Supplementary Material

Application of Plasma and UV/H_2O_2 for the Removal of Pharmaceuticals in Synthetic Urine

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Table S1: Physicochemical characteristics of the six target pharmaceuticals. References for rate constants can be found in figures 2, S1, and S2. Pharmaceutical structures and log K_{ow} values were found on pubchem. pKas were determined using the SPARC software.

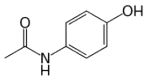
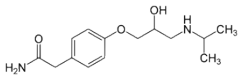
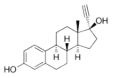
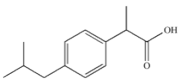
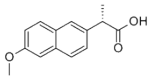
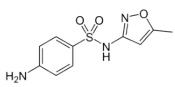
Compound	**Structure**	**pKa**	**log K_{ow}**	**$k_{OH\cdot,Pharm}$ [$M^{-1}s^{-1}$]**	**$k_{O_3,Pharm}$ [$M^{-1}s^{-1}$]**	**ϕ [mol Einstein^{-1}]**	**ε [m^2mol^{-1}]**	**$k_{OH\cdot,Pharm}$ / $k_{O_3,Pharm}$**
Acetaminophen		9.38	0.46	2.2E9	1.3E5	4.6E-2	742	1.7E4
Atenolol		9.60	0.16	8.0E9	1.7E3	3.6E-2	52.7	4.7E6
17α-ethinoestradiol		10.3	3.67	9.8E9	7.4E9	2.6E-2	75	5.4E6
Ibuprofen		5.30	3.97	7.4E9	9.6	8.6E-2	28.2	6.8E8
Naproxen		4.15	3.18	9.6E9	2.0E5	9.3E-3	490	4.8E4
Sulfamethoxazole		1.60; 5.70	0.89	6.3E9	2.5E6	2.1E-1	1189	2.5E3

Table S2: Recipes for fresh and hydrolyzed synthetic urine.

Chemical Formula	Molecular Weight (g mol^{-1})	Fresh Urine Concentration (mM)	Hydrolyzed Urine Concentration (mM)
$CaCl_2 \cdot H_2O$	129.98	5.0	
$MgCl_2 \cdot 6H_2O$	203.21	3.2	
NaCl	58.44	79	60
Na_2SO_4	142.04	16	15
$Na_3C_6H_8O_7 \cdot 2H_2O$	297.09	2.2	
$Na_2C_2O_4$	134.00	0.15	
NaH_2PO_4	119.98		14
KH_2PO_4	139.06	21	
KCl	74.55	21	40
NH_4Cl	53.49	19	
NH_4OH	35.04		250
NH_4HCO_3	79.06		250
$CO(NH_2)_2$	60.06	420	
$C_4H_7N_3O$	113.12	9.7	

Table S3: Synthetic urine characteristics.

Parameter	*Unit*	*Fresh Urine*	*Hydrolyzed Urine*
pH	-	5.6	9.6
Conductivity	$mS \cdot cm^{-1}$	16	36
UV Transmittance	%	0.03	75
Alkalinity	$meq \cdot L^{-1}$	22	490

Table S4: Target pharmaceuticals. with accurate mass and retention times used for quantification. Acceptable peaks ranged plus or minus 30 seconds from the retention times listed depending on the matrix sampled.

Compound	Formula	Accurate Mass (m/z)	Retention Time (min)	ESI Mode
Acetaminophen	C8H9NO2	152.07060	5.25	Positive
d3-Acetaminophen	C8H6D3NO2	155.08943	5.22	Positive
Atenolol	C14H22N2O3	267.17031	4.92	Positive
d7-atenolol	C14H15D7N2O3	274.21425	4.88	Positive
17α-ethinoestradiol	C20H24O2	279.17434	10.96	Positive
d4-17α-ethinoestradiol	C20H20D4O2	283.19944	10.95	Positive
Ibuprofen	C13H18O2	205.12231	11.61	Positive
d3-ibuprofen	C13H15D3O2	208.14241	11.60	Positive
Naproxen	C14H14O3	229.08592	10.64	Positive
d3-Naproxen	C14H11D3O3	232.10475	10.62	Positive
Sulfamethoxazole	C10H11N3O3S	254.05938	7.23	Positive
d4-sulfamethoxazole	C10H7D4N3O3S	258.08449	7.22	Positive

Table S5: Observed rate constants and for each pharmaceutical across several matrices. * denotes observed rate constants that were not statistically significantly non-zero.

	Observed Rate Constant (min^{-1})					
	Acetaminophen	**Atenolol**	**EE2**	**Ibuprofen**	**Naproxen**	**Sulfamethoxazole**
	UV/H_2O_2					
Nanopure Water	1.84E-04	1.25E-04	1.05E-04	1.17E-04	3.31E-04	6.75E-03
Hydrolyzed Urine	3.04E-04	9.67E-05	5.06E-04	1.06E-04	2.98E-04	1.31E-03
Fresh Urine	6.79E-06*	2.86E-06*	6.20E-06*	3.13E-06*	1.66E-05*	1.36E-04
	Plasma					
Nanopure Water	4.95E-04	9.72E-04	1.00E-03	1.46E-03	1.28E-03	7.44E-04
Hydrolyzed Urine	1.31E-04	1.50E-04	5.31E-04	3.79E-04	3.38E-04	7.68E-05
Fresh Urine	7.84E-05	7.98E-05	3.72E-04	2.64E-04	2.37E-04	1.27E-04

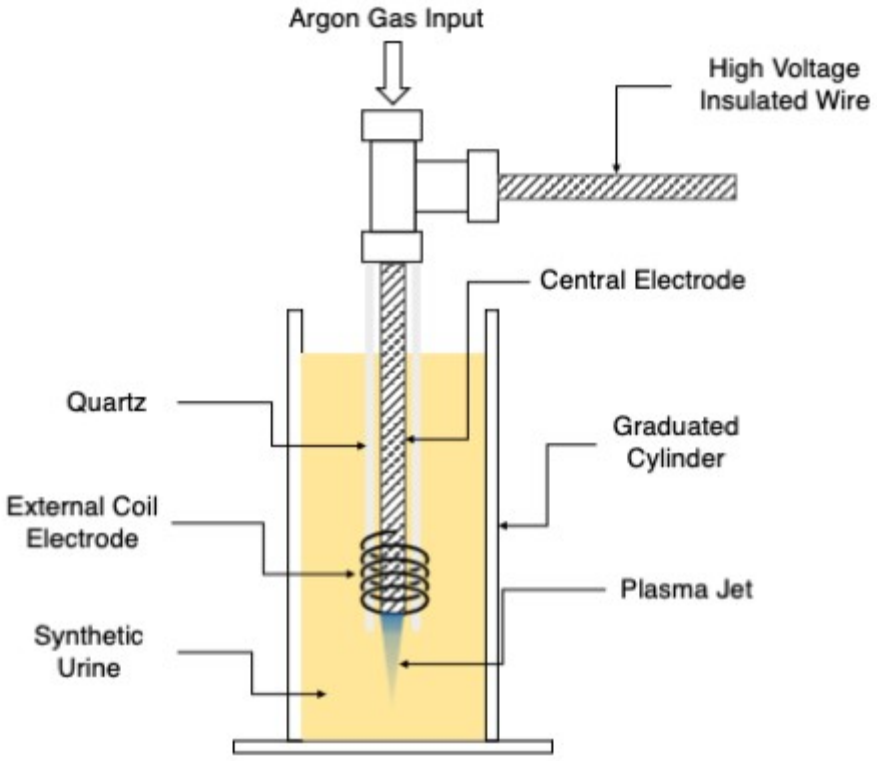


Figure S1: Plasma reactor schematic.

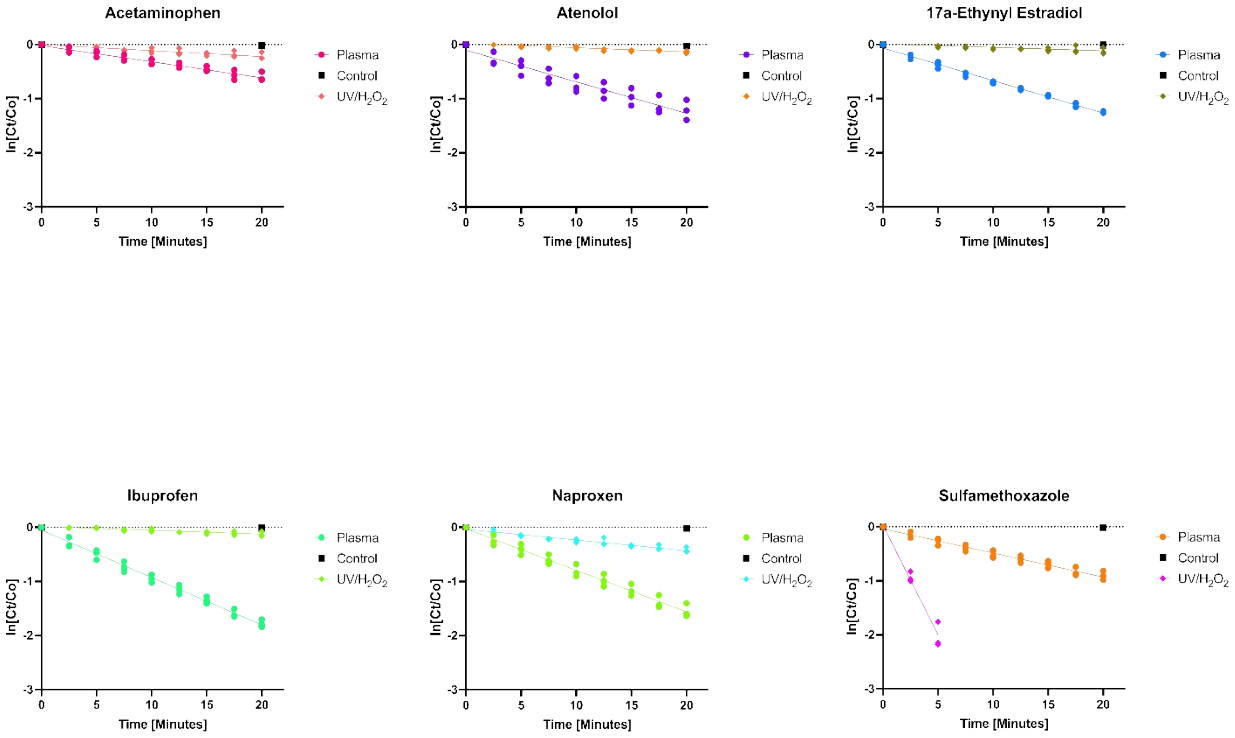


Figure S2: Degradation over time plots for each pharmaceutical in nanopure water undergoing treatment by plasma and UV/H_2O_2.

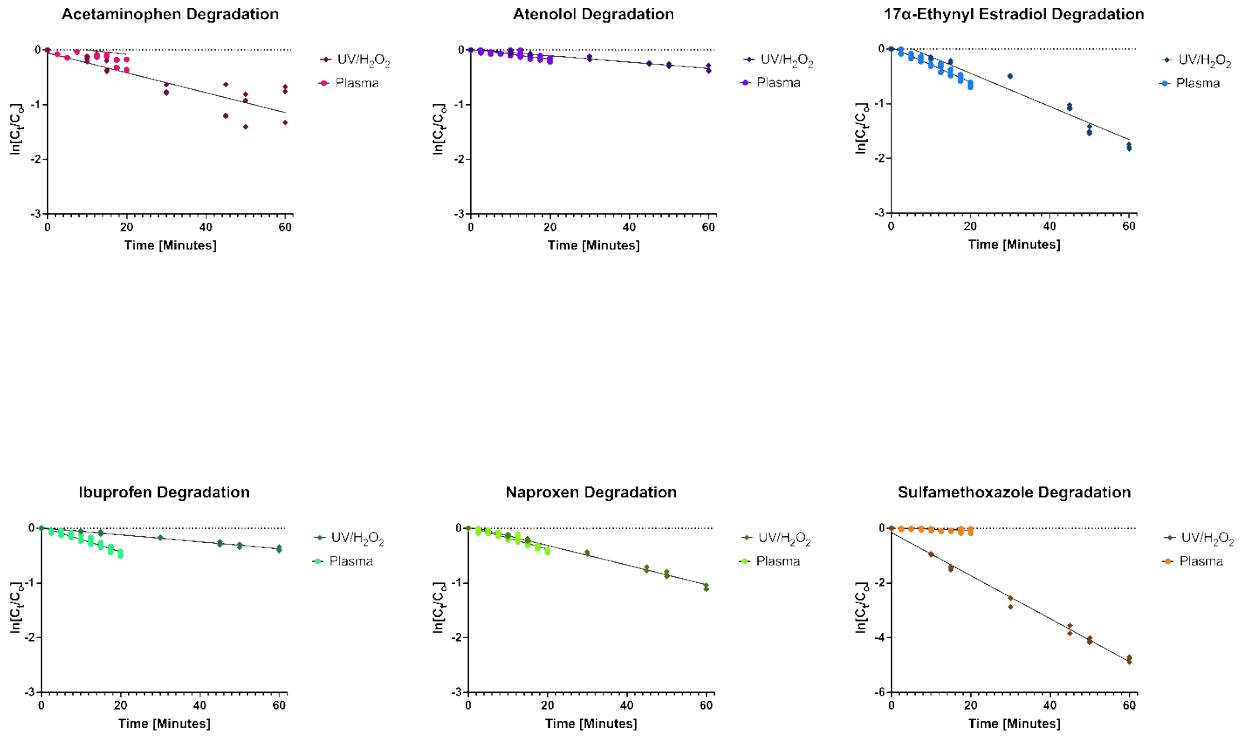


Figure S3: Degradation over time plots for each pharmaceutical in synthetic hydrolyzed urine undergoing treatment by plasma and UV/H_2O_2.

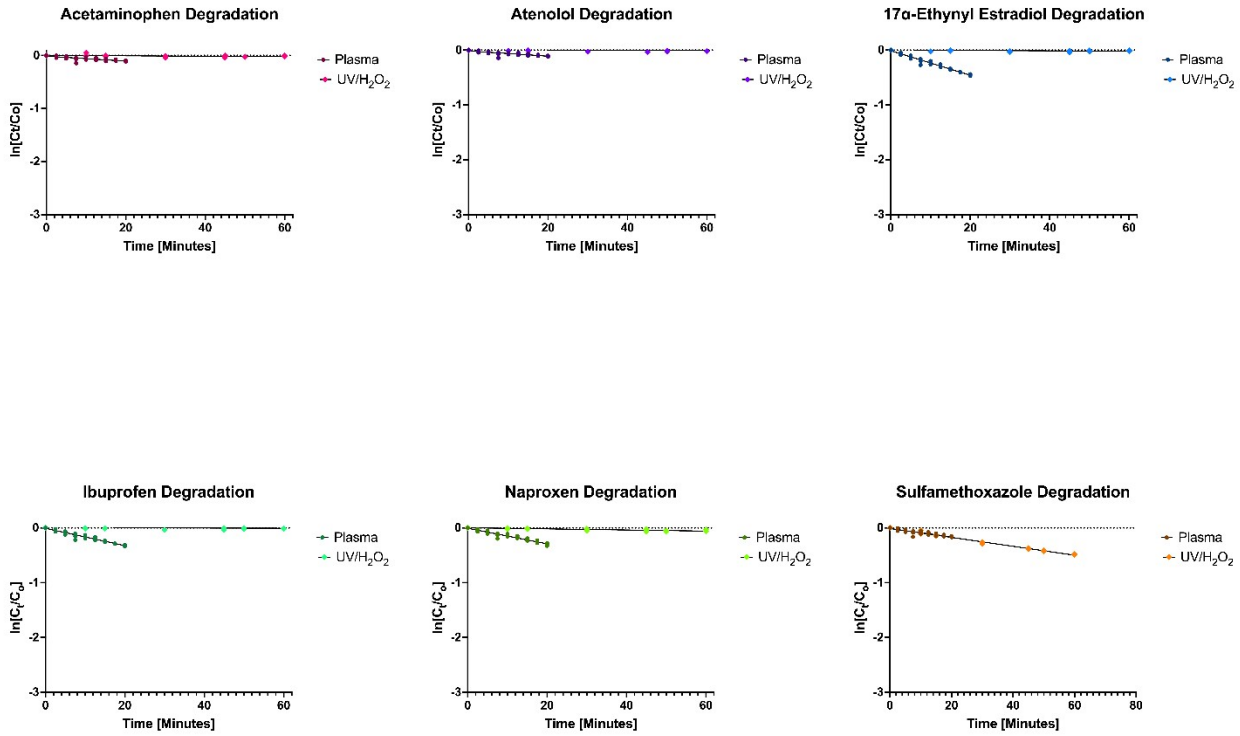


Figure S4: Degradation over time plots for each pharmaceutical in synthetic fresh urine undergoing treatment by plasma and UV/H_2O_2.

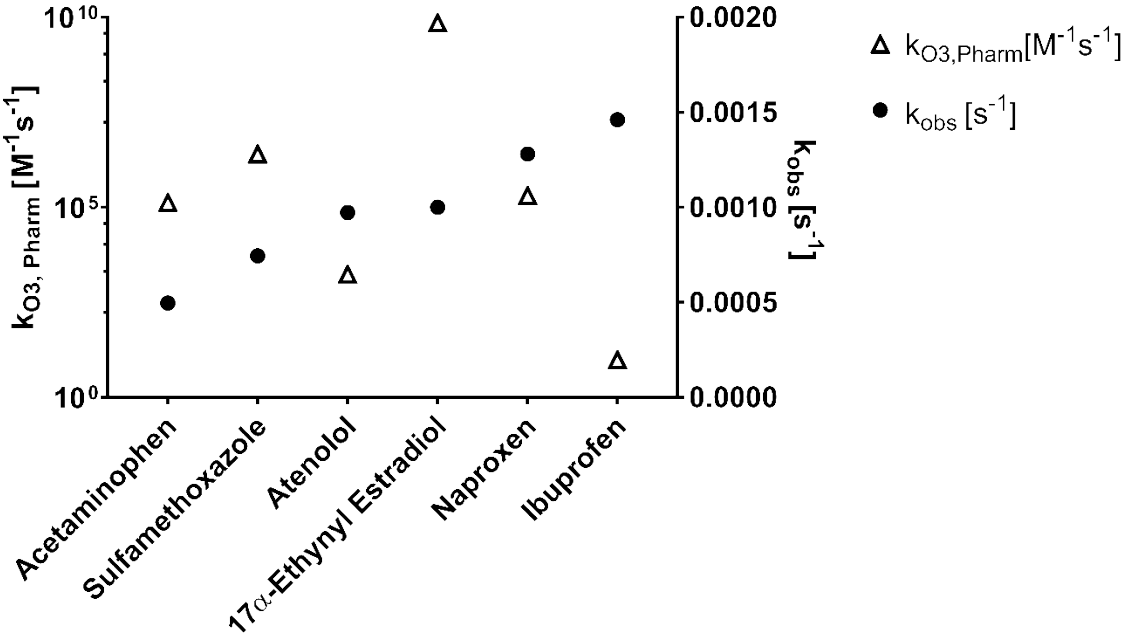


Figure S5: Second-order rate constants reported in the literature[1–4] for each pharmaceutical with ozone presented on the left y-axis. Values are presented using a log scale due to the large variation between each constant. Observed first-order rate constants for each pharmaceutical in nanopure water treated by plasma are presented on the right y-axis.

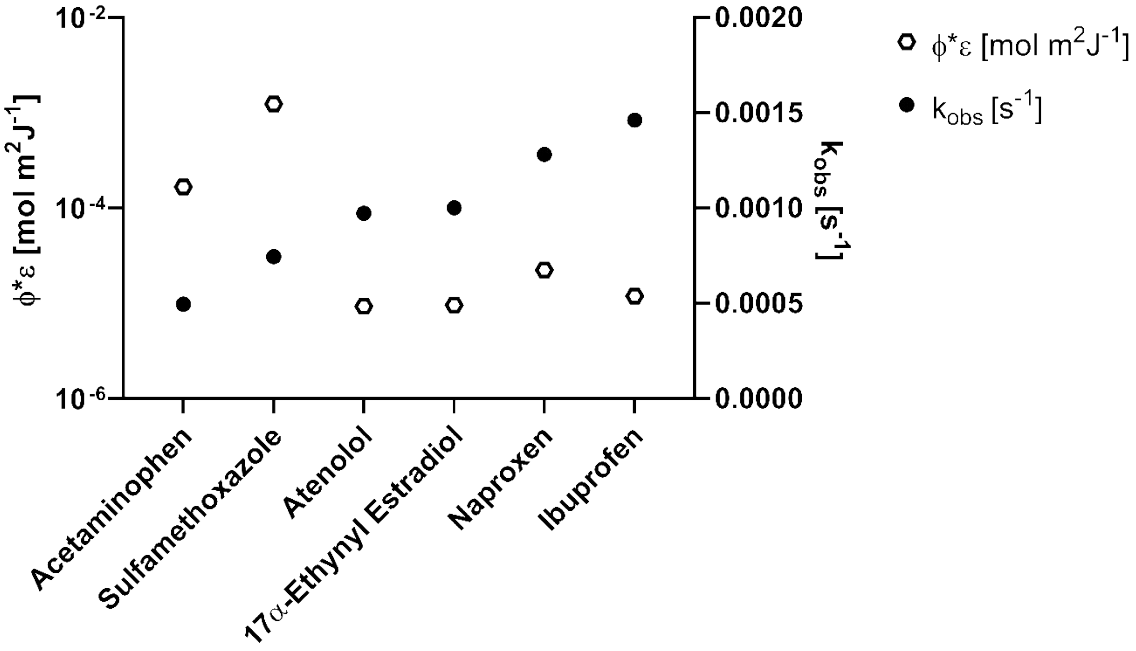


Figure S6: Susceptibility to direct photolysis is presented for each pharmaceutical by displaying the quantum yield (φ) multiplied by the molar extinction coefficient (ε).[5–7] The left y-axis is presented using a log scale to view the variability among constants. Observed first-order rate constants for each pharmaceutical in nanopure water treated by plasma are presented on the right y-axis.