Supplementary Information

Kinetics and mechanisms of Cr(VI) Removal by nZVI: Influencing parameters and modification

Submitted to

Catalysts

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Summary of contents:

Text S1.

1. The reduction rates of nZVI for Cr(VI) reduction were obtained by following formula [1]:

$$\text{Cr removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100\%$$

C_0: is the initial Cr(VI) concentration in the solution;

C_t: the concentration of Cr(VI)in the solution at min.

2. The kinetic equation for the removal of Cr (VI) by nZVI was as follows:

first-order [2]: $LnC = k_1t + C_0$

second-order [3]: $1/C = k_2t + C_1$

pseudo-first-order [4]: $Ln(q_e - q_t) = k_3t + C_2$

pseudo-second-order [5]: $t/q_t = k_4t + C_3$

C: the concentration of Cr(VI)in the solution at min.

3. The Langmuir and Freundlich isotherm models can be represented as follows:

Langmuir [6]: $q = kc^{1/n}$

Freundlich [7]: $q = qe*bc/(1+bc)$

q: adsorption capacity at different time($mg \cdot g^{-1}$)

4. Intraparticle [8]: $q_t=k*t^{0.5} + C$

5. Formula for calculating adsorption capacity[9]: $q = \frac{v(c_0 - c)}{m}$

q: Adsorption capacity at adsorption equilibrium, mg/g;

V: Solution volume, L;

C_0:Initial concentration of solution, mg/L;

C: The concentration of solution at adsorption equilibrium at min, mg/L;

Qt: adsorption capacity of solution at adsorption equilibrium at min , mg/g;

Qe: maximum adsorption capacity, mg/g.

Table S1. The EDS results of pre- and post-reaction of Cr(VI) with nZVI.

	Element	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
pre-reaction	Iron	74.01	95.16	84.92	6.03
	Oxygen	3.77	4.84	15.08	2.10
	Gold	0.00	0.00	0.00	0.00
	Total:	77.78	100.00	100.00	
post-reaction	Iron	69.72	70.93	42.04	5.67
	Oxygen	27.07	27.54	56.99	10.20
	Chromium	1.50	1.53	0.97	0.23
	Gold	0.00	0.00	0.00	0.00
	Total:	98.29	100.00	100.00	

Table S2. Comparison of R^2 values fitted by various kinetic models at different temperatures.

	First order	Second order	Pseudo-first order	Pseudo-second order
293K	LnC = 0.031t + 2.93 R^2 = 0.7075	1/C = 0.0001t + 0.054 R^2 = 0.6673	$Ln(Q_e-Q_t)$ = 0.0195t + 2.85 R^2 = 0.8123	t/Q_t = 0.019t + 0.075 R^2 = 0.9998
303K	LnC = 0.0109t + 2.29 R^2 = 0.2352	1/C = −0.0002t + 0.053 R^2 = 0.5492	$Ln(Q_e-Q_t)$ = 0.0361t + 0.068 R^2 = 0.6822	t/Q_t = 0.01972t + 0.049 R^2 = 0.9997
313K	LnC = 0.0033t + 2.89 R^2 = 0.6809	1/C = −9E-0.5t + 0.050 R^2 = 0.9122	$Ln(Q_e-Q_t)$ = -0.0407t + 3.63 R^2 = 0.8307	t/Q_t = 0.019t + 0.097 R^2 = 0.9983

Table S3. Comparison of R^2 values fitted by isothermal adsorption model.

T (K)	Langmuir			Freundlich		
	Q_m (mg/g)	K_L(L/mg)	R^2	n/1	K_F	R^2
293	57.077	1.46	0.9719	0.4329	25.11	0.9017

Table S4. Intraparticle diffusion coefficients and intercept values for Cr(VI) adsorption on nZVI particles at different temperatures.

Step.1

Temperature (K)	K ($mg \cdot g^{-1} \cdot h^{0.5}$)	Intercept values (C)	R^2
293 K	10.67	2.62	0.92
303 K	11.48	2.25	0.93
313 K	10.98	1.75	0.95

Step.2

Temperature (K)	K ($mg \cdot g^{-1} \cdot h^{0.5}$)	Intercept values (C)	R^2
293 K	37.82	1.39	1
303 K	41.49	0.98	1
313 K	32.85	1.71	1

Step.3

Temperature (K)	K ($mg \cdot g^{-1} \cdot h^{0.5}$)	Intercept values (C)	R^2
293 K	50	-8.95E-15	1
303 K	45.38	0.207	1
313 K	47.26	0.441	1

Table S5. Comparison of the Cr(VI) removal efficiency of nZVI and other related materials

Sorbent	pH	Adsorption rate (mg/g/h)	Adsorption capacity (mg/g)
nano-magnetite[10]	6.0	3.7	1.5
Fe_3O_4@poly(m-phenylenediamine) particle[11]	2.0	49.2	246.0
Magnetite[12]	2.0	7.5	12.5
liquid nitrogen treated zero-valent iron[13]	6.3	0.4	0.4
graphene oxide hydrogel with shrimp shell magnetic biochar[14]	1.0	28.6	85.9
ball milling synthesized FeS_2@biochar composite[15]	3.0	57.5	134.0
nZVI	3.0	25.0	50.0
H_2A-nZVI	3.0	66.7	50.0
Starch-nZVI	3.0	200.0	50.0
Fe-Cu	3.0	100.0	50.0

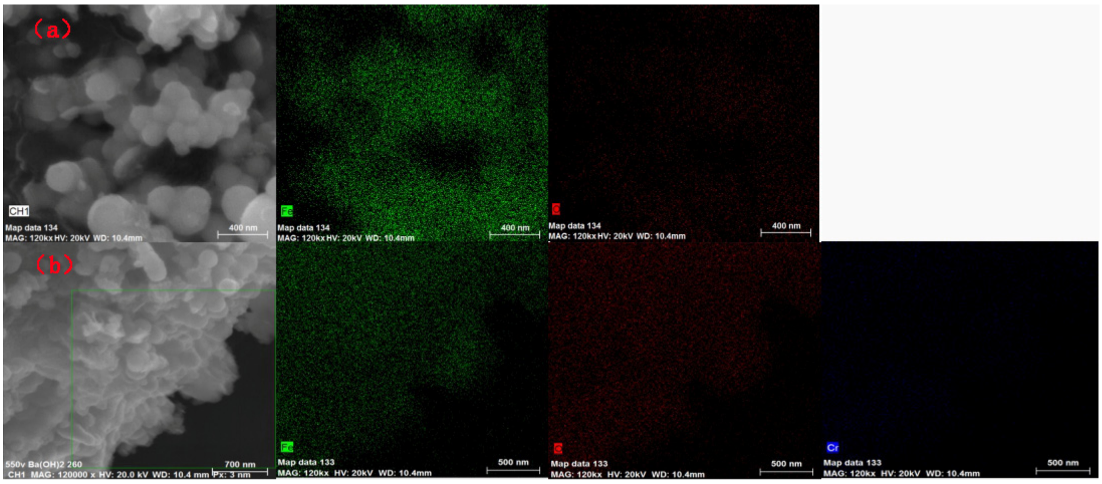

Figure S1. The EDS results of pre- (a) and post- (b) reaction of Cr(VI) with nZVI.

([Cr(VI)] = 25 mg/L, [nZVI] = 0.5 g/L, pH = 3, T = 293 K)

It can be seen from the Figure S1 that the content of Fe before the reaction is obviously higher than that after the reaction, while the content of O before the reaction is obviously lower than that after the reaction, which further proves that O participates in the removal of Cr(VI).

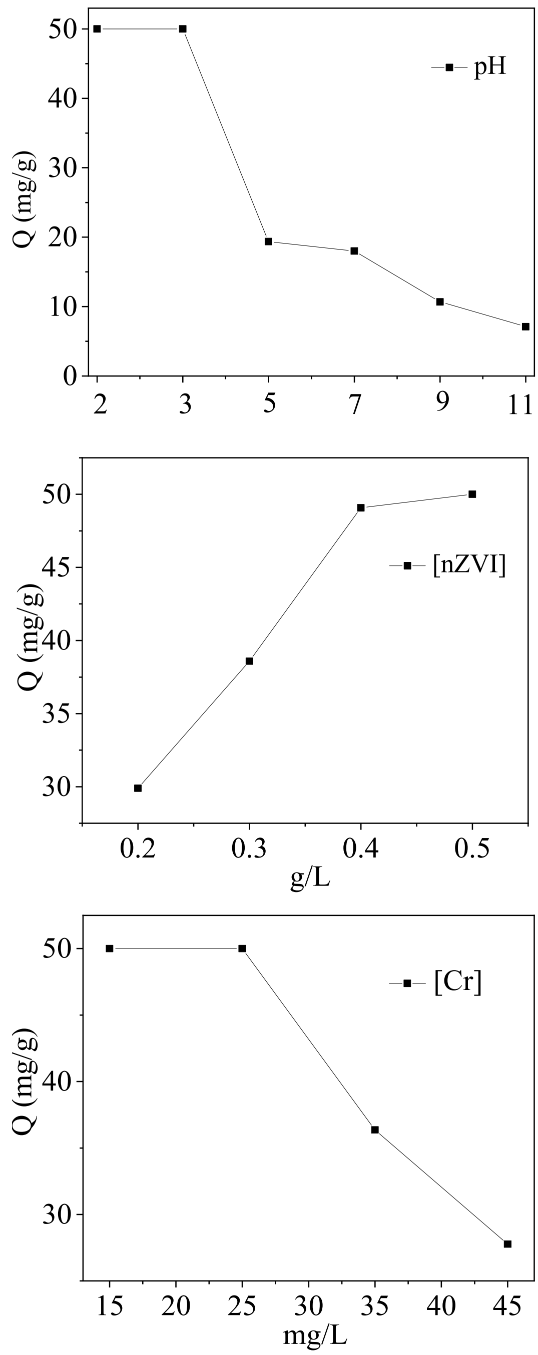

Figure S2. Changes of adsorption capacity with pH, initial concentration of Cr(VI) and dosage of nZVI.

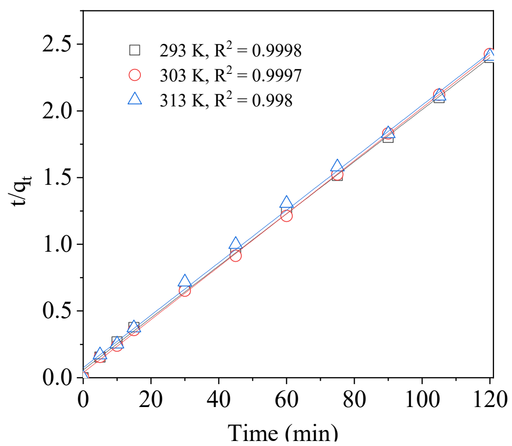

Figure S3. Pseudo-second-order kinetic fitting curve of Cr(VI) removal by nZVI.

([Cr(VI)] = 25 mg/L, [nZVI] = 0.5 g/L, pH = 3, T = 120 min)

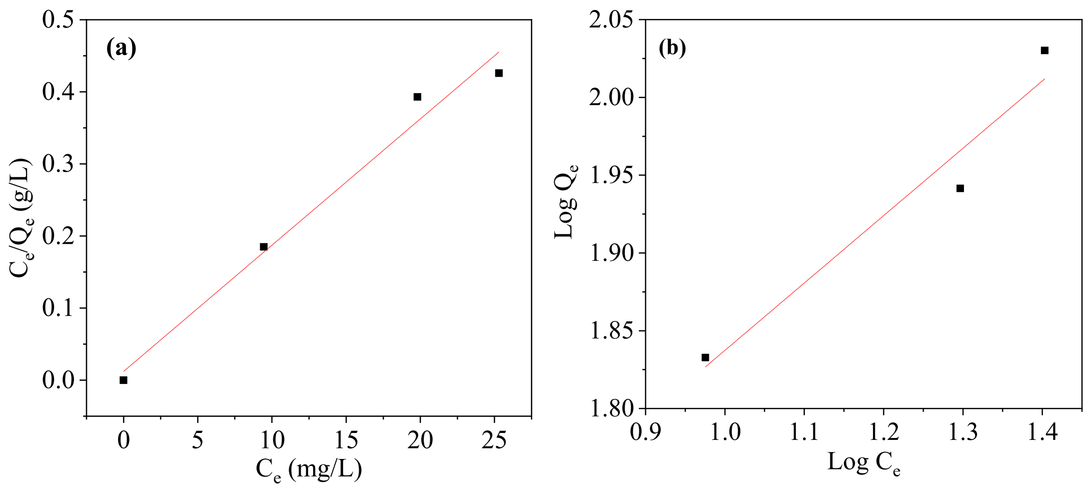

Figure S4. Fitting results of isotherm adsorption model (a: Langmuir; b: Freundlich).

([nZVI] = 0.5 g/L, pH = 3, T = 293 K)

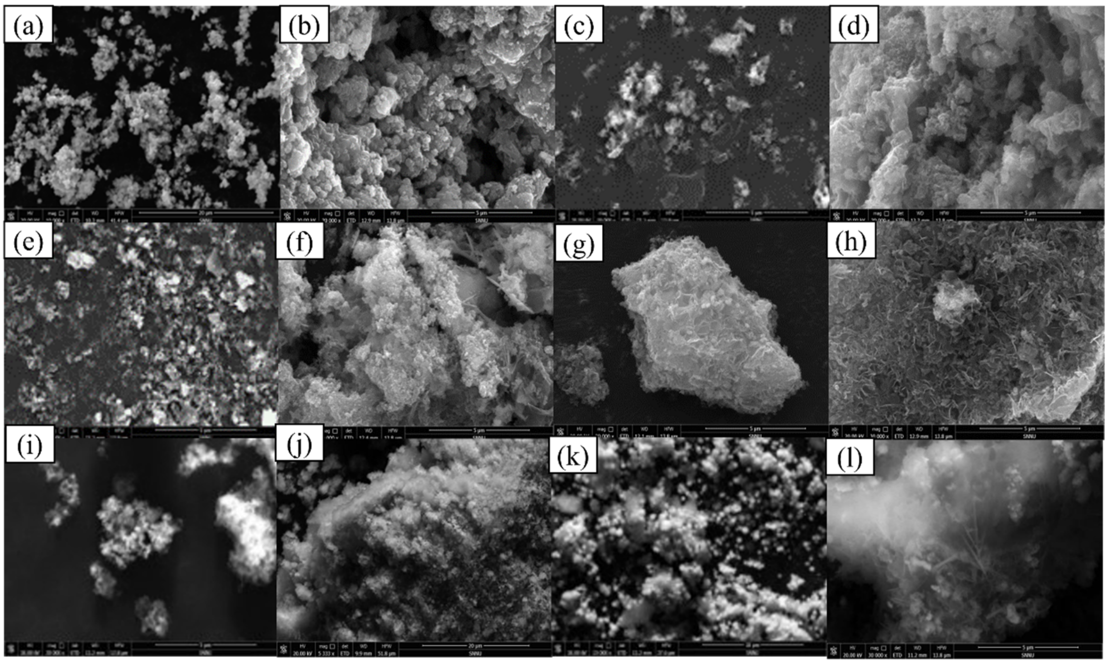

Figure S5. The SEM results of pre- and post- reaction of Cr(VI) with supported nZVI [(a,b) H_2A-nZVI; (c,d) Starch-nZVI; (e,f) Fe-Cu; (g,h) CMC-nZVI; (i,j) Fe-Zn; (k,l) Fe-Mn].

([Cr(VI)] = 25 mg/L, [nZVI] = 0.5 g/L, pH = 3, T = 293 K)

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