# Enhanced detoxification of Cr<sup>6+</sup> by *Shewanella oneidensis* via adsorption on spherical and flowerlike manganese ferrite nanostructures

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Figure S1: TEM images of spherical  $Mn_xFe_{3-x}O_4$  nanoparticles (NPs) prepared by solvothermal method at 250 °C. The precursor concentration ratio of (A-E) [ $Mn(acac)_2$ ] / [ $Fe(acac)_3$ ] and (F-J) [ $Mn(acac)_3$ ] / [ $Fe(acac)_3$ ] respectively were 0.14, 0.6, 1, 1.66 and 3.



*Figure S2: Polydispersity index (PDI) of NPs diameters varied with precursor concentration ratios calculated from TEM at annealing temperature (200 vs 250 °C).* 



Figure S3: XRD patterns of NPs prepared at 200 °C where (A) undoped  $Fe_3O_4$  NPs, (B)  $[Mn(acac)_2]/[Fe(acac)_3]$  was 0.33, (C)  $[Mn(acac)_3]/[Fe(acac)_3]$  was 0.33. The reference ICDD were  $Mn_3O_4$  (PDF card no. 01-080-0382),  $MnFe_2O_4$  (PDF card no 00-010-0319) and  $Fe_3O_4$  (PDF card no 01-089-0688).

$[Mn(acac)_{2 \text{ or } 3}] / [Fe(acac)_{3}]$	Ν	In(acac) <sub>2</sub>	Mn(acac) <sub>3</sub>			
-	2 <del>0</del> (311)	D <sub>XRD</sub> (nm)	20 (311)	D <sub>XRD</sub> (nm)		
0.14	41.33	7 ± 1	41.01	7 ± 1		
0.33	41.4	$7\pm0.5$	41.06	$6 \pm 1^*$		
0.6	41	7 ± 1	41.07	$7.5 \pm 1$		
1	41.1	7 ± 1	41.01	$6.5 \pm 1*$		
1.66	41	6.5 ± 1*	40.92	5 ± 1**		
3	41	6.5 ± 1.5*	40.87	5.5 ± 1.5**		
7	-	-	-	-		

Table S1: Summary of 311 peak positions and crystal size  $(D_{XRD})^a$  determined by XRD of  $Mn_xFe_{3-x}O_4$  NPs

<sup>*a*</sup> $D_{XRD}$  was presented as (mean  $\pm$  standard deviation) of 3 independent synthesis experiments and \*p < 0.05 and \*p < 0.01 showed the statistical confidence levels by comparing the crystal size with Fe<sub>3</sub>O<sub>4</sub> NPs (9  $\pm$  1.3 nm) synthesized in the same conditions.



Figure S4: XRD patterns of  $Mn_xFe_{3-x}O_4$  NPs where  $[Mn(acac)_3] / [Fe(acac)_3]$  were (A) 0.14, (B) 0.33, (C) 0.6, (D) 1 (E) 1.66 (F) 3. The reference ICDD were  $Mn_3O_4$  (PDF card no. 01-080-0382),  $MnFe_2O_4$  (PDF card no 00-010-0319) and  $Fe_3O_4$  (PDF card no 01-089-0688). A secondary phase appears to be present for NPs prepared from  $[1 \le [Mn(acac)_{2 \text{ or } 3}] / [Fe(acac)_3] \le 3]$  (D-F) which was identified as  $MnCO_3$  (Reference ICDD PDF card no. 00-044-1472). Perpendicular and horizontal arrows indicated the gradual increase in  $[Mn(acac)_3] / [Fe(acac)_3]$  from (A-F) and the shifting in the peak of 311 from the reference  $Fe_3O_4$  towards lower diffraction angle of  $MnFe_2O_4$ , respectively.



Figure S5: XRD patterns of TEG (A) before and (B) after thermal treatment at 250 °C for 6 h in autoclave.



Figure S6: Polydispersity index (PDI) of NP diameters varied with precursor concentration ratios calculated from XRD at the most intense peak of (311) at annealing temperature (200 vs 250 °C).



Figure S7: XRD patterns of produced sample where [Mn(acac)<sub>2</sub>] / [Fe(acac)<sub>3</sub>] was 7. Reference JCPDS card no. 00-044-1472, 00-029-0713, for MnCO<sub>3</sub>, FeOOH, respectively.

When [Mn(acac)<sub>2</sub>] / [Fe(acac)<sub>3</sub>] was 7, the observed XRD peaks of the solvothermal-produced material at 250 °C cannot be assigned to well-established crystal phases of ferrite materials (Figure S7). Hence, this sample was not selected for further analysis since it could not offer critical insights on metal substitution using the above precursors.

#### 2. Functionalization of NPs and nanoflowers (NFs)



Figure S8: Impact of variation in ratios between  $[Mn(acac)_{2 \text{ or } 3}] / [Fe(acac)_3]$  in  $Mn_xFe_{3-x}O_4$ nanostructures and synthesis temperature (200 vs 250 °C) on hydrodynamic size ( $D_{HD}$ ) of NPs and NFs coated by citrate.  $Fe_3O_4$  NPs and  $Mn_3O_4$  NPs were represented by grey and brown bars, respectively. \*\*p < 0.01 showed the statistical confidence levels when comparing the size with  $Fe_3O_4$  NPs synthesized at 250 °C.



Figure S9: Impact of variation in  $[Mn(acac)_{2 \text{ or } 3}] / [Fe(acac)_{3}]$  and synthesis temperature (200 vs 250 °C) on  $\zeta$ -potential of NPs and NFs coated by citrate.



Wavenumber (cm<sup>-1</sup>)

Figure S10: FTIR spectra of tri-sodium citrate alone, (A)  $Fe_3O_4$  NPs prepared at 250 °C for 6h of synthesis time,  $Mn_xFe_{3-x}O_4$  NPs prepared at 250 °C where (B)  $[Mn(acac)_2] / [Fe(acac)_3]$  and (C)  $[Mn(acac)_3] / [Fe(acac)_3]$  were 0.33, for 6h of synthesis time (D)  $[Mn(acac)_3] / [Fe(acac)_3]$  was 3, (E)  $MnFe_2O_4$  NFs  $[Mn(acac)_3] / [Fe(acac)_3]$  was 3 and (F)  $Mn_3O_4$  NPs. and all samples were coated by citrate.

3. Raman Spectra of the selected NPs



Figure S11: Raman spectra of (A)  $Fe_3O_4$  NPs, (B)  $Mn_{0.2}^{2+}Fe_{2.8}^{3+}O_4$  NPs.

### 4. The oxidation state of Mn and Fe in the prepared NPs



Figure S12: XPS spectra of  $Mn_xFe_{3-x}O_4$  NPs where orange and blue represent  $Mn_{0.2}^{2+}Fe_{2.8}^{3+}O_4$  and  $Mn_x^{3+}Fe_{3-x}^{3+}O_4$  respectively.

$Mn^{x+}$ .									
	$Mn_{0.2}^{2+}Fe_{2.8}^{3+}O_4$				$Mn_{x}^{3+}Fe_{3-x}^{3+}O_{4}$				
Binding Energy	640	642	645	651	653	640	642	651	653

1.9

15.7

2.2

21.7

2.25

22.1

2.7

26.6

3

29.6

*Table S2: Peak positions and full width at half maximum (FWHM) of the XPS of Mn 2p peak for* 

2.9

14

2.5

20.7

 $(BE)_{Mn}(eV)$ 

Peak weighting

2.7

22.3

2.1

10.2

FWHM

(%)

	$Mn_{0.2}^{2+}Fe_{2.8}^{3+}O_4$						$Mn_{x}^{3+}Fe_{3-x}^{3+}O_{4}$				
$BE_{Fe}(eV)$	710	712	718	723	726	732	710	713	718	723	726
FWHM	2.5	3.3	6.5	3.2	4.6	3.6	2.7	2.8	5.7	4	5.4
Peak weighting (%)	10.5	14	27.4	13.5	19.4	15.2	13.1	13.6	27.7	19.4	26.2

## 5. Biological studies

## Table S4: Molecular identification of the tested bacteria

Bacterial strain	16S rRNA gene sequence	BLAST bacterial matches at NCBI database
S. oneidensis MR-1	AAGNGTGAGCGCCCCCGAAGGTTA AGCTACCCACTTCTTTTGCAGCCCAC TCCCATGGTGTGACGGGCGGGTGTG TACAAGGCCCGGGAACGTATTCACC GA	CP053946.1, 98.98 %
S. loihica PV-4	GGTGAGCGCCCCCCGAAGGTTAAGC TACCCACTTCTTTTGCAGCCCACTCC CATGGTGTGACGGGCGGTGTGTACA AGGCCCGGGAACGTATTCACCGAA	CP053946.1, 100 %
S. oneidensis JG1486	TTGCAAAAGAAGCTAGNTAGCCTTA ACCTTCGGGAGGGCGCTTACCACTT TGTGATTCATGACTGGGGGTGAAGTC GTAACAAGGTAAC	EU567031.1, 96.6 %
S. oneidensis JG3355	CACTTAGGCGGCTGGCTCCAAAGGT TACCTCACCGACTTCGGGTGTTACA AACTCTCGTGGTGTGACGGGCGGTG TGTACAAGGCCCGGGAACGTATTCA CCGA	KT336053.1, 99.99 %