

Supplementary Material

Nanoscale zerovalent iron particles for magnetic-assisted soil washing of cadmium-contaminated paddy soil: proof of concept

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Table S1 Sequential extraction procedures used in this study. Dried soil (1.0 g) was extracted using the steps below (Tessier et al., 1979).

Step	Fraction	Reagent
1	Exchangeable (F1)	8 mL of 1 M MgCl_2 (pH 7), 1h with continuous agitation
2	Bound to carbonates (F2)	8 mL of 1 M NaOAc (pH 5; HOAc), 5 h with continuous agitation
3	Bound to Fe and Mn oxides (F3)	20 mL of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) HOAc , 6 h at 96 °C with occasional agitation
4	Bound to organic matter (F4)	5 mL of 0.02 M HNO_3 , 2 h at 85 °C with occasional agitation and 3 mL of 30% H_2O_2 (pH 2 with HNO_3) at 85 °C with occasional agitation again in 3 h After cooling, 3.2 M $\text{CH}_3\text{COONH}_2$ in 20% (v/v) HNO_3 was added and diluted by deionized water to 20 mL
5	Residual (F5)	digested with 10 mL of 65% nitric acid

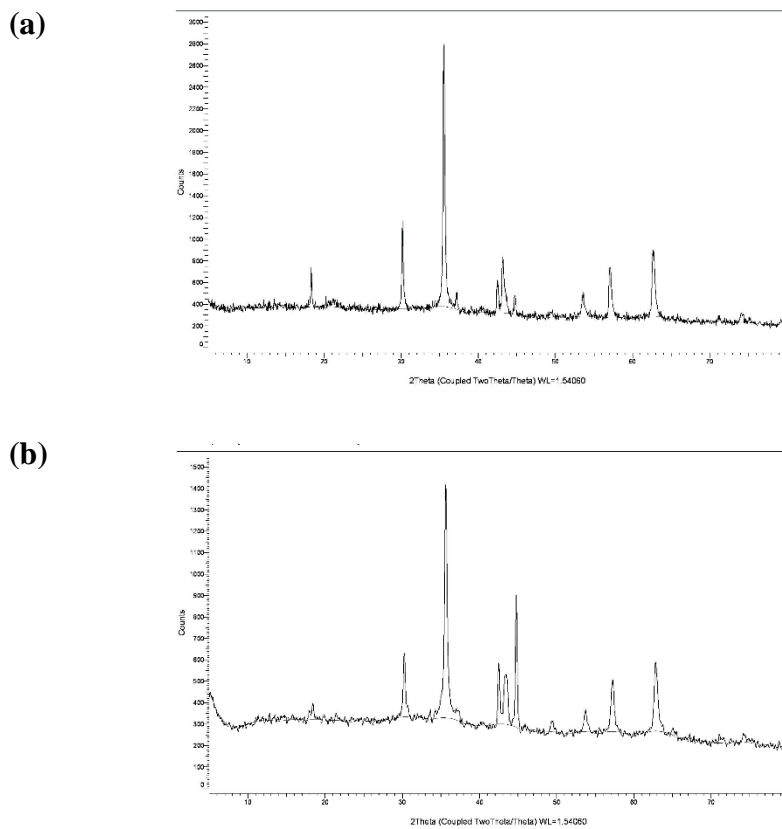
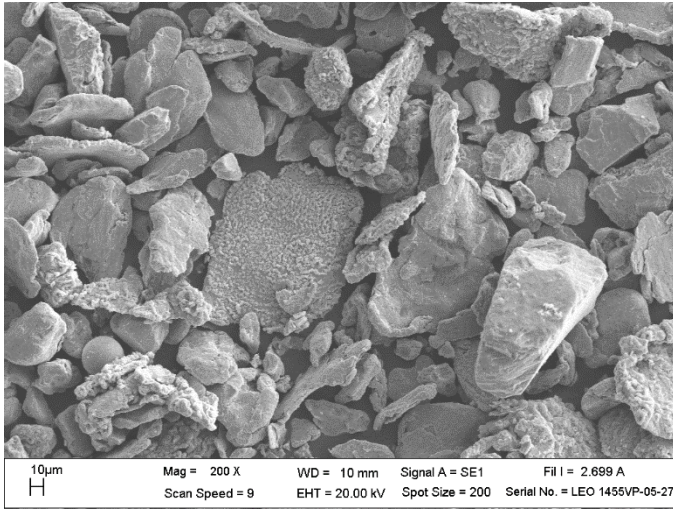


Fig. S1 XRD results of (a) NZVI and (b) MZVI

(a)



(b)

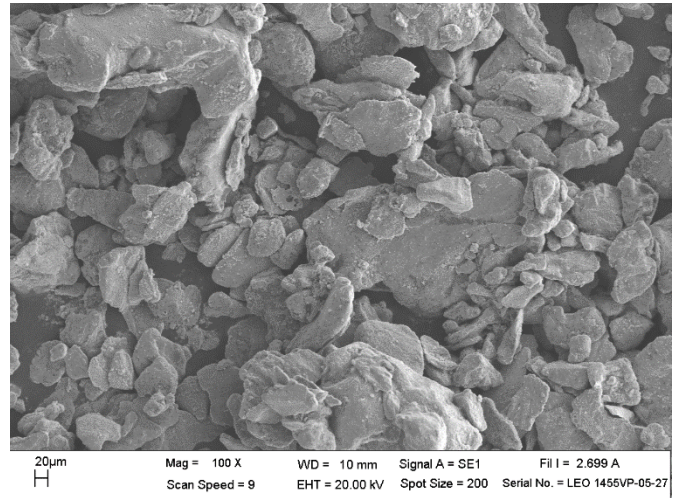
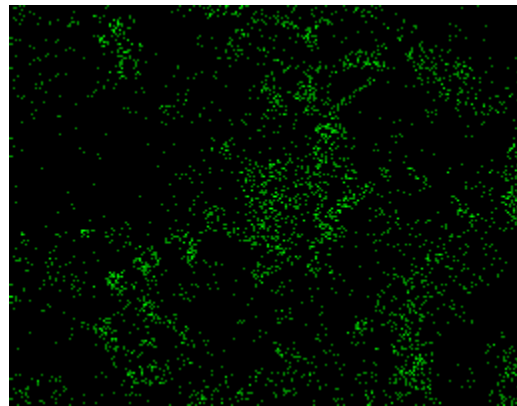


Fig. S2 SEM micrographs of MZVI (a) before using in soil washing and (b) recovered from the soil washing process.

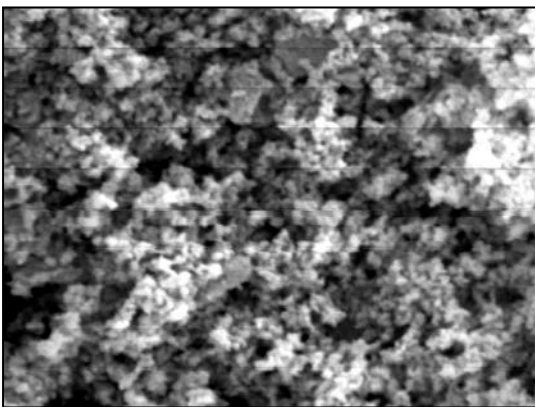
(a)



(b)



(c)



(d)

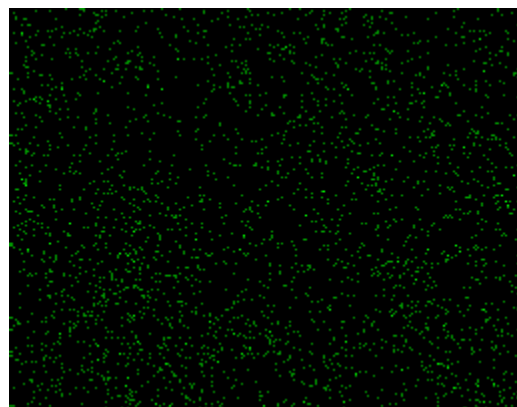


Fig. S3 SEM micrograph of (a) MZVI and (c) NZVI together with oxygen mapping by EDS for (b) MZVI and (d) NZVI

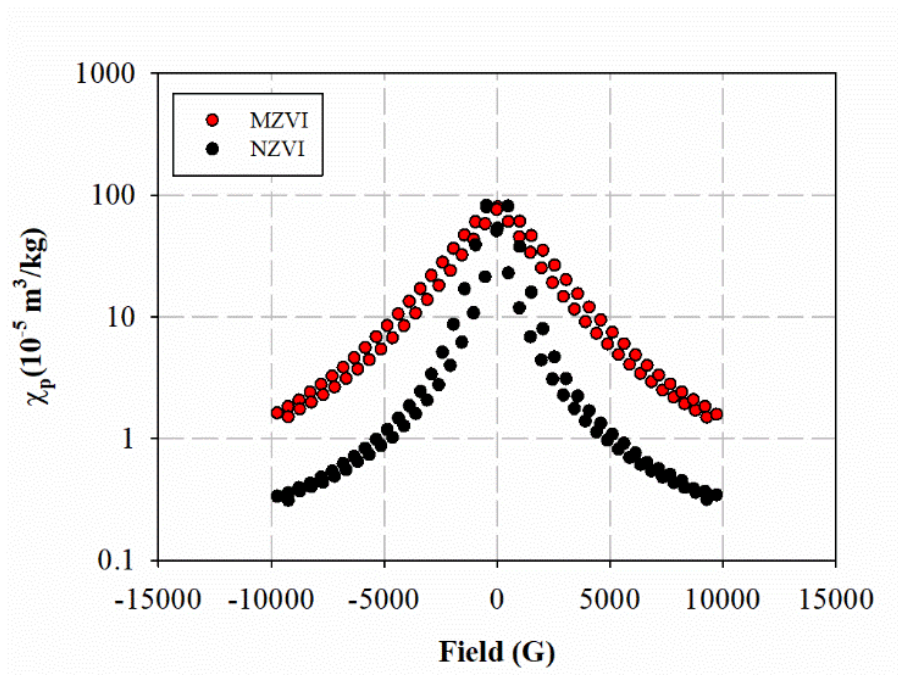


Fig. S4 Magnetic susceptibility of NZVI and micron-sized zerovalent iron (MZVI).

Table S2 Texture classification of the paddy soil samples from both yellow and red zones by hydrometer method

Sample Name	%Clay	%Silt	%Sand
<u>Lowland</u>	63.0±0.00	26.8±0.00	10.2±0.00

¹ calculated from the following information:

$$\% \text{ Sand} = 100 - \frac{100}{\text{weight of dry soil}} ((H1 - C1) + 0.36(T1 - 20))$$

$$\% \text{ Clay} = 100 - \frac{100}{\text{weight of dry soil}} ((H2 - C2) + 0.36(T2 - 20))$$

$$\% \text{ Silt} = 100 - (\% \text{ Sand} + \% \text{ Clay})$$

$$C1 = a1 - 0.5(T1 - b1)$$

$$C2 = a2 - 0.5(T2 - b2)$$

When H1 is hydrometer reading of sample in 30s

H1 is hydrometer reading of sample in 90s

T1 is temperature reading of sample in 30s

T2 is temperature reading of sample in 90s

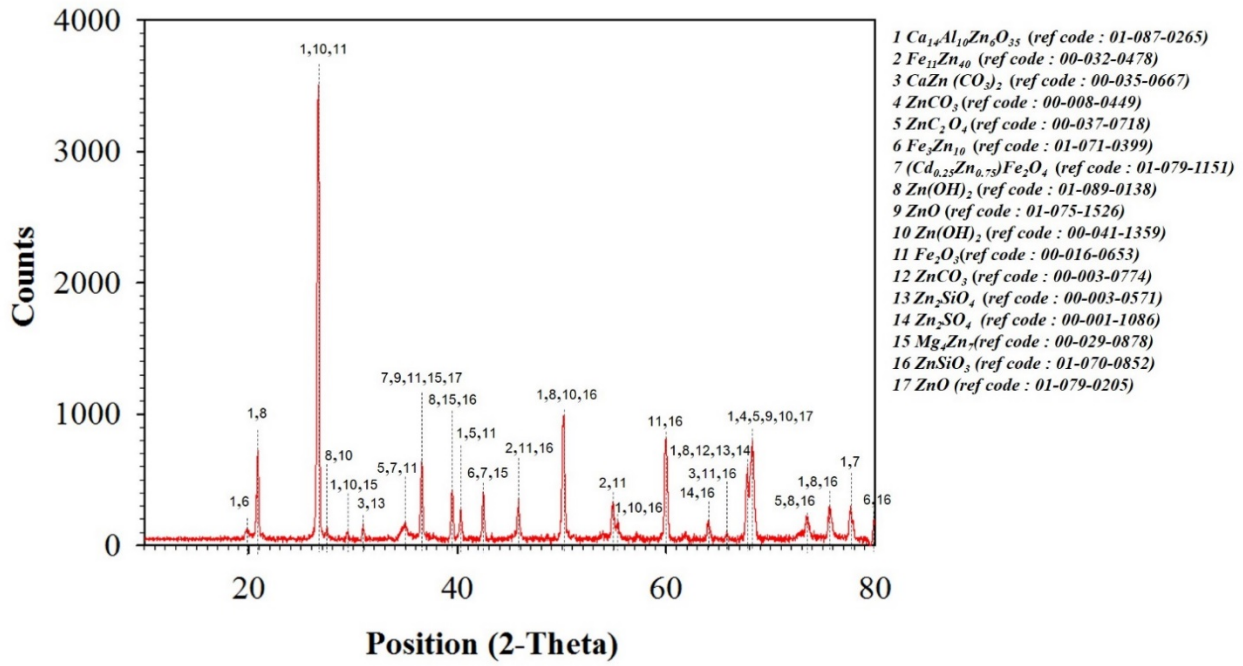
a1 is hydrometer reading of Calgon in 30s

a2 is hydrometer reading of Calgon in 90s

b1 is temperature reading of Calgon in 30s

b2 is temperature reading of Calgon in 90s

(a)



(b)

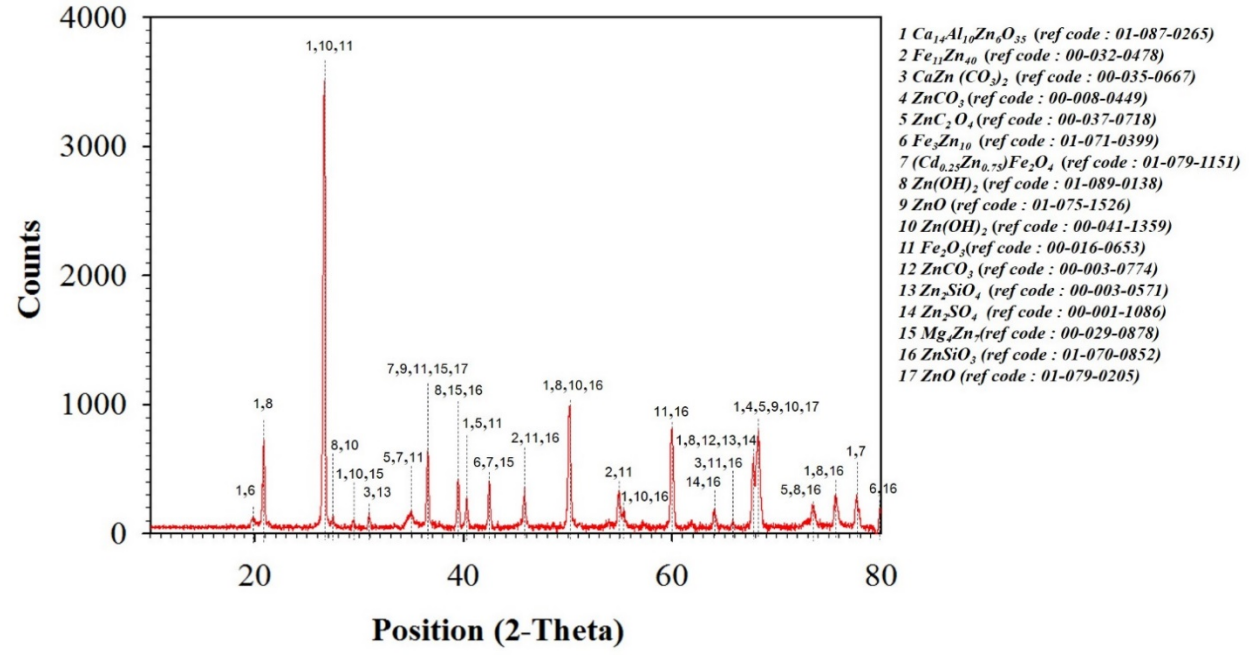
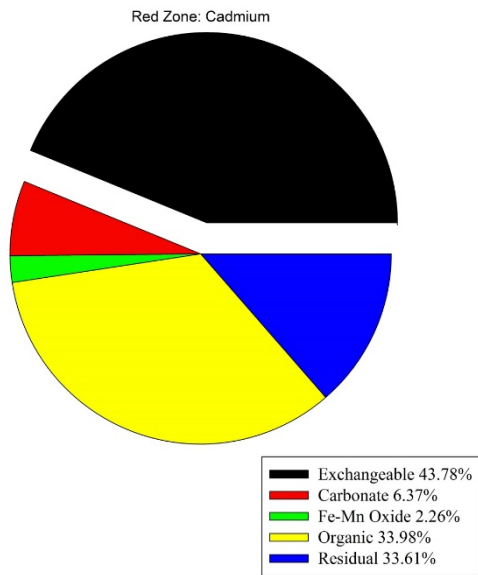


Fig. S5 XRD results of red and yellow zone soil samples

(a)



(b)

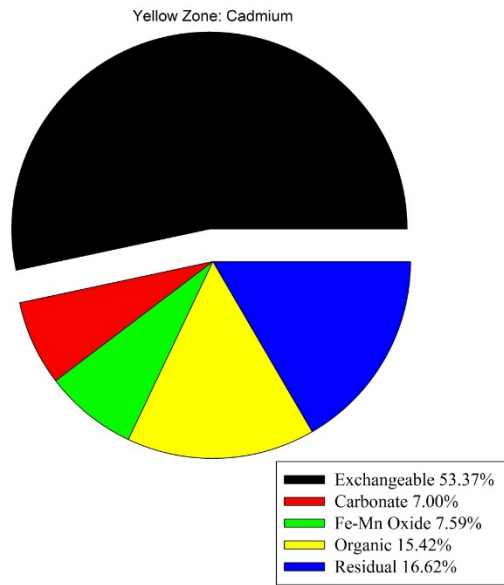


Fig. S6 Percentage of different Cd chemical fractions of (a) red zone and (b) yellow zone

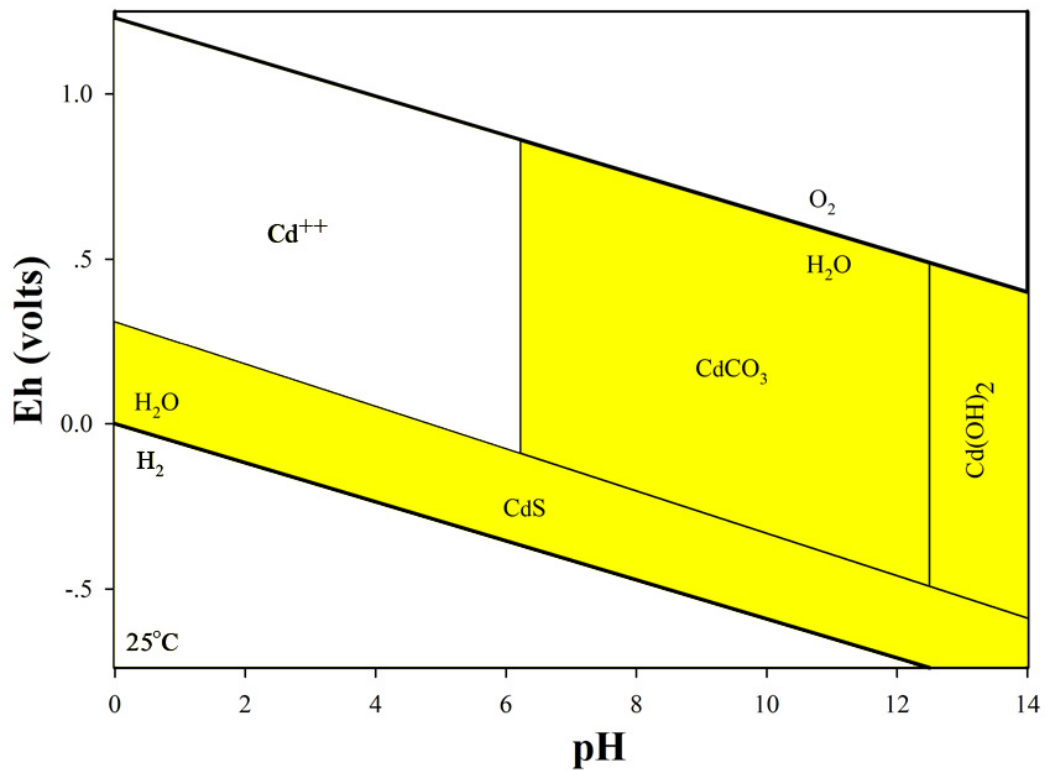


Fig. S7 Eh-pH diagram of Cd speciation in a carbonate, sulfide, H₂O system

Table S3 Cadmium (Cd) mass balance analysis for magnetic-assisted soil washing using nanoscale zerovalent iron (NZVI)

Phase of Cadmium (Cd)	Characteristics of the Phase	Cd Concentration in the Phase (mg/L or mg/kg)		Cd Mass in the Phase (mg)		Percentage (%)	
		Mass (g)	Ave	Std	Ave	Std	Ave
Dissolved in water ^a	20	0.027	0.028	0.0005	0.0004	0.03	0.03
NZVI remaining in the soil ^b	0.01	949.73	55.3	0.014	0.0008	0.78	0.05
Recovered NZVI ^c	0.99	949.73	55.3	0.936	0.0055	52.88	3.08
Soil ^c	10	43.85	8.7	0.439	0.0087	24.77	4.92
Sum of all phases ^d	-	-	-	1.39	0.0143	78.46	8.07
Cd Mass (input)	10	177		1.77		100.00	
Unbalanced ^d				0.381		21.54	

^a Obtained from the measurement of dissolved Cd in washing water for duplicate experiments.

^b Assume that Fe⁰ to Fe₃O₄ of NZVI is 0.65:0.35. Consequently, for NZVI, the Fe concentration measured by AAS can be transformed to NZVI by multiplying by 2.12. Thus, for NZVI, the increase of Fe in the soil (in comparison to untreated soil) after NZVI recovery was 6.83±0.41 g/kg. This was multiplied by 2.12 to obtain the value in the table. The increase of Fe in the soil in comparison to untreated soil after magnetic-assisted soil washing using ZVI materials is responsible for the remaining ZVI materials in the soil, irretrievable by magnetic separation.

^c Calculated from the following information. The apparent total Cd concentration on the washed soil using NZVI was 44.76±5.51 mg/kg. Nevertheless, based on note b, the washed soil has the remaining NZVI of 0.01 g. For this reason, the apparent Cd concentration (Cd_{A1}) was contributed from the real Cd in the soil (Cd_S) and the Cd sorbed onto the remaining NZVI (Cd_N). The total mass of soil after washing was 10 g (mass of soil) + 0.01 g (mass of remaining NZVI). Based on mass balance, we obtain the following:

$$Cd_{A1}*(10+0.01)=10*Cd_S+0.01*Cd_N \quad (S1) \text{ or}$$

$$44.76*(10+0.01)=10*Cd_S+0.01*Cd_N \quad (S1)$$

We recovered NZVI by magnetic recovery from soil and obtained the total mass of the NZVI mixture of 2.11±0.90 g. Some soil was mixed with magnetic-retrieved NZVI. We can calculate the mass of the soil mixed with magnetic-retrieved NZVI from the NZVI mass balance as follows. The total mass of NZVI (1 g) is the mass of NZVI remaining in the soil after recovery (0.01 g)+ the mass of recovered NZVI (mass of recovered NZVI=0.99 g). Thus, the mass of the soil mixed with magnetic-retrieved NZVI=2.75-0.99=1.76 g. In the mixture of soil and NZVI retrieved by magnetic separation, the Cd concentration (Cd_{A2}) was 370.24±27.81 mg/kg. Therefore, we can apply Cd mass balance as follows:

$$Cd_{A2}*(0.99+1.76)=1.76*Cd_S+0.99*Cd_N \quad (S2) \text{ or}$$

$$370*(0.99+1.76)=1.76*Cd_S+0.99*Cd_N \quad (S2)$$

We can determine Cd_S and Cd_N by solving Eqs. S1 and S2 together. Thus, for NZVI, $Cd_S=43.85$ mg/kg and $Cd_N=949.73$ mg/kg.

^d The sum of all phases was calculated by summing the Cd mass in all phases, while the unbalanced Cd mass was calculated by subtracting the total Cd mass in the input (untreated soil) with the sum of the Cd in all phases. The difference between the input and sum of all phases is the missing Cd or unbalanced Cd.

Table S4 Cadmium (Cd) mass balance analysis for magnetic-assisted soil washing using micron-sized zerovalent iron (MZVI)

Phase of Cadmium (Cd)	Characteristics of the Phase	Cd Concentration in the Phase (mg/L or mg/kg)		Cd Mass in the Phase (mg)		Percentage (%)	
		Mass (g)	Ave	Std	Ave	Std	Ave
Dissolved in water ^a	20.00	0.03	0.004	0.0006	0.0001	0.04	0.01
MZVI remaining in the soil ^b	0.01	586.69	43.130	0.004	0.0003	0.28	0.02
Recovered MZVI ^c	0.99	586.69	43.130	0.58	0.04	38.83	2.85
Soil ^c	10.00	38.61	6.410	0.39	0.06	25.74	4.27
Sum of all phases ^d				0.97	0.11	64.90	7.15
Cd Mass (input)	10.00	150.00		1.50		100.00	
Unbalanced ^d				0.53		35.10	

^a Obtained from the measurement of dissolved Cd in the washing water for duplicate experiments.

^b Assume that Fe⁰ to Fe₃O₄ of MZVI is 0.93:0.07. Consequently, for MZVI, the Fe concentration measured by AAS can be transformed to NZVI by multiplying by 1.22. Thus, for MZVI, the increase of Fe in the soil (in comparison to untreated soil) after NZVI recovery was 5.83±0.46 g/kg. This was multiplied by 1.22 to obtain the value in the table. The increase of Fe in the soil in comparison to untreated soil after magnetic-assisted soil washing using ZVI materials is responsible for the remaining ZVI materials in the soil, irretrievable by magnetic separation.

^c Calculated from the following information. The apparent total Cd concentration on the washed soil using MZVI was 39.16±6.41 mg/kg. Nevertheless, based on note b, the washed soil has a remaining MZVI of 0.01 g. Therefore, the apparent Cd concentration (Cd_{A1}) was contributed from the real Cd in the soil (Cd_S) and the Cd sorbed onto the remaining MZVI (Cd_N). The total mass of the soil after washing was 10 g (mass of soil) + 0.01 g (mass of remaining NZVI). Based on the mass balance, we obtain the following:

$$Cd_{A1}*(10+0.01)=10*Cd_S+0.01*Cd_N \quad (S1) \text{ or}$$

$$39.16*(10+0.01)=10*Cd_S+0.01*Cd_N \quad (S1)$$

We recovered NZVI by magnetic recovery from soil and obtained the total mass of the MZVI mixture of 1.80±0.30 g. Some soil was mixed with magnetic-retrieved MZVI. We can calculate the mass of the soil mixed with magnetic-retrieved MZVI from the MZVI mass balance as follows. The total mass of NZVI (1 g) is the mass of NZVI remaining in the soil after recovery (0.01 g)+ the mass of recovered NZVI (mass of recovered NZVI=0.99 g). Thus, the mass of the soil mixed with magnetic-retrieved NZVI=1.80-0.99=0.81 g. In the mixture of soil and MZVI retrieved by magnetic separation, the Cd concentration (Cd_{A2}) was 340.00±25.23 mg/kg. Thus, we can apply the Cd mass balance as follows:

$$Cd_{A2}*(0.99+0.81)=0.81*Cd_S+0.99*Cd_N \quad (S2) \text{ or}$$

$$340*(0.99+0.81)=0.81*Cd_S+0.99*Cd_N \quad (S2)$$

We can determine Cd_S and Cd_N by solving Eqs. S1 and S2 together. Thus, for MZVI, $Cd_S=38.61$ mg/kg and $Cd_N=586.59$ mg/kg.

^d The sum of all phases was calculated by summing the Cd mass in all phases, while the unbalanced Cd mass was calculated by subtracting the total Cd mass in the input (untreated soil) with the sum of the Cd in all phases. The difference between the input and the sum of all phases is the missing Cd or unbalanced Cd.

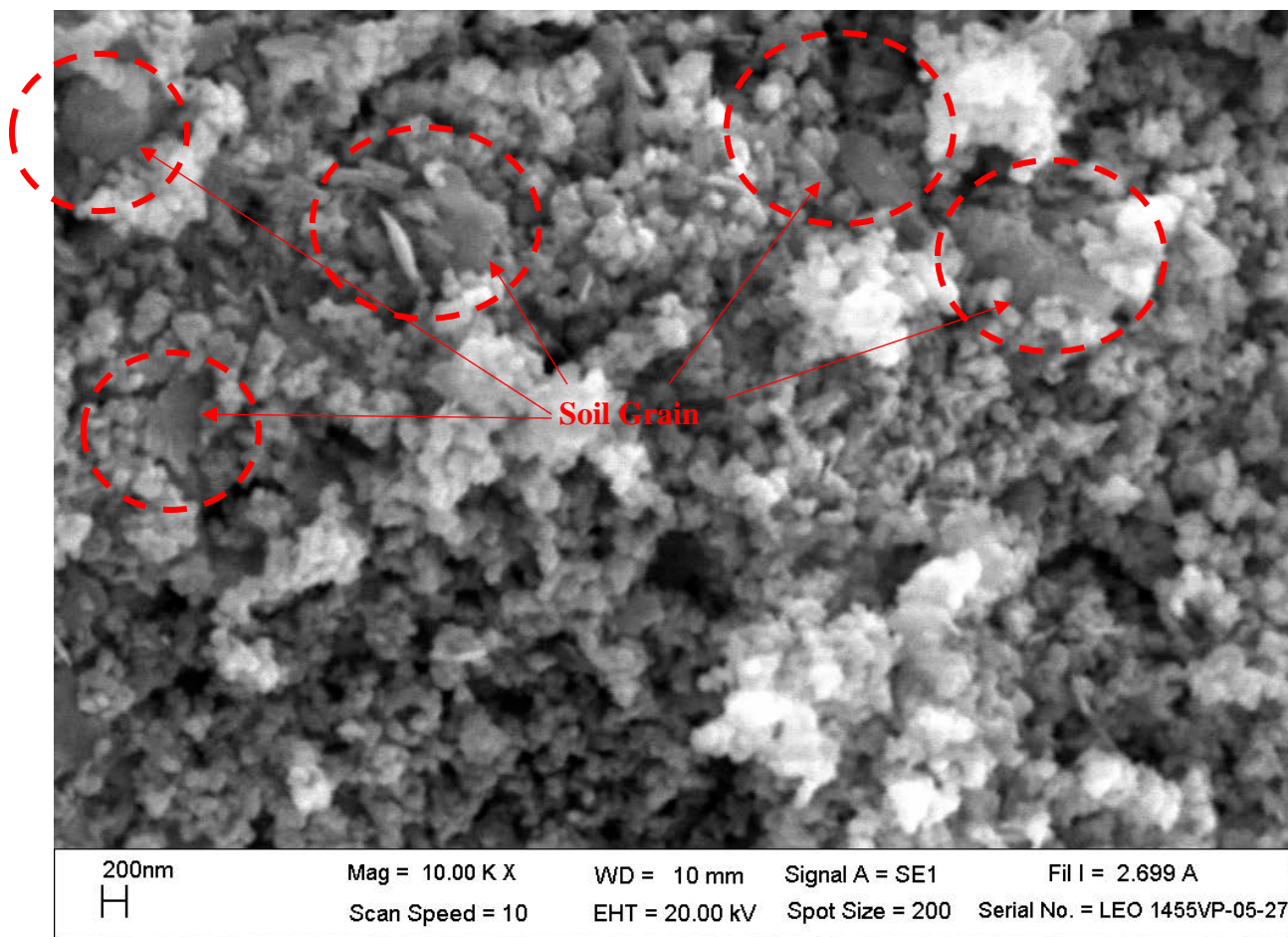


Fig. S8. Scanning electron microscope micrographs of nanoscale zerovalent iron (NZVI) recovered from soil washing