Supplementary Material

Can polymeric surface modification and sulfidation of nanoscale zerovalent iron (NZVI) improve arsenic-contaminated agricultural soil restoration via *ex situ* magnet-assisted soil washing?

Daoheuang Keochanh[A,B], *Saranya Tongkamnoi*[A,B] and *Tanapon Phenrat*[A,B,*]

[A]Department of Civil Engineering, Faculty of Engineering, Research Unit for Integrated Natural Resources Remediation and Reclamation (IN3R), Naresuan University, Phitsanulok, Thailand

[B]Center of Excellence for Sustainability of Health, Environment and Industry (SHEI), Faculty of Engineering, Naresuan University, Phitsanulok, Thailand

*Correspondence to: Email: pomphenrat@gmail.com

Supporting Information

Submitted to

Environmental Chemistry

1. Site History and Previous Studies

The site in this study is massively affected by the collapse of an embankment of the mine tailings storage pond in 2008 (Intamat et al., 2016) and seepage from the other side of the storage pond releasing As-contaminated suspended precipitate (205.53 to 2,000 mg/kg) to near agricultural lands and local creeks. Therefore, As was adsorbed onto clay particles and carbonate/clay aggregates (Zhang et al., 2014) in agricultural soil leading to As contamination ranging from 1.21 to 56.17 mg/kg, much higher than the maximum acceptable limit (20.0 mg/kg) recommended by the European Union (Rahaman et al., 2013). For more details on several aspects of this site characterization, please consult previous studies (Intamat et al., 2016; Weerasiri et al., 2012, 2013).

2. Method for Soil

Soil pH was measured using pH meter by suspending soil in deionized water at the ratio of 1:2 (Rayment & Higginson, 1992). The organic matter in soil was determined following the Walkley-black method (De Vos et al., 2007). The cation exchange capacity (CEC) and exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) was determined by the Kjeldahl distillation after saturating the samples with 1 M NH_4OAc. The concentrations of Ca^{2+}, Mg^{2+}, K^+ and Na^+ in each extractant were quantified using AAS (Stritsis et al., 2014). The soil texture and particle size analysis were also performed via sieving and sedimentation (IOf, 1998).

3. S-NZVI Synthesis

By the aqueous-solid sulfidation method (Xu et al., 2016), 15 mL of HAc-NaAc buffer solution (0.2M, pH 6.0) was prepared in a 50 mL centrifuge tube. The solution was deoxygenated by bubbling with N_2 for 30 min. Then, one gram of activated NZVI was added to the deoxygenated HAc-NaAc buffer solution in the centrifuge tube before being immediately sealed. The mixture was mixed by an end-to-end rotary at 30 rpm for 10 min at 25 ± 0.2 °C. Afterwards, various concentrations of sodium dithionite ($Na_2S_2O_4$) solution (1.5 mL at 0.1 to 4.0 M) was added to each 50 mL centrifuge tube to obtain S/NZVI molar ratios from 0.1 to 4.0 in the tube. Then, the centrifuge tubes were mixed for another 12 h. Consequently, S-NZVI was separated from the mixture via centrifugation, and the supernatant was decanted for analysis of sulfur residue concentration. The sulfur residue concentration in the solution was measured to determine the sulfur deposition on NZVI and the actual S/Fe molar ratio.

The mass of sulfur deposited on NZVI after sulfidation is calculated using the formula:

$$m_{actual\ S\ deposited\ on\ NZVI} = (C_{Initial\ S\ in\ solution} - C_{S\ residue\ in\ solution}) \times V_{solution}$$

$$m_{targeted\ S\ on\ NZVI} = C_{initial\ S\ in\ solution} \times V_{solution}$$

Where:

$m_{actual\ S\ deposited\ on\ NZVI}$: the mass of sulfur actually deposited on NZVI (mg)

$C_{initial\ S\ in\ solution}$: the initial concentration of sulfur in the solution (mg/L)

$C_{S\ residue\ in\ solution}$: the residue concentration of sulfur in the solution (mg/L)

$V_{solution}$: the volume of solution (L)

The number of moles of actual and targeted sulfur can be calculated using the formula:

$$n_{actual\ S\ deposited\ on\ NZVI} = \frac{m_{actual\ S\ deposited\ on\ NZVI}}{M_{mass\ of\ S}}$$

$$n_{targeted\ S\ deposited\ on\ NZVI} = \frac{m_{targeted\ S\ deposited\ on\ NZVI}}{M_{mass\ of\ S}}$$

where:

$m_{actual\ S\ deposited\ on\ NZVI}$: the mass of actual sulfur deposited on NZVI (mg)

$m_{targeted\ S\ deposited\ on\ NZVI}$: the mass of targeted sulfur on NZVI (mg)

$n_{actual\ S\ deposited\ on\ NZVI}$: the moles of actual sulfur deposited on NZVI (moles)

$n_{targeted\ S\ deposited\ on\ NZVI}$: the moles of targeted sulfur deposited on NZVI (moles)

50            $M_{mass\ of\ S}$: the molar mass of Sulfur (mg/mole).

51   The actual and targeted S/Fe molar ratio is calculated using the formula:

$$The\ actual\ S/Fe\ molar\ ratio = \frac{n_{actual\ S\ deposited\ on\ NZVI}}{n_{Fe}}$$

$$The\ targeted\ S/Fe\ molar\ ratio = \frac{n_{targeted\ S\ deposited\ on\ NZVI}}{n_{Fe}}$$

52   where:

53            $n_{actual\ S\ deposited\ on\ NZVI}$: the moles of actual sulfur deposited on NZVI (moles)

54            $n_{targeted\ S\ deposited\ on\ NZVI}$: the moles of targeted sulfur on NZVI (moles)

55   n_{Fe} : moles of iron of NZVI (moles)

56

57

4. CMC-modified NZVI Synthesis

59   Deionized water (250 mL) was purged with N_2 gas for 30 min to remove dissolved

60 oxygen (<0.2 mg/L). As a stock, de-oxygenated deionized water was used to prepare the CMC

61 solution (molecular weight =90,000 g/mol) at the concentration of 3.0 %. The CMC stock was

62 then used to prepare the CMC concentration of 0.5, 1.0, 2.0, 3.0% in 5 mL centrifuge tubes.

63 Activated NZVI (1 g) was added into different CMC solutions and mixed using vortex mixer

64 with 300 rpm for 15 min. CMC-coated NZVI suspension was then stirred for 6 hrs to produce

65 uniformly rheological phase at room temperature.

5. Frundlich and Langmuir isotherms

67   Langmuir and Freundlich are two-parameter adsorption isotherms that are widely used.

68 The Langmuir isotherm is applied to monolayer adsorption on homogeneous sites, whereas the

69 Freundlich isotherm suites are applied to multilayer adsorption on heterogeneous sites (Kalam et

70 al., 2021). Freundlich and Langmuir isotherm models were used in the equilibrium adsorption of

71 adsorbate that absorbed on the surface of the adsorbent. The parameters Q_0 and K_L of the

72 Langmuir isotherm and the parameters K_f and n of the Freundlich isotherm were determined

73 from the adsorption equilibrium data from the various samples (Okeola & Odebunmi, 2010).

74   *Langmuir adsorption isotherm*

75   Langmuir adsorption isotherms were used to describe quantitatively of a monolayer

76   adsorbate on the adsorbent surface. Langmuir isotherm shows the accuracy of monolayer

77   adsorption on the surface of the adsorbent. The model assumes equal energies of adsorption onto

78   the surface (Dada et al., 2012). The Langmuir adsorption isotherm is shown below.

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L Q_e}$$

79   The linear form of Langmuir adsorption isotherm is presented below:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$

80   Where: C_e (mg/L) is the equilibrium concentration of As; q_e (mg/g) is the amount of As

81   as adsorbed per gram of the biochar at equilibrium; Q_0 (mg/g) is the maximum monolayer

82   coverage capacity; K_L (L/mg) is the Langmuir isotherm constant. From the slope and intercept of

83   Langmuir isotherm plot of $1/q_e$ versus $1/Ce$, the Q_0 and K_L are calculated (Dada et al., 2012).

84   *Freundlich adsorption isotherm*

85   The Freundlich isotherm is an empirical equation that accounts for surface

86   heterogeneity caused by multilayer adsorption as well as the exponential distribution of

87   adsorbent active sites and their energies toward the adsorbate. At greater pressure, the Freundlich

88   adsorption isotherm failed. The Freundlich adsorption isotherm is used to describe the

89   heterogeneous adsorption on the surface (Kalam et al., 2021). It is expressed below.

$$q_e = K_f C_e^{1/n}$$

90   Where: K_f (mg/g) (mg/L)^{-n} is a Freundlich isotherm constant; n is the intensity of

91   adsorption

92   The linear form of the Freundlich adsorption isotherm is as below:

$$log q_e = log K_f + \frac{1}{n} log C_e$$

93   From the slope and intercept of the Freundlich isotherm plot of the log qe versus log Ce,

94   Kf and n were calculated (Dada et al., 2012; Kalam et al., 2021).

95

96   **6. Details for magnet-assisted separation of NZVI from soil**

97   A permanent magnetic bar was placed at the outer body of the 50 mL centrifuge tubes

98   where it magnetically attracted ZVI particles from the soil slurry to the inner body of the 50 mL

99   centrifuge tube. The tube was jogged to increase attachment of bare NZVI materials. The soil

100   slurry was then decanted into another 50 mL centrifuge tube while holding the magnet at the

101   outer body of the 50 mL centrifuge tube. The retrieve of bare NZVI materials using a permanent

102   magnetic was repeated in triplicate at the same manner to ensure that most of NZVI particles was

103   removed from soil slurry.

104

105   **7. As treatment efficacy**

$$As\ treatment\ efficacy = \left(\frac{(C_{initial\ As} - C_{residual\ As})}{C_{initial\ As}} \right) \times 100$$

106   Where:

107         $As\ treatment\ efficacy$: The percentage of As treatment efficacy in soil (%)

108         $C_{initial\ As}$: The initial As concentration of As in soil (%)

109         $C_{residual\ As}$: The residual concentration of As in soil after treatment (%)

110

111

112   **8. The kinetic of As removal using pseudo First order Kinetic**

113   The equation for describing first order elimination kinetics is shown below and can be

114   used to calculate at any time after both adsorption and distribution are complete (Laidler &

115   Keith, 1965). This equation is also used to calculate C_0.

$$C = C_0 \times e^{-Kt}$$

116   in which C is the concentration of the reactant at any time t and K is a constant, called the

117   velocity constant or specific reaction rate. If at the start of the reaction the initial concentration of

118   the reactant is C_0 then we have at $t=0$, $C = C_0$.

119

120   **9. The Nutrient loss and bioavailable nutrient**

121   Nutrient loss in soil due to each magnet-assisted soil washing protocol was calculated

122   following the formula below:

$$\underline{\%\ of\ nutrient\ loss} = \left(\frac{(C_{initial\ nutrients} - C_{residual\ nutrients})}{C_{initial\ nutrients}} \right) \times 100$$

$$\% \ of \ bioavailable \ nutrients = \left(\frac{C_{bioavailable \ nutrients}}{C_{initial \ nutrients}}\right) \times 100$$

123

124   Where:

125    $\% \ of \ Nutrient \ loss$: The percentage of nutrient loss after magnet-assisted soil washing

126   (%)

127    $\% \ of \ bioavailable \ nutrients$: The percentage of bioavailable nutrient in soil (%)

128    $C_{initial \ nutrients}$: The concentration of nutrients in soil before magnet NZVI-assisted soil

129   washing (mg/kg)

130    $C_{residual \ nutrients}$: The As residual concentration of nutrients in soil after magnet NZVI-

131   assisted soil washing (mg/kg)

132    $C_{bioavailable \ nutrients}$: The concentration of bioavailable nutrients in soil after magnet

133   NZVI-assisted soil washing (mg/kg). Sum of concentration of nutrients in

134   F1, F2 and F3 fractions.

135

136   **10. The mass balance and partition of As in soil, water and retrieved NZVI particles**

137   Mass balance of As in soil, water and retrieved NZVI particles was calculated by

138   formulas below:

$$M_{total \ As} = M_{As \ in \ soil} + M_{As \ in \ water} + M_{As \ in \ retrieved \ NZVI}$$

$$M_{As \ in \ soil} = C_{As \ in \ soil} \times m_{soil}$$

$$M_{As \ in \ water} = C_{As \ in \ water} \times V_{water}$$

$$M_{As \ in \ retrieved \ NZVI} = C_{As \ in \ retrieved \ NZVI} \times m_{retrieved \ NZVI}$$

139   The partition of As residue in soil, water and retrieved NZVI was calculated by formulas

140   below:

$$\% \ As \ in \ soil = \frac{M_{As \ in \ soil}}{M_{total \ As}} \times 100$$

$$\% \ As \ in \ water = \frac{M_{As \ in \ water}}{M_{total \ As}} \times 100$$

$$\% \ As \ in \ retrieved \ NZVI = \frac{M_{As \ in \ retrieved \ NZVI}}{M_{total \ As}} \times 100$$

141   Where:

142        $M_{total\ As}$ is total As mass in environment including soil, water and retrieved NZVI (mg)

143        $M_{As\ in\ soil}$ is As mass in soil (mg)

144        $M_{As\ in\ water}$ is As mass in water (mg)

145        $M_{As\ in\ retrieved\ NZVI}$ is As mass in retrieved NZVI (mg)

146   V_{water} is the volume of water (L)

147   m_{soil} and $m_{retrieved\ NZVI}$ is the mass of soil and retrieved NZVI (kg)

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149   **11. The phytotoxicity parameters of germination**

150   The germination percentage (*%G*), speed of germination (*SG*), mean germination time

151   (*MGT*), root length (*RL*), shoots length (*SL*), soot length inhibition (*SLI%*), root length inhibition

152   (*RLI%*) and the germination index (*GI%*) and vigor index (*Vi*) were measured in this study.

153   The percent inhibition of shoot and root length was calculated as

$$\text{Soot length inhibition } (SLI\%) = \left(\frac{SL \text{ of control } - \ SL \text{ of sample}}{SL \text{ of control}}\right) \times 100$$

$$\text{Root length inhibition}(RLI\%) = \left(\frac{RL \text{ of control } - \ RL \text{ of sample}}{RL \text{ of control}}\right) \times 100$$

154   Final germination percentage (*GR*) is the maximum average percentage of germinated

155   seeds.

$$GR = \left(\frac{No.\text{ of germinated seeds}}{No.\text{ of total planted seed}}\right) \times 100$$

156   The germination index (*GI%*) was calculated by counting the seeds that germinated in

157   each dish and by measuring the length of the roots of five germinated seeds that were chosen

158   randomly (Equation 1). The length of the roots was measured from the hypocotyl to the radicle,

159   that is, from the stem to the root tip.

$$GI = \%G.\left(\frac{Ls}{Lc}\right)$$

160   Where:

161   *GI*: Germination index

162   *%G*: Germination percentage in relation to control

163   *Ls*: Average length of the sample roots (cm)

164   *Lc*: Average length of control roots (cm)

165   Speed of Germination (*SG*) is the time course of seed germination, number of seed

166   germinated per day. Speed of germination was calculated by the following formula given by

$$SG = \sum \frac{N_i}{D_i}$$

167   where:

168   N_i = daily increase in seedling number,

169   Di = number of days from seed placement.

170   Vigor Index (*VI*) was calculated by multiplying seed germination (%) and seedling length

171   (cm) according to (Abdul-Baki & Anderson, 1970).

$$VI = (RL + SL) \times \%G$$

172   where:

173   *RL* = Length of the sample root

174   *SL*=Length of the sample soot

175   Mean Germination Time Mean is a measure of the time it takes for the seed to germinate,

176   focusing on the day at which most seeds have germinated (Ellis & Roberts, 1981).

$$MGT = \frac{\sum ni \times di}{N}$$

177   where:

178   *N*: Total number of seeds

179   *ni*: germinated seeds per day

180   *di*: counting day

181   Percent inhibition of seedling growth (*% iSG*) was calculated bythe given formula.

$$\%iSG = \left[\frac{(N - S)}{N}\right] \times 100$$

182   where:

183   $N = RL + SL$ of control or negative control

184   $S = RL + SL$ of sediment samples treated plants.

185   RL = root length, SL = shoot length.

186 **Table S1** Solvents used for 7-step sequential extraction of arsenic

No.	Fractions	Extract solvent
1	F1: Mobile (MB)	1 mol L^{-1} NH_4NO_3, 1:25 w/v for 24 h
2	F2: Weakly bound (WB)	1 mol L^{-1} CH_3COONH_4, 1:25 w/v for 24 h
3	F3: Mn oxides (MO)	0.1 mol L^{-1} NH2OH.HCl, 1:25 w/v for 30 min
4	F4: Organically bound (OB)	0.025 mol L^{-1} NH4EDTA, 1:25 w/v for 90 min
5	F5: Fe-Al amorphous oxides (FA)	0.2 mol L^{-1} $(COONH_4)_2$, 1:25 w/v for 4 h
6	F6: Fe-Al crystalline oxides (FC)	0.1 mol L^{-1} ascorbic acid + 0.2 mol L^{-1} $(COONH_4)_2$,
7	F7: Residue (RD)	Microwave-assisted acid digestion with 10 mL of 65% nitric acid in the EPA method (3051a)

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189 **Table S2** Physical-chemical properties of Soil

No.	Parameters	Value
1	Soil texture	Sandy loam
2	%clay	53
3	%Silt	49
4	Bulk density (g cm^{-3})	1.60
5	Drainage rate (cm hr^{-1})	1.05
6	pH	6.43
7	Conductivity (mV)	1,078
8	TDS (ppm)	761
9	Salt (ppm)	527
10	ORP (mV)	200
11	CEC (meq/100 g)	7.85

12	Organic carbon (OC) (%)	1.27
13	Nitrogen (N^+) (mg/kg)	54.67
14	Phosphorus (P^+) (mg/kg)	74.45
15	Potassium (K^+) (mg/kg)	35.21
16	Magnesium (Mg^+) (mg/kg)	676.73
17	Manganese (Mn^+) (mg/kg)	309.50

(a)

(b)
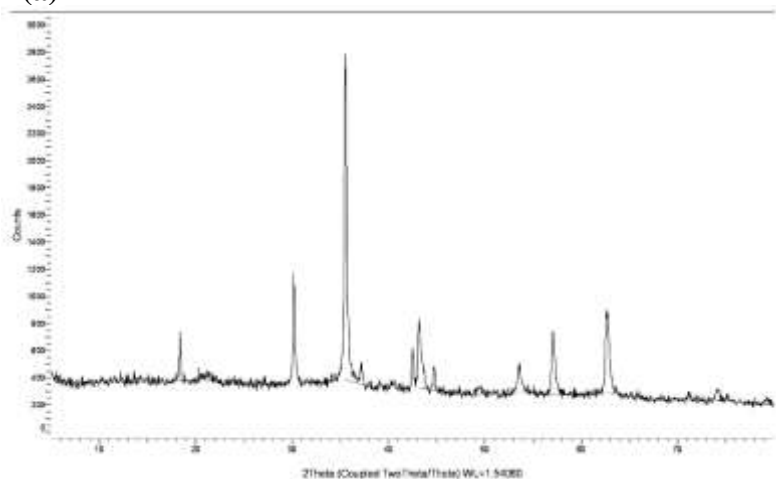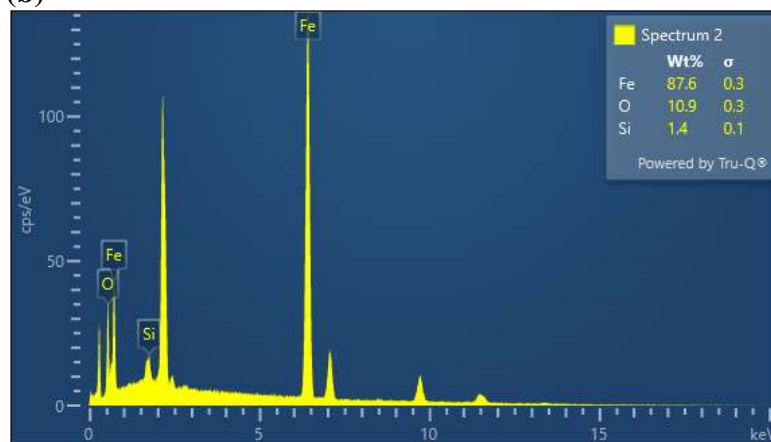
(c)

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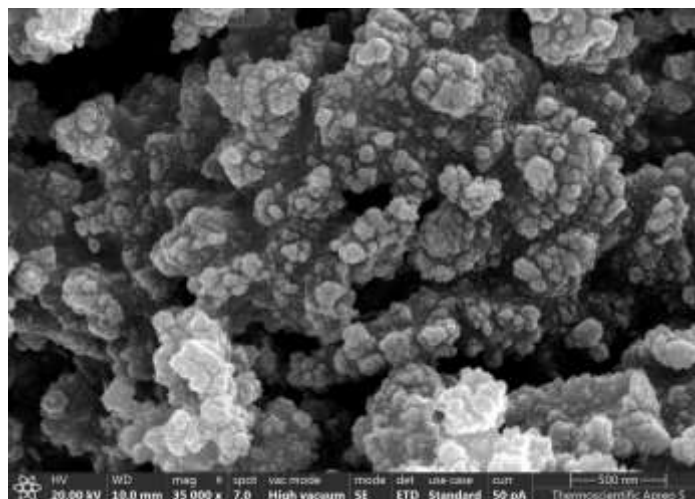
Figure S1 (a) XRD, (b) EDS, and (c) SEM of bare NZVI

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223
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Figure S2 SEM of (a) S-NZVI and (b) CMC-modified NZVI. The bars are 200 nm. EDS of (c) S-NZVI and (d) CMC-modified NZVI
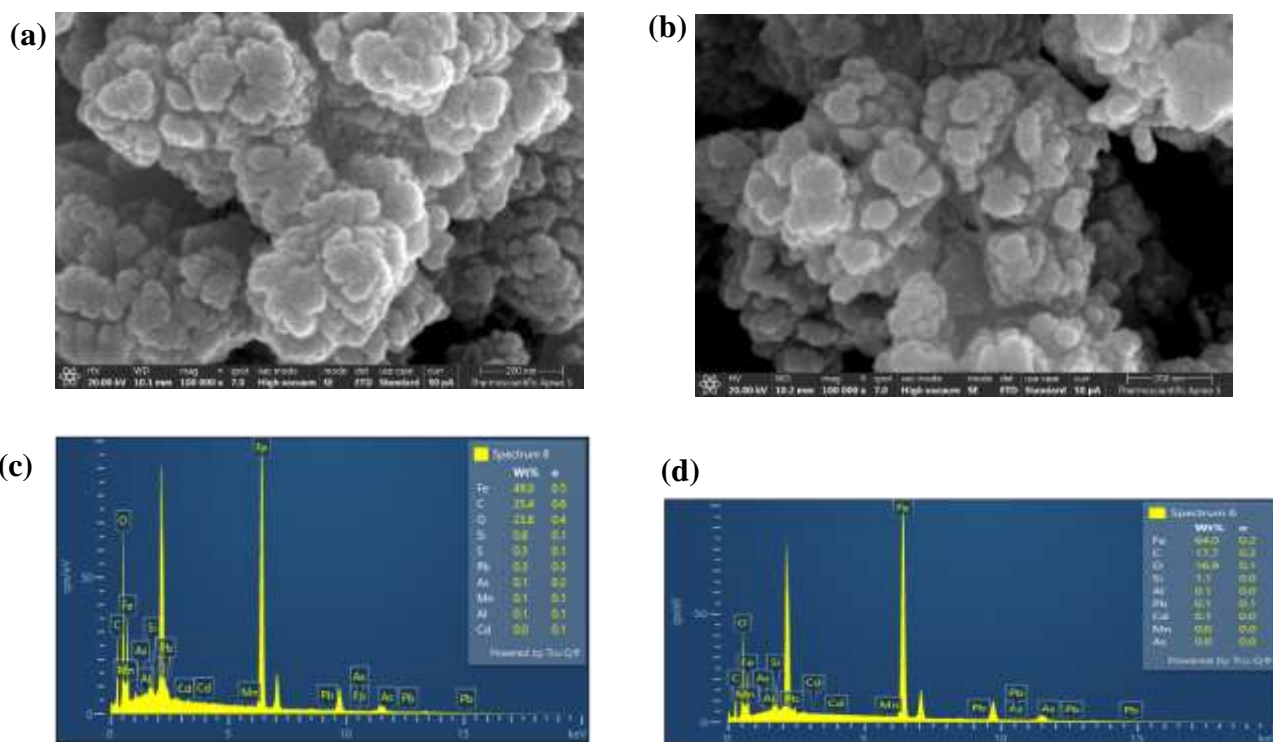
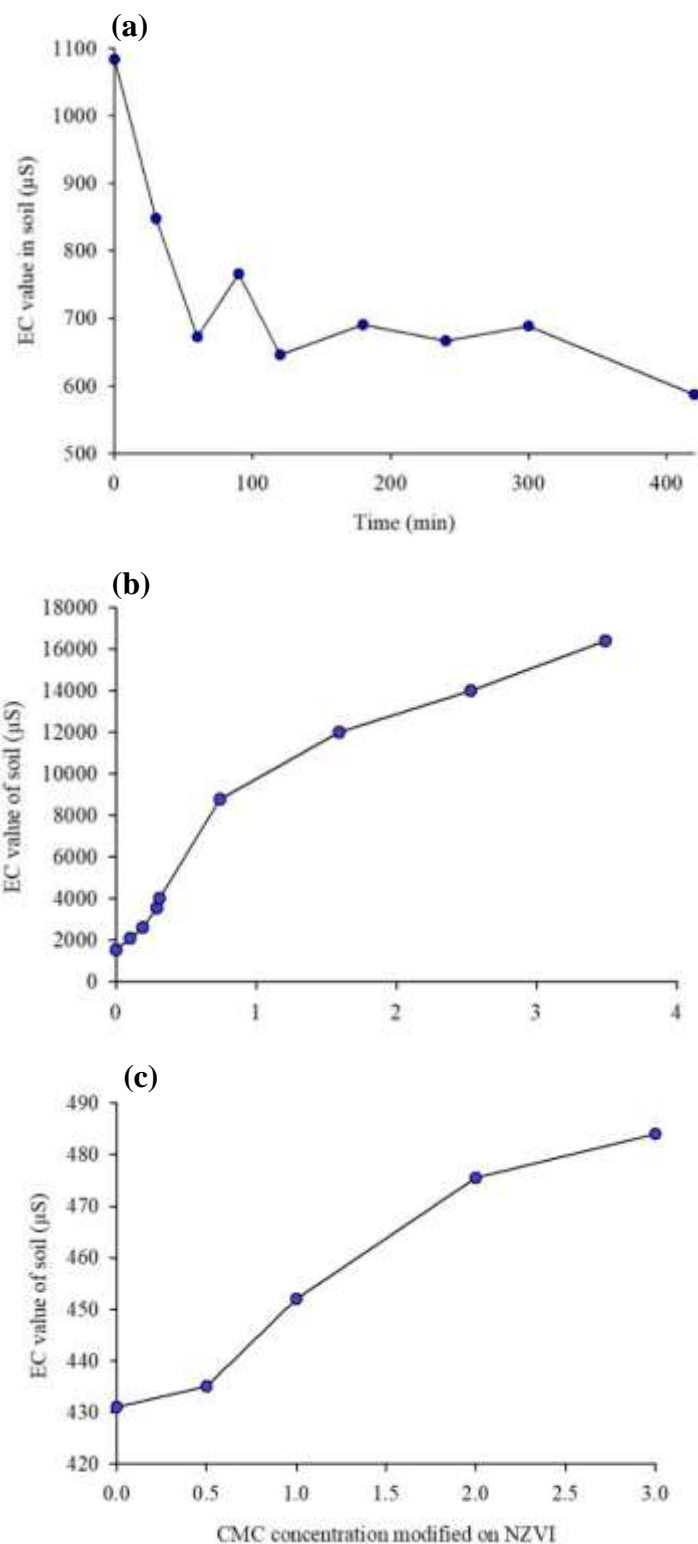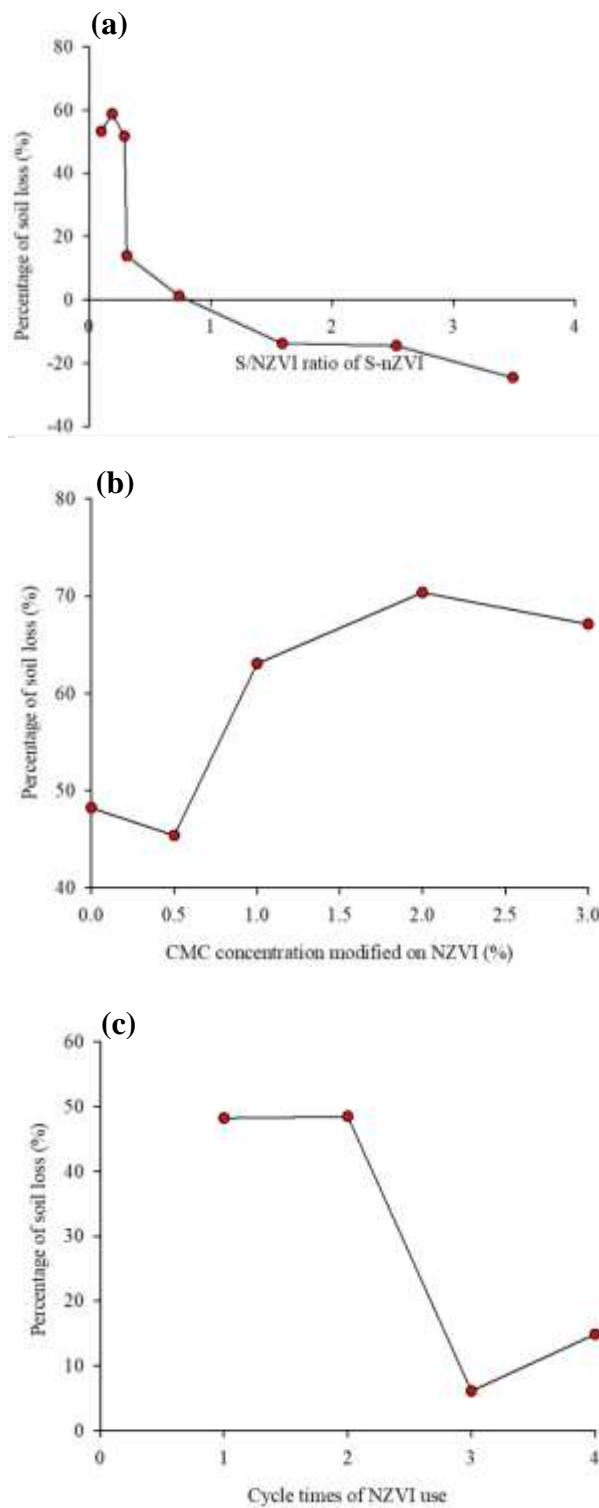**Figure S3** EC value in soil through the magnetic NZVI assisted soil washing with 10%(w/w) of
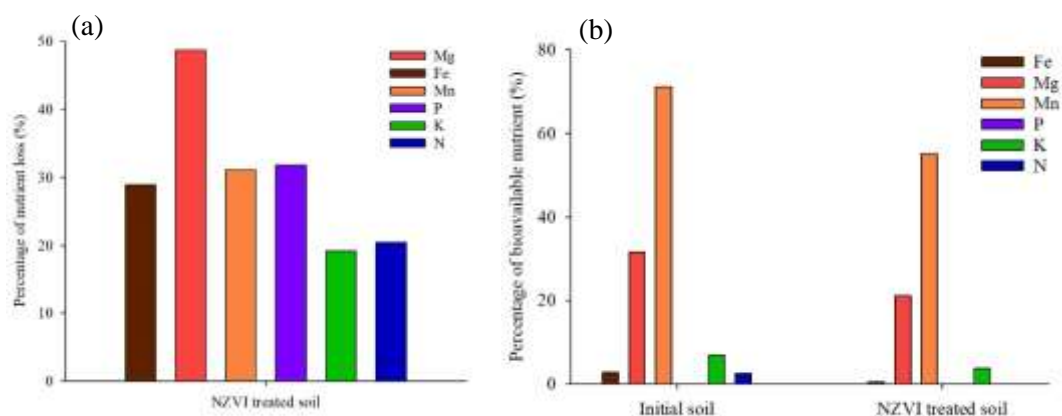(a) NZVI, (b) S-NZVI and (c) CMC-NZVI at 1:2 of soil:water ratio and 30 rpm of end-to-end
rotary

Figure S4 Soil loss for (a) S-NZVI with S/Fe ratios ranging from 0.1 to 3.49, (b) CMC-NZVI with CMC concentration ranging from 0.5 to 3.0% and (c) cycle of NZVI reuse.

Figure S5 (a) The percentage of nutrient loss and (b) the percentage of bioavailable nutrient after the magnetic NZVI assisted soil washing with 10%(w/w) of NZVI and dosage, 1:2 of soil:water ratio and 60 rpm of end-to-end rotary.

Table S3 The germination parameters of *Ipomoea aquatica Forsk* on As toxicity in soil

Soil condition	GR (%)	GI	SG	MGT	VI	% iSG	RLI%	SLI%
Control	93.33	93.33	4.33	1.15	0.18	0.00	0.00	0.00
Untreated	80.00	81.40	3.05	1.98	0.21	1.08	0.05	-0.0011
NZVI	100.0	126.39	3.11	1.00	0.20	-16.03	-0.26	-0.1218

Table S4 The germination parameters of *Oryza sativa L.* on As toxicity in soil

Soil condition	GR (%)	GI	SG	MGT	VI	% iSG	RLI%	SLI%
Control	96.67	96.67	3.13	3.70	0.19	0.00	0.00	0.0000
Untreated	70.00	41.46	2.87	3.00	0.29	0.99	0.41	-0.4154
NZVI	100.00	90.11	3.60	3.47	0.22	-0.11	0.10	-0.3545

Reference

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