Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.23660

145 (2019) 202–210
March

Adsorption mechanism of Cu(II) in water environment using chitosan-nano zero valent iron-activated carbon composite beads

Md. Tajuddin Sikder[a,b,c,*], Ryo Kubota[d], Mahmuda Akter[d], Md. Mostafizur Rahman[d], Kaniz Fatima Binte Hossain[d], Md. Shiblur Rahaman[d], Subrata Banik[d], Toshiyuki Hosokawa[e], Takeshi Saito[b], Masaaki Kurasaki[a,d]

[a]*Department of Public Health and Informatics, Jahangirnagar University, Dhaka-1342, Bangladesh, Tel. +88-027791045-51, email: sikder@ees.hokudai.ac.jp (M.T. Sikder)*
[b]*Faculty of Health Sciences, Hokkaido University, Sapporo 060-0812, Japan, Tel. +81-117063325, email: taksaito@med.hokudai.ac.jp (T. Saito)*
[c]*Faculty of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan, Tel. +81-117062243*
[d]*Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan, email: kubotar@ees.hokudai.ac.jp (R. Kubota), mahmuda@ees.hokudai.ac.jp (M. Akter), mmrahman@ees.hokudai.ac.jp (M.M. Rahman), rumana@ees.hokudai.ac.jp (K.F.B. Hossain), shiblu@ees.hokudai.ac.jp (M.S. Rahaman), sbanik@juniv.edu (S. Banik), Tel. +81-117062243, email: kura@ees.hokudai.ac.jp (M. Kurasaki)*
[e]*Research Division of Higher Education, Institute for the Advancement of Higher Education, Hokkaido University, Sapporo 060-0817, Japan, email: hoso@high.hokudai.ac.jp (T. Hosokawa)*

Received 2 July 2018; Accepted 22 December 2018

ABSTRACT

Copper ions (Cu(II)) produced from various industries can lead to pollution at toxic levels, eventually finding its way into food chains and resulting in serious health impairment. Among different treatment technologies practiced, adsorption is unique in terms of its versatility and economic feasibility. Here, the removal of Cu(II) was examined using chitosan-nano zero valent iron-activated carbon (CS-NZVI-AC) composite beads. Results indicate that the rate of Cu(II) adsorption onto the CS-NZVI-AC accelerated significantly in comparison with lonechitosan (CS), activated carbon (AC) and zero valent iron (NZVI). Moreover, the hybridization of CS-AC with NZVI endows an increase in the uptake of Cu(II) up to 30% compared to that of CS-AC alone. The adsorption mechanism is understood as chemisorptions along with the active Van der Waals forces, as supported by the best fit of sorption data with pseudo-second order kinetics and Freundlich isotherm model. The adsorption capacity of CS-NZVI-AC for Cu(II) increased with increasing pH of up to 5 and with 25°C water temperature. Thus, it is indicated that this hybrid CS-NZVI-AC composites have great potential for environmental remediation efforts for Cu(II) and other similar heavy metal ions.

Keywords: Chitosan; Activated carbon; Zero valent iron; Adsorption; Kinetic; Equilibrium; Remediation

1. Introduction

Water pollution due to toxic heavy metals is a significant environmental concern [1]. Being one of the most toxic heavy metals, copper (Cu(II)) is persistent, carcinogenic at higher doses, and leads serious threats to the environment and health [2,3]. Its bioaccumulation tendency, along with the non-biodegradable nature, contributes serious public health concern and causes various diseases and disorders e.g. depression, gastrointestinal and nervous system disorder. The leaching of Cu(II) from waste disposal sites, along with industrial discharge and erosion of natural deposits,

---

*Corresponding author.

all eventually pollute the surface and ground water. Alongside, exposed mine tailing wastes can release considerable amounts of hazardous Cu(II) into soil and water under transient chemical and physical conditions [4–6]. Therefore, it's very important to remove Cu(II) from aqueous solution [7,8].

In the past years, efforts were given to remove Cu(II) from solution in a variety of ways e.g. chemical precipitation, coagulation, ion exchange and adsorption [8–13]. A huge number of reports recognized adsorption as a superb method of Cu(II) remediation from polluted water. An ongoing endeavor is to make hybrid or composites adsorbents using high efficient adsorbents such as activated carbon (AC), chitosan (CS), alginate, cyclodextrin, etc. [3,9,12–19]. Recently, several research groups have been trying to optimize different types of synthesized composites from both inexpensive natural and synthetic materials. In our previous studies, we have successfully synthesized different types of composites and reported their high metal removal efficiency. For example, β-cyclodextrin polymer entrapped in functionalized CS yielded a composite for cadmium removal from waste water [9]; crab shell-derived CS [20], and its composites mixed with caboxymethyl-β-cyclodextrin-entrapped nanozerovalent iron, were efficient in removing chromium and arsenic, respectively [21]; micro particle prussian blue-synthesized alginate gel beads were superb in removing cesium ions in water [22]; cross-linked β-cyclodextrin polymer and its composites were used to remove copper ions from solution [7,23]; and modified α, β, and γ-cyclodextrin polymers were also tested for removing two toxic heavy metals: cadmium and chromium [24,25]. The application of CS and alginate as stabilizing agents for zerovalent iron and functionalized cyclodextrin often resulted synergistic metal removal capability. Inspired from results of previous studies, AC (in a composite of CS and NZVI) is used in this research to imply its well-known sorption capacity of Cu(II) [26,27].

Chitosan (CS) is an important biocompatible, biodegradable and non-toxic natural polymer, obtained through the deacetylation of chitin. It is positively charged and well soluble in acidic-to-neutral solution, having a pKa value from 6.2 to 7.0. Through exertion of its bio-adhesive properties, stable nanoparticles and chelation complexes can be formed by CS with different metals in solution [28,29]. The chelation of CS depends on $-NH_2$ groups in C-2 position and the reaction easily performed here by the quaternization of the $-NH_2$ groups [30]. Chelation also depends on the physical state of CS (powder, gel, fiber, film) and better chelation is obtained for greater degrees of deacetylation of Chitin [31]. In addition, introduction of carboxyl groups into chitosan is an efficient way of sorption due to the formation of stable chelate rings with metal ions. At acidic pH, CS presents remarkable chelating ability for several metal ions [32]. Zerovalent iron powders (NZVI) have been extensively used for remediation of heavy metal-polluted water due to its insoluble form, large surface area, tremendous reducing capacity, magnetite forming ability, and rapid separation from solution [33,34]. Activated carbon (AC), the top most adsorbent for the treatment of both organic and inorganic contaminants in wastewater, is unique due to its porosity, surface area and surface functional groups [35,36]. If the AC and NZVI are incorporated into a surface stabilizer CS to yield CS-impregnated zerovalent iron-activated carbon composites (CS-NZVI-AC), then the overall remediation process can be accelerated. This hypothesis was tested in this study using copper ions as a model pollutant. Each raw compounds will take part in adsorption of Cu(II). CS will impede the disintegration and dissociation of both NZVI and AC, so that, they can effectively sorb Cu(II) ions from water. NZVI will give strength to CS-NZVI-AC beads and facilitates magnetic separation. In addition, the adsorption mechanism, characteristics, kinetics, and isotherms of the synthesized CS-NZVI-AC beads were also evaluated and discussed.

2. Materials and methods

2.1. Materials

Deacytylated chitosan (≥75%) was purchased from Sigma–Aldrich (St. Louis, MA, USA). Iron, Electrolytic, powder was obtained from Kanto Chemical (Tokyo, Japan). Activated Charcoal powder (treated with HCl) was purchased from Nacalai Tesque (Kyoto, Japan). Copper(II) sulfate pentahydrate with 97% purity was used for Cu(II) adsorption, and it was purchased from Wako Pure Chemical Industries (Osaka, Japan). Acetic acid, Sodium hydroxide, Ethanol (99.5%), Hydrochloric acid and other reagents were purchased from Wako Pure Chemical Industries (Osaka, Japan). All chemicals and materials were used in this study without any prior treatment. For preparation and measurement of reagents, distilled water was used in all cases.

2.2. Preparation of CS-NZVI-AC composite beads

Firstly, 100 mL of water was equilibrated with 5% (v/v) acetic acid. Subsequently, 0.25 g of AC (finely grained powder, surface area - 770 m^2/g, size - 60 μm) and 4.0 g of CS flakes were added in small portions to the acetic acid solution at 50°C, which would be stirred for 2 h to get CS-AC gel. Then, 0.45 g of NZVI (zero-valent, powder, size-20–100 nm) was added to the CS-AC gel followed by vigorous stirring to yield CS-NZVI-AC gel. The solution was cooled down in room temperature with continuous stirring. An alkaline bead forming solution was prepared using 3.75 M NaOH, 100 mL of 99.50% ethanol and 100 mL of water, and was cooled to room temperature. The mixture gel of CS-NZVI-AC was dropped into the alkaline solution using a syringe with constant stirring to form beads. After 8 h, the beads were washed with distilled water for lowering the pH under 7. Two kinds of other mixtures were also prepared without NZVI or AC for producing CS and CS-AC beads as controls.

2.3. Characterization of CS-NZVI-AC

The morphology of the synthesized CS-NZVI-AC beads was assessed using scanning electron microscope (SEM), JEOL (Tokyo, Japan), FE-SEM JSM-6500F, operated at 20 kV, attached an Energy dispersive X-ray spectrometer, EDS. To enhance the electron conductivity, the sample was dried on aluminum stubs adhered to graphite support units using carbon tape. To measure the surface area, Brunauer–

Emmett–Teller (BET) analysis was conducted on an automated gas adsorption analyzer Belsorp-max, (S/N = 240) Ver. 1.2.7t (BEL Japan, Inc.).

2.4. Adsorption study

Artificial wastewater was prepared by spiking ultrapure water with copper (II) sulfate pentahydrate at environmentally relevant concentrations. Adsorption experiments were carried out in aqueous solutions at pH 2–7 and 25–45°C. Except some special cases, the adsorbent dosage was defined as 1 g at wet condition per 10 mL of the test solution, the pH was employed as 5 and the sample volume was 10 mL. Atomic absorption spectrophotometer (AAS); Hitachi (Tokyo, Japan) was used to measure the concentration of Cu(II).

3. Results and discussion

3.1. Characterization of the CS-NZVI-AC beads

Energy-dispersive X-ray spectrophotometric analysis (EDS) imaging of CS-NZVI-AC beads was used to know the presence of characteristic element as a function of energy and to check the presence of C and O fused in beads preparation (Fig. 1). Strong peak of C and O indicated the presence of CS and AC, while some peaks for Fe indicated the presence of NZVI as well. Interestingly, some peaks for Cu were also reflected in EDS (Fig. 1B) which suggested the presence of Cu in CS-NZVI-AC beads. Thus, the presence of Cu peaks in the EDS analysis confirmed the adsorption capacity of CS-NZVI-AC beads, as the said peaks were not present in the beads prior to adsorption; thereby indicating that there was binding of the metal ions with the beads. However, some weaker peaks also indicated the presence of platinum (Pt), might be reflected from the Pt plate that was used to hold beads during EDS analysis.

To study the morphological analysis, SEM was performed (Fig. 2). At 10 kV, SEM showed oval shaped micro-structured CS-NZVI-AC beads with a rough and porous body surface. The beads were black in color with a diameter ranged from 2.20 to 2.50 mm. Cross-section of the beads showed mesh-like pore structures around the whole surfaces, which accounts for the beads' high adsorption capability (Fig. 2A). There was a strong structural difference visualized between the outer and inner surface of the beads. From the results of EDS and SEM analysis, it might be confirmed that after adsorption, Cu was contained into the adsorbent wherein the porous structure of the beads played a vital contribution in the adsorption mechanism.

The BET surface area of the CS-NZVI-AC beads was obtained as 8.58 m²/g, and it was calculated by using the following equations:

$$\frac{p}{v(p_0-p)}=\frac{1}{v_mC}+\frac{c-1}{v_mC}*\frac{p}{p_0} \tag{1}$$

$$A_s=v_m*N*\frac{a_m}{22400}*10^{-18} \tag{2}$$

where V_m is the monomolecular layer adsorption and A_s is the surface area. The value of N is the Avogadro's number (6.02×10^{23}) and a_m represents molecular occupied cross section, in which for this case it was 0.162 nm² [7]. From the adsorption-desorption (BET) isotherms (Fig. 3A), the volume of adsorbed N_2 was found slightly increased with increasing P/P_0, indicating a small pore size distribution in the adsorbent beads. The average weight of a wet bead was 0.043 g (standard deviation was 0.0045, n = 20) and the average weight of a dry bead was 0.003 g.

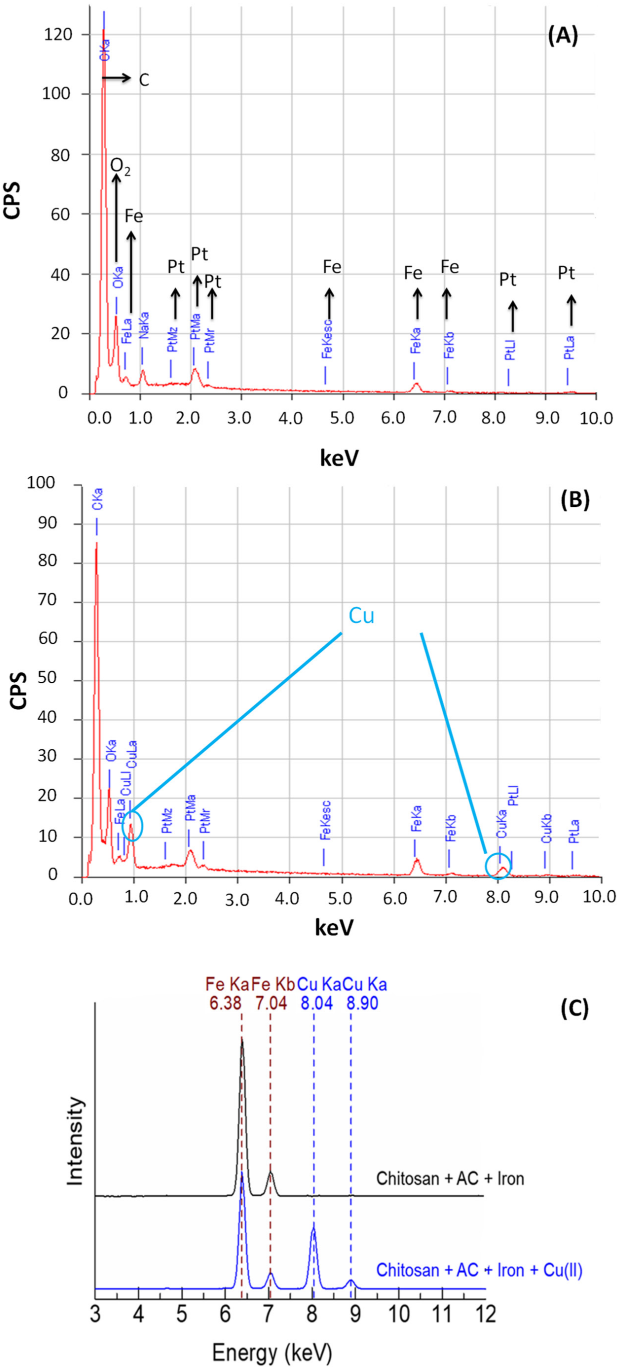

Fig. 1. EDS analysis of CS-NZVI-AC beads (A) before; (B) after adsorption of Cu(II) and, (C) elemental analysis of chitosan, activated carbon, iron as shown in black line and, chitosan, activated carbon, iron and Cu (II) as shown in blue line.

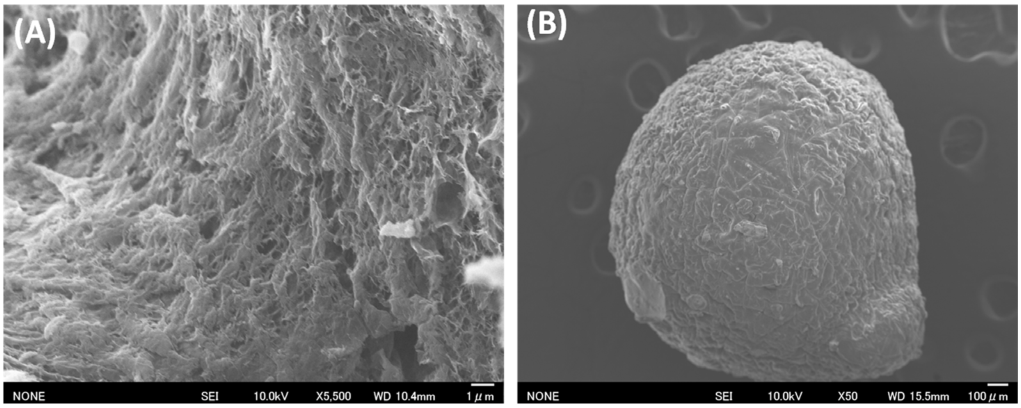

Fig. 2. SEM images of CS-NZVI-AC beads at different magnifications. (A) internal network of the pore spaces for CS-NZVI-AC beads, and (B) the size and shape of the beads.

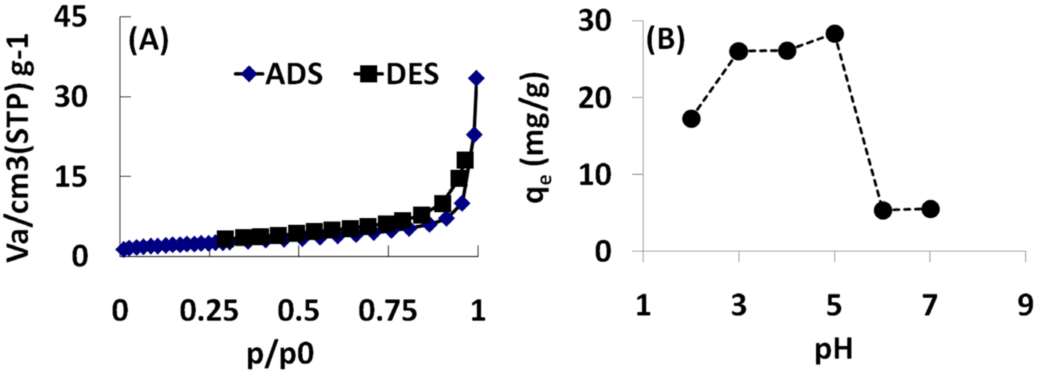

Fig. 3. (A) BET adsorption desorption isotherm; (B) Effects of pH to the adsorption of Cu(II) onto CS-NZVI-AC beads.

3.2. Effects of initial pH

pH of the solution usually control the sorption process [37]. The pH condition of the solution can generate a suitable surface environment for the sorbent through controlling electrostatic interactions between sorbent and sorbate by charge-regulation [21]. In this study, characterization of CS-NZVI-AC composite beads were carried out at pH value range 2–7 in order to determine the effect of pH on Cu(II) removal (Fig. 3B). There was an observed increasing trend of adsorption capacity of CS-NZVI-AC with increasing pH up to 5. However, above pH 6 the adsorption capacity of CS-NZVI-AC was significantly decreased. In solution, Cu can appear at different forms, such as Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, and $Cu(OH)_4^{2-}$, and among them Cu(II) is the most dominant form at $pH < 6$ [23]. Due to the high solubility of the CS in acidic solution, CS-NZVI-AC beads remain dissociated in the solution at pH 2. Thus the results demonstrate the high adsorption capacity of CS-NZVI-AC beads to Cu(II) but low adsorption capacity for other forms of copper.

3.3. Effects of temperature

For the investigation of the changes in the transition of the adsorption rate caused by temperature, three different temperatures of 25°C, 35°C and 45°C were considered. Adsorption ability of CS-NZVI-AC beads in the three temperature set-ups was assessed at concentration range of 5–1000 ppm. High rate of adsorption capability was observed in the lower temperature of 25°C (Fig. 4). According to Le Chatleir principle, low temperature conditions would favor the forward direction and thus adsorption process is exothermic in nature. But, the results of changing temperature showed that increasing temperature enhanced the adsorption rate, which is a clear characteristic of chemisorptions [38–40]. This result indicated the endothermic nature of this process. It is just like as the temperature increases the rate of the reaction also increases. The surface becomes activated and thus the adsorption capacity increases. The temperature results also depicted that high concentration of adsorbate enhance Cu(II) adsorption rate of the beads (Figs. 4B, 4D and 4F). In low concentrations, the equilibrium reached earlier within 2–4 h whereas, in higher concentrations, the equilibrium attained slowly within 8 h (Figs. 4A, 4C and 4E).

3.4. Kinetics of Cu(II) removal over CS-NZVI-AC beads

To understand the adsorption rate and behavior, measurement of adsorption kinetics is important. To analyze adsorption kinetics, well established Lagergren's pseu-

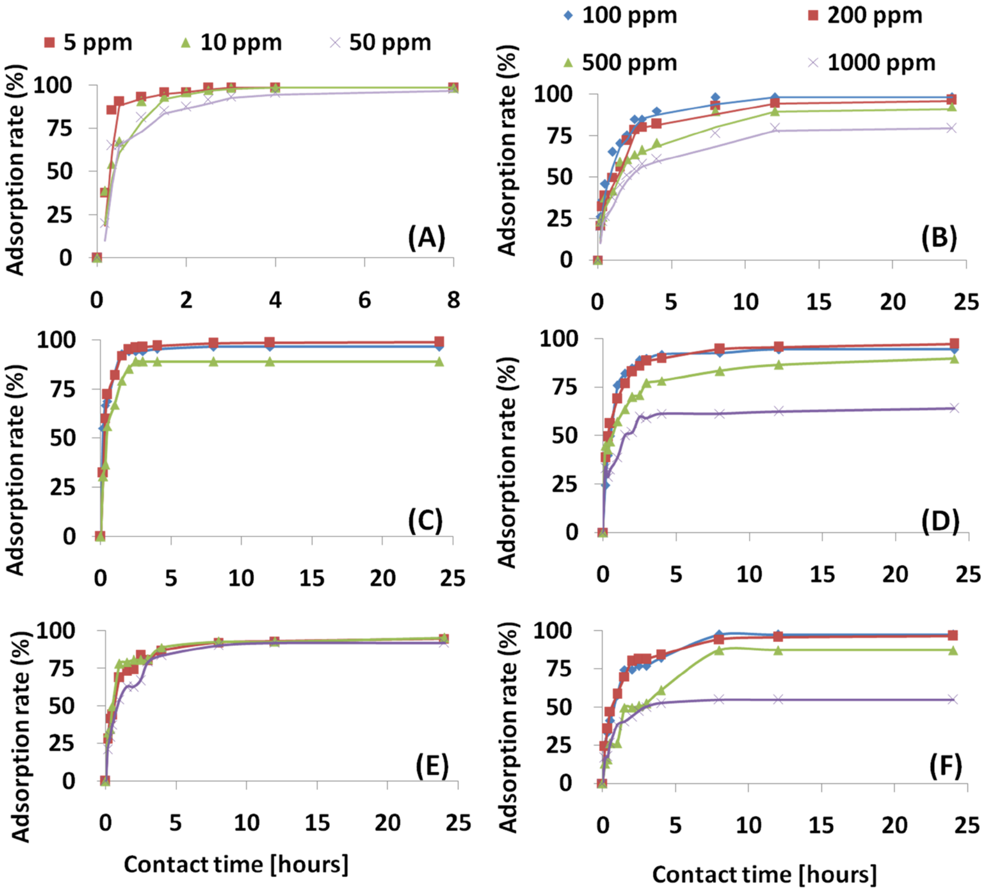

Fig. 4. Adsorption rate at different concentrations and contact time of Cu(II) ion onto the CS-NZVI-AC beads at (A, B) 25°C, (C, D) 35°C and (E, F) 45°C.

do-first order and pseudo-second order kinetic models were used. Lagergren's first order equation measures the rate of adsorption by assuming one ion is sorbed onto one adsorption site and this is expressed as follows [21,41]:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{3}$$

where

$$q_e = \frac{C_i - C_e}{m} V \tag{4}$$

where q_t is the quantity adsorption of adsorbate (mg·g^{-1}) at time t, and k_1 is Lagergren's first-order rate constant (min^{-1}). Values of k_1 and q_e at 298 K calculated from the intercept and slope of the plot of ln (q_e – q_t) vs. t were considered (Fig. 5A) for the analysis of chemisorption kinetics in the solution where the pseudo-second order model was typically applied [41]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \tag{5}$$

where k_2 is the rate constant (g/mg min) of second order. The values of k_2 and q_e were determined experimentally by plotting t/q_t vs. t (Fig 5B).

Our kinetic results clearly demonstrated that the correlation coefficients of the second order equation support the experimental observation in comparison with the pseudo-first order model. This result suggests that adsorption of Cu(II) ions onto the CS-NZVI-AC took place following pseudo-second order kinetics via chemical interactions [42].

In addition, adsorption rate of Cu(II) onto CS-NZVI-AC composite beads was significantly influenced by the initial concentration of the adsorbate. The quantity of Cu(II) adsorbed at equilibrium increased from 0.86 to 101 mg/g when the adsorbate concentration was varied from 5 to1000 mg/L at pH 5 and 25°C. Thus, the adsorption efficiency of CS-NZVI-AC beads was dependent on the initial concentration of the metal.

3.5. Equilibrium isotherms

The adsorption isotherms provide insight into the sorbate/sorbent interactions and thus lead to improved understanding of the sorption mechanism [7,43]. Several models have been used to understand the distribution of the sorbate molecules on the sorbent surface. In this study, Langmuir and Freundlich isotherm models were used to understand the adsorption mechanism of CS-NZVI-AC at varying temperatures (Fig. 6). From the temperature study,

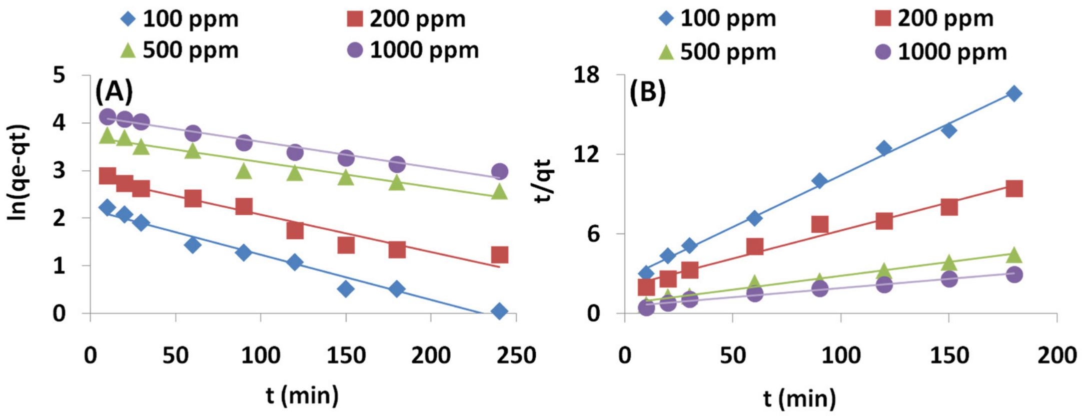

Fig. 5. (A) Pseudo-first-order kinetic model for Cu(II) adsorption; (B) Pseudo-second-order kinetic model for Cu(II) adsorption onto CS-NZVI-AC beads.

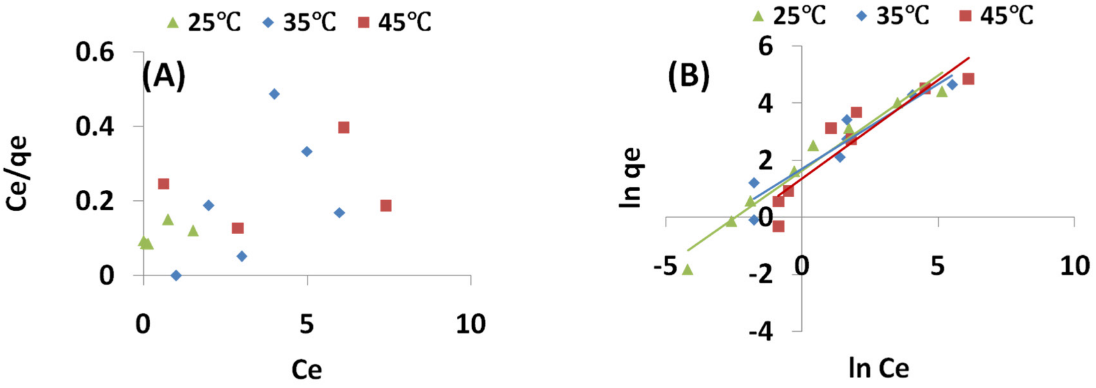

Fig. 6. Equilibrium isotherms (A) Langmuir and (B) Freundlich isotherm for Cu(II) adsorption onto CS-NZVI-AC beads at different temperatures.

it is evident that an increase of the Cu(II) concentration results in an increase of sorption capacity until a saturation plateau is achieved. The sorption data at the equilibrium point were used to analyze every isotherm models. The Langmuir model describes the sorption process on a homogeneous surface with energetically identical binding sites that permits the adsorbate to form only monolayer coverage. The linear form of the Langmuir equation is described as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \tag{6}$$

where Q_0 and b are the maximum capacity or "Langmuir" monolayer sorption capacity (mg/g) and the Langmuir adsorption constant (L/mg), respectively.

The Freundlich isotherm is generally applied to model both monolayer (chemisorption) and multilayer (physisorption) adsorption on heterogeneous surfaces [44]. The linear form of the Freundlich equation is represented as follows:

$$\ln q_e = \frac{1}{n}\ln C_e + \ln K_f \tag{7}$$

where K_f and n are the Freundlich adsorption constant (mg/L) and the adsorption constant, respectively. Values of K_f and n were determined from the intercept and slope of the plot of $ln\ q_e$ versus $ln\ C_e$. Value of greater than unity was classified as L-type isotherms, indicating chemisorptions for Cu(II) and reflecting a high affinity between adsorbate and adsorbent [24]. The Freundlich isotherm parameter for Cu(II) adsorption on CS-NZVI-AC beads are in good agreement with observed behavior ($R^2 = 0.95$ at 25°C). Since the Freundlich equation is suitable when there are multiple adsorption sites to the adsorbate, it is considered that Cu(II) bonds with multiple adsorption sites in CS-NZVI-AC beads.

3.6. Comparison of effectiveness of CS, CS-AC, and CS-NZVI-AC beads in Cu(II) removal

Experiments were also conducted to compare the efficiency of CS, CS-AC and CS-NZVI-AC beads to remove Cu(II). At initial concentrations, equilibrium adsorption of each adsorbent is shown in Fig. 7. Among the three beads, CS-NZVI-AC beads showed highest efficiency while CS-AC beads showed the lowest efficiency at each initial concentration. Table 1 shows a comparison of CS-NZVI-AC beads with other synthesized adsorbents which used CS, NZVI or AC. We have chosen adsorbents made by similar kinds of ingredients or their hybrid form e.g. CS and/or AC and/ or NZVI. Every ingredient put

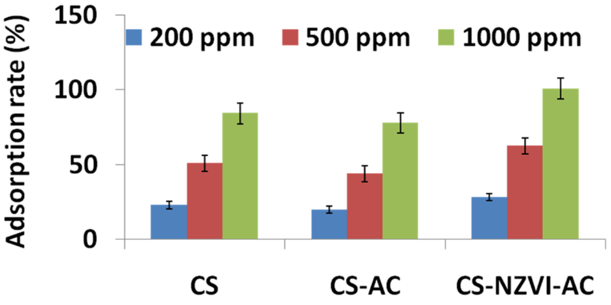

Fig. 7. Equilibrium adsorption amount of Cu(II) for each ingredients of CS-NZVI-AC beads.

Table 1
Cu(II) adsorption efficiency of different adsorbents at each initial concentration

Adsorbents	Adsorption amount (mg/g)	Reference
CS-NZVI-AC	101	This study
Activated carbon (hulls)	19.50	[8]
Chitosan bound Fe_{3O4} nanoparticles	21.50	[11]
Chitosan–cellulose	53.20	[28]
NZVI-cashew nut shell	48.10	[34]
Activated carbon(coconut)	75.80	[35]

in their contribution into the beads and eventually made it an effective one. From the table, CS-NZVI-AC beads showed the highest metal adsorption efficiency among the six studied adsorbents.

3.7. A brief discussion

This study aimed to synthesize hybrid composites wherein individual sorption attributes of every raw material were incorporated into it. Here, all key ingredients have well known affinity towards Cu(II) but have limitation with respect to pre/post treatment affinity, stability, easy separation, mechanical strength, etc. The synthesized CS-NZVI-AC composite beads was able to remove all limitations without compromising its high affinity towards Cu(II). To understand the sorption mechanism of the composites, it is first important to understand each key ingredient's mechanisms of adsorption. AC mainly interacted with the metal ions electron donor-acceptor complex, the π–π dispersion interactions and the solvent effects [2,8,12,18]. The amino (NH_2^-) group of the CS is the key functional group which can interact with metal ions [9,10,20,21,28,29,37]. The NZVI usually have tremendous reducing capacity for heavy metals [9,12,15,16,21,26,27]. The basic surface of the composites utilized their functional groups for necessary bonding with metal ions [13,25]. The amino groups of CS confirmed by the FTIR, (data not shown) along with the oxygen containing groups of AC (confirmed by the EDS), played a key role in Cu(II) uptake from solution. In addition to these was NZVI's great reducing capacity for heavy metals which made the CS-NZVI-AC hybrid efficient in Cu(II) removal from the solution [9,23].

The kinetics uptakes or potential gradient between sorbent and sorbate are usually controlled by different mechanisms e.g. bulk diffusion, film diffusion, intraparticle diffusion and reaction rate [45,46]. The sorbent data suggested that intraparticle diffusion was acted in this study to ensure the flow of Cu(II) into the sorbent which was also supported by our previous study [9]. After necessary surface accumulation of the Cu(II), the metal ions entered the CS-NZVI-AC beads by redox potential forces and was then reduced by NZVI (Fig. 8). The isotherm data also supported this given mechanism [9,23]. The removal uptakes of the composites were in agreement with the values obtained in the pH study. At pH below or higher than 5, the adsorption rate was decreased. This result is solely due to adsorption because no precipitation was detected at the given initial concentration. At alkaline pH, hydroxide precipitation is observed. On the other hand, at lower pH, the functional groups are usually protonated and gained a positive surface charge. Thus, H_3O^+ occupied most of the adsorbent surface which eventually induced electrostatic repulsion to resist the Cu(II) ions.

The results also suggested that the introduction of AC and NZVI into the CS skeleton increased the affinity and selectivity of the sorbed ions; which is useful for the treatment of industrial effluents. However, the sorption capacity does not reflect an expected increase of more than 50% from the capacity of the key ingredients. It might be due to the introduction of the extractant into the composite, reducing its total volume for hosting copper ions. The results also indicated a good fit of Freundlich isotherms to the experimental data. To add, the experimental data best fit with the pseudo-second order kinetic model. Taking up both results together, it can be concluded that both chemisorptions and Van der Waals electrostatic forces worked together to place Cu(II) into a multilayer format onto the adsorbent surface. The objects of chemical reaction is CS and its $–NH_2$ groups in C-2 position and chelation reaction easily performed by the quaternization of the $–NH_2$ groups. The carboxyl group of CS along with the hydroxyl group of AC also triggered the chemical reaction [38–40]. Finally, the oxidation of NZVI with oxygen in the presence of water resulted to the formation of magnetite depending on redox condition and pH of the medium [9]. This process resulted in making iron a magnetic material facilitating the separation of adsorbents from aqueous medium.

4. Conclusion

In this study, CS-NZVI-AC beads were successfully synthesized and were found suitable for copper removal from waters. Though the final surface area of the beads was reduced due to the hybrid composition, the copper removal efficiency was eventually enhanced along with other associated benefits e.g. magnetic separation, ease regeneration, low diffusion and high stability. The sorption mechanism was found to be pH dependent, wherein the best removal efficiency was ensured at pH 5. Kinetic model of Cu(II) removal using CS-NZVI-AC beads followed a pseudo-second order kinetics, and indicated that Cu(II) ions were

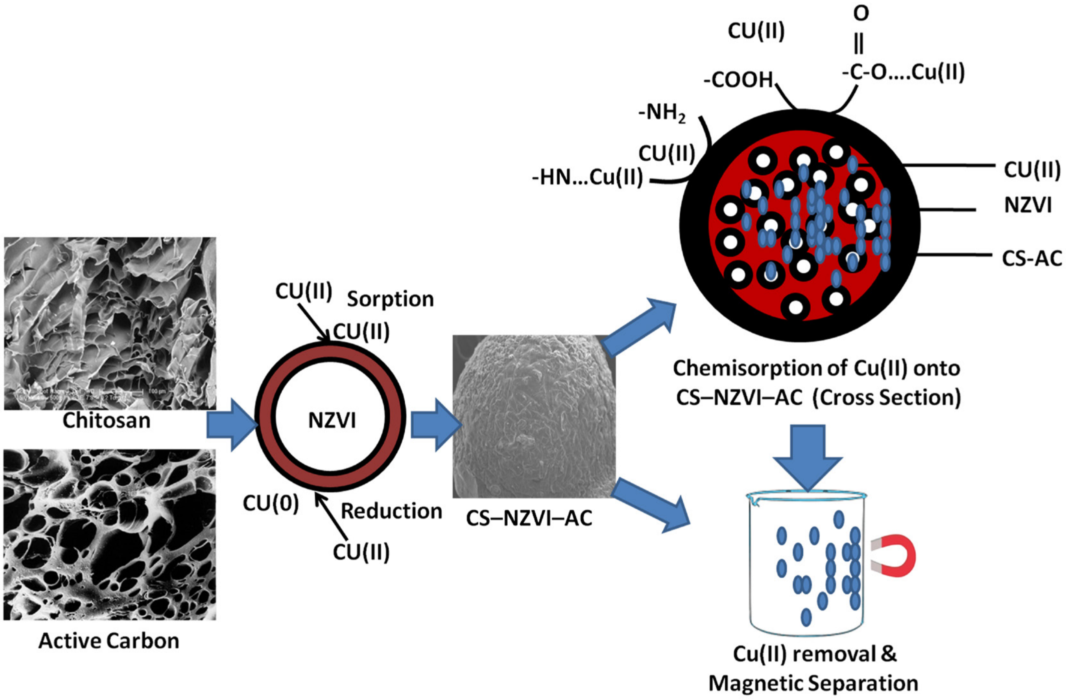

Fig. 8. A flow chart showing steps involved in the adsorption process of Cu(II) onto CS-NZVI-AC.

adsorbed onto the CS-NZVI-AC surface via chemical interactions. The best fit of Freundlich isotherm parameter for Cu(II) adsorption on CS-NZVI-AC beads indicated multilayer adsorption onto the adsorbent surface by chemisorptions. Finally, the study showed that the simplicity of the manufacturing procedure and high sorption capacity proved to be an advantage of using CS-NZVI-AC beads as compared with existing similar sorbents.

Acknowledgements

This work was supported by the Division of Environmental Science Development, Graduate School of Environmental Science, Hokkaido University. The authors are largely indebted to every members of Kurasaki Laboratory for their useful assistance during conduction of this work. Special thanks to Dr. Hakim Siddiqui, Institute for Catalysis, Hokkaido University for his kind assistance to conduct EDS.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no competing interests.

References

[1] M.T. Sikder, Y. Kihara, M. Yasuda, Yustiawati, Y. Mihara, S. Tanaka, D. Odgerel, B. Mijiddorj, S.M. Syawal, T. Hosokawa, T. Saito, M. Kurasaki, River water pollution in developed and developing countries: judge and assessment of physicochemical characteristics and selected dissolved metal concentration, Clean: Soil Air Water, 41 (2013) 60–68.

[2] N.D. Tumin, A.L. Chuah, Z. Zawani, S.A. Rashid, Adsorption of copper from aqueous solution by ElaisGuineensis kernel activated carbon, J. Environ. Sci. Technol., 3 (2008) 180–189.

[3] A.Z.M. Badruddoza, A.S.H. Tay, P.Y. Tan, K. Hidajat, M.S. Uddin, Carboxymethyl β-cyclodextrin conjugated magnetic nanoparticles as nano-adsorbents for removal of copper ions: synthesis and adsorption studies, J. Hazard. Mater., 185 (2011) 1177–1186.

[4] C. Lu, Y. Wu, S. Hu, M.A. Raza, Y. Fu, Mobilization and transport of metal-rich colloidal particles from mine tailings into soil under transient chemical and physical conditions, Environ. Sci. Pollut. Res. Int., 23 (2016) 8021–8034.

[5] W. Yaoguo, X. Youning, Z. Jianghua, H. Sihai, K. Liu, Heavy metals pollution and the identification of their sources in soil over Xiaoqinling gold-mining region, Shaanxi, China, Environ. Earth Sci., 64 (2011) 1585–1592.

[6] W. Yaoguo, X. Youning, Z. Jianghua, H. Sihai, Evaluation of ecological risk and primary empirical research on heavy metals in polluted soil over Xiaoqinling gold mining region, Shaanxi, China. Trans. Nonferrous Met. Soc. China, 20 (2010) 688–694.

[7] T. Aman, A.A. Kazi, M.U. Sabri, Q. Bano, Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent, Colloids Surface B., 63 (2008) 116–121.

[8] M.M. Rao, A. Ramesh, G.P.C. Rao, K. Seshaiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceibapentandra* hulls, J. Hazard. Mater., 129 (2006) 123–129.

[9] M.T. Sikder, Y. Mihara, M.S. Islam, T. Saito, S. Tanaka, M. Kurasaki, Preparation and characterization of chitosan–carboxymethyl-β-cyclodextrin entrapped nano zero-valent iron composite for Cu(II) and Cr(IV) removal from wastewater, Chem. Eng. J., 236 (2014) 378–387.

[10] A.J. Varma, S.V. Deshpande, J.F. Kennedy, Metal complexation by chitosan andits derivatives: a review, Carbohyd. Polym., 55 (2004) 77–93.

[11] Y.C. Chang, D.H. Chen, Preparation and adsorption properties of monodisperse chitosan-bound Fe_3O_4 magnetic nanoparticles for removal of Cu(II) ions, J. Colloid Interface Sci., 283 (2005) 446–451.

[12] H. Zhua, Y. Jia, X. Wua, H. Wanga, Removal of arsenic from water by supported nanozero-valent iron on activated carbon, J. Hazard. Mater., 172 (2009) 1591–1596.

[13] A.L. Roberts, L.A. Totten, W.A. Arnold, D.R. Burris, T.J. Campbell, Reductive elimination of chlorinated ethylenes by zero-valent metals, Environ. Sci. Technol., 30 (1996) 2654–2659.

[14] B. Geng, Z. Jin, T. Li, X. Qi, Kinetics of hexavalent chromium removal from water by chitosan-Fe^0 nanoparticles, Chemosphere, 75 (2009) 825–830.

[15] S.M. Ponder, J.G. Darab, T.E. Mallouk, Remediation of Cr(VI) and Pb(II) aqueous solutions using supported nano scale zero valent iron, Environ. Sci. Technol., 34 (2000) 2564–2569.

[16] S.R. Kanel, B. Manning, L. Charlet, H. Choi, Removal of arsenic (III) from ground water by nanoscale zero-valent iron, Environ. Sci. Technol., 39 (2005) 1291–1298.

[17] Q. Liu, T. Zheng, P. Wang, J. Jiang, N. Li, Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers, Chem. Eng. J., 157 (2010) 348–356.

[18] F. He, D. Zhao, Preparation and characterization of a new class of starch stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water, Environ. Sci. Technol., 39 (2005) 3314–3320.

[19] M.T. Sikder, M.M. Rahman, M. Jakariya, T. Hosokawa, M. Kurasaki, T. Saito, Remediation of water pollution with native cyclodextrins and modified cyclodextrins: A comparative overview and perspectives, Chem. Eng. J., 355 (2019) 920–941.

[20] K.F.B. Hossain, M.T. Sikder, M.M. Rahman, M.K. Uddin, Investigation of chromium removal efficacy from tannery effluent by synthesized chitosan from crab shell, Environmental Nanotechnology, Arabian J. Sci. Technol., 42(4) (2017) 1569–1577.

[21] M.T. Sikder, S. Tanaka, T. Saito, M. Kurasaki, Synthesis and application of an arsenic sorbent using zerovalent iron impregnated chitosan-caboxymethyl-β-cyclodextrin composite beads, J. Environ. Chem. Eng., 2 (2014) 370–376.

[22] Y. Mihara, M.T. Sikder, T. Sasaki, M. Kurasaki, S. Ito, S. Tanaka, Adsorption kinetic model of alginate gel beads synthesized micro particle-Prussian blue to remove cesium ions from water, J. Water Process Eng., 10 (2016) 9–19.

[23] M.T. Sikder, M.S. Islam, T. Kikuchi, J. Suzuki, T. Saito, M. Kurasaki, Removal of copper ions from water using epichlorohydrin cross-linked β-cyclodextrin polymer: Characterization, isotherms and kinetics, Water Environ. Res., 86 (2014) 296–304.

[24] M.T. Sikder, T. Kikuchi, J. Suzuki, T. Hosokawa, T. Saito, M. Kurasaki, Removal of cadmium and chromium ions using modified α, β, and γ-cyclodextrin polymers, Sep. Sci. Technol., 48(4) (2013) 587–597.

[25] M.T. Sikder, M. Jakariya, M.M. Rahman, S. Fujita, T. Saito, M. Kurasaki, Epichlorohydrin cross-linked β- cyclodextrin polymer entrapped in funtionalized chitosan for cadmium removal from waste water, J. Environ. Chem. Eng., 5 (2017) 3395–3304.

[26] S.M. Ponder, J.G. Darab, T.E. Mallouk, Remediation of Cr(VI) and Pb(II) aqueous solutions using supported nanoscale zerovalent iron, Environ. Sci. Technol., 34 (2000) 2564–2569.

[27] S.R. Kanel, B. Manning, L. Charlet, H. Choi, Removal of arsenic (III) from groundwater by nanoscale zero-valent iron, Environ. Sci. Technol., 39 (2005) 1291–1298.

[28] N. Li, R.B. Bai, Copper adsorption on chitosan–cellulose hydrogel beads: behaviors and mechanisms, Sep. Purif. Technol., 42 (2005) 237–247.

[29] X. Wang, Y. Zheng, A. Wang, Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite composites, J. Hazard Mater., 168 (2009) 970–977.

[30] M. Rhazi, J. Desbrie, A. Tolaimate, M. Rinaudo, P. Vottero, A. Alagui, Michael reaction of chitosan with various acryl reagents in water, Biomacromolecules, 4 (2003) 1250–1254.

[31] P.C. Da Silva Mira, L.E. Souza-Flamini, D.F. da Costa Guedes, A.M. Da Cruz-Filho, Evaluation of the chelating effect of chitosan solubilized in different acids, J. Conserv. Dent., 20 (2017) 297–301.

[32] M.M. Naim, H.E.M. Abdel Razek, Chelation and permeation of heavy metals using affinity membranes from cellulose acetate–chitosan blends, Desal. Water Treat., 51 (2013) 644–657.

[33] H.K. Boparai, M. Joseph, D.M. O'Carroll, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nanozerovalent iron particles, J. Hazard. Mater., 186 (2011) 458–465.

[34] D. Prabu, R. Parthiban, P.S. Kumar, N. Kumari, P. Saiki, Adsorption of copper ions onto nano-scale zero-valent iron impregnated cashew nut shell, Desal. Water Treat., 57 (2016) 6487–6502.

[35] T.S. Anirudhan, S.S. Sreekumari, Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons, J. Environ. Sci., 23 (2011) 1989–1998.

[36] J. Shou, M. Qiu, Adsorption of copper ions onto activated carbon from capsicum straw, Desal. Water Treat., 57 (2016) 353–359.

[37] V. Patrulea, A. Negrulescu, M.M Mincea, L.D. Pitulice, O.B. Spiridon, V. Ostafe, Optimization of the removal of copper(II) ions from aqueous solution on chitosan and cross-linked chitosan beads, BioResources, 8 (2013) 1147–1165.

[38] X. Xin, W. Yaoguo, H. Sihai, Y. Zhang, Preparation and performance analysis of chitosan/polyacrylamide/poly(vinyl alcohol)/Fe/glutaraldehyde copolymer for Cr(VI) adsorption, Desal. Water Treat., 102 (2018) 151–164.

[39] W. Yaoguo, Y. Zhang, J. Qian, X. Xin, S. Hu, S. Zhang, J. Wei, An exploratory study on low concentration hexavalent chromium adsorption by Fe(III)-crosslinked chitosan beads, R Soc Open Sci., 4 (2017) 170905.

[40] Y. Na, W. Yaoguo, W. Jianguo, et al., Adsorption of the low concentration Cr (VI) on magnetic chitosan/Pvahydrogel beads, Fresen Environ. Bull., 25 (2016) 2174–2182.

[41] M.J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, Acta Phys. URSS, 12 (1940) 217–222.

[42] B.H. Hameed, D.K. Mahmoud, A.L. Ahmad, Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocosnucifera*) bunch waste, J. Hazard. Mater., 158 (2008) 65–72.

[43] G. Huang, C. Yang, K. Zhang, J. Shi, Adsorptive removal of copper ions from aqueous solution using cross-linked magnetic chitosan beads, Chinese J. Chem. Eng., 17 (2009) 960–966.

[44] A.B. Dichiara, M.R. Webber, W.R. Gorman, R.E. Rogers, Removal of copper ions from aqueous solutions via adsorption on carbon nanocomposites, ACS Appl. Mater. Interfaces, 7 (2015) 15674–15680.

[45] L. Darmayanti, S. Notodarmodjo, E. Damanhuri, R.R. Mukti, Removal of copper (II) ions in aqueous solutions by sorption onto alkali activated fly ash, MATEC Web Conf., 147 (2018) 04007.

[46] T. Benzaoui, A. Selatnia, D. Djabali, Adsorption of copper (II) ions from aqueous solution using bottom ash of expired drugs incineration, Ads. Sci. Technol., 36 (2018) 114–129.