Electronic Supplemental Information (ESI): Removal of estrogenic compounds via iron electrocoagulation: removal mechanisms and impact of water quality

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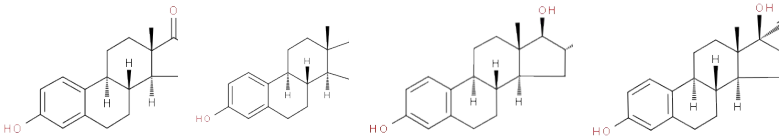
S1: Physical-chemical properties of estrogenic compounds

Table S1. Physical-chemical properties of estrogenic steroids

Property	Estrone (E1)	17β-Estradiol (E2)	Estriol (E3)	17α-Ethynylestradiol (EE2)
Molecular Formula	$C_{18}H_{22}O_2$	$C_{18}H_{24}O_2$	$C_{18}H_{24}O_3$	$C_{20}H_{24}O_2$
CAS No.	53-16-7	50-28-2	50-27-1	57-63-6
Structure[1]				
Type	Natural	Natural	Natural	Synthetic
Molecular Weight (g mol^{-1})[2]	270.4	272.4	288.4	296.403
Log K_{OW} [2]	3.43	3.94	2.81	4.15
pKa [3]	10.5-10.7	10.3-10.8	10.3-10.8	10.4 [4]
Water Solubility[2]	13	13	13	4.8
Henry's Law Constant (atm m^3 mol^{-1})[5]	3.8×10^{-10}	3.64×10^{-11}	1.33×10^{-12}	7.94×10^{-12}
Vapor Pressure[2]	2.3×10^{-10}	2.3×10^{-10}	6.7×10^{-15}	4.5×10^{-11}

S2: X-Ray Diffraction Patterns

X-ray diffraction (XRD) patterns of the ferric and ferrous flocs were obtained using a Bruker D8 Discover A25 diffractometer with a copper Kα radiation to determine their crystalline phases. The XRD scans were recorded from 2θ of 10º - 70º using a step size of 0.02º and a count time of 0.4 s per step.

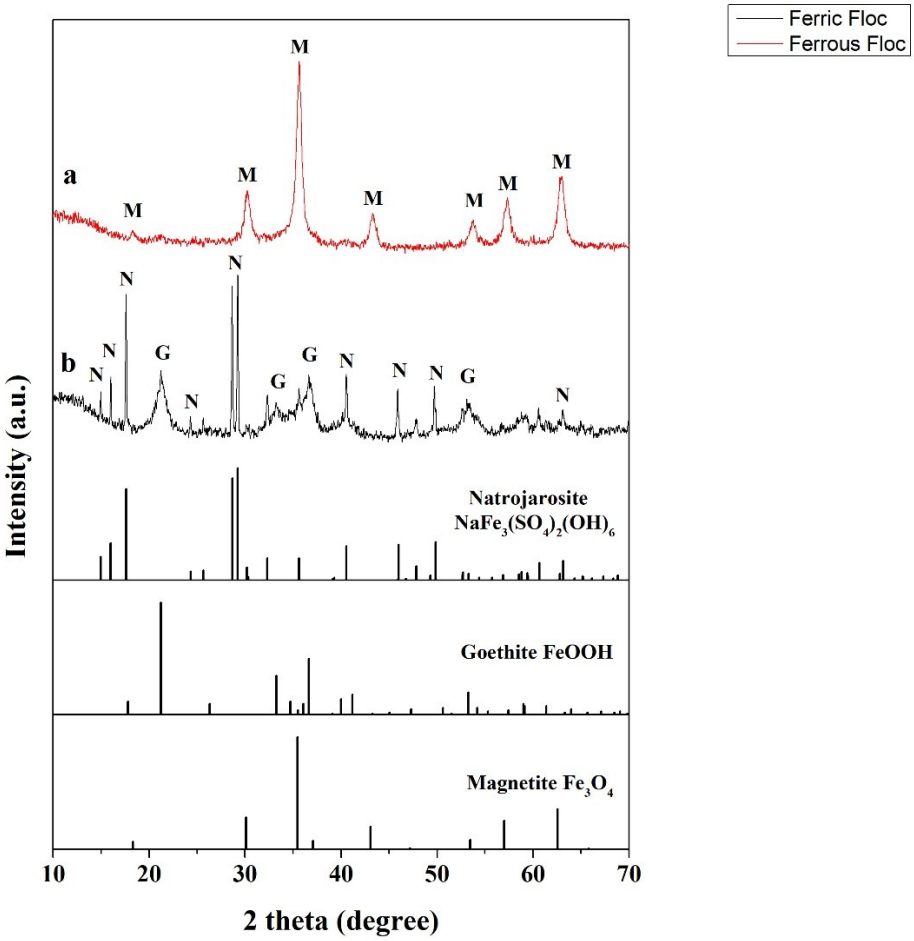


Figure S1. XRD patterns of iron flocs produced from conventional coagulation jar tests using (a) $FeSO_4$ and (b) $Fe_2(SO_4)_3$. The reference patterns for goethite (G, 29-0713), magnetite (M, 65-3107), and natrojarosite (N, 51-1567) are included for comparison.

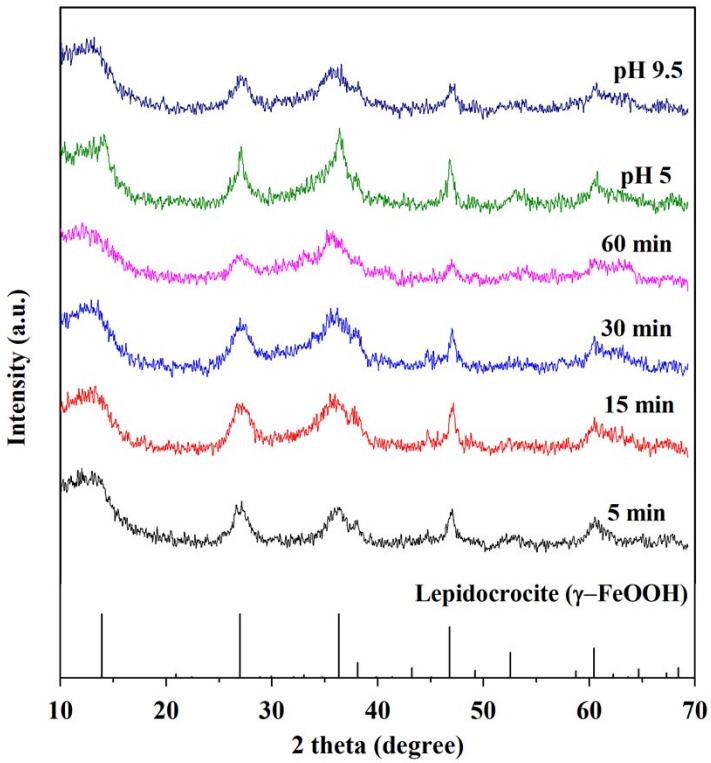


Figure S2. XRD patterns of iron floc produced at different pH values and electrocoagulation times. The reference pattern for lepidocrocite (01-0136) is included for comparison.

S3: Post-hoc Statistical Analysis P-values

Table S2. Post-hoc p-values with Fisher's LSD for Multiple Comparisons at Variable pH

Estradiol (E1)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
pH 5.5 vs. pH 7.0	-0.3738	-0.4897 to -0.2579	Yes	0.0002
pH 5.5 vs. pH 9.5	-0.7919	-0.9078 to -0.676	Yes	<0.0001
pH 7.0 vs. pH 9.5	-0.4181	-0.534 to -0.3022	Yes	0.0001
17β- Estradiol (E2)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
pH 5.5 vs. pH 7.0	-0.571	-0.6584 to -0.4835	Yes	<0.0001
pH 5.5 vs. pH 9.5	-0.9274	-1.015 to -0.8399	Yes	<0.0001
pH 7.0 vs. pH 9.5	-0.3564	-0.4439 to -0.2689	Yes	<0.0001
Estriol (E3)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
pH 5.5 vs. pH 7.0	-0.424	-0.5426 to -0.3053	Yes	0.0001
pH 5.5 vs. pH 9.5	-0.7667	-0.8854 to -0.648	Yes	<0.0001
pH 7.0 vs. pH 9.5	-0.3427	-0.4614 to -0.2241	Yes	0.0004
17α-Ethynylestradiol (EE2)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
pH 5.5 vs. pH 7.0	-0.1295	-0.1772 to -0.08182	Yes	0.0006
pH 5.5 vs. pH 9.5	0.2091	0.1614 to 0.2567	Yes	<0.0001
pH 7.0 vs. pH 9.5	0.3386	0.2909 to 0.3862	Yes	<0.0001

Table S3. Post-hoc p-values with Fisher's LSD for Multiple Comparisons at Variable Turbidities

Estradiol (E1)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
0.0 NTU vs. 2.0 NTU	0.1251	-0.02172 to 0.272	No	0.085
0.0 NTU vs. 60.0 NTU	-0.05162	-0.1985 to 0.09522	No	0.441
2.0 NTU vs. 60.0 NTU	-0.1768	-0.3127 to -0.0408	Yes	0.0171
17β- Estradiol (E2)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
0.0 NTU vs. 2.0 NTU	0.321	0.1744 to 0.4676	Yes	0.001
0.0 NTU vs. 60.0 NTU	0.09973	-0.04685 to 0.2463	No	0.1553
2.0 NTU vs. 60.0 NTU	-0.2213	-0.357 to -0.08554	Yes	0.0055
17α-Ethynylestradiol (EE2)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
0.0 NTU vs. 2.0 NTU	0.2854	0.1568 to 0.4141	Yes	0.0009
0.0 NTU vs. 60.0 NTU	0.2728	0.1441 to 0.4015	Yes	0.0012
2.0 NTU vs. 60.0 NTU	-0.01262	-0.1318 to 0.1065	No	0.8131

Table S4. Post-hoc p-values with Fisher's LSD for Multiple Comparisons at Variable DOC Concentrations

17β- Estradiol (E2)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
0.0 vs. 0.5 mg L^{-1}	-0.117	-0.4257 to 0.1918	No	0.4078
0.0 vs. 15.0 mg L^{-1}	0.3051	-0.00363 to 0.6139	No	0.0522
0.5 vs. 15.0 mg L^{-1}	0.4221	0.1362 to 0.708	Yes	0.0093

Table S5. Post-hoc p-values for Fisher's LSD for Multiple Comparisons with EC vs Conventional Coagulation

Estradiol (E1)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
EC with Iron vs. CC - Ferric	0.9123	0.6593 to 1.165	Yes	<0.0001
EC with Iron vs. CC - Ferrous	0.6917	0.4387 to 0.9447	Yes	0.0001
CC - Ferric vs. CC - Ferrous	-0.2205	-0.4735 to 0.03248	No	0.0808
17β- Estradiol (E2)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
EC with Iron vs. CC - Ferric	0.9149	0.6642 to 1.166	Yes	<0.0001
EC with Iron vs. CC - Ferrous	0.6829	0.4322 to 0.9336	Yes	0.0001
CC - Ferric vs. CC - Ferrous	-0.232	-0.4827 to 0.01872	No	0.0662
Estriol (E3)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
EC with Iron vs. CC - Ferric	0.7493	0.5818 to 0.9167	Yes	<0.0001
EC with Iron vs. CC - Ferrous	0.6917	0.5242 to 0.8592	Yes	<0.0001
CC - Ferric vs. CC - Ferrous	-0.05757	-0.225 to 0.1099	No	0.4614
17α-Ethynylestradiol (EE2)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
EC with Iron vs. CC - Ferric	0.7493	0.5818 to 0.9167	Yes	<0.0001
EC with Iron vs. CC - Ferrous	0.6917	0.5242 to 0.8592	Yes	<0.0001
CC - Ferric vs. CC - Ferrous	-0.05757	-0.225 to 0.1099	No	0.4614

Table S6. Post-hoc p-values for Fisher's LSD for Multiple Comparisons for EC and Oxidant Scavenging Tests

Estradiol (E1)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
EC Only vs. EC with t-BuOH	0.1824	0.01885 to 0.346	Yes	0.0342
EC Only vs. EC with MeOH	0.3384	0.1749 to 0.502	Yes	0.0023
EC with t-BuOH vs. EC with MeOH	0.156	-0.00752 to 0.3196	No	0.0583
17β- Estradiol (E2)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
EC Only vs. EC with t-BuOH	0.38	0.2492 to 0.5107	Yes	0.0004
EC Only vs. EC with MeOH	0.5553	0.4246 to 0.6861	Yes	<0.0001
EC with t-BuOH vs. EC with MeOH	0.1754	0.04461 to 0.3061	Yes	0.0168
Estriol (E3)				
Fisher's LSD	Mean Diff.	95.00% CI of diff.	Significant?	P Value
EC Only vs. EC with t-BuOH	0.225	0.04136 to 0.4086	Yes	0.0241
EC Only vs. EC with MeOH	0.487	0.3034 to 0.6706	Yes	0.0006
EC with t-BuOH vs. EC with MeOH	0.262	0.07836 to 0.4456	Yes	0.013

*EE2 was removed below the detection limit.

S4: Ultrasonic Assisted Extraction

Table S7.

		Estradiol (E1)	17β-Estradiol (E2)	Estriol (E3)	17α-Ethynylestradiol (EE2)
LOD (µg L-1)		27	3	3	13
LOQ (µg L-1)		107	14	14	51
Initial Concentration (µg L^{-1})		460	440	469	452
Final Concentration (µg L^{-1})		N.D.	<14	<14	<51
Percent Removal (%)		100	98	98	97
Spiked Sample* (µg L-1)	1	130	80	87	65
	2	121	87	94	69
	3	138	96	101	77
Unspiked Sample (µg L-1)	1	N.D.	<14	<14	N.D.
	2	N.D.	<14	<14	N.D.
	3	N.D.	<14	<14	N.D.
Average Percent Recovery (%)		137	116	126	108
Standard Deviation		19	9	8	7

*Spiked concentration were 68 µg L-1 for E1, 69 µg L-1 for E2 and E3, and 65 µg L-1 for EE2.

N.D. = Non-detect

S5: Oxidation

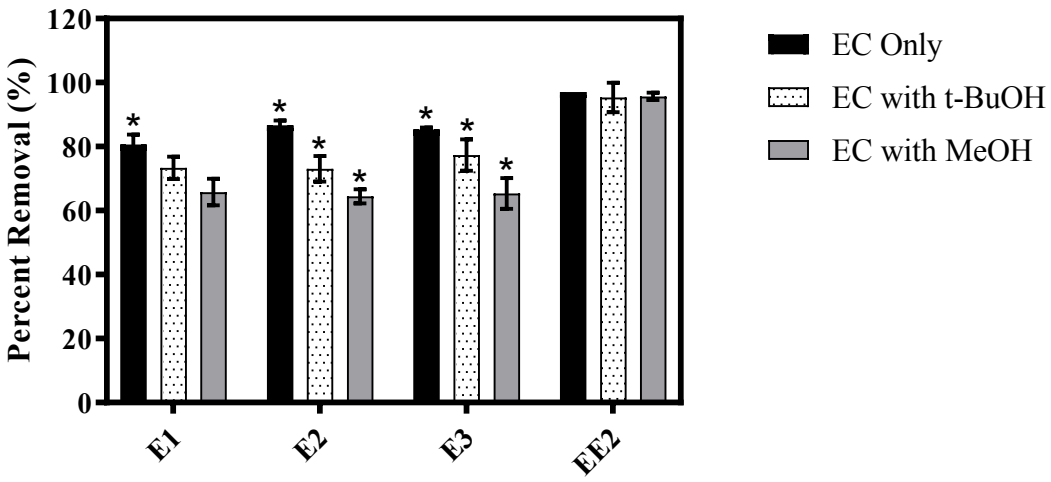


Figure S3. Removal of E1, E2, E3, and EE2 for an EC test with iron electrodes (n=3) compared to a test with oxidant scavengers of 0.25 M t-BuOH (n=3) or 0.95 M MeOH (n=3). E1, E2, and E3 were significantly different for all tests (p-values < 0.007). There was no significant difference for EE2 (p-value =0.77). The error bars represent the standard error of the mean. Asterisks indicate significant difference between all other conditions within a single estrogenic compound. Bars indicate difference between specific conditions.

Table S8. EE2 dosed EC reactor results for transformation to E1, E2, and E3

		E1		E2		E3		EE2	
Test	Time (min.)	Area	S/N* Ratio	Area	S/N Ratio	Area	S/N Ratio	Area	S/N Ratio
1	0	N.P.	N.P.	N.P.	N.P.	N.P.	N.P.	290053	140.19
	5	4675	3.6	N.P.	N.P.	N.P.	N.P.	223636	123.24
	120	12701	3.98	N.P.	N.P.	N.P.	N.P.	N.P.	N.P.
2	0	N.P.	N.P.	N.P.	N.P.	N.P.	N.P.	286970	137.65
	5	9614	3.72	N.P.	N.P.	N.P.	N.P.	246019	119.68
	120	12719	4.89	N.P.	N.P.	N.P.	N.P.	N.P.	N.P.

N.P. = No peak

S/N Ratio = signal-to-noise ratio

*S/N Ratio ≥ 3.0 sample is detectable; S/N Ratio ≥ 10.0 sample is quantifiable.

Data indicate that E1 was formed from oxidation of EE2

Table S9. E2 dosed EC reactor results for transformation to E1, EE2, and E3

Test	Time (min.)	E1 Area	E1 S/N* Ratio	E2 Area	E2 S/N Ratio	E3 Area	E3 S/N Ratio	EE2 Area	EE2 S/N Ratio
1	0	N.P.	N.P.	47574	118.9	N.P.	N.P.	N.P.	N.P.
	120	N.P.	N.P.	19042	25.62	1651	3.45	N.P.	N.P.
2	0	N.P.	N.P.	133863	318.1	N.P.	N.P.	N.P.	N.P.
	120	N.P.	N.P.	26517	5.1	8750	8.25	N.P.	N.P.

N.P. = No peak

S/N Ratio = signal-to-noise ratio

*S/N Ratio ≥ 3.0 sample is detectable; S/N Ratio ≥ 10.0 sample is quantifiable.

Data indicate that E3 was formed from oxidation of E2

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