyde group of GA and the amido of chitosan is dominant. It is expected that cross-linked chitosan bead material with EP or GA improves the adsorption ability of Cr(VI) as well as Cu(II) and Co(II) [11, 12].

The aim of this paper is to investigate the adsorption efficiency of chitosan cross-linked with EP or GA for more practical use in the future. Experiments were conducted to determine the optimum conditions of time, pH, dosage and temperature for the adsorption. Adsorption isotherms of Cr(VI) were studied and analyzed using Langmuir and Freundlich equations, kinetics and thermodynamic analyses were also carried out. In addition, to evaluate the characteristics of the adsorbents, the surface morphology of the materials were determined by SEM (Scanning Electron Microscope), BET (Brunauer, Emmet and Teller) method and FT-IR (Fourier Transform Infrared Spectroscopy).

2. Experimental

2.1 Materials and Reagents

Chemical reagents including chitosan was purchased from Tokyo Chemical Industry Co., Inc., acetic acid, NaOH, EP and GA were purchased from Kanto Chemical Industry Co., Inc., and all reagents used were of analytical grade. The water ($> 18.2 \text{ M}\Omega$) which was treated by an ultrapure water system (RFU 424TA, Advantech Aquarius) was employed

throughout the work. Cr(VI) standard solutions used for calibration curve were prepared by diluting the standard solution (Kanto Chemical Co., Inc., 1,000 mg/L K_2CrO_7 solution). The experimental solution was prepared at 0.05-5.0 mg/L by serial dilution from the stock solution of 1,000 mg/L.

2.2 Preparation of Cross-Linked Chitosan Beads

Chitosan was stirred with the acetic acid solution 200 mL (2.0%) and added drop-wise to 100 mL of 0.5 M NaOH [13, 14].

Each cross-linked chitosan was prepared as follows. Chitosan was added to 1.0 wt% of EP, adjust the pH to 14. After keeping the mixed solution at 60 °C for 6 h, can get cross-linking with EP. Furthermore, chitosan was added to 1.0 wt% of GA, adjust the pH to 7. After keeping the mixed solution at room temperature for 24 h, can get cross-linking with GA. Chitosan cross-linked with EP or GA were described as EP and GA, respectively as below.

2.3 Characterization of These Adsorbents

Various characterization methods have been used to determine physicochemical properties of pristine and modified chitosan. The surface morphologies of these cross-linked chitosan beads were surveyed by using a SEM (Hitachi S-4300). Surface areas of these cross-linked chitosan beads before and after Cr(VI) adsorption were carried out by N_2 adsorption/desorption tests (Micromeritics TriStar 3020). Surface functional groups were identified by FT-IR spectrometer (FTIR-4200, Jasco, Japan).

2.4 Adsorption Experiments

For investigating the effects of pH, contact time, adsorbent dose, temperature and initial concentration on the adsorption of Cr(VI), the following batch adsorption experiments were conducted using cross-linked chitosan bead. The bead was thoroughly mixed with 100 dm^3 of containing known amount of Cr(VI) in a 200 dm^3 conical flask, and the

suspensions was shaken in a water bath at prescribed temperature. Adsorption experiments were performed in the pH range of 1-7, contact time from 0.5 h to 24 h, adsorbent dosage 0.10-0.50 g·dm⁻³, temperature at 288 K-318 K and initial Cr(VI) concentration from 0.05-5.0 mg·dm⁻³. The pH of each solution was adjusted by using 0.1 mol·dm⁻³ NaOH or HNO₃.

Following each adsorption experiment, the cross-linked chitosan bead and the above Cr(VI) solution was filtered to remove Cr(VI) that have been absorbed into the cross-linked chitosan bead, and the concentration of Cr(VI) in the filtrate was determined with an ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

The adsorption capacities of Cr(VI) using modified chitosan with GA and EP at equilibrium (q_e : mg·g⁻¹) was calculated using the Eq. (1):

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

Where q_e is the adsorption capacities at equilibrium (mg·g⁻¹), C_i and C_e are the initial and equilibrium concentrations of Cr(VI) in a batch system respectively (mg·L⁻¹), V is the volume of the solution (L), and m is the weight of adsorbent (g).

2.5 Adsorption Isotherm Model

Adsorption isotherms are commonly used to reflect the performance of adsorbents in adsorption processes. To examine the relationship between the metal uptake (q_e) and the concentration of metal ion (C_e) at equilibrium, adsorption isotherm models are widely employed for fitting the data. To get the equilibrium data, initial concentrations of metals were varied while the adsorbent weight of each sample was kept constant. Langmuir and Freundlich isotherms model was applied to evaluate the adsorption data obtained in this study.

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 and q_e are the concentration of Cr(VI) at equilibrium (mg·L⁻¹) and the amount of adsorption of Cr(VI) at equilibrium (mg·g⁻¹) respectively, q_{\max} is the maximum adsorption capacity on the surface of hybrid membrane (mg·g⁻¹), and K_L is the equilibrium adsorption constant (L·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 $1/(K_L q_{\max})$.

On the other hand, the linearized Freundlich model isotherm is represented by 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, $1/n$ indicate 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.

2.6 Kinetic Studies

Kinetic models have been proposed to determine the mechanism of the adsorption process which provided useful data to improve the efficiency of the adsorption and feasibility of process scale-up. In the present investigation, the mechanism of the adsorption process was studied by fitting first-order and second-order reactions to the experimental data.

The pseudo first-order model is given by 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 chitosan at equilibrium and time t , respectively (mol·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 Eq. (5):

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

Where q_e and q_t are the adsorption capacities of Cr(VI) using the hybrid membrane at equilibrium and time t , respectively (mol·g⁻¹), and k is the rate constant of the pseudo-second-order adsorption (g·mol⁻¹·h⁻¹).

3. Results and Discussion

3.1 Characterization of Prepared Materials

SEM pictures of the pristine and cross-linked chitosan beads are shown in Fig. 1. It can be observed that surface textures were changed. The FT-IR spectra of the pristine and the cross-linked chitosan beads are presented in Fig. 2. The broad and intense peak at 3,400 to 3,500 cm^{-1} corresponds to the -OH and -NH₂

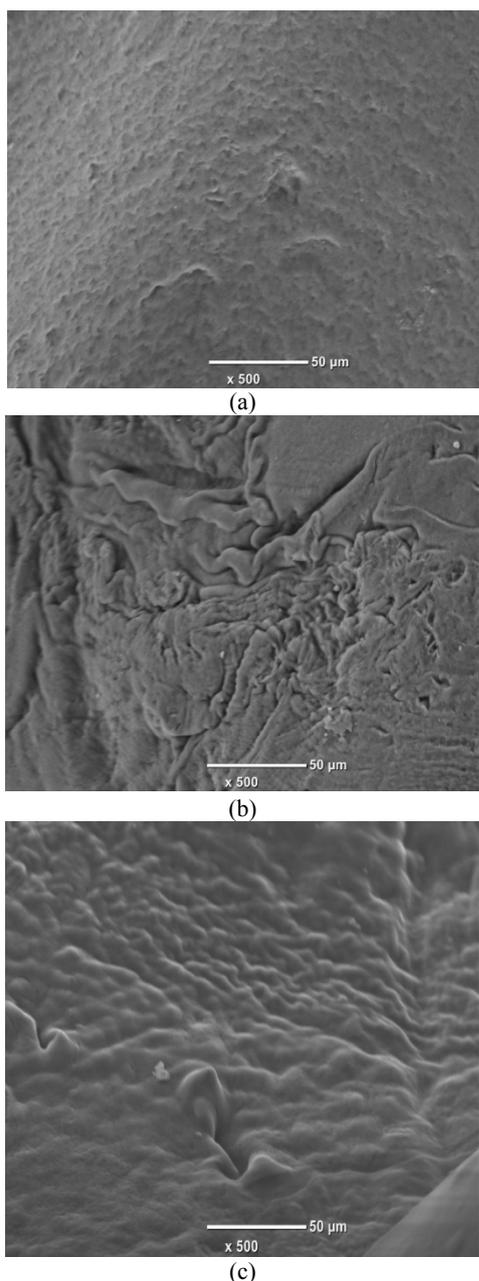


Fig. 1 SEM photomicrographs of (a) chitosan, (b) crosslinking with EP (c) crosslinking with GA.

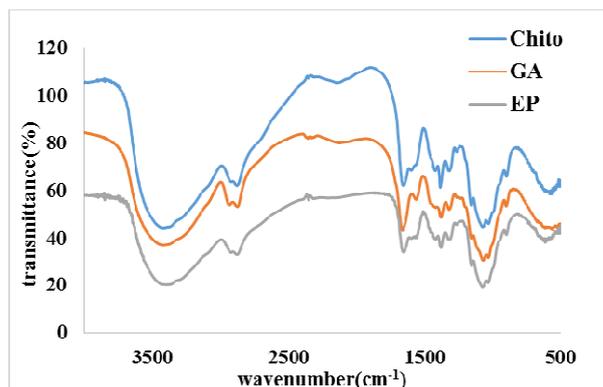


Fig. 2 FT-IR spectra of the chitosan, EP and GA.

stretching vibration of hydroxyl groups in chitosan and the cross-linked chitosan. [12, 15, 16]. The peak at 2,871 cm^{-1} is related to aliphatic methylene group. Moreover, the wide peak at 1,560 to 1,640 cm^{-1} shows the amine group which is remarkable for GA [12].

The properties of the chitosan and the cross-linked chitosan beads were investigated by N₂ adsorption (TriStar II 3020 Micromeritics); and the pore size was calculated from adsorption average pore width (4V/A by BET) in this work is shown in Table 1. From Fig. 1 and Table 1, it is found that the surface textures were changed, and that the specific surface areas were remarkably increased after cross-linking.

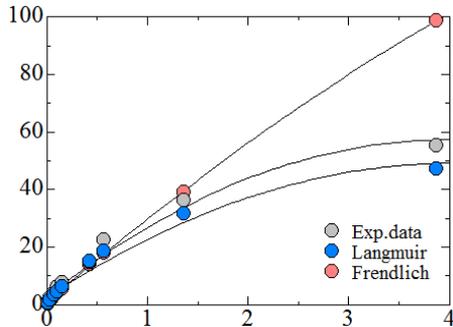
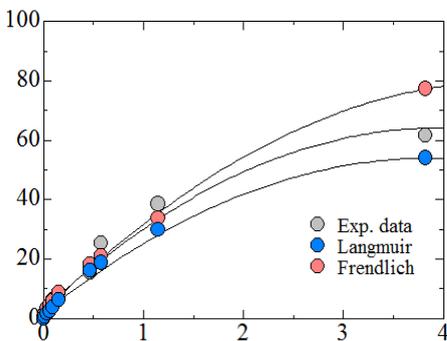
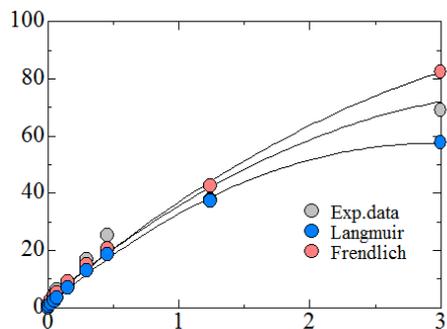
3.2 Adsorption of Cr(VI) on Chitosan, EP and GA

3.2.1 Adsorption Isotherms

Langmuir and Freundlich isotherms were applied to the data obtained in this work. The linear plots of C_e and Q_e for these materials were presented for Langmuir and Freundlich models (Fig. 3: chitosan, Fig. 4: GA, Fig. 5: EP). The coefficients of both isotherms are shown in Table 2 (Langmuir) and Table 3 (Freundlich). From Figs. 3-5, it is also found that chitosan is more fitted to Langmuir isotherm; and that EP and GA were fitted to Freundlich isotherm as well as Langmuir isotherm compared to Chitosan. Adsorption isotherms of Cr on these materials can be generally described by Langmuir isotherm more satisfactorily. The adsorption may have occurred mainly by monolayer reaction.

Table 1 Surface areas of these cross-linked chitosan beads.

Adsorbent	Chitosan	EP	GA
BET surface area (m^2/g)	0.80	8.26	52.1


Fig. 3 Adsorption isotherm of Cr(VI) on Chitosan.

Fig. 4 Adsorption isotherm of Cr(VI) on GA.

Fig. 5 Adsorption isotherm of Cr(VI) on EP.

From Tables 2 and 3, the maximum adsorption capacity of modified chitosan reached 90.9 mg/g from 49.8 mg/g by cross-linking with EP under our experimental conditions. That is to say, modified chitosan by cross-linking can be an efficient adsorbent for Cr(VI).

3.2.2 Kinetic Studies

The linear plot of q_e versus time t for Cr(VI)

adsorption under the conditions (dose: $0.20 \text{ g}\cdot\text{dm}^{-3}$, Cr: $500 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$, pH: 4) is shown in Figs. 6-8 (Fig. 6: chitosan, Fig. 7: GA, Fig. 8: EP). The pseudo-first and pseudo-second-order rate constant (k) and the amount of adsorbed Cr(VI) (q_e), obtained from the intercept and slope of the plot of t/q_t vs. t are listed in Tables 4 and 5 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 rather than pseudo first-order model.

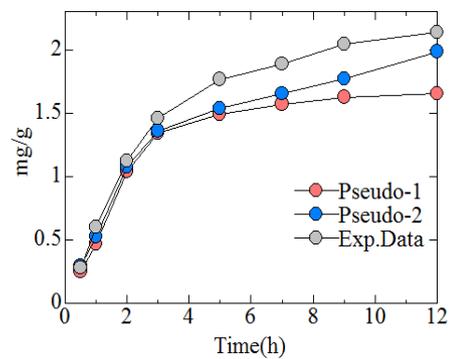
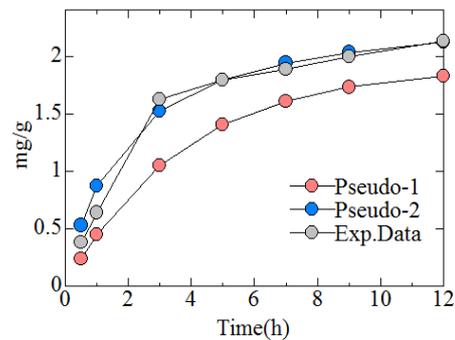

Fig. 6 Adsorption kinetics of Cr(VI) on chitosan.

Fig. 7 Adsorption kinetics of Cr(VI) on EP.

Table 2 Langmuir isotherm parameters for Cr(VI).

	Chitosan	EP	GA
a (mg/g)	49.8	90.9	73.5
b (L/mg)	2.87	0.558	0.594
R_L	0.0337	0.152	0.144
R^2	0.979	0.989	0.997

Table 3 Freundlich isotherm parameters for Cr(VI).

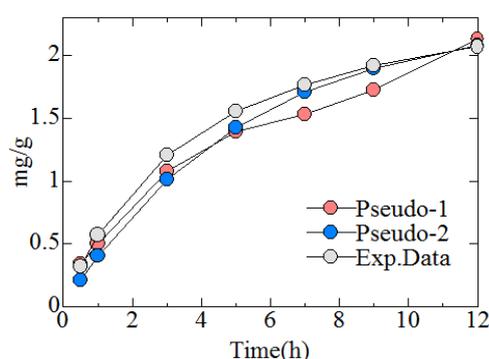
	Chitosan	EP	GA
K_F	26.4	36.2	30.8
$1/n$	0.841	0.721	0.685
R^2	0.941	0.980	0.977

Table 4 Pseudo-first-order model kinetic parameters.

	Chitosan	EP	GA
K_1 (h^{-1})	0.330	0.267	0.192
q_e (mg/g) _{exp}	2.23	2.21	2.29
q_e (mg/g) _{cal}	1.66	1.90	2.31
R^2	0.980	0.973	0.943

Table 5 Pseudo-second-order model kinetic parameters.

	Chitosan	EP	GA
K_2 (g/mg h)	0.135	0.226	0.0975
q_e (mg/g) _{exp}	2.23	2.21	2.29
q_e (mg/g) _{cal}	2.26	2.44	2.72
R^2	0.983	0.989	0.935

**Fig. 8 Adsorption kinetics of Cr(VI) on GA.**

4. Conclusions

The maximum adsorption capacity of modified chitosan reached 90.9 mg/g from 49.8 mg/g by cross-linking with EP under the experimental conditions. Adsorption isotherms of Cr on the modified chitosan can be generally described by Langmuir isotherm more satisfactorily. The adsorption may have occurred mainly by monolayer reaction. The rates of adsorption using the modified chitosan for the removal of Cr were found to conform to pseudo-second order kinetics. Modified chitosan by cross-linking can be an efficient adsorbent for Cr.

Acknowledgements

The present work was partially supported by a Grant-in-Aid for Scientific Research (Research Program (C), No. 16K00599) of the Japan Society for the Promotion of Science. This research was also supported by a fund for the promotion of Niigata

University KAAB Projects from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

The authors are also grateful to Mr. M. Ohizumi of Office for Environment and Safety in Niigata University, Dr. M. Teraguchi, Mr. T. Hatamachi, Mr. T. Nomoto and Prof. T. Tanaka of Fac. of Eng. in Niigata University for permitting the use of ICP-MS, FT-IR, Surface Area Analyzer and SEM for giving helpful advice in measurement.

References

- [1] Laus, R., Costa, T. G., Szpoganicz, B., and Fávere V. T. 2010. "Adsorption and Desorption of Cu(II), Cd(II) and Pb(II) Ions Using Chitosan crosslinked with Epichlorohydrin-triphosphate as the Adsorbent." *J. J. Hazard Matter* 183 (1-3): 233-41.
- [2] Aydin, Y. A., and Aksoy, N. D. 2009. "Adsorption of Chromium on Chitosan: Optimization, Kinetics and Thermodynamic." *Chem. Eng. J.* 151 (1-3): 188-94.
- [3] Li, X., Zhou, H., Wu, W., Wei, S., Xu, Y., and Kuang, Y. 2015. "Studies of Heavy Metal Ion on Chitosan/Sulfhydryl-functionalized Graphene Oxide Composites." *J. Colloid. Interf. Sci.* 448: 389-97.
- [4] Kołodynska, D. 2011. "Chitosan as an Effective Low-cost Sorbent of Heavy Metal Complexes with the Polyaspartic Acid." *Chem. Eng. J.* 173 (2): 520-9.
- [5] Baroni, P., Vieira, R. S., Meneghetti, E., da Silva, M., and Beppu, M. M. 2008. "Evaluation of Batch Adsorption of Chromium Ions on Natural and Crosslinked Chitosan Membranes." *J. J. Hazard Matter* 152 (3): 1155-63.
- [6] Huang, G., Zhang, H., Shi, J. X., and Langrish, T. S. G. 2009. "Adsorption of Chromium(VI) from Aqueous Solutions Using Cross-Linked Magnetic Chitosan Beads." *J. Ind. Eng. Chem. Res.* 48 (5): 2646-51.
- [7] Ngah, W. S., Ghani, S. A., and Kamari, A. 2005. "Adsorption Behaviour of Fe(II) and Fe(III) Ions in Aqueous Solution on Chitosan and Cross-linked Chitosan Beads." *Bioresour. Technol.* 96 (4): 443-50.
- [8] Modrzejewska, Z., Sujka, W., Dorabalska, M., and Zarzycki, R. 2006. "Adsorption of Cr(VI) on Cross-linked Chitosan Beads." *Separat. Sci. Technol.* 41 (1): 111-22.
- [9] Jaros, K., Kaminski, W., Albinska, J., and Nowak, U. 2005. "Removal of Heavy Metal Ions: Copper, Zinc and Chromium from Water on Chitosan Beads." *Environ. Prot. Eng.* 31 (3-4): 153-62.
- [10] Zarzycki, R., Sujka, W., Dorabalska, M., and Modrzejewska, Z. 2002. "Adsorption of Cr(VI) on

- Chitosan Beads." *Chem. Inz. Ekol.* 9: 1561-70.
- [11] Ngah, W. S., Endud, C. S., and Mayanar, R. 2002. "Removal of Copper(II) Ions from Aqueous Solution onto Chitosan and Cross-linked Chitosan Beads." *React. Funct. Polym.* 50 (2): 181-90.
- [12] Cestari, A. R., Vieira, E. F. S., Oliveira, I. A., and Bruns, R. E. 2007. "The Removal of Cu(II) and Co(II) from Aqueous Solutions Using Cross-linked Chitosan-evaluation by the Factorial Design Methodology." *J. Hazard Matter* 143 (1-2): 8-16.
- [13] Ngah, W. S. W., Teong, L. C., and Hanafiah, M. A. K. M. 2011. "Adsorption of Dyes and Heavy Metal Ions by Chitosan Composites." *A Review Carbohydr. Polym.* 83 (4): 1446-56.
- [14] Sushanta, D., Arjun, M., and Kriveshini, P. 2014. "Magnetic Chitosa-GO Nanocomposite: Synthesis, Characterization and Batch Adsorbed Design for Cr(VI) Removal." *J. Environ. Chem. Eng.* 2 (2): 963-73.
- [15] Motawie, A. M., Mahmoud, K. F., El-Sawy, A. A., Kamal, H. M., Hefni, H., and Ibrahiem, H. A. 2014. "Preparation of Chitosan from the Shrimp Shells and Its Application for Pre-concentration of Uranium after Cross-linking with Epichlorohydrin." *J. Egyptian Journal of Petroleum* 23 (2): 221-8.
- [16] Ngah, W. S., Endud, C. S., and Mayanar, R. 2002. "Removal of Copper(II) Ions from Aqueous Solution onto Chitosan and Cross-linked Chitosan Beads." *React. Funct. Polym.* 50 (2): 181-90.