SUPPLEMENTARY MATERIAL

Treatment of Antihypertensive and Cardiovascular Drugs in Supercritical Water: An Experimental and Modeled Approach

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Table of contents

1. Materials and methods....3
1.1 Physical-chemical characterization....3
1.2 Reference....3
2. Chemical compounds in the outflow....4
3. The feed operating conditions considered for thermodynamic analysis of ScW system. 5
4. Results of ANOVA....6

1. Materials and methods

1.1 Physical-chemical characterization

Samples were characterized before and after treatment. The Standard Methods for the Examination of Water and Wastewater (Baird et al., 2017) was used as guideline.

In the liquid phase, total organic carbon analysis was performed in a carbon analyzer, model TOC-L CSH (Shimadzu) using method 5310B. As calibration standard for organic carbon, a solution of potassium phthalate (1000 mgC/L) was used, while a solution of sodium carbonate and bicarbonate (1000 mgC/L) was used for inorganic carbon. Chemical oxygen demand (COD) analyzes were performed following method 5220D. For this, a closed reflux digestion was carried out and detection performed using a colorimeter, model DR-900 produced by Hach. Biochemistry oxygen demand (BOD) analyzes followed the method 5210B, which used an optical oximeter coupled to a multiparameter meter (model HQ40D, Hach) in a BOD incubator (Tecnal). Nitrite (4500-NO_2-B) and nitrate (4500-NO_3-B) determination were carried out using molecular absorption spectroscopy within the UV-Vis region, utilizing a Perkin Elmer model 365 spectrophotometer. Sulfate quantification was achieved through gravimetry, following the 4500-$SO_4$2-D method. pH analysis was carried out at 25°C using a Quimis model Q400MA pH meter. Metal analysis was performed using inductively coupled plasma optical emission spectrometry (ICP-OES), Perkin Elmer model 7300 DV instrument. A certified multi-element standard solution (1000 mg/L) from SpecSol was used for calibration, following the method 3120B. High-resolution mass spectrometry analyses were performed using an Exactive HCD Plus system equipped with an Ion Max API ionization source featuring a HESI probe (Heated Electrospray Ionization – HESI), by Thermo Scientific, Bremen, Germany. The instrument was operated in the mode of direct infusion at a flow rate of 15 μL/min. Sample solutions were prepared by diluting 5 μL of the sample into 1 mL of methanol. The analyses were performed in positive mode, with the following conditions: a spray voltage of 3.0 kV, vaporization region heating at 50 °C, capillary temperature set at 300 °C, sheath gas at 15 au, auxiliary gas at 5 au, and sweep gas at 5 au. Mass spectra were acquired within the m/z range of 150 to 800.

In the gaseous phase, determinations were performed using a gas chromatograph (GC) equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID), specifically the Perkin Elmer Clarus 580 GC model. The separation system is composed by a packed molsieve 13X 60/80 mesh column (1.83 m x 2 mm) and a HaySep 60/80 mesh column (1.83 m x 2 mm x 3.18 mm), both supplied by Perkin Elmer. The equipment was calibrated using a certified gas mixture, provided by White Martins, consisting of the following composition (v/v): H_2 (50.01%), CO_2 (2.04%), C_2H_4 (9.95%), C_2H_6 (10.02%), N_2 (21.11%), CH_4 (4.86%), and CO (2.01%). Analyses were conducted at 60 °C, employing argon as the carrier gas at a constant flow rate for a duration of 15 minutes.

1.2 Reference

Baird, R.B., Eaton, A.D., Rice, E.W., 2017. Standard Methods for the Examination of Water and Wasterwater, 23rd ed. American Public Health Association.

2. Chemical compounds in the outflow

Table S1. Considered compounds during simulations and their thermodynamic properties (POLING et al., 2001).

Compound	Chemical Formula	TC (K)a	PC (MPa)a	VC (m3/kmol)a	ω (−)a
Chloroform	$CHCl_3$	536.4	5.47	0.024	0.218
Methanol	CH_3OH	512.6	8.09	0.012	0.556
Acetonitrile	C_2H_3N	545.5	4.83	0.017	0.278
Water	H_2O	647.3	22.10	0.056	0.348
Hydrogen	H_2	33.0	1.30	0.064	0.000
Ethane	C_2H_6	305.4	4.82	0.148	0.105
Propane	C_3H_8	369.9	4.20	0.200	0.152
Ethylene	C_2H_4	283.1	5.05	0.124	0.073
Propylene	C_3H_6	369.9	4.54	0.182	0.143
Carbon monoxide	CO	133.0	3.50	0.093	0.041
Carbon dioxide	CO_2	304.2	7.39	0.094	0.420
Methane	CH_4	191.1	4.58	0.099	0.013
Ammonia	NH_3	405.6	11.35	0.072	0.250
Nitric oxide	NO	180.0	6.48	0.058	0.607
Nitrogen dioxide	NO_2	431.0	10.10	0.169	0.860
Nitrogen	N_2	126.2	3.39	0.086	0.040
Hydrogen chloride	HCl	324.7	8.31	0.081	0.133
Chlorine	Cl_2	416.9	7.99	0.124	0.090
Hydrogen peroxide	H_2O_2	728.0	22.00	0.073	0.359
Hydrogen sulfide	H_2S	373.2	8.94	0.099	0.081
Sulfuric acid	H_2SO_4	590.8	12.94	0.200	1.916
Sulfur oxide	SO_2	430.8	7.88	0.122	0.256
Sulfur trioxide	SO_3	490.9	8.21	0.127	0.481

3. The feed operating conditions considered for thermodynamic analysis of SCW system.

Table S2. Operational conditions used in the SCW thermodynamic analysis via Gibbs energy minimization [30].

Variable		Minimum	Maximum	Unit
Atenolol	$C_{14}H_{22}N_2O_3$	5	20	% wt
Captopril	$C_9H_{15}NO_3S$	5	20	% wt
Propranolol hydrochloride	$C_{16}H_{21}NO_2$	5	20	% wt
Trimetazidine	$C_{14}H_{22}N_2O_3$	5	20	% wt
Diosmin	$C_{28}H_{32}O_{15}$	5	20	% wt
Hesperidin	$C_{28}H_{34}O_{15}$	5	20	% wt
Losartan potassium	$C_{22}H_{23}ClN_6O$	5	20	% wt
Hydrochlorothiazide	$C_7H_8N_3ClO_4S_2$	5	20	% wt
Hydrogen peroxide	H_2O_2	10	10	% wt
Water	H_2O	70	85	% wt
Temperature	T	77	527	° C
Pressure	P	30	230	bar

4. Results of ANOVA

Table S3. Results of ANOVA table

Factor	Df	Sum Sq	Mean Sq	F valor	p-value
First-order	3	8710.4	2903.46	15.548	1.89×10^{-4}
Pure quadratic	3	3881.5	1293.86	6.928	0.0069
Lack-of-fit	8	2046.2	255.77	96.757	0.0015
Pure Error	3	7.9	2.64		
Total SS	11	2054.1	186.74		

Multiple R-squared: 0.8597, Adjusted R-squared: 0.7832, MS residual = 2055.13