Electronic Supplementary Material (ESI) for Environmental Science: Nano.

# Supporting Information

## Enhanced simultaneous removal of Cr(VI) and Cd(II) from aqueous solution and soil: A novel carbon microspheres-calcium alginate supported sulfide-modified nZVI composite

Weiyu Liang[a], Yihao Shen[c], Chen Xu[d], Dongqing Cai[c], Dongfang Wang[c], Kailun Luo[a], Xuechun Shao[a], Zhihua Qiao[a], Wei Zhang[a,b], Cheng Peng[a, b*]

[a] State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, School of Resource and Environmental Engineering, East China University of Science and Technology, Shanghai, 200237, China.

[b] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China

[c] College of Environmental Science and Engineering, Donghua University, Shanghai, 201620, China.

[d] Zhejiang Jiahe Eco Envitech Co., Ltd., Hangzhou, 310000, China.

*Corresponding author.

E-mail: cpeng@ecust.edu.cn (C. Peng)

This Supplementary Material included 5 text (Text S1 to S5), 5 figures (Figure S1 to S5), and 2 tables (Table S1 and S2).

## Text S1 Materials

All chemicals were of analytical reagent grade without further treatment. The glucose, sodium alginate, $CaCl_2$, $FeCl_3 \cdot 6H_2O$, $NaBH_4$, $Na_2S_2O_4$, $K_2Cr_2O_7$, $Cd(NO_3)_2 \cdot 4H_2O$, KCl, $Ca(NO_3)_2$, $Mg(NO_3)_2 \cdot 6H_2O$, $KH_2PO_4$, and $K_2SO_4$ were purchased from China National Medicines Corporation Ltd. The sodium humate (HA) was purchased from Sigma Aldrich. All solution in this research was prepared by ultrapure water which has the resistivity of 18.25 MΩ cm

## Text S2 Preparation of CMS, CA, and S-nZVI

The carbon microspheres (CMS) were prepared by traditional hydrothermal method [1]. In brief, 6 g glucose was dissolved in 20 mL ultrapure water, stirred at room temperature for 2 h, then transferred to hydrothermal reaction kettle. After 180°C hydrothermal reaction for 12 h in the oven, it was cleaned with deionized water and anhydrous ethanol at least 3 times, and then dried and grinded for later use.

The preparation process of calcium alginate (CA) was as follow. Firstly, 2.5% (m/v) of sodium alginate (SA) was dissolved and stirred magnetically for 4 h, then stood 6 h to form a homogeneous solution. Then it was slowly added to 0.3M $CaCl_2$ solution for crosslinking under magnetic stirring and aged 6 h. The hydrogel was filtered and washed with ultra-pure water for several times to remove uncross linked calcium ions on the surface. The calcium alginate aerogel was obtained by freeze-drying for 24 h. The preparation process of CMS@CA was similar to CA, in which the SA was replaced with mixed powder of SA and CMS.

The S-nZVI nanoparticle were synthesized based on one-step process adapt from the previous study [2]. $Na_2S_2O_4$ and $NaBH_4$ mixed solution was added into the $FeCl_3 \cdot 6H_2O$ solution drop by drop, S/Fe=0.75. It was continuously stirred uniformly at a slow speed, and $N_2$ was injected to maintain the anoxic environment. The products were cleaned with anhydrous ethanol for at least three times, and the obtained nanoparticles were freeze-dried for 24 h, and stored in vacuum drying oven for later use. The synthesis of nZVI was the same without adding $Na_2S_2O_4$.

## Text S3 Characterization of S-nZVI@CMS@CA ternary composite

The morphology, surface structure, and surface elements of the ternary composite were analyzed by scanning electron microscopy (SEM, S-3400N, Japan) and energy dispersive spectrometer (EDS, Falion 60S, U.S.A). The functional groups of the ternary composite were identified by fourier transform infrared spectrometer (FTIR, Nicolet 6700, U.S.A.). The elemental valence and composition of the ternary composite before and after removal experiments were detected by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, USA). The pore size distributions of CA, CMS@CA, and S-nZVI@CMS@CA were obtained by $N_2$ adsorption-desorption at 77 K (ASAP 2460, U.S.A), and the specific surface area of S-nZVI@CMS@CA was calculated by Brunauer-Emmette-Teller (BET) method.

## Text S4 Batch experiments

Stock solution (1000 mg $L^{-1}$) were prepared by dissolving certain amount of $K_2Cr_2O_7$ and $Cd(NO_3)_2 \cdot 4H_2O$ respectively in ultrapure water and then diluted to required concentrations. The batch adsorption experiment was carried out in a 50 mL centrifugal tube with 25 mL reaction liquid, placed in a constant-temperature water-bathing shaker to react at 25 ± 1 °C at 200 rpm. After that, samples were taken from the flask and filtered by a 0.22 m water-phase filter.

For the adsorption kinetics study, the react time was set within 0, 5, 10, 20, 30, 40, 50, 60, and 120 min to detect the adsorption amount of Cr(VI) and Cd(II) by S-nZVI@CMS@CA. The optimal dosage of S-nZVI@CMS@CA (0.05 g, 0.1 g, and 0.2 g) for the best removal efficiency was investigated as well. Meanwhile, the effects of initial pH at a range from 2.0 to 10.0. The pH of the solution was adjusted using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide. In addition, different co-existence ions ($Mg^{2+}$, $Ca^{2+}$, $H_2PO_4^-$, $SO_4^{2-}$, and $Cl^-$ (0.01M) and co-existence matter (humic acid, 1 and 10 M) on the adsorption performance were also measured.

**Text S5**

The removal percentage (R, %) and adsorption capacity were calculated as follows (Eq. (1-2)):

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{1}$$

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where Qe (mg $g^{-1}$) is the adsorption capacity, $C_0$ and Ce (mg $L^{-1}$) are the initial concentration and equilibrium concentration, respectively.

The fitting equation model of adsorption kinetics models (Pseudo first-order (Eq. 3), Pseudo second-order (Eq. 4), and Elovich models (Eq. 5)) are as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{3}$$

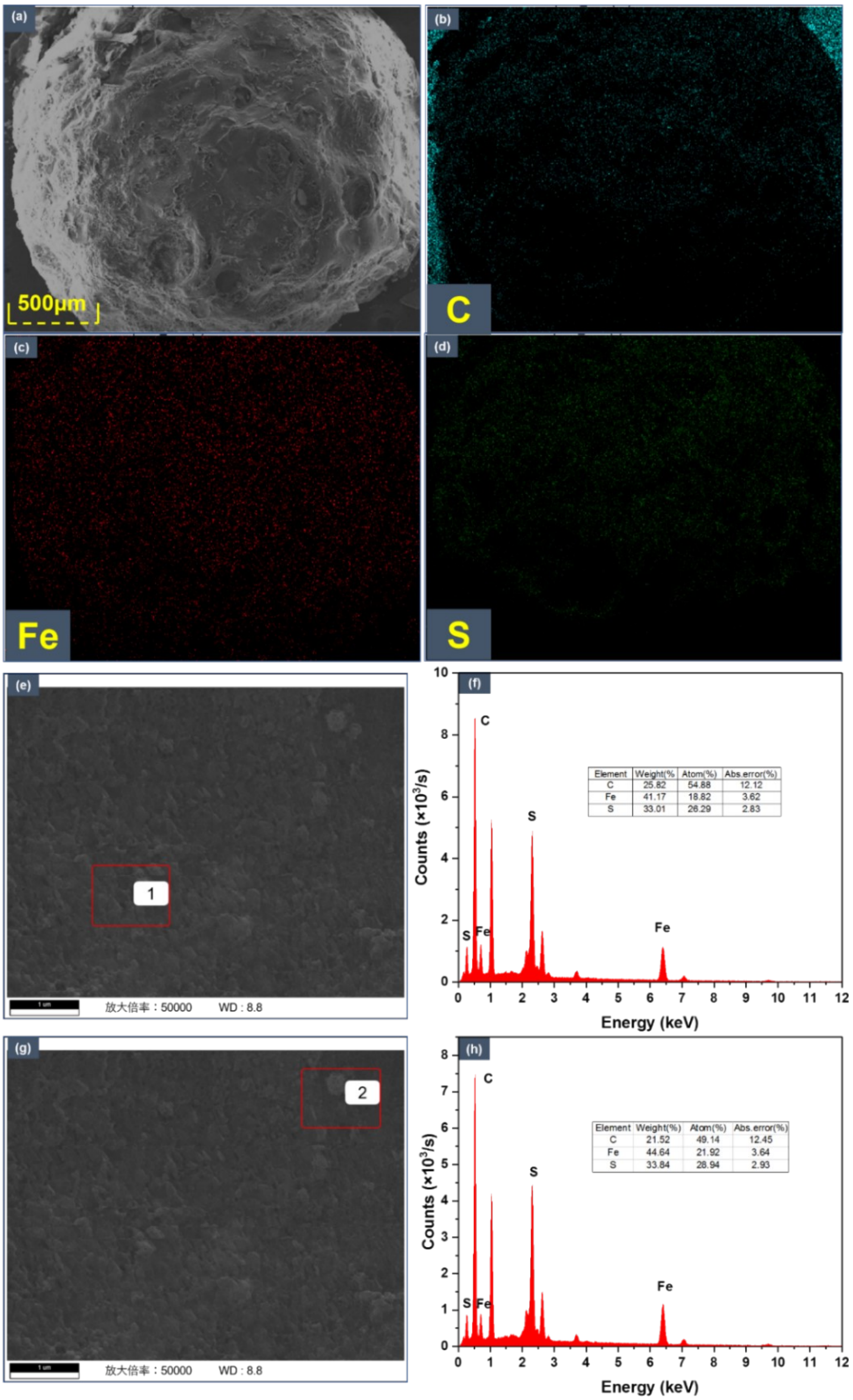
$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{4}$$

$$\frac{C_t}{C_0} = 1 - \frac{m}{\beta V C_0}\ln(1 + \alpha\beta t) \tag{5}$$

where $Q_e$ and $Q_t$ are the amounts adsorbed at equilibrium and at time t, mg $g^{-1}$; $C_0$ and $C_t$ are the concentration of solute at initial and time t, mg $L^{-1}$; V (L) is the volume and m (mg) is the amount of adsorbent; $k_1$ is the rate constant of pseudo-first-order adsorption, $min^{-1}$; $k_2$ is the rate constant of pseudo-second-order adsorption, $g\cdot(mg\ min)^{-1}$; α and β are the rate constants of Elovich model; t is contact time, min.

## Figures (including 5 figures)

**Fig. S1**



| Element | Weight(% | Atom(%) | Abs.error(%) |
|---|---|---|---|
| C | 25.82 | 54.88 | 12.12 |
| Fe | 41.17 | 18.82 | 3.62 |
| S | 33.01 | 26.29 | 2.83 |

| Element | Weight(%) | Atom(%) | Abs.error(%) |
|---|---|---|---|
| C | 21.52 | 49.14 | 12.45 |
| Fe | 44.64 | 21.92 | 3.64 |
| S | 33.84 | 28.94 | 2.93 |

**Fig. S1.** SEM-EDS images of S-nZVI@CMS@CA.

**Fig. S2**

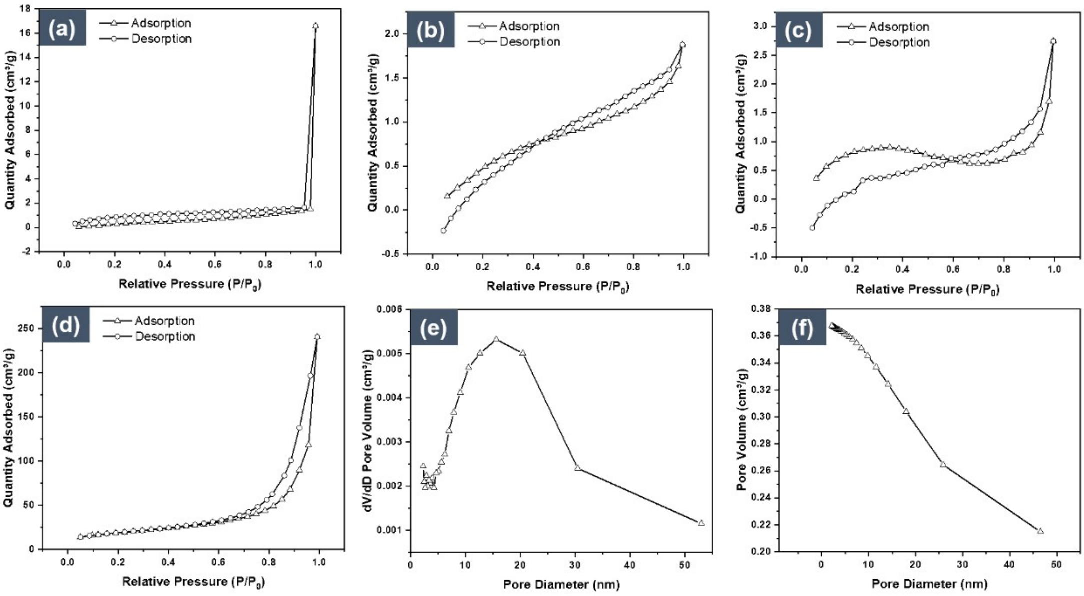


**Fig. S2.** $N_2$ adsorption-desorption isotherms, pore size distributions and cumulative pore volume of CA (a); CMS@CA (b); S-nZVI@CMS@CA-in (c); S-nZVI@CMS@CA-out (d-f).

**Fig. S3**

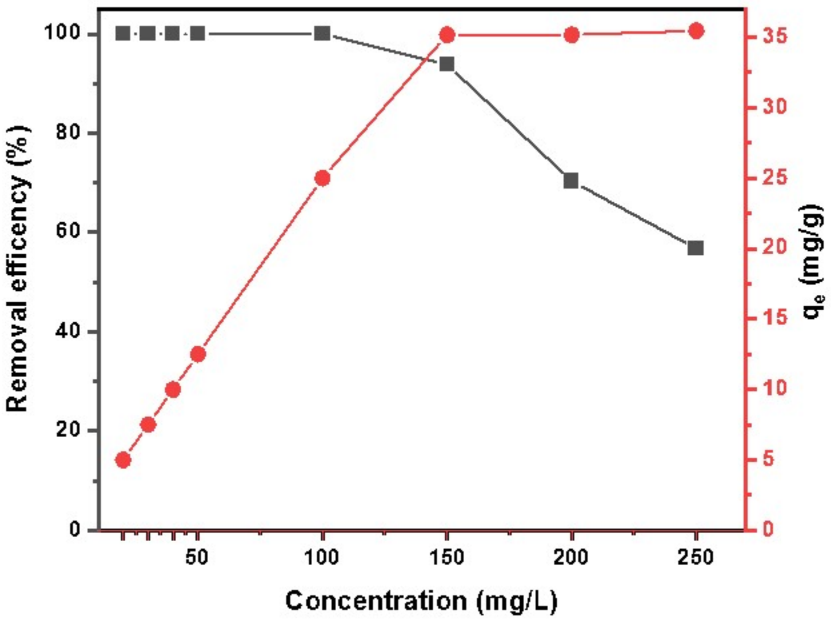


**Fig. S3.** Removal efficiency and adsorption capacity for Cr(VI).

**Fig. S4**

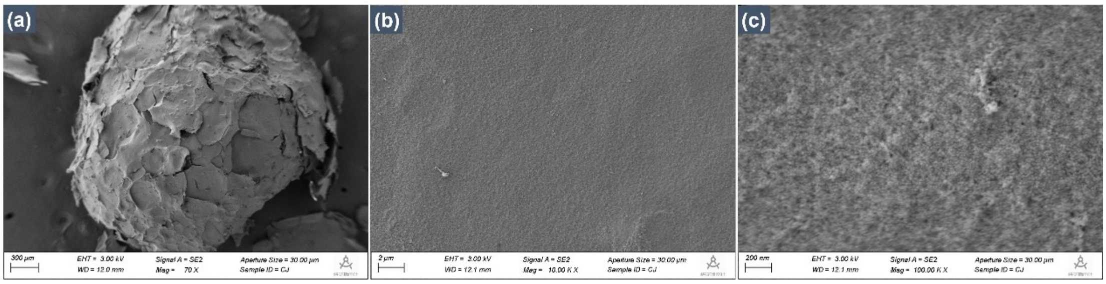


**Fig. S4.** SEM images of S-nZVI@CMS@CA after Cd(II) adsorption.

**Fig. S5**

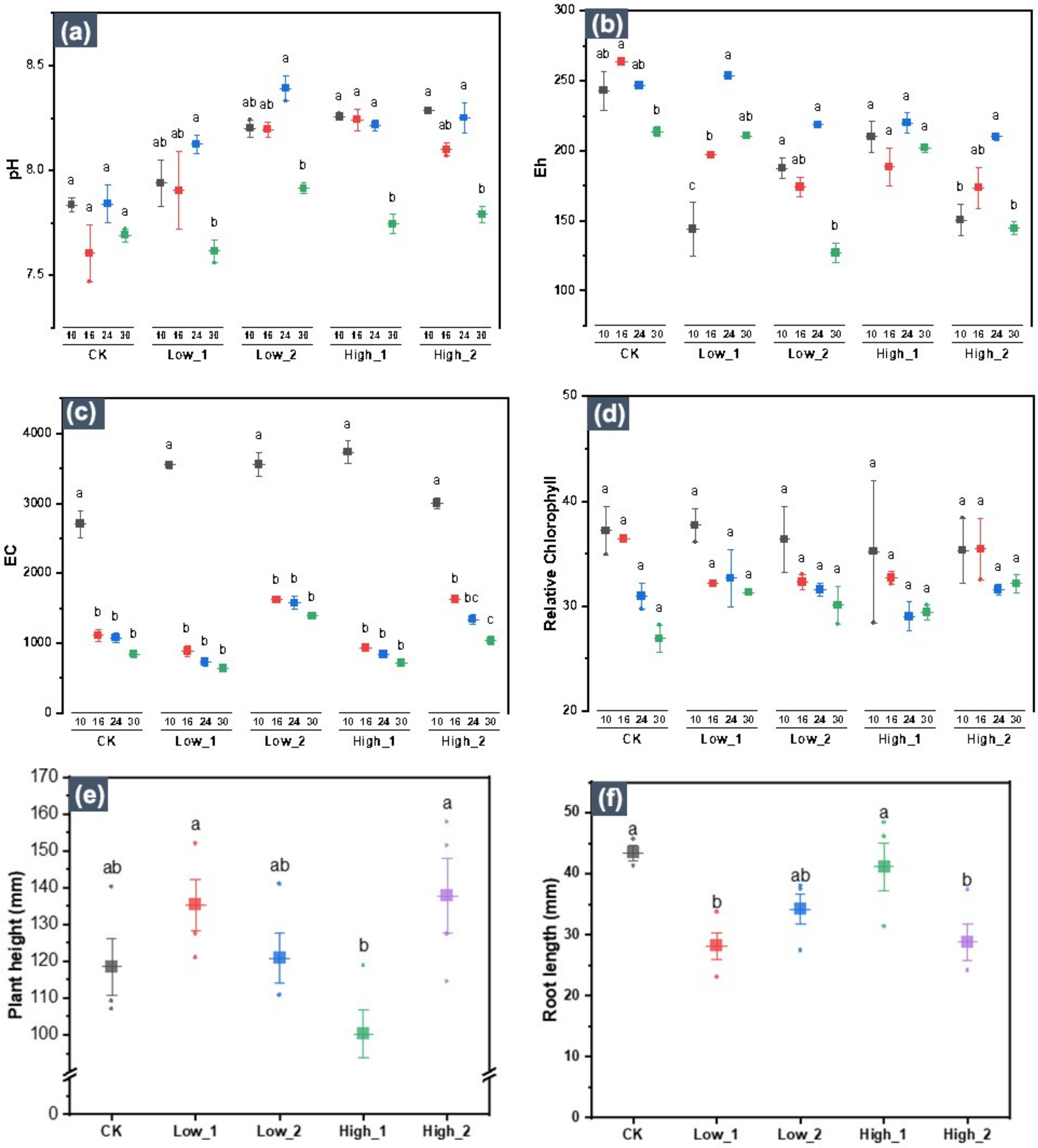


**Fig. S5.** Changes of *Brassica rapa L.* cultivation: day 10, 16, 24 and 30; different letters indicated marked differences in results among treating groups ($p < 0.05$): (a) soil pH; (b) soil Eh; (c) soil EC; (d) relative chlorophyll of *Brassica rapa L.*; (e) plant height of *Brassica rapa L.*; and (f) root length of *Brassica rapa L.*.

## Tables (including 2 tables)

**Table S1.** Pot experiment treatment group settings (mg kg$^{-1}$).

| | CK | Low-1 | Low-2 | High-1 | High-2 |
|---|---|---|---|---|---|
| S-nZVI@CMS@CA | / | / | 2000 | / | 2000 |
| Cr(VI) | / | 20 | 20 | 200 | 200 |
| Cd(II) | / | 5 | 5 | 50 | 50 |

**Table S2.** Effect of S-nZVI@CMS@CA addition on the growth of *Brassica rapa L.*

| Growth index | CK | Low-1 | Low-2 | High-1 | High-2 |
|---|---|---|---|---|---|
| Plant height (mm) | 118.45 | 135.32 | 120.75 | 100.31 | 137.71 |
| Root length (mm) | 43.44 | 28.13 | 34.19 | 41.13 | 28.78 |
| Fresh weight (mg) | 749.28 | 1025.91 | 896.20 | 897.83 | 778.90 |
| Dry weight (mg) | 95.78 | 106.35 | 86.69 | 92.33 | 83.63 |
| $K_{F/D}$ | 7.82 | 9.65 | 10.34 | 9.72 | 9.31 |

## References

[1] S. Huang, S. Song, R. Zhang, T. Wen, X. Wang, S. Yu, W. Song, T. Hayat, A. Alsaedi, X. Wang, Construction of Layered Double Hydroxides/Hollow Carbon Microsphere Composites and Its Applications for Mutual Removal of Pb(II) and Humic Acid from Aqueous Solutions, ACS Sustainable Chem. Eng. 5 (2017) 11268-11279.

[2] W. Yan, A.A. Herzing, C.J. Kiely, W.-x. Zhang, Nanoscale zero-valent iron (nZVI): Aspects of the core-shell structure and reactions with inorganic species in water, J. Contam. Hydrol. 118 (2010) 96-104.