

SUPPORTING INFORMATION

Comparison of nitrilotriacetic acid and [S,S]-ethylenediamine-N,N'-disuccinic acid in UV-Fenton for the treatment of oil sands process-affected water at natural pH

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Figures: 9

Tables: 3

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Cyclic voltammetry:

Platinum electrode, silver chloride electrode, and glassy carbon electrode were used as counter, reference, and working electrodes, respectively. The electrolyte used in this study was 0.1 M NaCl. Scan rate was 1.2 V/s. The buffer solutions used in this part of the research were Tris buffer at pH 7 (a mixture of 0.1 M Tris solution and 0.1 M HCl), and borate buffers at pHs 8 and 9 (a mixture of 0.05 M sodium tetraborate solution and 0.1 M HCl).

Nitrilotriacetic acid (NTA) measurement:

NTA in the form of Fe-NTA was measured using a HPLC-UV instrument (Agilent Technologies, 1260 Infinity) at 254 nm with a C18 column of 5 μ m, 250 mm \times 4.6 mm, from Phenomenex. The mobile phase consisted of 0.03 M sodium acetate/0.002 M tetrabutylammonium bromide/5% methanol. The pH of the solution was adjusted to 2.78 using acetic acid. Flow rate was 0.8 mL/min.

Ethylenediamine-N,N'-disuccinic acid (EDDS) measurement:

The analyses were performed with a mobile phase of a 10/90% mixture of methanol and formate buffer (2 mM tetrabutylammonium hydrogen sulfate and 15 mM sodium formate) at a flow rate of 0.8 mL/min. The pH of the sodium formate solution was adjusted to 4 using formic acid. The detection of EDDS in the form of Fe-EDDS was performed by UV absorbance at a wavelength of 240 nm.

Metal ion measurement:

The metal ion measurements were conducted using an ICP-MS instrument (Perkin Elmer's Elan 6000). The instrument conditions were set at: ICP RF power of 1300 W; dual detector mode; subtract blank after internal standard correction; measurement units in cps (counts per second); auto lens on; and Bi, Sc and In used as internal standards. The running conditions were: flow rate

of 1 mL/min; and 35 sweeps/reading, 1 reading/replicate and 3 replicates, dwell times were 10 ms for Na, Al, K, Cu, Zn and Sr, and the others were 20 ms except Se (150 ms). The integration time were dwell time times number sweeps (35 in this case), i.e. 350 ms for Al, K, Cu, Zn and Sr, 5250 ms for Se, and 700 ms for the others. The final results were the average of 3 replicates. The instrument conditions were: 4 points calibration curves (0, 0.25, 0.50, 1.00 ppm for Na, Ca, Mg, Fe, K and P; and 0, 0.005, 0.010, 0.020 ppm for rest elements); typical count rates for 10 ppb Pb were 150000 cps to 200000 cps.

Fourier transform infrared (FT-IR) analysis:

The 25 mL samples for FT-IR analysis were filtered with 0.45 μ m nylon membrane filters. The pH of the samples was adjusted to 2.2. Then, the samples were extracted twice with 25 mL HPLC grade methylene chloride (DCM) and the extract was transferred to 50-mL glass tubes and evaporated to dryness. The residual in the tubes was reconstituted in 7 mL Optima grade DCM and injected into a KBr cell for analysis.

^1H nuclear magnetic resonance (NMR) analysis:

The organic matters in the samples were extracted by HPLC grade DCM and the extract was evaporated with dry air overnight to dryness. The extract was reconstituted in 1 mL deuterated DMSO and transferred into NMR tubes with 5 mm outside diameter for analysis. Parameters for the analysis were: ^1H resonance frequency: 399.950 MHz; pw30 (i.e., 30 degree pulse): 3.3 ms; acquisition time: 5s; spectral width: 10000Hz or 25 ppm; transmitter offset: 989.9; relaxation delay: 0.1 s. Data analysis was done using VNMRJ 4.2A software¹.

Naphthenic acids (NAs) quantification in UPLC TOF-MS:

The column used for the chromatographic separation was a Waters UPLC Phenyl BEH column (1.7 μ m, 150 mm \times 1 mm). Mobile phases were 10 mM ammonium acetate in water (A) and 10

mM ammonium acetate in 50/50 methanol/acetonitrile (B). Typically, the raw OSPW was injected and analyzed for quality control. The injection solution (1 mL) contained 0.5 mL sample, 0.1 mL of 4.0 mg/L internal standard (myristic acid-1-¹³C) in methanol and 0.4 mL methanol. A high-resolution time-of-flight mass spectrometer (Synapt G2, Waters, Milford, MA, USA) was used to analyze samples with the electrospray ionization (ESI) working at negative ion mode and TOF analyzer at high-resolution mode. Masslynx (Waters) and Targetlynx (Waters, Milford, MA, USA) were used to process data acquisition and data extraction from spectra, respectively. The quantification of each NA species was based on its empirical formula $C_nH_{2n+2}O_x$ ($x=2, 3, 4$) and was done by comparing its peak area with that of the internal standard. The chromatographic conditions were: 0-2 min, 1% B; 2-3 min, B increased from 1% to 60%; 3-7 min, B increased to 70%; 7-13 min, 95% B; 13-14 min, B decreased to 1% and was maintained at 1% to 20 min to equilibrate the column with a flow rate of 100 μ L/min. The temperature of the column was set at 50 °C and the sample was kept at 10 °C.

Toxicity towards *Vibrio fischeri*:

The toxicity (% inhibition effect) of the samples was calculated based on the change of the luminescence intensity. Reagent without inhibitors was used as a negative control to acquire the correction factor.

Table S1. Characterization of Oil Sands Process-Affected Water (OSPW).⁷⁻¹²

Parameter	Range
pH	8.3-8.7
Turbidity (NTU)	71.6-213.3
Conductivity ($\mu\text{S}/\text{cm}$)	3459-4500
Total suspended solids (TSS) (mg/L)	97-221
Total dissolved solids (TDS) (mg/L)	2477-2859
Zeta potential (mV)	(-40.0)-(-41.3)
Alkalinity (mg/L as CaCO_3)	609.3-776.9
Chloride (mg/L)	641.0-715.7
Sulfate (mg/L)	274.7-602.6
Sodium (mg/L)	840.6-846.7
Potassium (mg/L)	14.7-17.0
Magnesium (mg/L)	8.6-15.1
Calcium (mg/L)	10.1-25.3
Organic Parameters	
Chemical oxygen demand (COD) (mg/L)	204-302
Total organic carbon (TOC) (mg/L)	48.3-75.0
Biochemical oxygen demand (BOD_5) (mg/L)	2.7-3.30
UV_{254} (cm^{-1})	0.476 \pm 0.512
Naphthenic acids (NAs) (mg/L)	8.92-39.2
Acid extractable fraction (AEF) (mg/L)	48.5-64.2
BTEX (benzene, toluene, ethyl benzene, and xylenes) (mg/L)	<0.01
PAHs (polyaromatic hydrocarbons) (mg/L)	0.01
Phenols (mg/L)	0.008-1.8

Table S1 (concluded).

Trace Metals	Range
Silicon (mg/L)	6.95±0.13
Aluminum (µg/L)	7.66±0.24
Vanadium (µg/L)	8.84±0.62
Chromium (µg/L)	19.29±0.31
Manganese (µg/L)	2.74±1.02
Cobalt (µg/L)	2.13±0.05
Nickel (µg/L)	7.40±0.48
Copper (µg/L)	30.12±4.51
Zinc (µg/L)	1.34±0.15
Arsenic (µg/L)	6.05±0.19
Selenium (µg/L)	11.69±0.35
Strontium (mg/L)	0.67±0.01
Molybdenum (mg/L)	0.19±0.01
Cadmium (µg/L)	0.31±0.02
Antimony (µg/L)	2.76±0.09
Barium (µg/L)	63.67±1.02
Lead (µg/L)	0.10±0.01
Uranium (µg/L)	6.99±0.14
Titanium (mg/L)	0.09±0.03
Gallium (mg/L)	0.001±0.000
Iron (mg/L)	1.0±0.0

Table S2. Metal ions in the OSPW used in this study and the stability constants (log K) of metal-NTA/EDDS.

Metal ion	Conc. (mg/L)	log K for metal-EDDS	log K for metal-NTA
Li	0.18	-	2.50* ²
B	1.78	-	-
Na	600	-	1.20* ²
Mg	25.10	6.09 ³⁻⁵	5.24 ⁶ , 5.41 ⁷
Al	0.0076	16.27 for Al(III) ⁸	13.70* for Al(III) ⁹
Si	3.38	-	-
K	29.00	-	-
Ca	41.4	4.72 ³⁻⁵	6.40* ^{2, 7}
Ti	0.010	-	-
V	0.0089	-	-
Cr	0.014	-	7.10* ²
Fe	< Detection limit	20.60 for Fe(III) ¹⁰	15.90* for Fe(III), ¹¹⁻¹³ 8.80* for Fe(II) ²
Mn	0.0015	8.95 ³⁻⁵	7.40* ²
Co	0.0017	14.02 ^{3, 4, 14}	11.70* ⁹ , 10.30* ²
Ni	0.0089	18.02 ^{3, 4, 14}	12.80* ⁹ , 11.50* ²
Cu	0.0098	18.45 ^{3, 4, 15}	14.20* ⁹ , 13.10* ²
As	0.0038	-	-
Rb	0.036	-	0.10* ²
Sr	1.09	3.37 ³⁻⁵	6.16* ¹⁶
Zr	0.0019	-	-
Nb	0.00038	-	-
Mo	0.088	-	-
Ru	0.00006	-	-
Cd	0.00014	10.80 ³⁻⁵	9.83 ⁷
Sn	0.00085	-	-
Sb	0.0032	-	-
Cs	0.00022	-	-
Ba	0.14	3.10 ³⁻⁵	4.80* ²
Hf	0.0011	-	-
Ta	0.00058	-	-
W	0.0070	-	-
Pb	0.0001	12.70* ³⁻⁵	12.10 ¹⁷
Th	0.0024	-	16.90* for Th(IV) ²
U	0.010	-	-

Note: values refer to 20 °C except values marked*, which are at 25 °C. Values without valence notification are for divalent metal ions.

Table S3. NA distributions in the OSPW.

-z	c-NAs (%)	Carbon number	c-NAs (%)
0	2.7	9	0.04
2	2.4	10	0.5
4	25.9	11	1.5
6	21.9	12	5.1
8	5.8	13	12.8
10	7.1	14	17.1
12	14.1	15	14.7
14	8.8	16	14.2
16	7.6	17	11.6
18	3.7	18	10.6
		19	6.3
		20	3.6
		21	1.4
		22	0.5

Note: c-NAs: classical NAs.



Figure S1. Medium-pressure UV lamp apparatus.

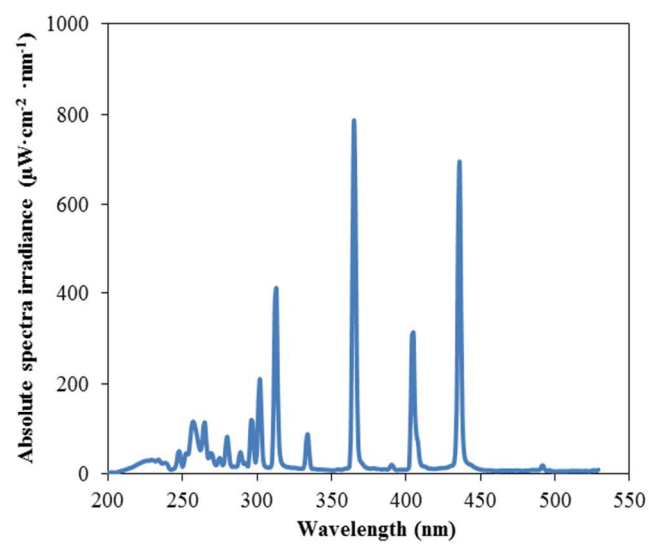


Figure S2. Absolute spectrum irradiance of the MP lamp.

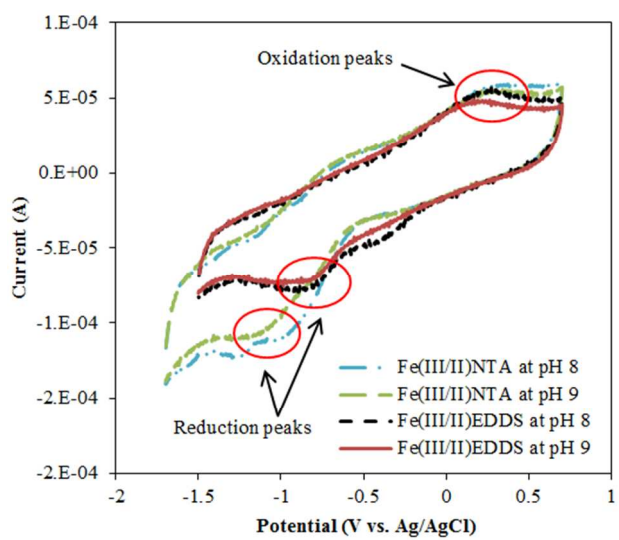


Figure S3. Cyclic voltammograms of Fe(III/II)NTA and Fe(III/II)EDDS at pHs 8 and 9 ($[\text{Fe}]_0 = 1 \text{ mM}$ and $[\text{NTA}]_0 = [\text{EDDS}]_0 = 2 \text{ mM}$).

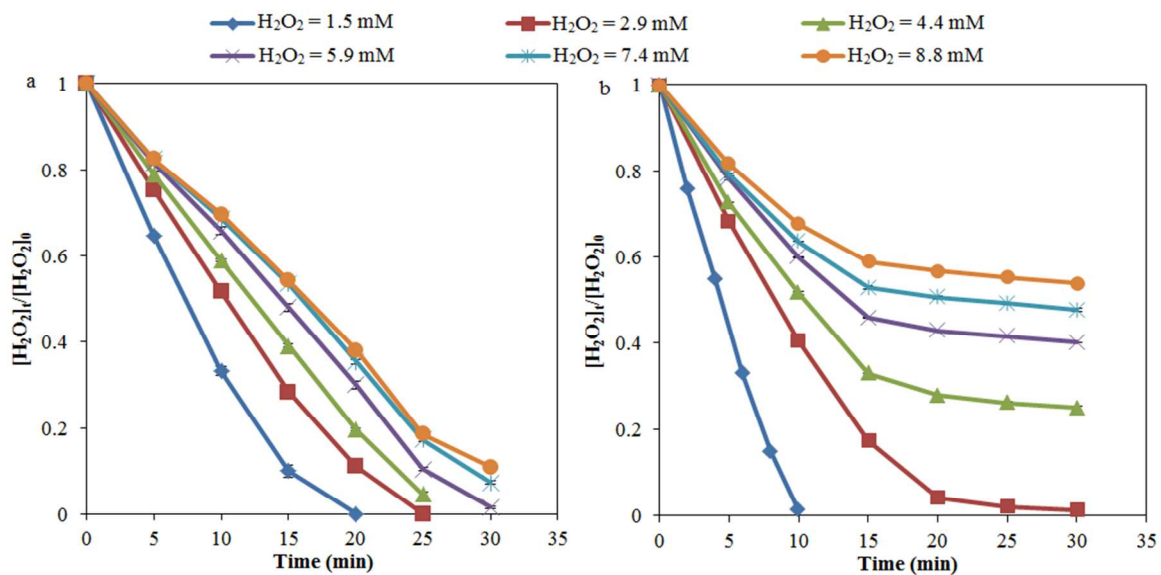


Figure S4. H_2O_2 decomposition in the treatment of OSPW by a) UV-NTA-Fenton process and b) UV-EDDS-Fenton process ($[\text{Fe}]_0 = 0.089 \text{ mM}$, $[\text{NTA}]_0 = [\text{EDDS}]_0 = 0.72 \text{ mM}$, and 30 min UV irradiation).

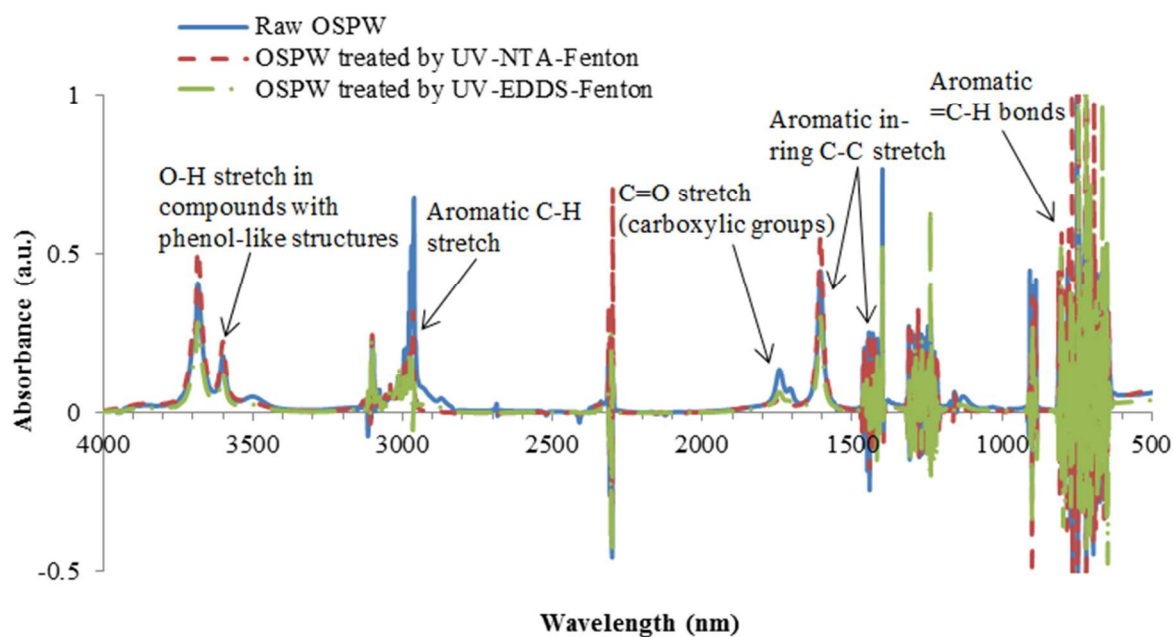


Figure S5. FT-IR spectra of the raw OSPW and OSPW treated by UV-NTA/EDDS-Fenton processes ($[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$ and 4.4 mM for UV-NTA-Fenton and UV-EDDS-Fenton, respectively. $[\text{Fe}]_0 = 0.089 \text{ mM}$, $[\text{NTA}]_0 = [\text{EDDS}]_0 = 0.72 \text{ mM}$, and 30 min UV irradiation).

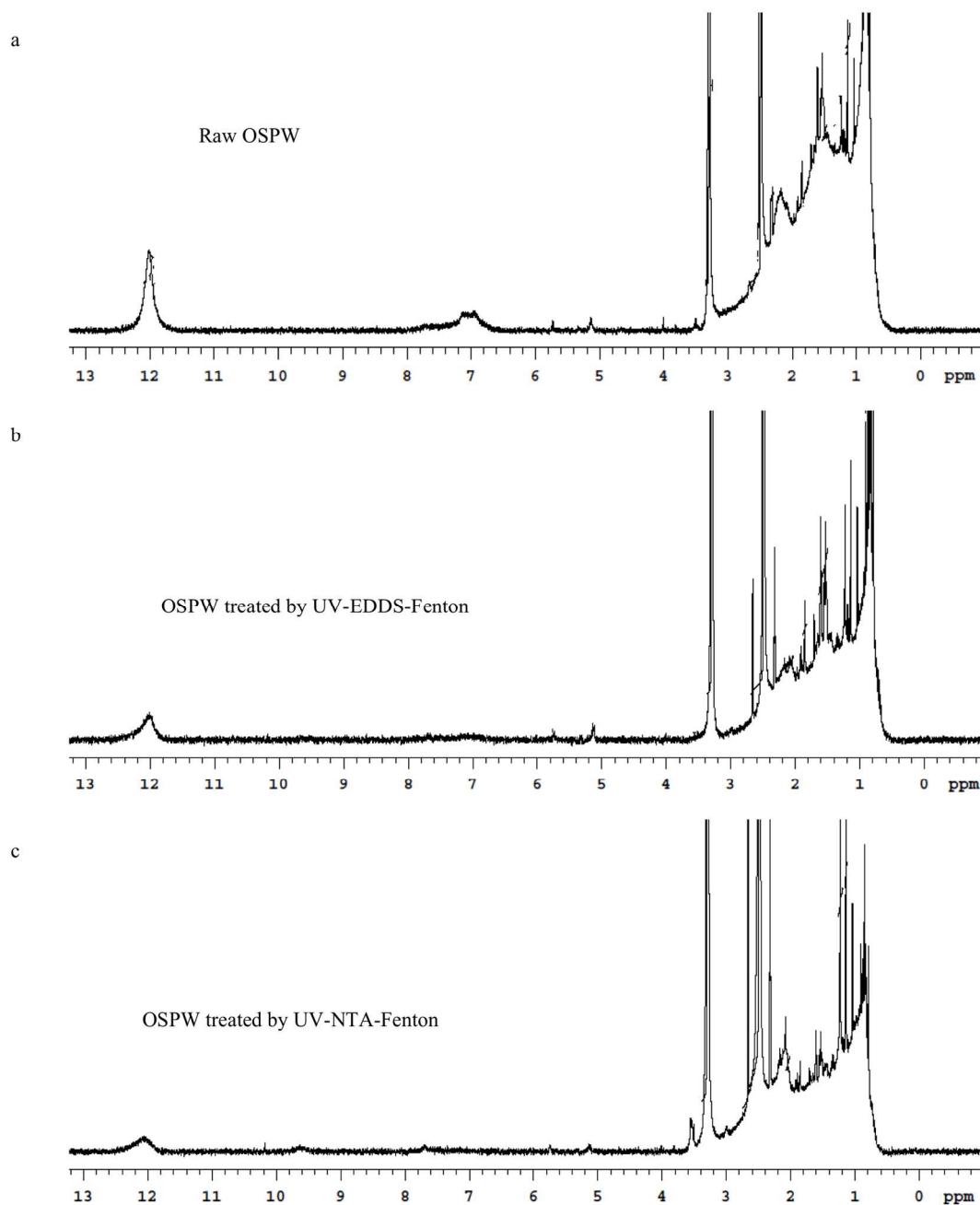


Figure S6. ^1H NMR spectra for a) raw OSPW, b) OSPW treated with the UV-EDDS-Fenton process, and c) OSPW treated with the UV-NTA-Fenton process ($[\text{H}_2\text{O}_2]_0 = 5.88$ mM and 4.41 mM for the UV-NTA-Fenton and UV-EDDS-Fenton processes, respectively. $[\text{Fe}]_0 = 0.089$ mM and $[\text{NTA}]_0 = [\text{EDDS}]_0 = 0.72$ mM, and 30 min UV irradiation) (the values above the peaks are the relative peak area with the peak of the internal standard DMSO set as 100).

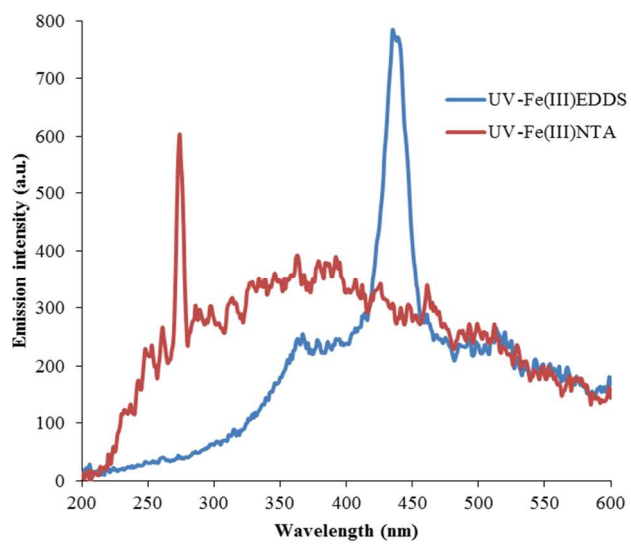


Figure S7. SFS of UV irradiated Fe(III)NTA/EDDS in MilliQ water ($[\text{Fe}]_0 = 0.089 \text{ mM}$, $[\text{NTA}]_0 = [\text{EDDS}]_0 = 0.72 \text{ mM}$, and 30 min UV irradiation).

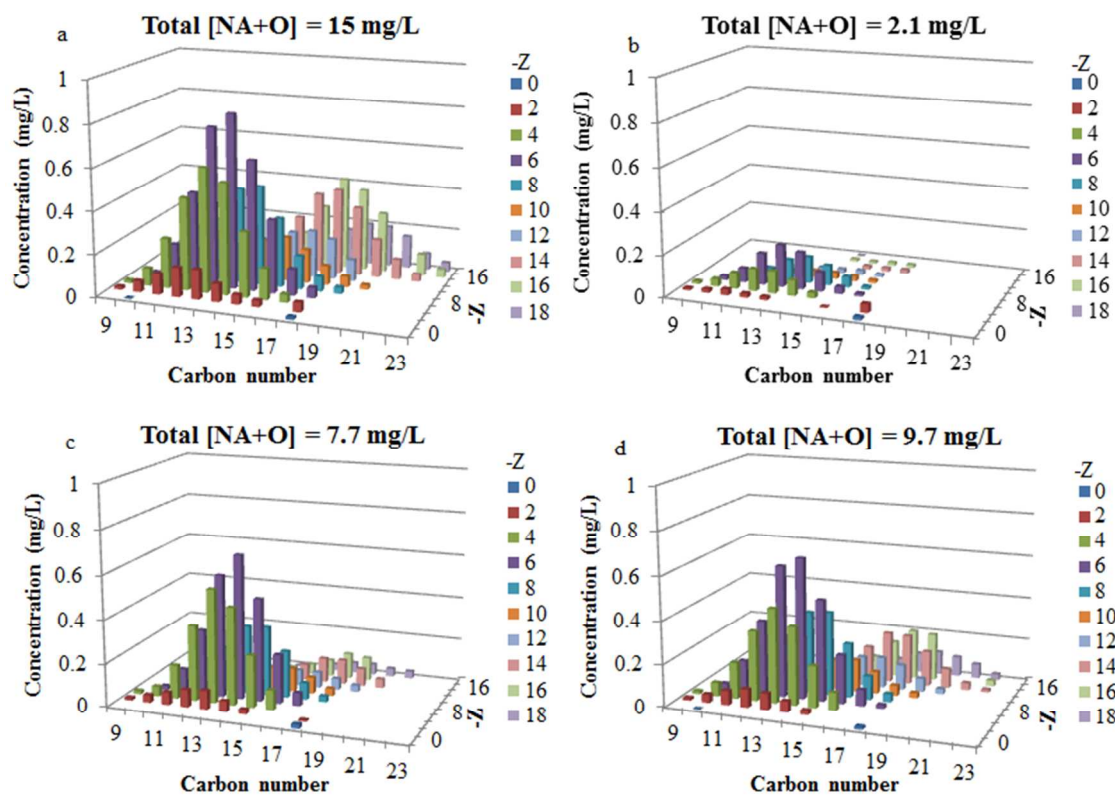


Figure S8. NAs+O distribution in a) the raw OSPW, b) OSPW treated by UV-NTA-Fenton ($[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$, $[\text{Fe}]_0 = 0.089 \text{ mM}$, $[\text{NTA}]_0 = 0.72 \text{ mM}$, and 30 min UV irradiation), c) OSPW treated by UV- H_2O_2 ($[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$), and d) OSPW treated by NTA-Fenton ($[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$, $[\text{Fe}]_0 = 0.089 \text{ mM}$, $[\text{NTA}]_0 = 0.72 \text{ mM}$, and 30 min UV irradiation).

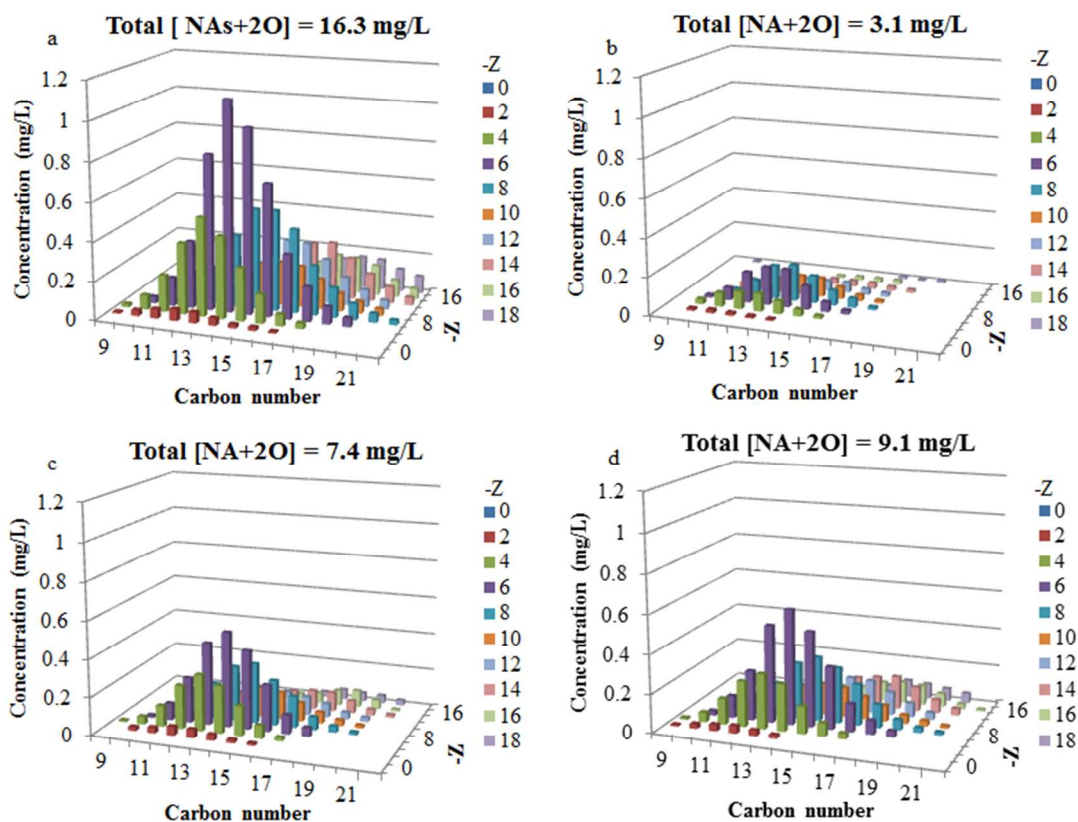


Figure S9. NAs+2O distribution in a) the raw OSPW, b) OSPW treated by UV-NTA-Fenton ($[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$, $[\text{Fe}]_0 = 0.089 \text{ mM}$, $[\text{NTA}]_0 = 0.72 \text{ mM}$, and 30 min UV irradiation), c) OSPW treated by UV- H_2O_2 ($[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$), and d) OSPW treated by NTA-Fenton ($[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$, $[\text{Fe}]_0 = 0.089 \text{ mM}$, $[\text{NTA}]_0 = 0.72 \text{ mM}$, and 30 min UV irradiation).

References

1. Wang, C.; Klammerth, N.; Huang, R.; Elnakar, H.; Gamal El-Din, M., Oxidation of Oil Sand Process-affected Water by Potassium Ferrate (VI). *Environ. Sci. Technol.* **2016**.
2. Smith, R. M.; Martell, A. E., Critical stability constants, enthalpies and entropies for the formation of metal complexes of aminopolycarboxylic acids and carboxylic acids. *Sci. Total. Environ.* **1987**, *64*, (1-2), 125-147.
3. Whitburn, J. S.; Wilkinson, S. D.; Williams, D. R., Chemical speciation of ethylenediamine-N, N' -disuccinic acid (EDDS) and its metal complexes in solution. *Chem. Spec. Bioavailab.* **1999**, *11*, (3), 85-93.
4. Martell, A. E.; Smith, R. M., *Critical stability constants*. Plenum Press: New York, 1974-1989; Vol. 1-6.
5. Majer, J.; Jokl, V.; Dvorakova, E.; Juracova, M., New complexones. XIII. Potentiometric and electrophoretic study of ethylenediamine-N, N' -disuccinic acid and its metal chelates. *Chem Zvesti* **1968**, *22*, 415-423.
6. Tomita, Y.; Ando, T.; Ueno, K., Infrared Spectra of Nitrilotriacetate Chelates in Aqueous Solution. *J. Phys. Chem.* **1965**, *69*, (2), 404-407.
7. Sunda, W. G.; Engel, D. W.; Thuotte, R. M., Effect of chemical speciation on toxicity of cadmium to grass shrimp, *Palaemonetes pugio*: importance of free cadmium ion. *Environ. Sci. Technol.* **1978**, *12*, (4), 409-413.
8. Tolkacheva, L.; Saprunova, T.; Nikolskii, V.; Yakovlev, A., Environmentally friendly complexones. The thermodynamic characteristics of the formation of Al^{3+} ion complexes with ethylenediaminedisuccinic acid in aqueous solutions. *Chem. J. Mold.*, **2012**, *7*, (1), 70-73.
9. Bolton, H.; Girvin, D. C.; Plymale, A. E.; Harvey, S. D.; Workman, D. J., Degradation of metal-nitrilotriacetate complexes by *Chelatobacter heintzii*. *Environ. Sci. Technol.* **1996**, *30*, (3), 931-938.
10. Orama, M.; Hyvönen, H.; Saarinen, H.; Aksela, R., Complexation of [S, S] and mixed stereoisomers of N, N' -ethylenediaminedisuccinic acid (EDDS) with Fe (III), Cu (II), Zn (II) and Mn (II) ions in aqueous solution. *J. Chem. Soc., Dalton Trans.* **2002**, (24), 4644-4648.
11. Cuculić, V.; Pižeta, I.; Branica, M., Voltammetry of Dissolved Iron (III)–Nitrilotriacetate–Hydroxide System in Water Solution. *Electroanalysis* **2005**, *17*, (23), 2129-2136.
12. Andrianirinaravelo, S. L.; Pilichowski, J. F.; Bolte, M., Nitrilotriacetic acid transformation photo-induced by complexation with iron (III) in aqueous solution. *Transition Met. Chem.* **1993**, *18*, (1), 37-41.
13. Anderegg, G., The stability of iron (III) complexes formed below pH= 3 with glycinate, iminodiacetate, β -hydroxyethyliminodiacetate, N, N-di-(Hydroxyethyl)-glycinate, nitrilotriacetate and triethanolamine. *Inorg. Chim. Acta* **1986**, *121*, (2), 229-231.
14. Majer, J.; Springer, V.; Kopecka, B., New complexones. VIII. Ethylenediamino-N, N' -disuccinic acid and investigation of its heavy metal complexes by spectrophotometry. *Chem. Zvesti* **1966**, *20*, 414-422.
15. Gorelova, R.; Babich, V.; Gorelov, I., Potentiometric study of copper complex formation with ethylenediaminedisuccinic and ethylenediaminetetraacetic acids. *ZHURNAL NEORGANICHESKOI KHIMII* **1971**, *16*, (7), 1873-&.
16. Chowdhury, M. J.; Blust, R., Bioavailability of waterborne strontium to the common carp, *Cyprinus carpio*, in complexing environments. *Aquat Toxicol* **2002**, *58*, (3), 215-227.

17. Krishnan, K. A.; Sheela, A.; Anirudhan, T., Kinetic and equilibrium modeling of liquid - phase adsorption of lead and lead chelates on activated carbons. *J. Chem. Technol. Biot.* **2003**, 78, (6), 642-653.