Instructions for use

Preparation and characterization of chitosan-caboxymethyl-β-cyclodextrin entrapped nano zero-valent iron composite for Cu (II) and Cr (IV) removal from wastewater

Md. Tajuddin Sikder[a, b], Yoshihiro Mihara[c], Md. Shariful Islam[a], Takeshi Saito[d], Shunitz Tanaka[a, e], Masaaki Kurasaki[a, e, *]

[a]Division of Environmental Science Development, Graduate School of Environmental Science, Hokkaido University, 060-0810 Sapporo, Japan.

[b]Department of Environmental Science, Stamford University Bangladesh, Dhaka-1209, Bangladesh

[c]Division of Environmental Materials Science, Graduate School of Environmental Science, Hokkaido University, 060-0810 Sapporo, Japan.

[d]Group of Environmental Adaptation Science, Faculty of Environmental Earth Science, Hokkaido University, 060-0812 Sapporo, Japan.

[e]Laboratory of Environmental Health Sciences, Faculty of Health Sciences, Hokkaido University, 060-0812 Sapporo, Japan.

[*]**Corresponding author**: Dr. Masaaki Kurasaki, Group of Environmental Adaptation Science, Faculty of Environmental Earth Science, Hokkaido University. Kita 10, Nishi 5, Kita-ku, Sapporo 060-0810, Japan.
Tel: +81-11-706-2243; fax: +81-11-706-4864
E-mail: kura@ees.hokudai.ac.jp

Abstract

The entrapment of Fe^0 nanoparticles within a chitosan-carboxymethyl β-cyclodextrin complex, a nontoxic and biodegradable stabilizer, yields chitosan-Fe^0 nanoparticle-carboxymethyl β-cyclodextrin beads that are 2.5 mm in diameter and contain 50% iron by weight. The complete disappearance of Cr (VI) and Cu (II) may involve both physical adsorption and reduction of Cr (VI) to Cr (III) and Cu (II) to Cu (0) while oxidizing Fe^0 to Fe (III). The rate of reduction can be expressed by pseudo-second-order reaction kinetics. The rate constants increased with increasing iron loading and initial concentration at pH 6, while the adsorption of Cr (VI) and Cu (II) was found to be endothermic and exothermic, respectively. The apparent activation energies for Cr (VI) and Cu (II) were found to be 71.99 and 18.38 $kJ\ mol^{-1}$, respectively. X-ray photoelectron spectroscopy confirmed the reduction process. The equilibrium data could be well described by both Langmuir and Temkin isotherms for describing monolayer adsorption and chemisorption processes, respectively. Both film diffusion and intraparticle diffusion were found to be the rate-limiting steps from the analysis of an intraparticle diffusion model. Thus, the synthesized chitosan-Fe^0-nanoparticle-carboxymethyl β-cyclodextrin beads can be a potential material for *in situ* remediation of contaminated surface and ground water.

Keywords: Chitosan, zero-valent iron, remediation, cyclodextrin polymer, heavy metals, water pollution.

1. Introduction

Toxic heavy-metal pollution is of significant environmental and occupational concern because of the tendency of heavy metals to enter the food chain. Among metals of concern, chromate (Cr (VI)) is the 16th most toxic and carcinogenic material released into the environment through numerous industrial operations [1]. Cu (II) is toxic at elevated concentrations, and is persistent and bioaccumulative in the environment. Cr (VI) concentrations range from 0.5 to 270 mg L^{-1} in industrial wastewater [2, 3], though the US Environmental Protection Agency (EPA) permissible limit of Cr (VI) is only 0.1 mg L^{-1}. The acceptable limits for Cu (II) set by the EPA and WHO (2011) are 1.2 and 2 mg L^{-1}, respectively [4-6]. Numerous studies have investigated adsorption and redox processes as removal mechanisms of Cu (II) and Cr (VI) from water using of a variety of materials including natural adsorbents, waste materials, microorganisms and macromolecules [3, 7-14]. Recently, adsorption using nano zero-valent iron (NZVI), chitosan (CS), and carboxymethyl β-cyclodextrin (CMβ-CD) has attracted increased attention for use in environmental remediation of heavy-metal ions.

Zero-valent iron powders (Fe^{0}) have been extensively used for in situ remediation of water polluted with As [15], chlorinated hydrocarbons [16], nitrate [12], Cr (VI), and Pb (II) [17]. Special attention has recently given to insoluble form of NZVI because of its large surface area and tremendous reducing capacity for heavy metals [17]. In addition, the oxidation of NZVI by water and oxygen produces ferrous iron to give magnetite, depending upon redox conditions and pH [18]. This process, rendering the iron magnetic, facilitates the rapid separation of adsorbents from solution.

CS is an important natural polymer, obtained by the deacetylation of chitin, in which the amino group has a pKa value from 6.2 to 7.0, positively charged and soluble in acidic-to-neutral

solution, and has found extensive application in the green synthesis of nanoscale materials because of its excellent biocompatibility, biodegradability, and lack of toxicity. Recently, adsorption of metal ions to CS has been extensively studied because CS exerts bioadhesive properties to form stable nanoparticles with different metals in solution [19, 20]. Because the amino groups of CS have the ability to form chelation complexes with various heavy-metal ions, CS has been used as a material for environmental remediation [21].

β-CD is a cyclic oligosaccharide containing a hydrophobic, a polar cavity with hydroxyl groups present on the inside and outside of the cavity. There is evidence that both organic and inorganic compounds can complex with β-CD through its cavity and hydroxyl groups [7, 22]. Recently, β-CD has been immobilized or grafted with supportive materials, and active functional groups have been introduced to enhance its adsorption capacity for metal ions, e.g., CMβ-CD. The coupling of CMβ-CD with functionalized CS followed by the entrapment of NZVI is expected in this study to facilitate the removal of metals from wastewater.

In water treatment systems, direct application of NZVI may cause iron pollution because of its tiny particle size. In addition, NZVI exhibits high agglomeration, high mobility, lack of stability, and low reducing specificity in water, and thus must be used with surface stabilizers such as CS, alginate, activated carbon, and others porous structures [23]. If these supporting materials also have high affinity for metal ions, the combination with NZVI accelerates the overall remediation process. The use of CS as stabilizer can facilitate detoxification of metal ions in solution and act as effective electron donor. In addition, the sorption mechanism along with the degree of detoxification of heavy metal ions is also known [12, 24-26]. Some papers have reported only CS bearing NZVI beads for Cr (VI) and Cu (II) removal, but have not specially studied the thermodynamics, kinetics and isotherms extensively; and the removal mechanism was not

elucidated clearly for metal ions [12, 21, 24-30]. In this study, NZVI was entrapped in a highly-functioning, porous polymer CS already cross-linked with CMβ-CD to yield CS-NZVI-CMβ-CD beads. The adsorption behavior of CS-NZVI-CMβ-CD beads were fabricated and their adsorption behavior was characterized using Cu (II) and Cr (VI) ions in solution. The adsorption mechanism, characteristics, thermodynamics, influence of different factors, kinetics, and isotherms of CS-NZVI-CMβ-CD beads were also evaluated.

2. Materials and methods

2.1 Materials

Deacetylated CS flakes (75%), called 2-amino-2-deoxy-(1-4)-β-D-glucopyranan or poly-(1,4)-β-D-glucopyranose amine, derived from shrimp shells and CMβ-CD sodium salt were purchased from Sigma-Aldrich (St. Louis, MA, USA). NZVI electrolytic powder finer than 100 mesh, 98% purity, was purchased from Kanto Chemical (Tokyo, Japan). Condensation reagent for the synthesis of 1,3-bis(2,2-diethyl-1,3-dioxolan-4-yl-methyl) carbodiimide was purchased from Tokyo Chemical Industry (Tokyo, Japan). All other chemicals were of analytical grade. Milli-Q water (Millipore-Gradient A10, Milli-Q Gradient ZMQG) was used in the experiments.

2.2 Preparation of CS-CMβ-CD gel

CS-NZVI-CMβ-CD beads were prepared using the commercially available CS flakes, CMβ-CD sodium salt, and NZVI. First, 1,000 ppm CM-β-CD sodium salt in 500 mL of water was equilibrated with 2% (v/v) acetic acid. The mixture was stirred for 8 h at room temperature. Then, CS flakes without depolymerization (4.0 g) were added in small portions to 200 mL of the mixture at 333 K, which was stirred for 6 h followed by cooling to 293 K to obtain CS-CMβ-CD

gel. Next, 0.1 g of a solution of 1,3-bis(2,2-diethyl-1,3-dioxolan-4-yl-methyl) carbodiimide in water (1 mL) as the condensing agent was added dropwise to the CS-CMβ-CD gel. The CS-CMβ-CD gel reacted with carbodiimide was then divided between two beakers, and used to produce both CS-CMβ-CD beads and CS-NZVI-CMβ-CD beads. In addition, CS gel was prepared by adding CS flakes (4-5 g) in small portions into 2% acetic acid as a control.

2.3 Preparation of CS-NZVI-CMβ-CD beads

First, 0.1, 0.5, 1.0, or 2.0 g of NZVI was gently added to 30 mL of CS-CMβ-CD gel in centrifuge tubes. The mixture was then shaken repeatedly after every 15 min using a Vortex Genie 2 (USA) to achieve homogeneous mixing of NZVI with the CS-CMβ-CD gel. The resulting mixture was then poured into a 50 mL syringe (Terumo ss-50ESz, Japan) prior to bead formation. An alkaline bead forming solution was prepared using 3.75 M NaOH and 200 mL ethanol, and was cooled to room temperature. The mixture was dropped into the alkaline solution with constant stirring to form CS-NZVI-CMβ-CD beads [12, 27]. The addition of ethanol to the alkaline solution prevented the immediate rusting of NZVI. A mixture was also prepared without NZVI to produce CS-CMβ-CD beads as a control.

2.4 Characterization of CS-NZVI-CMβ-CD beads

Images of the polymer were recorded using a Hitachi S-4000 scanning electron microscope (SEM; Ibaraki, Japan) on aluminum stubs adhered to graphite support units using carbon tape. For Brunauer-Emmett-Teller (BET) analysis, an automated gas adsorption analyzer Belsorp-max, (S/N=240) Ver. 1.2.7t (BEL Japan, Inc.) were used to measure the surface area. The size distribution of the CS-NZVI-CMβ-CD beads was ascertained visually with a ruler. The

homogeneity of NZVI within the CS-NZVI-CMβ-CD beads was visualized using fluorescence microscopy (Olympus IX70). Fourier transform infrared (FTIR) spectroscopy (FT210, Horiba, Japan) was used to determine the presence of functional groups on and within the CS-NZVI-CMβ-CD beads at room temperature using KBr as the background over the range of 4000–400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) analysis was used to detect elements such as C, O, Cr, and Cu in the CS-NZVI-CMβ-CD beads.

2.5 Adsorption study

Adsorption experiments were carried out using a batch equilibrium technique in aqueous solutions at pH 2–9 and 298–323 K. Excepting some special cases, the adsorbent dosage was 0.1 g, the adsorbate dosage was 100 mgL^{-1}, the pH was 6.0, the sample volume was 30 mL and the shaking time was 5 h to achieve complete equilibrium. The concentrations of Cr (VI) and Cu (II) were measured using a flame-type atomic absorption spectrophotometer (AAS; model 180–80, Hitachi, Japan). The lower limit of sensitivity was 0.01 µg mL^{-1}. To conduct equilibrium isotherm studies, 30 mL Cu (II) or Cr (VI) solutions of different concentrations were mixed with 100 mg of CS-NZVI-CMβ-CD beads at pH 6.0 and were shaken for 6 h at 298 K, 313 K, and 323 K.

3. Results and discussion

3.1 Adsorbent characterization and adsorption mechanisms

3.1.1 SEM characterization

The SEM images of the synthesized CS-NZVI-CMβ-CD beads are shown in Fig. 1. The beads were nearly blackish with a mean diameter of 2.5 mm (standard deviation is 0.10) (Fig. 1a).

Fluorescence microscopy images indicated that NZVI are homogeneously distributed in the interior of CS-CMβ-CD with no agglomeration (Fig. 1b). Fig. 1c shows the macroporous morphology of CS-CMβ-CD beads prior to the entrapment of NZVI. The entrapment of NZVI into CS-CMβ-CD complexes was confirmed by the ashen color (Fig. 1d). The distribution of NZVI throughout the network of pores in the beads is further illustrated in Fig. 1e with magnification, and the internal pore wall morphology of the beads can be seen in Fig. 1f. From these images, NZVI was completely entrapped in the pores rather than within cracks on the outer surface. This enables repeated use in water treatment facilities without the loss of iron particles or corrosion. The pore size distribution of the CS-NZVI-CMβ-CD beads was calculated to be 3.5–8.7 μm, which is similar to previously reported sizes for CS beads (4.9–15.8 μm) [31]. Figs. 2a and b show the dry and wet forms of the synthesized CS-NZVI-CMβ-CD beads, respectively. The batch adsorption technique is shown in Fig. 2c for Cr (VI) removal followed by the magnetic separation of the CS-NZVI-CMβ-CD beads (Fig. 2d).

3.1.2 BET Analysis

CS beads formed in alkaline solution undergo shrinkage, reducing the surface area significantly. But, an increase in the dosage of NZVI nanoparticles can lead to an increase in total surface area. Accordingly, the BET surface area of the CS-NZVI-CMβ-CD beads is obtained as 12.1 m^2 g^{-1} and the pore volume was 2.78 cm^3 g^{-1} [27, 32-33]. The weight of a single dry bead was ~0.005 g, with NZVI constituting 50% of the total weight, and the total shrinkage of the surface area was around 74%. NZVI may have blocked the largest pores of the CS-NZVI-CMβ-CD beads. From the adsorption-desorption (BET) isotherms, the volume of adsorbed N_2 slightly increased with increasing P/P_0, indicating a small pore size distribution. In addition, the contents of bound Cr

(VI) and Cu (II) per m^2 of surface area of the CS-NZVI-CMβ-CD beads were calculated to be 16.65 and 20.81 mg m^{-2}, respectively.

3.1.3 FTIR analysis

To identify possible interactions between the CS-NZVI-CMβ-CD beads and Cr (VI) or Cu (II), the surface functional groups of the adsorbent were characterized by FTIR before and after adsorption (Fig. 3). CS-NZVI-CMβ-CD has two characteristic peaks at 1654 and 3423 cm^{-1}, which are contributions from the N–H or C=O and O–H bending vibrations, respectively [34] (line a in Fig. 3). The peaks at 1091 and 1165 cm^{-1} corresponded to the glycosidic vibrations of C-O-C or C-C/C-O stretch vibrations, indicating the presence of CMβ-CD in the adsorbent [7]. After Cr (VI) reduction, the expected peak shifted to 1654–1653 cm^{-1}, 3423–3443 cm^{-1}, and 1091–1101 cm^{-1} (line b in Fig. 3). The peak at 569 cm^{-1} (line b in Fig. 3) ascribe to Fe–O group which is supported by [35]. A characteristic sharp peak was observed after Cr (VI) adsorption at 2365.26, indicating the interaction of Cr (VI) with oxygen-containing functional groups on the surface and the interior of the CS-NZVI-CMβ-CD beads [20].

The FTIR spectrum of Cu (II) sorbed onto CS-NZVI-CMβ-CD beads revealed that the peaks expected at 1091, 1654, and 3423 cm^{-1} shifted to 1092, 1660, and 3443 cm^{-1}, respectively (line c in Fig. 3c). These peak shifts may also have arisen from the interaction of Cu (II) with the corresponding functional groups of the beads (mainly N–H, O–H, and COOH). It is reasonable to assume that oxygen atoms were the main binding sites of Cu (II) based on the shifts of peaks arising from oxygen containing groups [7, 27].

3.1.4 XPS characterization

XPS studies were also employed in order to understand the adsorption mechanism of CS-NZVI-CMβ-CD beads before and after Cr (VI) or Cu (II) reduction (Fig. 4). New peaks were observed at 580 and 933 eV after Cr (VI) and Cu (II) reduction, respectively, corresponding to the photoelectron peaks of Cr (III) and Cu (0) (Fig. 4a). The N 1s spectra before Cr (VI) and Cu (II) reduction exhibited a peak at 398 eV, which corresponds to $-NH_2$, but a new peak appeared after Cr (VI) and Cu (II) reduction at 397.0 eV (line II in Fig. 4a). This new peak confirmed the formation of metal-NH_2 complexes, indicating either mono- or bidentate ligands between Fe (III) and Cr (III) [19]. This process leads to protection of the metal precipitation in solution. Photoelectron peaks for the $2p_{3/2}$ and $2p_{1/2}$ levels of oxidized iron Fe (III) were found at 711 and 724.5 eV, respectively (Fig. 4b). Notably, the characteristic peak for NZVI at 706.5 eV was absent because of the extensive oxidation of iron. Fig. 4c shows the Cu $2p_{3/2}$ spectrum of Cu (II) at 936 eV and the presence of the Cu $2p_{1/2}$ satellite band at 957 eV, indicating that reduction had taken place. The Cr 2p spectrum of CS-NZVI-CMβ-CD beads exhibited two characteristic peaks at 577.3 and 586.6 eV for Cr $2p_{3/2}$ and Cr $2p_{1/2}$, respectively (Fig. 4d). These results are similar to the binding energies of Cr (III) and are in good agreement with previous reports [36]. Thus, Cr (VI) was solely reduced by NZVI in the pores of CS-NZVI-CMβ-CD beads.

3.2 Kinetics of Cu (II) and Cr (VI) removal over CS-NZVI-CMβ-CD beads

Lagergren's pseudo-first-order, pseudo-second-order, and diffusion models were used to analyze the adsorption kinetics. Lagergren's first-order equation measures the rate of adsorption by assuming that one ion is sorbed onto one adsorption site, and can be expressed as follows [37]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

where q_t is the amount of adsorbate adsorbed (mg g^{-1}) at time t, and k_1 is Lagergren's first-order rate constant (min^{-1}). k_1 and q_e at 298 K were calculated from the intercept and slope of the plot of ln (q_e-q_t) versus t (Figs. 5a and c). The pseudo-second-order model is typically applied to the analysis of chemisorption kinetics in solution [13]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

where k_2 (g mg^{-1}min^{-1}) is the second order rate constant and q_e is the equilibrium sorption capacity. The values of k_2 and q_e can be determined experimentally by plotting t/q_t versus t (Figs. 5b and d). The corresponding correlation coefficients derived from the second order equation were in close agreement with those observed experimentally in compare with pseudo-first-order model. This result suggests that the adsorption followed pseudo-second-order kinetics, and that Cr (VI) and Cu (II) ions were adsorbed onto the CS-NZVI-CMβ-CD surface via chemical interactions [38]. Similar trends have been observed in the adsorption of Cr (VI) and Cu (II) from aqueous solution onto other adsorbents [7].

In addition, the initial concentration of the adsorbate significantly influenced the adsorption rate of Cr (VI) and Cu (II) onto CS-NZVI-CMβ-CD beads. For example, the rate constants of the removal of both Cr (VI) and Cu (II) increased with increasing initial adsorbate concentration. The results obtained for Cr (VI) were different from those reported by previously [12, 27]. The amount of Cu (II) adsorbed at equilibrium increased from 12.4 to 44.7 mg g^{-1} when the adsorbate concentration was varied from 50 to 200 mgL^{-1} at pH 6.0 and 298 K. Thus, the initial metal concentration plays a key role in the adsorption efficiency of CS-NZVI-CMβ-CD beads.

The Weber-Morris intraparticle diffusion model has been applied to know the rate-limiting steps of the adsorption process,

$$q_t = k_d t^{0.5} + C \tag{3}$$

where k_d is the intraparticle diffusion rate constant (mg g^{-1}min$^{-0.5}$) and C is the intercept [39]. As shown in Figs. 6a and b, the initial steep section represents surface sorption or film diffusion, while the subsequent linear section indicates that intraparticle or pore diffusion is the rate limiting step.

3.2.1 Effects of adsorbent dosage and NZVI loadings

Adsorbent dosage is an important parameter in the removal of metal ions by adsorption. Our studies showed that the removal of both Cr (VI) and Cu (II) increased from 60 to 80% when the dose of CS-NZVI-CMβ-CD increased from 0.1 to 1 g/30 mL for initial Cr (VI) and Cu (II) concentrations of 100 mg L^{-1} (Figs. 6c and d). In addition, the influence of the presence of NZVI entrapped in the CS-NZVI-CMβ-CD beads on the removal rates was also determined for Cr (VI) and Cu (II) (inset in Fig. 6c). The removal rates of Cr (VI) and Cu (II) increased with increasing iron loadings. This phenomenon can be explained by the increased number of active sites on the CS-NZVI-CMβ-CD surface. However, the NZVI loading was found to be dependent on the size of the adsorbent. For example, for the 2.5 mm beads used in this study, the maximum NZVI load was 1 g/30 mL to avoid oxidation, corrosion, and loss of iron particles.

3.2.2 Effects of initial pH

The effect of pH on Cr (VI) and Cu (II) removal using CS-NZVI-CMβ-CD beads was characterized for the pH values ranging from 2–9 (Figs. 7a and b). The removal rate of Cr (VI) dramatically decreased with increasing pH (Fig. 7a), indicating that acidity played an important role in the reduction rate of Cr (VI) and its interaction with CS-NZVI-CMβ-CD beads. Cr (VI)

has three predominant salt forms—H_2CrO_4, $HCrO_4^-$, and CrO_4^{2-}—among which H_2CrO_4 is the dominant species at pH <1.0, $HCrO_4^-$ is the dominant species at pH 1.0–6.0, and CrO_4^{2-} is dominant at pH <6.0 [27]. Generally, Fe^0 donates its electrons to protons or chromate anions and is oxidized to Fe (III). The protons are reduced to hydrogen gas, and Cr (VI) is converted into Cr (III) [27]. As a result, the bead surface becomes more positively charged, establishing an electrostatic attraction between adsorbent and adsorbate. In contrast, the adsorption capacity of CS-NZVI-CMβ-CD for Cu (II) increased with increasing pH (Fig. 7b). In solution, Cu can take different forms such as Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, and $Cu(OH)_4^{2-}$, among which Cu^{2+} is the dominant species at pH <6.0. Cu adsorption decreased at pH <6.0, and the ionic mobility of $[H_3O]^+$ in water was abnormally high as compared with most other ions [13, 40]. Thus, not only by virtue of its high concentration but also of its high mobility in solution, protons favorably competed with metallic ions such as Cu^{2+} for surface active sites of the adsorbent.

3.3 Equilibrium isotherms

The adsorption isotherms provide insight into the relationship between the equilibrium concentration of adsorbate in the bulk and the amounts adsorbed on the surface of adsorbent [41]. Langmuir, Freundlich, and Temkin isotherm models were used to understand the adsorption mechanism of CS-NZVI-CMβ-CD at varying temperatures (Fig. 8).

The linear form of the Langmuir equation can be described as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \tag{4}$$

The Langmuir isotherm parameter fits for Cr (VI) and Cu (II) adsorption on CS-NZVI-CMβ-CD beads are in good agreement with observed behavior ($R^2 \geq 0.99$) (Figs. 8a and b). The adsorption capacities of Cr (VI) and Cu (II) on CS-NZVI-CMβ-CD beads at room temperature (298 K) were 142.8 and 250 mg g^{-1}, respectively. This capacity was high in comparison with some existing high performance adsorbents listed in Table 1.

The Freundlich isotherm [42] is generally applied to model both monolayer (chemisorption) and multilayer (physisorption) adsorption on heterogeneous surfaces [38, 43]. The linear form of the Freundlich equation can be represented as follows:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \tag{5}$$

Values of K_f and n were determined from the intercept and slope of the plot of log q_e versus log C_e. Values of n greater than unity were classified as L-type isotherms, indicating chemisorption for both Cr (VI) and Cu (II) and reflecting a high affinity between adsorbate and adsorbent (Figs. 8c and d) [44].

The Temkin isotherm model describes indirect adsorbent-adsorbate interactions and assumes that the adsorption energy in the layer decreases linearly with coverage [44, 45]. The Temkin isotherm model is given in the following form:

$$q_e = B \ln A + B \ln C_e \tag{6}$$

where B = RT/b, b is the Temkin constant related to the heat of sorption (J mol^{-1}), A represents the Temkin isotherm constant (L g^{-1}), R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$), and T is the absolute temperature (K). The Temkin adsorption isotherm achieved a good fit for the adsorption data, with correlation coefficients ≥ 0.97, indicating chemisorption of the adsorbate

onto CS-NZVI-CMβ-CD beads (Figs. 8e and f). On the basis of earlier findings [46], we concluded that the adsorption of Cr (VI) and Cu (II) onto CS-NZVI-CMβ-CD beads was entirely a chemisorption process.

3.3.1 Comparison of effectiveness of bare NZVI, CS, CS-CMβ-CD, and CS-NZVI-CMβ-CD beads in Cr (VI) and Cu (II) removal

Experiments were also conducted to compare the effectiveness of bare NZVI, CS, CS-CMβ-CD, and CS-NZVI-CMβ-CD beads in the removal of Cr (VI) and Cu (II). NZVI was expected to increase the removal efficiency for both Cr (VI) and Cu (II), but in reality, low removal rates were found because of its instability, leading to facile oxidization in solution (Table 2). Furthermore, both CS and CS-CMβ-CD also exhibited low removal rates of Cr (VI) and Cu (II) similar to those of NZVI. In contrast, CS-NZVI-CMβ-CD adsorbed Cr (VI) and Cu (II) with more than twice the efficiency of bare NZVI, CS, and CS-CMβ-CD, indicating that multiple amide, hydroxyl, and carboxyl functional groups enhanced the adsorption capability. CS-NZVI-CMβ-CD beads were also used to treat a mixture of additional types of metal ions, and good adsorption efficiency was found for each metal ion (Table 2).

3.4 Adsorption activation energy

The activation energy provides a basis for understanding whether the adsorption process is physical or chemical adsorption [47]. The activation energy required for physical adsorption ranges from 5 to 40 kJ mol^{-1}. Chemical adsorption is specific and involves stronger forces, and thus requires larger activation energies (e.g., 40–800 kJ mol^{-1}). Thus, the activation energy provides a basis for understanding whether the adsorption process is physical or chemical

adsorption [48]. The Arrhenius equation can be used to estimate the activation energy involved between the adsorbent and adsorbate as follows:

$$K_2 = K \exp\left(\frac{E_a}{RT}\right)$$

(7)

where k is the temperature-independent factor (g mg^{-1} h^{-1}), E_a is the activation energy of sorption (kJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K), and T is the temperature of the solution (K) [38].

The pseudo-second-order kinetics rate constants were also empirically determined for Cr (VI) and Cu (II) adsorption onto CS-NZVI-CMβ-CD beads in the temperature range of 298–323 K and at pH 6. The activation energy for Cu (II) adsorption onto CS-NZVI-CMβ-CD beads was calculated as 71.99 kJ mol^{-1}, suggesting that the Cu (II) ions were chemically adsorbed onto the CS-NZVI-CMβ-CD surface. The low activation energy of Cr (VI) at 18.38 kJ mol^{-1} suggests the occurrence of a redox process and both physical and chemical adsorption processes. The standard redox potentials of Cr (VI) and Cu (II) (1.33 and 0.34 V, respectively) were different from that of NZVI (-0.41 V) [49].

3.5 Thermodynamic studies

An adsorption isotherm study was conducted under isothermal conditions at pH 6 at temperatures ranging from 298–323 K. The thermodynamic parameters were determined from the thermodynamic equilibrium constant, K_0 (or the thermodynamic distribution coefficient). The standard Gibbs free energy change $\Delta G°$ (kJ mol^{-1}), standard enthalpy change $\Delta H°$ (kJ mol^{-1}), and standard entropy change $\Delta S°$ (J mol^{-1} K^{-1}) were also determined [38] The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes for Cr (VI) were 11.39 KJ mol^{-1} and 0.041 KJ mol^{-1} K^{-1}, respectively,

suggesting endothermic adsorption onto CS-NZVI-CMβ-CD beads [7, 38]. In contrast, the negative values of $\Delta H°$ (-6.24) and $\Delta S°$ (-0.01) confirmed the exothermic nature of adsorption for Cu (II). They indicate the affinity of Cu (II) towards the surface functional groups of the CS-NZVI-CMβ-CD beads [7, 38].

3.6. A possible mechanism of metal adsorption in CS-NZVI-CMβ-CD

This study was conducted to develop a new composite for the remediation of wastewater polluted with heavy metals. The removal efficiency and mechanisms were investigated by fitting the data into different sorption kinetics, isotherm, and thermodynamic models. The results affirmed the successful synthesis of CS-NZVI-CMβ-CD beads with enhanced removal efficiency. In addition, the detailed removal mechanism of Cr (VI) and Cu (II) by CS-NZVI-CMβ-CD beads was remarkably well-characterized, as outlined in Fig. 9. The entrapment process yielded a stable and spherical composite bead with magnetic characteristics, as shown in Fig. 9a. The surface of the beads featured the free amino and hydroxyl groups of CS in addition to the hydroxyl and carboxylate groups introduced by CMβ-CD. Thus, the surface was enriched with functional groups that facilitated the accumulation of both Cr (VI) and Cu (II) on the surface or inside the adsorbent (Fig. 9b). After sufficient surface adsorption, the metal ions entered the CS-NZVI-CMβ-CD beads by redox potential forces and reacted with NZVI. Cr (VI) and Cu (II) were reduced to Cr (III) and Cu (0), respectively, while NZVI was oxidized to Fe (III) on the pore surface of CS-NZVI-CMβ-CD (Fig. 9c). By combining the above mechanisms, we concluded that the reduction of metal ions and the oxidation of NZVI to Fe (III) occurred synergistically, and that the reactions proceeded to complete under our experimental conditions [12]. The results of the sorption kinetics and isotherm studies conclusively confirmed the

mechanism described above. The CS-NZVI-CMβ-CD beads are not only an ideal candidate as a high-efficiency adsorbent for the removal of Cu (II) and Cr (VI) from water but are also easily magnetically collected after adsorption. It is anticipated that the versatile method presented here can be extended to induce the assembly of functional NZVI, CS, and CMβ-CD into different composites with multi-functionalities for different applications.

4. Conclusion

CS-NZVI-CMβ-CD beads have been successfully produced by simple impregnation methods of NZVI in CS-CMβ-CD complex. SEM, FTIR, BET and fluorescence microscopy analyses showed that the NZVI particles were homogeneously entrapped into the pore spaces of CS-CMβ-CD complex. Batch adsorption studies showed higher removal efficiency via chemical reduction of NZVI and sorption by the functional groups of CS and CMβ-CD. The synthesized CS-NZVI-CMβ-CD beads showed that combined effects of highly-dispersed NZVI particles and highly functional CS-CMβ-CD surface give a fast kinetics to remove both Cr (VI) and Cu (II). Removal rates increased with increasing initial concentration of metals and NZVI dosage at pH 6. The adsorption capacity was found to be 200 mg/g and 250 mg/g for Cr (VI) and Cu (II), respectively. These values are higher than some existing adsorbents. The adsorption mechanism is mostly chemisorption with surface sorption and pore diffusion as the rate-limiting step. In addition, the enrichment of Cr (VI) and Cu (II) inside the beads trespassed by strong redox potential of NZVI facilitates the metal to reduce into Cr (III) and Cu (0). The free amino groups, hydroxyl groups and carboxylic groups were considered to be also responsible for adsorption of metal ions. The equilibrium data showed a better fit by both Langmuir and Temkin isotherm indicating monolayer adsorption and chemisorption technique, respectively. Thermodynamic data reveals

that the adsorption of Cr (VI) and Cu (II) was endothermic and exothermic, respectively. The strong magnetic properties of the CS-NZVI-CMβ-CD beads facilitated easy separation from solution.

Conflict of interest statement

The authors declare that there are no conflicts of interest.

Acknowledgements

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Figure Captions

Fig. 1. SEM and fluorescence images of CS-NZVI-CMβ-CD beads at different magnifications; (a) SEM image; (b) fluorescence image showing the homogeneous distribution of NZVI within the beads; (c) the internal network of the pores of CS-CMβ-CD beads; (d) the incorporation of NZVI into the pores; (e) incorporation of NZVI at higher magnification; (f) the morphology of the pore wall.

Fig. 2. The size and shape of the synthesized CS-NZVI-CMβ-CD beads: (a) dry beads; (b) wet beads; (c) application of the synthesized beads in batch adsorption for Cr (VI) removal; (d) magnetic separation of the beads after treatment.

Fig. 3. FTIR spectra of CS-NZVI-CMβ-CD beads. Spectrum a: before metal ion adsorption; spectrum b: after Cr (VI) sorption; spectrum c: after Cu (II) sorption. Initial Cr (VI) and Cu (II) concentrations, 100 mg L^{-1}; adsorbent dose, 0.12 g; pH 6; temperature, 298 K.

Fig. 4. XPS general spectra of CS-NZVI-CMβ-CD beads. (a) Typical wide range spectrum (1) before and after (2) Cr (VI) and (3) Cu (II) adsorption; (b) high resolution Fe $2p_{3/2}$ XPS spectrum of CS-NZVI-CMβ-CD beads; (c) Cu $2p_{3/2}$ core level spectrum; (d) Cr $2p_{3/2}$ spectrum. Initial Cr (VI) and Cu (II) concentrations, 100 mg L^{-1}; adsorbent dose, 0.12 g; pH 6; temperature, 298 K.

Fig. 5. Pseudo-first-order kinetic model for (a) Cr (VI) and (c) Cu (II) adsorption as well as pseudo-second-order kinetic model for (b) Cr (VI) and (d) Cu (II) adsorption by CS-NZVI-CMβ-CD beads at various concentrations.

Fig. 6. Intraparticle diffusion model fit for (a) Cr (VI) and (b) Cu (II) adsorption on CS-NZVI-CMβ-CD beads at different concentrations. Effects of adsorbent dose on (c) NZVI loadings (c, inset).

Fig. 7. Effect of pH on the adsorption of (a) Cr (VI) and (b) Cu (II) by CS-NZVI-CMβ-CD beads. Initial Cr (VI) and Cu (II) concentrations, 100 mg L^{-1}; pH 6; temperature, 298 K.

Fig. 8. Linearized equilibrium isotherms. (a) Langmuir; (b) Freundlich; (c) Temkin isotherms for Cr (VI) and Cu (II) adsorption on CS-NZVI-CMβ-CD beads at different temperatures.

Fig. 9. Removal mechanism of Cr (VI) and Cu (II) by CS-NZVI-CMβ-CD beads in schematic form. (a) Functional groups are exposed on the surface of the newly synthesized CS-NZVI-CMβ-CD beads; (b) the beads are exposed to solution containing Cr (VI) and Cu (II), which initially accumulate on the surface; (c) after some time, the ions enter the interior of the beads and react with NZVI, leading to reduction to Cr (III) and Cu (0).