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1 Application of zerovalent iron impregnated chitosan-
2 caboxymethyl- β -cyclodextrin composite beads as a arsenic
3 sorbent

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18 **Abstract**

19 Nano zerovalent iron impregnated chitosan-carboxymethyl β -cyclodextrin complex has
20 been successfully tested for arsenic removal. Addition of chitosan enhances the stability of
21 Fe^0 particles and the carboxymethyl β -cyclodextrin gives the composite more active sites to
22 interact with the target ions. Removal of arsenic (III) and arsenic (V) was studied through
23 batch adsorption at pH 6.0 under equilibrium and dynamic conditions. Prepared beads were
24 characterized by FT-IR, SEM, BET and XPS. The rate of reduction can be expressed by
25 pseudo-second-order reaction kinetics plus the equilibrium data were well fitted to
26 Langmuir adsorption models. Equilibrium is achieved after 3 h and As (III) and As (V)
27 were reduced to $<20 \mu\text{g/L}$ which accounts 99% of the total removal below the Bangladesh
28 standard ($50 \mu\text{g L}^{-1}$). The adsorption capacity was calculated from Langmuir model and
29 found to be 18.51 mg/g and 13.51 mg/g for As (III) and As (V), respectively. The adsorbent
30 can be separated magnetically and thus reused successfully for the removal of total
31 inorganic arsenic from water. So, this adsorbent can be a potential material for the
32 remediation of contaminated surface and ground water.

33

34 **Key words:** Arsenic, Removal, Chitosan, Zero valent iron, cyclodextrin, Nanocomposite,
35 Adsorption,

36

37 **1. Introduction**

38 Arsenic (As) is a dangerous toxicant that poses risk to humans and environment. As
39 contaminated groundwater have been reported in many regions of the world such as
40 Argentina, Bangladesh, Chile, China, India, Japan, Mexico, Mongolia, Nepal, Philippines,
41 Poland, Taiwan, Thailand, Vietnam, and some parts of the United States [1-5]. In
42 Bangladesh, approximately half of the total population is at risk of drinking As-
43 contaminated water from tube wells which resulted in approximately 9,100 deaths and
44 125,000 disability in 2001 [6]. A nationwide survey reported 27% arsenic contaminated
45 shallow-tube wells (STWs) with elevated As contamination above the Bangladesh standard
46 of 0.05 mg/L [7]. It was also reported by another study that more than 8,000 villages had
47 As contamination in 80% of all STWs above the Bangladesh standard of 0.05 mg/L [8].
48 The presence of arsenic in water is extremely detrimental to human health [9, 10]. Thus,
49 there is a growing interest in using low-cost methods and materials to remove arsenic from
50 potable water before it may cause significant contamination.

51 The removal of arsenic by various methods has been adequately reviewed where activated
52 carbon [11], activated alumina [12] and Red mud [13] have extensively used. Zero-valent
53 iron powders (Fe^0) have been extensively used for in situ remediation of water polluted
54 with As in aqueous solution [14-16]. The oxidation of nano-zerovalent iron (NZVI) by
55 water and oxygen produces ferrous iron to give magnetite, depending upon redox
56 conditions and pH which eventually facilitates the magnetic separation [14].

57



61

62 However, low adsorption due to high diffusion and initial cost has made these technologies
63 incompetent. In addition, NZVI exhibits high agglomeration, high mobility, lack of stability,
64 and low reducing specificity in water, and thus must be used with surface stabilizers such as
65 chitosan (CS), alginate, activated carbon, and others porous structures [17].

66 CS (2-Amino-2-deoxy- β -D-glucopyranose; $\text{C}_6\text{H}_{13}\text{NO}_5$) is an important natural polymer has
67 found extensive application of adsorbing several metal ions because of its excellent
68 biocompatibility, biodegradability, and lack of toxicity [18]. Because the amino groups of
69 CS have the ability to form chelating complexes with various heavy-metal ions, CS-NZVI
70 should have the removal applicability of total inorganic arsenic.

71 In addition, β -cyclodextrin (β -CD; $\text{C}_{42}\text{H}_{70}\text{O}_{35}$), a cyclic oligosaccharide has been
72 immobilized or grafted with supportive materials, and active functional groups have been
73 introduced to enhance its adsorption capacity for metal ions, e.g., carboxymethyl β -CD
74 (CM β -CD) [19]. The coupling of CM β -CD with functionalized CS followed by the
75 entrapment of NZVI is expected in this study to facilitate the removal of arsenic from
76 wastewater. Accordingly, a new CS-NZVI-CM β -CD bead was synthesized in our previous
77 study by incorporating all the above mentioned potent of CS, CM β -CD and NZVI and the
78 bead was successfully tested for chromate anion (CrO_4^{2-}) and cationic copper (Cu^{2+})

79 removal and the removal mechanism was elucidated clearly for metal ions. It was also said
80 about the potentiality of this bead for the arsenic removal [20]. Some papers have reported
81 only CS and activated carbon bearing NZVI beads for As (III) and As (V) removal, but
82 haven't specially studied the combine effects of CS, CM β -CD and NZVI onto arsenic
83 removal [21-25]. In the current studies, both As (III) and As (V) were aimed to remove
84 down to minimum contamination limit (MCL) of 50 μ g/L recommend by Bangladesh
85 Government in the near neutral pH. Herein, a novel arsenic sorbent, NZVI-impregnated
86 porous CS-CM β -CD complex, which has been previously synthesized and successfully
87 tested, is reported. These beads were then evaluated and applied towards the removal of
88 arsenic from arsenic contaminated water.

89

90 **2. Materials and methods**

91 2.1 Reagents, bead preparation and characterization

92 Stock solutions of As (III) and As (V) were prepared by dissolving NaAsO₂ (Sigma
93 Aldrich) and Na₂HAsO₄·7H₂O (Fisher Scientific), respectively in deionized water. All other
94 chemicals were of analytical grade purity and were used without further purification. Milli-
95 Q water (Millipore-Gradient A10, Milli-Q Gradient ZMGG) was used in every step where
96 necessary.

97 CS-NZVI-CM β -CD beads were prepared according to the procedures described in detail in
98 our previous study [20]. Briefly, CM- β -CD sodium salt was complexed with CS flakes in
99 2% (v/v) acetic acid followed by the addition of 1,3-bis (2,2-diethyl-1,3-dioxolan-4-yl-

100 methyl) carbodiimide in water to obtain CS-CM β -CD gel. Then, different proportion of
101 NZVI (electrolytic powder finer than 100 mesh, 98% purity) was gently added to CS-CM β -
102 CD gel in centrifuge tubes and the resulting mixture was then dropped into the alkaline
103 solution with constant stirring to form CS-NZVI-CM β -CD beads [20, 26, 27]. The
104 characterization of the bead was performed with a Hitachi S-4000 scanning electron
105 microscope (SEM) (Ibaraki, Japan); brunauer-emmet-teller (BET) (Bel-Japan-Inc);
106 fluorescence microscopy (Olympus IX70); fourier transform infrared (FTIR) spectroscopy
107 (FT210, Horiba, Japan) and x-ray photoelectron spectroscopy (XPS) as per the methods
108 described by Sikder et al. 2013 [20]. The beads are reported nearly spherical in shape,
109 blackish and uniform in size with a mean diameter of 2.5 ± 0.10 μ m (Fig. 1a). The result
110 from the image of fluorescence microscopy also suggests the presence of NZVI in CS-
111 CM β -CD interior with no agglomeration. Fig. 1b shows the ashen color macroporous
112 morphology of CS-NZVI-CM β -CD beads [20].

113

114 2.2 The adsorption batch experiment

115 Adsorption experiments were carried out using batch equilibrium technique in aqueous
116 solutions at pH 2-9 and 298-323 K. In general, a known amount of CS-NZVI-CM β -CD
117 beads with 30 mL aqueous solution of As (III) and As (V) of the desired concentration was
118 taken and shaking in a thermostatic water bath incubator (Hi TEC; BT-23, Japan) or in a
119 shaking mixture (SHM-100) with 120 rpm for a given time. The pH of the solution was
120 carefully checked with a pH meter (Model HM-25R, DKK-TOA Corporation, Tokyo,

121 Japan) and adjusted with NaOH or HCl solution, if necessary. Except some special cases,
122 the adsorbent mass was 0.1 g; adsorbate dosage was 1 to 20 mg/L; pH was 6.0; and the
123 shaking time was 12 h to achieve complete equilibrium. After a shaking time completed,
124 the CS-NZVI-CM β -CD beads were removed using a strong permanent magnet followed by
125 centrifugation at 2,500 rpm for 5 min. The obtained supernatant was filtered by 0.45 μ m
126 pore size Millipore membrane filters (OmniporeTM, Ireland) to remove the insoluble
127 materials. The As (III) and As (V) contents were measured using an inductively coupled
128 plasma-mass spectrophotometer (ICP-MS; SPQ 6500, Plasma Quadrupole Mass Analyzer,
129 SII-Seiko Instrument, Japan). The lower limit of sensitivity was 0.01 μ g/mL. The accuracy
130 of the analysis was checked by the use of certified standard reference material for As (013–
131 15481, Lot ALK 9912, 1000 ppm) obtained from Wako Pure Chemical Ind. Ltd., Japan.
132 Each equilibrium experiment was performed at triplicate

133 The accumulated amount of metal ions onto the CS-NZVI-CM β -CD beads was calculated
134 by the following numerical formula;

$$135 \quad q_t = \frac{C_i - C_e}{W} \times V \quad (4)$$

136 Where, q_t (mg/g) is the total adsorbed amount in time t (min) C_i and C_e are the initial and
137 equilibrium concentrations (mg/L) of metal ion in the solution, V is the volume and W is the
138 weight (g) of the adsorbent. To describe the efficiency of metal ion removal from the
139 solution, the recovery factor (RF) or percent (%) removal was calculated as follows;

140
$$RF(\%) = \frac{C_i - C}{C_i} \times 100 \quad (5)$$

141 Kinetic experiments were performed using different concentration of As (III) and As (V) as
142 initial concentrations with 100 mg of CS-NZVI-CM β -CD beads at pH 6. The suspension
143 was stirred from 0-300 min at 298 K. Samples were collected at different time intervals by
144 the procedure mentioned in the above adsorption experiment. To conduct the equilibrium
145 isotherm studies, 30 mL As (III) and As (V) ions of different concentrations were mixed
146 with 100 mg of CS-NZVI-CM β -CD beads at pH 6.0 and were shaken for 12 h at 298 K,
147 313 K AND 323 K.

148

149 2.3 The desorption study

150 Desorption study was accomplished using 0.1M NaOH (pH 13) or Na₂EDTA (pH 7) as
151 desorption eluants. After adsorption experiments of 1 mg/L As (III) and As (V) ion solution
152 with 100 mg CS-NZVI-CM β -CD beads for 12 h at pH 6.0, the concentration of metal ions
153 in the sorbent were measured. The beads were then washed gently with distilled water to
154 remove unadsorbed metal ions. The amounts of unadsorbed As washed gently with distilled
155 water were measured and found negligible or insignificant and thus it was not considered
156 during desorption study. Desorption was then studied by adding 30 mL of 0.1M NaOH
157 solution to the As (III) and As (V) sorbed CS-NZVI-CM β -CD beads. The regenerated

158 adsorbent sample was reused in the next cycle of the adsorption experiment. The
159 adsorption-desorption experiments were conducted for five cycles.

160

161 **3. Results and discussion**

162 3.1 BET analysis

163 Bigger pore spaces present in the adsorbent are believed to facilitate the mass transfer
164 between the adsorbent and wastewater. In this study, this statement was highly supported
165 by the quick equilibrium achieved within the first 3 hours (Fig. 2a). The pore size
166 distribution of the CS-NZVI-CM β -CD beads was calculated to be 3.5–8.7 μm . BET surface
167 area of the CS-NZVI-CM β -CD beads is obtained as $12.1 \text{ m}^2 \text{ g}^{-1}$ and the pore volume was
168 $2.78 \text{ cm}^3 \text{ g}^{-1}$ (16.35 v/v). The density of the bead was around $>5.85 \text{ g/cm}^3$ where NZVI
169 contributed $>5.0 \text{ g/cm}^3$ indicated the CS-CM β -CD complex can dominate the composite
170 volumetrically and serves as a host for the NZVI particles. The weight of a single dry bead
171 was $\sim 0.005 \text{ g}$, with NZVI constituting 50% of the total weight, and the total shrinkage of
172 the surface area was around 74%. This indicates that NZVI blocked the maximum pores of
173 the CS-NZVI-CM β -CD beads. From the adsorption-desorption (BET) isotherms, the
174 volume of adsorbed N_2 slightly increased with increasing P/P_0 , indicating a small pore size
175 distribution (Fig. 2b).

176

177 3.2 Fourier-transform infrared (FTIR) evaluation

178

179 To identify possible interactions between CS-NZVI-CM β -CD beads and As (III), the
180 surface functional groups of the adsorbent were observed by FT-IR spectrum before and
181 after the adsorption (Fig. 3). CS-NZVI-CM β -CD has two characteristic peaks at 1654 and
182 3423 cm⁻¹ are contributed to the N-H or C=O and O-H bending vibration, respectively [20,
183 28, 29]. The peaks at 1091, 1165 and 1399 cm⁻¹ corresponds to the glycosidic vibration of
184 C-O-C or C-C/ C-O stretch vibration indicating the presence of CM β -CD into the adsorbent
185 (line a in Fig. 3) [20, 28]. A weak bands at 2877 cm⁻¹ ascribes C-H stretch. Adsorption of
186 arsenite species (H₃AsO₃) was evident from the weak band at 710 cm⁻¹ corresponding to
187 the asymmetrical and symmetrical stretching of As-O bond [20, 30]. This infrared
188 absorption must arise from As-O stretch vibrations of adsorbed arsenite species. The
189 results from FTIR showed the complexation between Fe and Arsenic. The characteristic
190 absorption bands for N-H and C-O shifted to 1590 and 1081 cm⁻¹, respectively (line b in
191 Fig. 3) [31, 32]. The peak at 569 cm⁻¹ ascribe to Fe-O group.

192

193 3.3 XPS analysis

194

195 XPS studies were also employed to comprehend the adsorption mechanism of As (III) and
196 As (V) onto CS-NZVI-CM β -CD beads. The high resolution XPS spectra for the CS-NZVI-
197 CM β -CD beads after As (III) and As (V) reduction were shown in Fig. 4. A single
198 photoelectron peak at 45.5 eV indicates the retention of the oxidation state of As (V) treated
199 with CS-NZVI-CM β -CD beads. In addition, two characteristic peaks corresponding to As

200 (III) and As (V) were observed at 43.5 and 45.5 eV, respectively (Fig. 4). The earlier XPS
201 studies also support these results [33, 34]. Metal–NH₂ complexes act as mono or bidentate
202 ligands between Fe (III) and As (III) [32]. This process leads to protect the metal
203 precipitation in solution. Photoelectron peaks for 2p_{3/2} and 2p_{1/2} of oxidized iron Fe (III)
204 were found at 711 and 724.5 eV [20]. Of note, the characteristic peak for NZVI at 706.5 eV
205 was absent due to the extensive oxidation of iron by the oxidation-reduction reaction.
206 Hence it could be concluded that after adsorption, partial oxidation of arsenite takes place
207 on the surface of the sorbent.

208

209 3.4 Effects of adsorbent dosage and pH

210 Adsorbent dosage is an important parameter in the removal of metal ions by adsorption.
211 Our studies showed that the removal of both As (III) and As (V) increased when the dose of
212 CS-NZVI-CMβ-CD increased from 0.1 to 1 g/30 mL for initial metal concentrations of 1
213 mg/L (Fig. 5a). It is evident from Fig. 5a that As (III) and As (V) can be lowered below the
214 Bangladesh standard (50 ppb) and eventually to the international standard level (10 ppb)
215 by increasing the adsorbent dosage. In addition, the removal rates of As (III) and As (V)
216 increased with increasing iron loadings (data not shown). However, the NZVI loading was
217 found to be dependent on the size of the adsorbent. For example, for the 2.5 mm beads used
218 in this study, the maximum NZVI load was 1 g/30 mL to avoid oxidation, corrosion, and
219 loss of iron particles.

220

221 The effect of pH on As (III) and As (V) removal was tested using CS-NZVI-CM β -CD
222 beads at the concentration level 2 mg/L for the pH values ranging from 2–9 (Fig. 5b).
223 Elemental As is water insoluble but As salts exhibit a wide range of solubilities depending
224 on pH and the ionic environment. From the pH-pE relation of As (when pH = 0, pE \approx 11) it
225 is known that As can exist in four valency states: –3, 0,+3,+5. Under reducing conditions,
226 the +3 valency state as arsenite, As (III) is the dominant form in water; the +5 valency state
227 as arsenate, As (V) is generally the more stable form in oxygenized environments [11, 35].
228 Efficient adsorption was found over the wide range of pH where NZVI present in the
229 adsorbent reduced As (V) to As (III) which subsequently gets complexed with oxidized
230 iron and chitosan. Generally, Fe⁰ donates its electrons to protons and is oxidized to Fe (III)
231 whereas the protons are reduced to hydrogen gas [26]. As a result, the bead surface
232 becomes more positively charged, establishing an electrostatic attraction between adsorbent
233 and adsorbate. More than 98% of As (III) and As (V) species were adsorbed at pH ranges
234 from 5 to 7. The adsorption decreased significantly at pH <5.0 and >7.0, because of the
235 high ionic mobility of [H₃O]⁺ in water as compared with most other ions [32, 36, 37].

236

237 3.5 Adsorption kinetics

238 The adsorption of As (III) and As (V) on the CS-NZVI-CM β -CD composite beads was fast
239 and reached equilibrium within 3 h. Adsorption increased with an increase in contact time
240 due to due to the efficient reaction caused by the adsorbent composition of the materials.
241 Pseudo-first-order and pseudo-second-order models were tested. The Lagergren's first-order

242 equation measures the rate sorption by assuming that one ion is sorbed onto one sorption
243 site and can be expressed as follows [38]:

$$244 \quad \ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

245 where q_t is the amount of adsorbate adsorbed (mg/g) at time t , k_1 is the Lagergren's first-
246 order rate constant (min^{-1}). k_1 and q_e at 298K were calculated from the intercept and slope
247 of the plot $\ln (q_e - q_t)$ versus t (Figures not shown). The corresponding correlation
248 coefficients suggest that the pseudo first-order model did not fit well (Table 1). Pseudo
249 second-order model usually applied for analyzing chemisorptions kinetics in solution and
250 the equation can be represented as [38]:

$$251 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

252 Where k_2 (g/mg min) is the second order rate constant and q_e is the equilibrium sorption
253 capacity. k_2 and q_e can be determined experimentally by plotting t/q_t versus t (Figures not
254 shown). The corresponding correlation coefficients derived from the second order equation
255 are healthy and thus assume that one metal ion is sorbed onto two sorption sites on the
256 adsorbent with chemisorptions process (Table 1). Removal of As with iron coated particle
257 has been attributed to ion exchange, specific adsorption to surface hydroxyl groups, or
258 coprecipitation. Improved As adsorption in near alkaline pH range was attributed to a
259 depression of negative solid surface charges in the alkaline region, caused by the presence

260 of the inorganic electrolyte, enhancing the interactions between the surface sites and arsenic
261 oxyanions.

262 The removal of As (III) and As (V) can be explained by the respective speciation
263 differences. As(V) in solution above pH 3 is present in anionic forms (AsO_4^{3-} , HAsO_4^{2-} ,
264 H_2AsO_4^-) and therefore can be effectively removed by iron hydroxide attached to the
265 surface of the beads [11].

266 On the other hand, As (III) is present as an anion exclusively above pH 9 (AsO_3^{3-} , HAsO_3^{2-} ,
267 H_2AsO_3^- whereas in the pH interval 6–9 only a small percentage of H_3AsO_3 is dissociated.
268 The responsible mechanism for the removal of arsenic was adsorption on iron-modified
269 adsorbents, which refers to the formation of surface complexes between soluble arsenic
270 species and the surface hydroxyl groups, as arsenic gets in contact with the iron sites [14].

271 3.6 Equilibrium isotherms

272 The adsorption isotherms notify specific relation between the equilibrium concentration of
273 adsorbate in the bulk and the adsorbed amount at the surface of adsorbent. The Langmuir
274 adsorption isotherm has been successfully used in many monolayer adsorption processes.
275 The Freundlich isotherm is generally applied to model both monolayer (chemisorption) and
276 multilayer (physisorption) adsorption on heterogeneous surfaces [39-41]. Temkin isotherm
277 model describes indirect adsorbent-adsorbate interaction and assumes that the adsorption
278 energy in the layer would decrease linearly with coverage (Fig. 6) [33].

279 Langmuir isotherm parameter fits for As (III) and As (V) adsorption on CS-NZVI-CM β -
280 CD beads are in good agreement with observed behavior ($R^2 \geq 0.99$) (Table 2). The
281 adsorption capacity of As (III) and As (V) on CS-NZVI-CM β -CD beads at room
282 temperature (298 K) were 18.51 and 13.51 mg/g, respectively (Fig. 6a) (Table 2). This
283 capacity was observed as high in compare with some existing high performance adsorbents
284 reported in the literature especially, iron chitosan granules (2.24 mg/g for As (V) and 2.32
285 mg/g for As (III)) [23]; TiO₂-impregnated chitosan bead (6.4 mg/g for As (III) and 4.9
286 mg/g for As (V)) [42]; activated alumina grains (3.48 mg/g for As (III) and 15.9 mg/g for
287 As (V)) [12]; iron doped activated carbons (0.036 mg/g for As (III)) [24]; Activated carbon
288 (Draco) (3.75 mg/g for As (V)) [43]; Iron-Treated Activated Carbon (25.58 mg/g for As
289 (V)) [11]. In case of Freundlich isotherm, the n values greater than unity are classified as
290 L-type isotherms indicating chemisorption for both As (III) and As (V) and reflecting a
291 high affinity between adsorbate and adsorbent (Fig. 6b) (Table 2). The adsorption data were
292 fitted well with Temkin adsorption isotherm with correlation coefficients ≥ 0.91 indicating
293 chemisorption of the adsorbate onto CS-NZVI-CM β -CD beads (Fig. 6c). The earlier
294 findings were further proved that the adsorption of As (III) and As (V) onto CS-NZVI-
295 CM β -CD beads is a complete chemisorption process. The homogeneous distribution of
296 active sites on CS-NZVI-CM β -CD bead surface and uniform distribution of NZVI into the
297 interior may lead to the experimental data fitted well with Langmuir isotherm model.

298 3.7. Reusability of the adsorbent

299 Reusability of any adsorbent is of great importance in view of sustainability and cost-
300 effectiveness. Desorption experiment of As (III) and As (V) was conducted using 0.1 M
301 NaOH at room temperature. The effectiveness of CS-NZVI-CM β -CD beads was checked
302 by following the adsorption-desorption process for five cycles with 1 ppm each of As (III)
303 and As (V) (Fig. 7a). The desorption study was carried out using the fresh desorption
304 solution each time. Subsequent washing of the adsorbent was carried out with distilled
305 water and the cycle was repeated. The beads used in the adsorption experiment were
306 regenerated and reused for five times. It can be clearly observed that both the adsorption
307 and desorption efficiency decrease slightly in each cycle. Around 74% of load were found
308 to be desorbed during desorption cycles. In addition, uniform adsorption-desorption trend
309 was evident from the N₂ adsorption-desorption isotherm (BET isotherm) of CS-NZVI-
310 CM β -CD beads (Fig. 2b). Apparently, the repeated adsorption and desorption performance
311 indicates the CS-NZVI-CM β -CD beads as mechanically and chemically robust for the
312 wastewater treatment. Desorption was sufficiently high at the first 4 cycles and decrease
313 sharply at the fifth cycle. In contrast, the adsorption rate of As (III) and As (V) was
314 identical from cycle 1 to cycle 3. The decrease of both adsorption and desorption may be
315 due to the fact of excessive exhaustion of NZVI by reduction process. Further study and
316 improvement are needed to enhance both the adsorption and desorption performance of CS-
317 NZVI-CM β -CD beads.

318 The entrapment of NZVI into the CS-CM β -CD complex given them suitability, stability
319 and introduce multiple amide, hydroxyl and carboxyl functional groups could enhance the

320 adsorption capabilities. CS-NZVI-CM β -CD beads were also tested to treat the mixture of
321 multiple metal ions and good adsorption efficiency was found for each metal. Cadmium
322 (Cd (II)), copper (Cu (II)) and chromium (Cr (VI)) were also evaluated with CS-NZVI-
323 CM β -CD beads and high removal rate was observed in each case (Fig. 7b). This result
324 clearly supports the suitability of this adsorbent for both drinking water and waste water
325 treatment.

326 **4. Conclusion**

327 CS-NZVI-CM β -CD beads have been successfully tested for As (III) and As (V) removal by
328 batch adsorption experiments. This CS-NZVI-CM β -CD bead showed that a combined
329 effect of highly-dispersed NZVI particles and highly functional CS-CM β -CD surface gives
330 a fast kinetics to remove both As (III) and As (V) supported by early equilibrium with high
331 adsorption and respective speciation. The adsorption capacity was found to be 18.51 mg/g
332 and 13.51 mg/g for As (III) and As (V), respectively. It has been demonstrated that CS-
333 NZVI-CM β -CD is capable of adsorption in a wide range of pH. The adsorption mechanism
334 is mostly chemisorption. The strong magnetic property of CS-NZVI-CM β -CD beads
335 facilitates easy separation from solution and could be effectively regenerated with 0.1 M
336 NaOH for repeated usage. So, this study may possibly offer a way to effectively use NZVI
337 in many surface or groundwater remediation situations. Detailed investigation and long-
338 term continued experiments are absolutely necessary to treat contaminated water, to
339 understand the regeneration, and to reuse of the beads. Further specialized study must be
340 carried out to verify whether these beads are applicable to realistic As-contaminated

341 groundwater or surface water based on ionic strength, natural organic matter, etc. or to
342 develop applicable alternatives.

343

344 **Conflict of interest statement**

345 The authors declare that there are no conflicts of interest.

346

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352

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480 **Figure Captions**

481 **Fig. 1.** SEM image of CS-NZVI-CM β -CD beads; (a) size and spherical shape of the wet
482 beads and (b) the internal network of the pores of CS-NZVI-CM β -CD beads.

483 **Fig. 2.** (a) As (III) and As (V) removal efficiency of CS-NZVI-CM β -CD beads (b)
484 Adsorption (ADS) and desorption (DES) isothermal curve of CS-NZVI-CM β -CD beads
485 from BET.

486 **Fig. 3.** FTIR spectra of CS-NZVI-CM β -CD beads. Spectrum a: before As (III) ion
487 adsorption; spectrum b: after As (III) adsorption. Initial As (III) concentrations, 1 mg/L;
488 adsorbent dose, 0.10 g; pH 6; temperature, 298 K.

489 **Fig. 4.** XPS general spectra of CS-NZVI-CM β -CD beads. CS-NZVI-CM β -CD beads
490 loaded with As (III) and As (V). Initial As (III) and As (V) concentrations, 1 mg/L;
491 adsorbent dose, 0.10 g; pH 6; temperature, 298 K.

492 **Fig. 5.** (a) Effects of pH and (b) adsorbent dosage on the adsorption of As (III) and As (V).

493 **Fig. 6.** Linearized equilibrium isotherms. (a) Langmuir; (b) Freundlich; (c) Temkin
494 isotherms for As (III) and As (V) adsorption on CS-NZVI-CM β -CD beads.

495 **Fig. 7.** Reusability studies of the CS-NZVI-CM β -CD beads with As (III) and As (V).

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497

498 Table 1 Adsorption kinetics for As (III) and As (V) on CS-NZVI-CM β -CD composite
 499 beads.
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Initial concentration (mg/L)	Pseudo-first-order model			Pseudo-second-order model		
	K_1 (min ⁻¹)	$q_{e,cal}$ (mg/g)	R^2	K_2 g/(mg.min)	q_e (mg/g)	R^2
As (III)						
1	0.004	1.18	0.82	1.62	0.28	0.99
2	0.007	0.78	0.92	0.20	0.59	0.99
As (V)						
50	0.013	1.01	0.98	0.50	0.29	0.99
100	0.024	0.35	0.97	0.22	0.60	0.99

501
 502

503 Table 2 Langmuir, Freundlich and Temkin isotherm model constants and correlation
 504 coefficients for sorption of As (III) and As (V) onto CS-NZVI-CM β -CD beads at 298 K
 505 and pH 6.

Metal	Langmuir			Freundlich			Temkin		
	b (L/mg)	Q_0 (mg/g)	R^2	K_f (mg/g (L/mg) ^{1/n})	n	R^2	A (L/mg)	B	R^2
As (III)	0.18	18.51	0.99	2.60	1.11	0.91	13.23	3.75	0.91
As (V)	0.06	13.51	0.99	2.70	1.23	0.83	13.67	3.69	0.94

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