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

Supporting Information

Influence of nickel manganese cobalt oxide nanoparticle composition on toxicity toward *Shewanella oneidensis* MR-1: Redesigning for reduced biological impact

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Table S1. Aggregation Analysis via Dynamic Light Scattering (DLS).

To assess the aggregation states of the different NMC nanomaterials, DLS was used. Analogous to the toxicity studies, 5 mg/L of each NMC was prepared in growth medium (no bacteria was added). The exposure was completed for 24 h without any agitation. Immediately before DLS analysis (Malvern Zetasizer Nano-ZS), the solutions were agitated for 10 seconds using a Mini Vortexer (Fisher Scientific) and aliquots were removed for analysis. Measurements were obtained at 0 h (initial) and 24 h after exposure to medium.

Table S1 shows that initially after exposure to growth medium, the number mean diameter are similar across the different NMC compositions. Table S1 shows that number mean diameters measurements made after 24 h do not significantly change as compared to initial measurements. Moreover, for DLS measurements, only spherical objects can be accurately described by a single hydrodynamic diameter value. As the NMC nanosheets are anisotopic in shape, aggregate sizes cannot be accurately be quantified by DLS. Therefore, the DLS data can only qualitatively suggest that the NMC nanosheets of different compositions have similar aggregation behavior.

	0 h after exposure to growth medium, diameter (nm)	**24 h** after exposure to growth medium, diameter (nm)
X_{Mn}=0.39	426 ± 73	482 ± 72
X_{Mn}=0.55	478 ± 105	531 ± 51
X_{Mn}=0.72	465 ± 82	450 ± 62

Figure S1. Photographs of a green laser pointer aimed at vials of 5 mg/L NMCs in bacterial growth medium immediately and 24 h after exposure to growth medium. Vials in images A-D are the same. Image A and C is of the vials with the lights turned off for greater contrast of the green laser and solutions. Images B and D is of the vials with the lights on. The suspensions of NMCs in growth medium are similar across different NMC compositions and between the different time points.

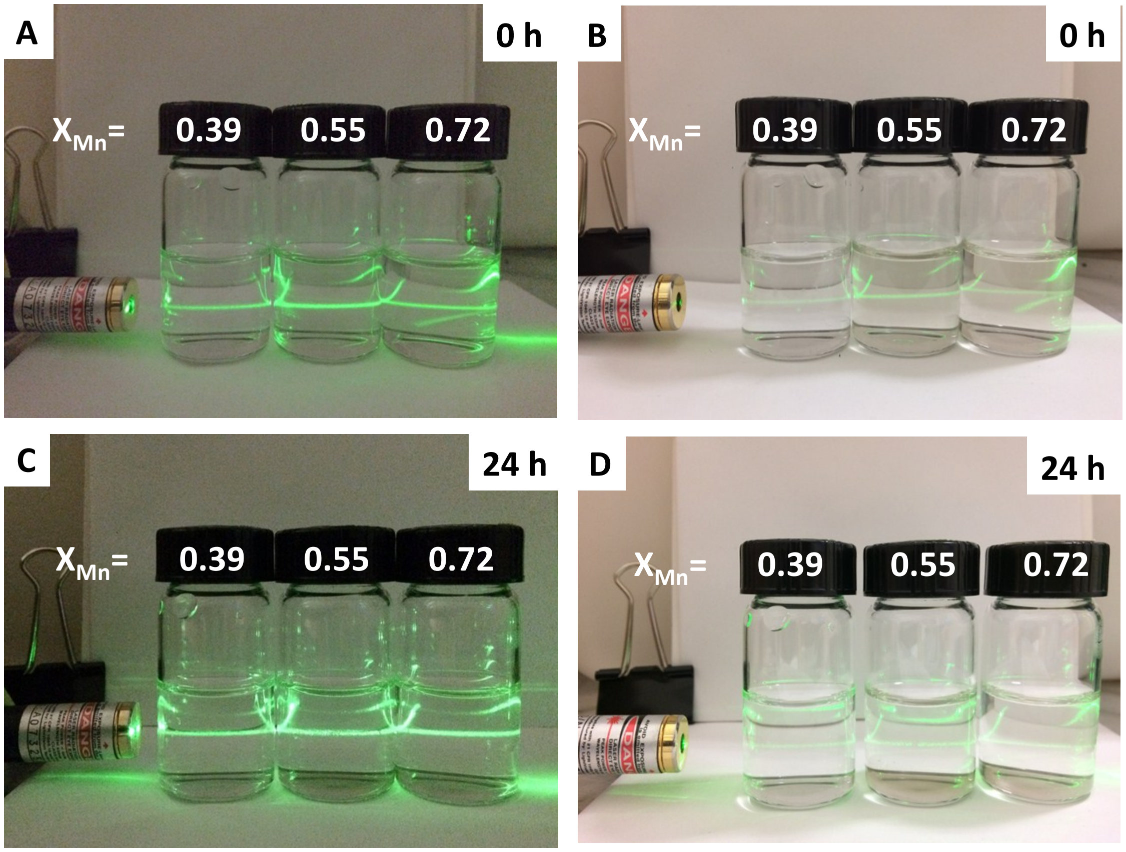


Table S2. Correlation coefficients for curves from Figures 6-7. Correlation coefficients for respirometry curves are presented as calculated in Excel by the correlation function of the Analysis Tool Pak Add-in. The highest correlation coefficient in a set has a shaded cell. The highest correlation coefficient for each type of NMC is bolded.

	Control Avg	*NMC 39 Average*	*39 ions average*
Control Avg	1.0000		
NMC 39 Avg	0.9497	1.0000	
39 ions Avg	0.9492	**0.9980**	1.0000

	Control Avg	*NMC 39 Avg*	*39 Ni, Co Avg*
Control Avg	1.0000		
NMC 39 Avg	0.8168	1.0000	
39 Ni, Co Avg	0.8376	0.9921	1.0000

	Control Average	*NMC 55 Average*	*55 ions Average*
Control Avg	1.0000		
NMC 55 Avg	0.9387	1.0000	
55 ions	0.9651	**0.9938**	1.0000

	Control Avg	*NMC 55 Avg*	*55 Ni, Co Avg*
Control Avg	1.0000		
NMC 55 Avg	0.8761	1.0000	
55 Ni, Co	0.9136	0.9931	1.0000

Avg			
	Control Avg	*NMC 72 Avg*	*72 ions Avg*
Control Avg	1.0000		
NMC 72 Avg	0.9765	1.0000	
72 ions Avg	0.9879	0.9973	1.0000

Avg			
	Control Avg	*72 NMC Avg*	*72 Ni, Co Avg*
Control Avg	1.0000		
72 NMC Avg	0.9578	1.0000	
72 Ni, Co Avg	0.9711	**0.9982**	1.0000

Visual Minteq modeling of solution species

Speciation of soluble metals in bacterial growth medium in the presence of LiCl, $NiCl_2$, $MnCl_2$, $CoCl_2$ to mimic the amount of free Li, Ni, Mn, and Co dissolved from the various NMC nanomaterials after 72 h in medium.

Table S3. Analysis of soluble metals leaching from 5 mg/L of NMC (X_{Mn}=0.39). Speciation of soluble metals in bacterial growth medium in the presence of 38.3 µM LiCl, 12.9 µM $NiCl_2$, 11.5 µM $MnCl_2$, and 10.3 µM $CoCl_2$

Component	% of total concentration	Species name
Li^+	80.357	Li^+
	3.119	$LiCl_{(aq)}$
	0.168	$LiSO_4^-$
	11.225	$LiHPO_4^-$
	5.129	Li-Lactate $_{(aq)}$
Ni^{+2}	9.802	Ni^{+2}
	0.052	$NiOH^+$
	0.119	$NiCl^+$
	0.253	$NiSO_{4\,(aq)}$
	0.57	$NiNH_3^{+2}$
	0.064	$NiH_2PO_4^+$
	22.499	$NiHPO_{4\,(aq)}$
	4.175	Ni-(Lactate)$_3^-$
	26.641	Ni-(Lactate)$_{2\,(aq)}$
	35.813	Ni-Lactate$^+$
Mn^{+2}	11.614	Mn^{+2}
	0.013	$MnOH^+$
	0.037	$MnCl_{2\,(aq)}$
	0.375	$MnCl^+$
	0.273	$MnSO_{4\,(aq)}$

	78.672	$MnHPO_{4\ (aq)}$
	0.156	Mn-(Lactate)$_3^-$
	1.603	Mn-(Lactate)$_{2\ (aq)}$
	7.245	Mn-Lactate$^+$
Co^{+2}	14.242	Co^{+2}
	0.086	$CoOH_+$
	0.208	$CoCl^+$
	0.369	$CoSO_{4\ (aq)}$
	0.171	$Co(NH_3)^{+2}$
	41.154	$CoHPO_{4\ (aq)}$
	1.524	Co-(Lactate)$_3^-$
	16.023	Co-(Lactate)$_{2\ (aq)}$
	26.219	Co-Lactate$^+$

Table S4. Analysis of soluble metals leaching from 5 mg/L of NMC (X_{Mn}=0.55). Speciation of soluble metals in bacterial growth medium in the presence of 40.7 µM LiCl, 9.56 µM $NiCl_2$, 16.0 µM $MnCl_2$, and 7.35 µM $CoCl_2$.

Component	% of total concentration	Species name
Li^+	80.357	Li^+
	3.119	$LiCl_{\ (aq)}$
	0.168	$LiSO_4^-$
	11.225	$LiHPO_4^-$
	5.129	Li-Lactate $_{(aq)}$
Ni^{+2}	9.802	Ni^{+2}
	0.052	$NiOH^+$
	0.119	$NiCl^+$
	0.253	$NiSO_{4\ (aq)}$
	0.57	$NiNH_3^{+2}$
	0.064	$NiH_2PO_4^+$
	22.497	$NiHPO_{4\ (aq)}$
	4.176	Ni-(Lactate)$_3^-$
	26.642	Ni-(Lactate)$_{2\ (aq)}$
	35.814	Ni-Lactate$^+$
Mn^{+2}	11.614	Mn^{+2}
	0.013	$MnOH^+$
	0.037	$MnCl_{2\ (aq)}$
	0.375	$MnCl^+$
	0.273	$MnSO_{4\ (aq)}$
	78.672	$MnHPO_{4\ (aq)}$
	0.156	Mn-(Lactate)$_3^-$
	1.603	Mn-(Lactate)$_{2\ (aq)}$
	7.245	Mn-Lactate$^+$

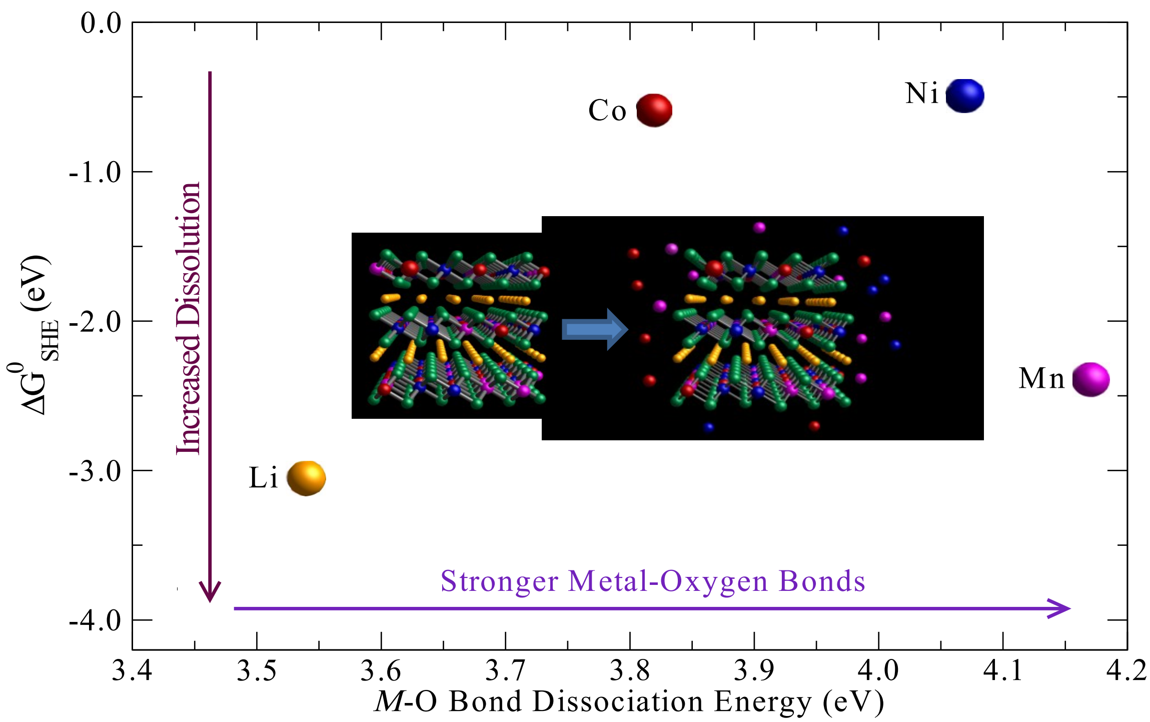
Co^{+2}	14.242	Co^{+2}
	0.086	$CoOH_{+}$
	0.208	$CoCl^{+}$
	0.369	$CoSO_{4\ (aq)}$
	0.171	$Co(NH_3)^{+2}$
	41.152	$CoHPO_{4\ (aq)}$
	1.524	$Co\text{-}(Lactate)_3^-$
	16.024	$Co\text{-}(Lactate)_{2\ (aq)}$
	26.22	$Co\text{-}Lactate^{+}$

Table S5. Analysis of soluble metals leaching from 5 mg/L of NMC (X_{Mn}=0.72). Speciation of soluble metals in bacterial growth medium in the presence of 41.9 µM LiCl, 5.99 µM $NiCl_2$, 20.5 µM $MnCl_2$, and 4.51 µM $CoCl_2$

Component	% of total concentration	Species name
Li^{+}	80.357	Li^{+}
	3.119	$LiCl_{\ (aq)}$
	0.168	$LiSO_4^-$
	11.225	$LiHPO_4^-$
	5.129	$Li\text{-}Lactate_{\ (aq)}$
Ni^{+2}	9.801	Ni^{+2}
	0.052	$NiOH^{+}$
	0.119	$NiCl^{+}$
	0.253	$NiSO_{4\ (aq)}$
	0.57	$NiNH_3^{+2}$
	0.064	$NiH_2PO_4^{+}$
	22.496	$NiHPO_{4\ (aq)}$
	4.176	$Ni\text{-}(Lactate)_3^-$
	26.643	$Ni\text{-}(Lactate)_{2\ (aq)}$
	35.814	$Ni\text{-}Lactate^{+}$
Mn^{+2}	11.614	Mn^{+2}
	0.013	$MnOH^{+}$
	0.037	$MnCl_{2\ (aq)}$
	0.375	$MnCl^{+}$
	0.273	$MnSO_{4\ (aq)}$
	78.671	$MnHPO_{4\ (aq)}$
	0.156	$Mn\text{-}(Lactate)_3^-$
	1.604	$Mn\text{-}(Lactate)_{2\ (aq)}$
	7.246	$Mn\text{-}Lactate^{+}$
Co^{+2}	14.242	Co^{+2}
	0.086	$CoOH_{+}$

	0.208	$CoCl^{+}$
	0.369	$CoSO_{4\ (aq)}$
	0.171	$Co(NH_3)^{+2}$
	41.151	$CoHPO_{4\ (aq)}$
	1.524	$Co\text{-}(Lactate)_3^{-}$
	16.025	$Co\text{-}(Lactate)_{2\ (aq)}$
	26.22	$Co\text{-}Lactate^{+}$

Figure S2. DG$^0_{SHE}$ vs. Bond Dissociation Energy to oxygen for the cations present in NMC, in units of eV.[1] Li will dissolve first, as its solvation is most exothermic (-3.039 eV), and it has the weakest bonds to oxygen (3.534 eV). Even though Mn has the next largest negative value for dissolution -2.363 eV), it forms the strongest bonds to oxygen (4.166 eV), and is most likely going to dissolve last, which is observed experimentally.



[1]Lange's Handbook of Chemistry, Fifteenth Edition. Ed: John A. Dean, Publisher: McGraw-Hill Company, Year: 1998

Table S6. Electrophoretic mobilities of NMC nanosheets. Data averages are of six replicates.

	NMC-39	NMC-55	NMC-72
Electrophoretic Mobility (µm*cm/V*s)	-0.462	-0.403	-0.614
Standard Deviation	0.063	0.071	0.024