Supplementary Data

Adsorption of Tetracycline to Nano-NiO: Effect of Co-existing Cu(II) Ion and Environmental Implications

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Adsorption kinetics experiments

Batch experiments were conducted to examine the adsorption kinetics of tetracycline to nano-NiO or bulk-NiO. First, 100 mg of nano-NiO or bulk NiO was transferred to a 250-mL glass vial, followed by a full volume of tetracycline aqueous solution and then covered with aluminum foil to prevent exposure to light. The initial spiked concentration of tetracycline was 0.11 mmol/L. The vial was repeatedly sampled (<0.5 ml aliquot each time) at a predetermined time intervals (0 h, 0.5 h, 1 h, 4 h, 8 h, 16 h, 24 h, 36 h, 48 h, 60 h, 72 h, 84h, 96 h) to determine the aqueous phase concentration of tetracycline. Control experiments were conducted using vials receiving the same treatment as the adsorption samples but without nano-NiO or bulk-NiO.

Table S1. Surface area, pore volume and average pore size distribution of nano-NiO and bulk NiO.

		nano-NiO	bulk-NiO
Surface Area	BET Surface Area	52.70 m^2/g	5.82 m^2/g
Pore Volume	Single point adsorption total pore volume of pores less than 160.1 Å diameter at P/Po = 0.987:	0.153 cm^3/g	0.011 cm^3/g
	BJH adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter:	0.168 cm^3/g	0.022 cm^3/g
	BJH desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter:	0.168 cm^3/g	0.021 cm^3/g
	HK maximum pore volume at P/P_0 = 0.01:	0.013 cm^3/g	0.001 cm^3/g
Pore Size	Adsorption average pore width (4V/A by BET):	11.66 nm	7.52 nm
	BJH adsorption average pore diameter (4V/A):	10.68 nm	19.80 nm
	BJH desorption average pore diameter (4V/A):	9.69 nm	17.92 nm
	HK median pore width:	0.64 nm	0.81 nm

Table S2. Freundlich model parameters for adsorption of tetracycline to nano-NiO and bulk-NiO.

	K_F ($mmol^{1-n}L^nkg^{-1}$)	n	R^2	K_d (L/kg)
nano-NiO	370 ± 20	0.550 ± 0.015	0.9971	$10^{3.1}$-$10^{4.2}$
nano-NiO + Cu^{2+}	210 ± 20	0.059 ± 0.027	0.6543	$10^{3.0}$-$10^{5.5}$
bulk-NiO	90 ± 10	0.421 ± 0.026	0.9849	$10^{2.6}$-$10^{3.9}$
bulk-NiO + Cu^{2+}	240 ± 10	0.040 ± 0.008	0.8423	$10^{3.1}$-$10^{5.3}$

Table S3. Adsorption distribution coefficient (K_d) of tetracycline to selected natural geosorbents and carbonaceous materials, corresponding to an equilibrium aqueous phase concentration (C_w) of 0.01 mmol/L.

Adsorbent/conditions	K_d (L/kg)	Reference
montmorillonite	2.97×10^3	[17]
soil humic acid	1.32×10^3	[23]
coal humic acid	2.11×10^3	[23]
soil	7.42×10^2, 9.50×10^2,1.34×10^2	[30,34]
sediment	1.53×10^3,1.18×10^3,7.30×10^2	[30,36]
clays	7.40×10^1 , 1.71×10^2	[36]
aluminum hydrous oxides	2.67×10^2	[28]
iron hydrous oxides	3.32×10^2	[28]
SWNTs	5.45×10^4	[18]
MWNTs	1.08×10^4	[18]
graphite	8.61×10^2	[18]
nano-NiO	2.94×10^3	present study
bulk-NiO	1.31×10^3	present study
montmorillonite/0.25 mM Cu(II)	1.18×10^4	[17]
SWNTs/ 0.12 mM Cu(II)	6.03×10^4	[18]
MWNTs/0.12 mM Cu(II)	1.94×10^4	[18]
graphite/0.12 mM Cu(II)	1.00×10^3	[18]
nano-NiO/ 0.10 mM Cu(II)	1.60×10^4	present study
bulk-NiO/ 0.10 mM Cu(II)	1.99×10^4	present study

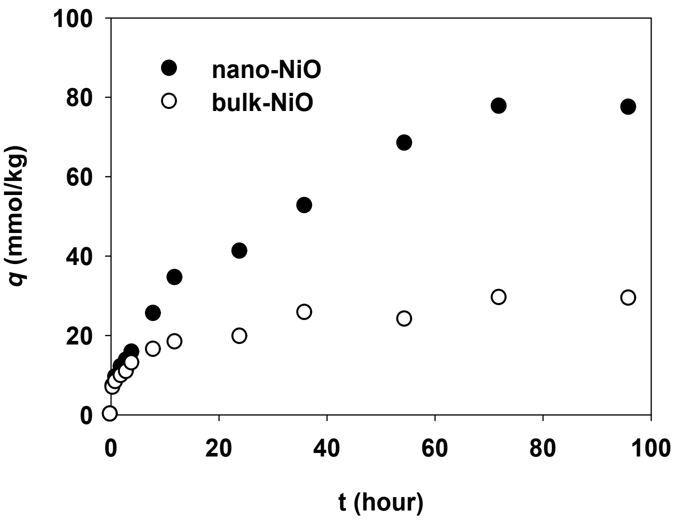

Fig. S1. Adsorption kinetic of tetracycline to nano-NiO and bulk-NiO under neutral pH, the initial spiked concentration of tetracycline was 0.11 mmol/L.

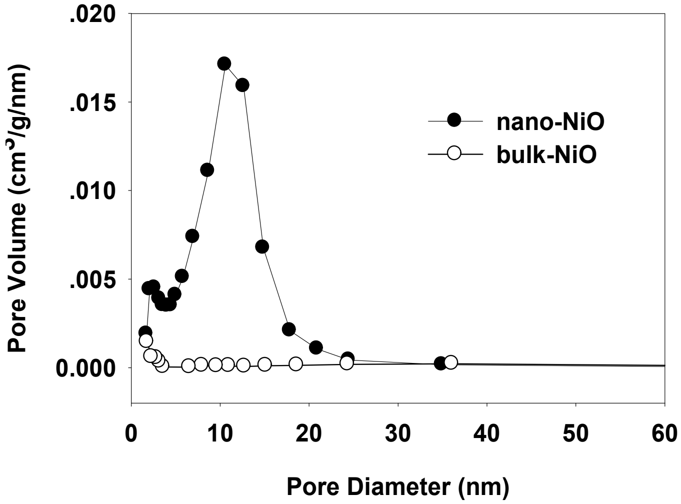

Fig. S2. Pore size distributions of nano-NiO and bulk-NiO measured by N_2 desorption.

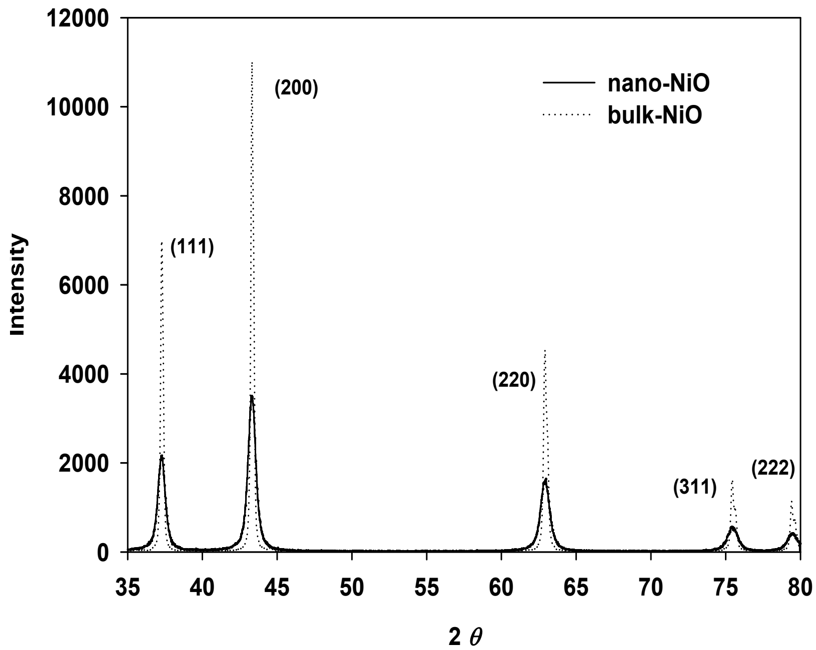

Fig. S3. X-ray diffraction data of nano-NiO and bulk NiO.

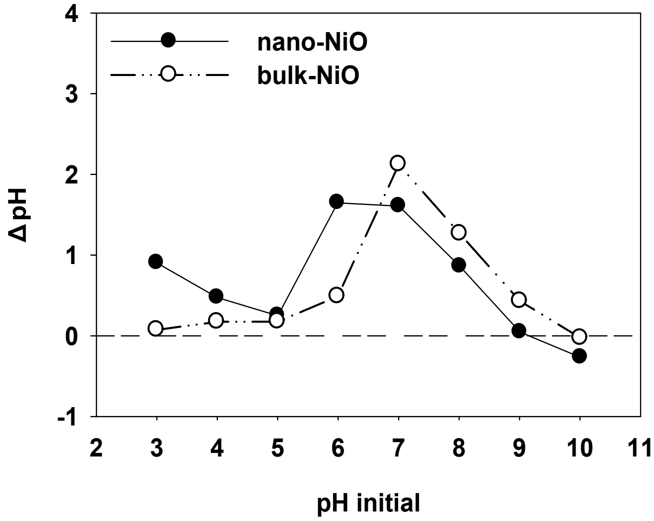

Fig. S4. ΔpH versus initial pH of nano-NiO and bulk-NiO suspensions.

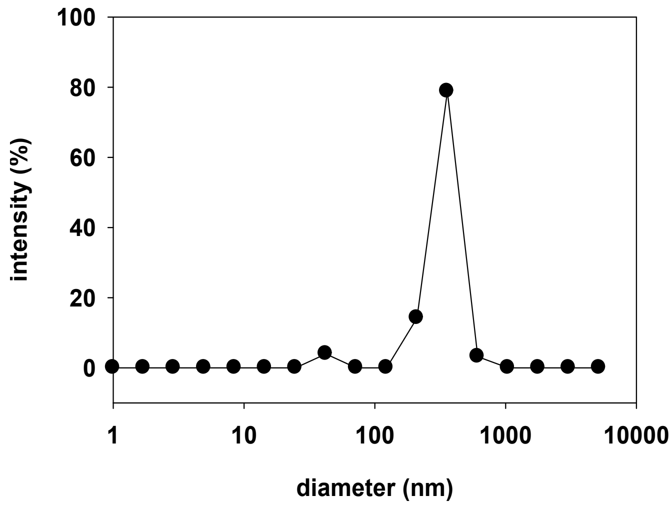

Fig. S5. Intensity-weighted particle size distribution of nano-NiO.

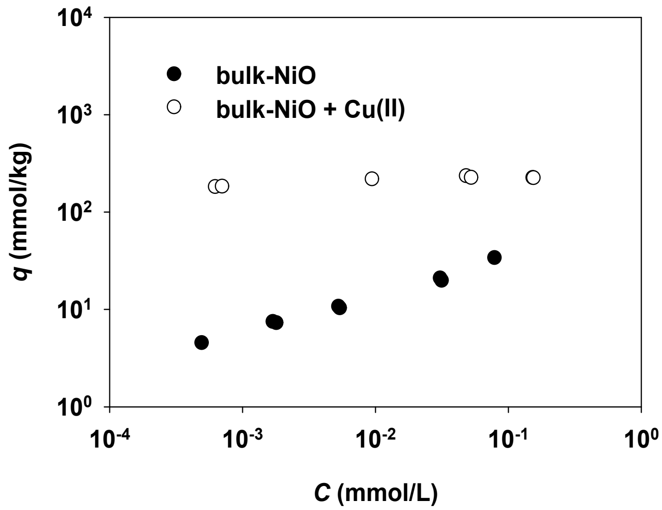

Fig. S6. Adsorption isotherms of tetracycline to bulk-NiO in the absence and presence of Cu(II) (initially at 0.1 mM).

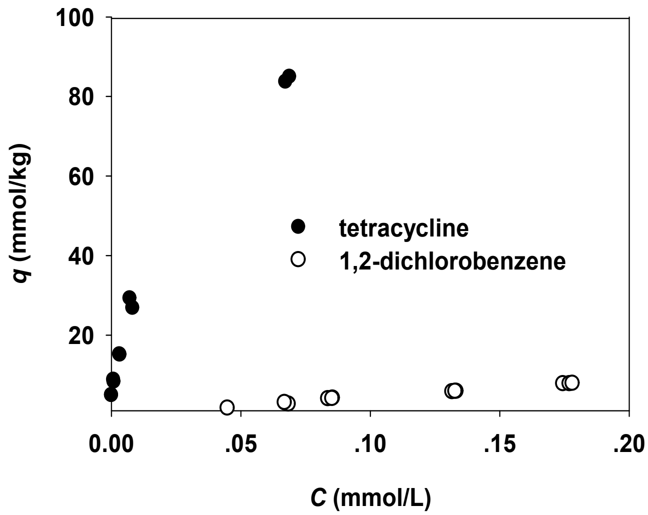

Fig. S7. Comparison of adsorption isotherms of tetracycline and 1,2-dichlorobenzene onto nano-NiO plotted as solid-phase concentration (*q*) versus aqueous-phase concentration (*C*).

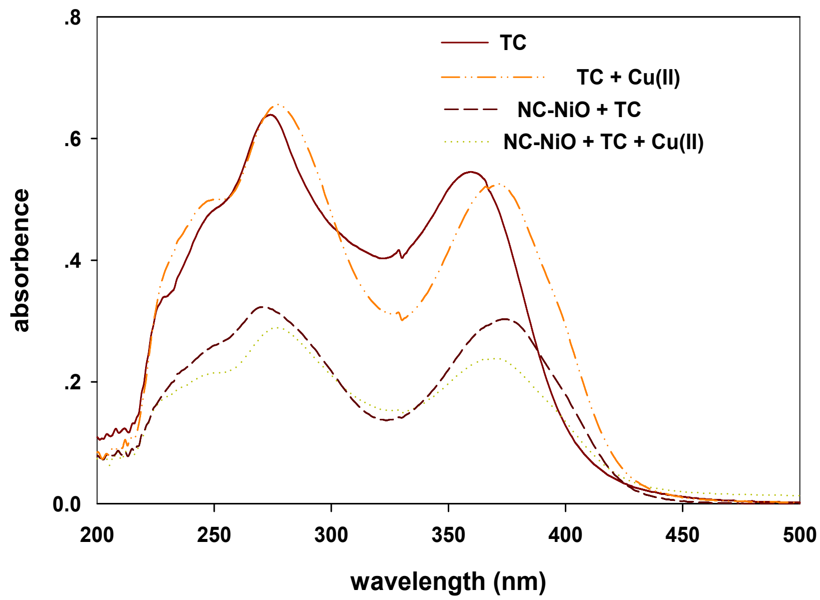

Fig. S8. UV spectra of an aqueous solution of tetracycline (0.2 mmol/L), an aqueous solution of tetracycline (0.2 mmol/L) and Cu(II) (0.05 mmol/L), an aqueous suspension of tetracycline (0.2 mmol/L) and nano-NiO (0.5 g/L), and an aqueous suspension of tetracycline (0.2 mmol/L), Cu(II) (0.05 mmol/L) and nano-NiO (0.5 g/L) (spectra were obtained under neutral initial pH; solutions/suspensions were pre-equilibrated for 24 h before UV measurement).

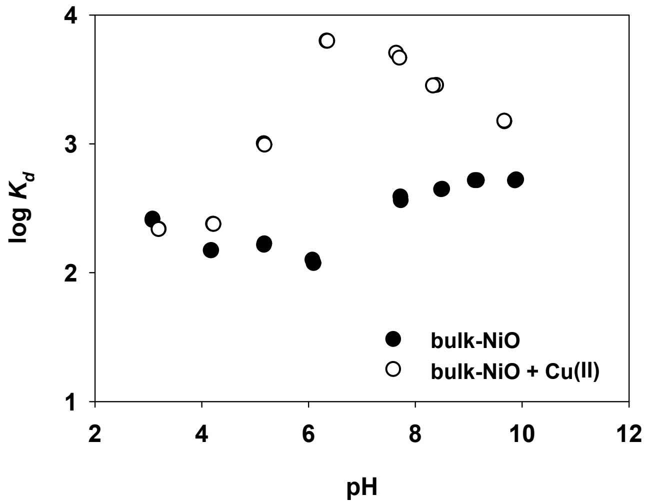

Fig. S9. Adsorption affinity of tetracycline to bulk-NiO (indicated by the distribution coefficient, K_d) as a function of pH (at adsorption equilibrium) in the absence and presence of Cu(II) (initially at 0.1 mM). The initial concentration of tetracycline is 0.1 mM..

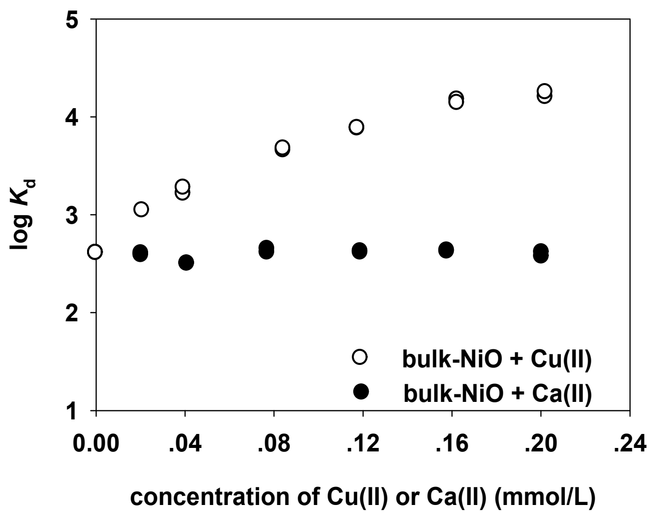

Fig. S10. Effects of Cu(II) and Ca(II) on the distribution coefficient (K_d) of tetracycline to bulk-NiO under neutral pH. The x-axis shows the initial concentrations of Cu(II) or Ca(II).