



Spectroscopic (UV-vis and Fluorescence) and Chromatographic (HPLC) Studies of Pharmaceuticals in Nacogdoches Wastewater Treatment Plant

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1. Abstract

Pharmaceutical compounds are introduced into the environment and may pose adverse environmental and human health effects. The sources of pharmaceuticals include sewage, animal waste, and/or improper disposal from homes and hospitals. In this study, the spectroscopic, and chromatographic properties of carbamazepine (CBZ), diclofenac (DF), and ketoprofen (KT) were analyzed by using UV-Vis, fluorescence and HPLC. Via UV-VIS spectroscopy, CBZ, DF, and KT exhibited absorption peaks at 285 nm, 284 nm and 255.6 nm, respectively. The determined fluorescence quantum yield (Φ_f) for CBZ, DF, and KT were $\Phi_f = 0.226$, 0.287, and 0.327, respectively. Retention times was observed at 3.84 (CBZ), 4.84 (KT), and 9.84 (DF) min. The removal efficiencies is in the range 8.8% (KT) to 39.2% (CBZ). This study is useful for the quantitation of these pharmaceuticals in wastewater treatment plants and possible risks.

2. Objectives for study

- To determine concentration of carbamazepine, ketoprofen, diclofenac in wastewater treatment plants in east Texas via spectroscopic [FT-IR, UV-Vis, and Fluorescence] and chromatographic [HPLC] methods.
- To examine removal efficiencies of pharmaceuticals in WWTP.
- Provide data for health risk assessment

3. Nacogdoches Wastewater Treatment Plant

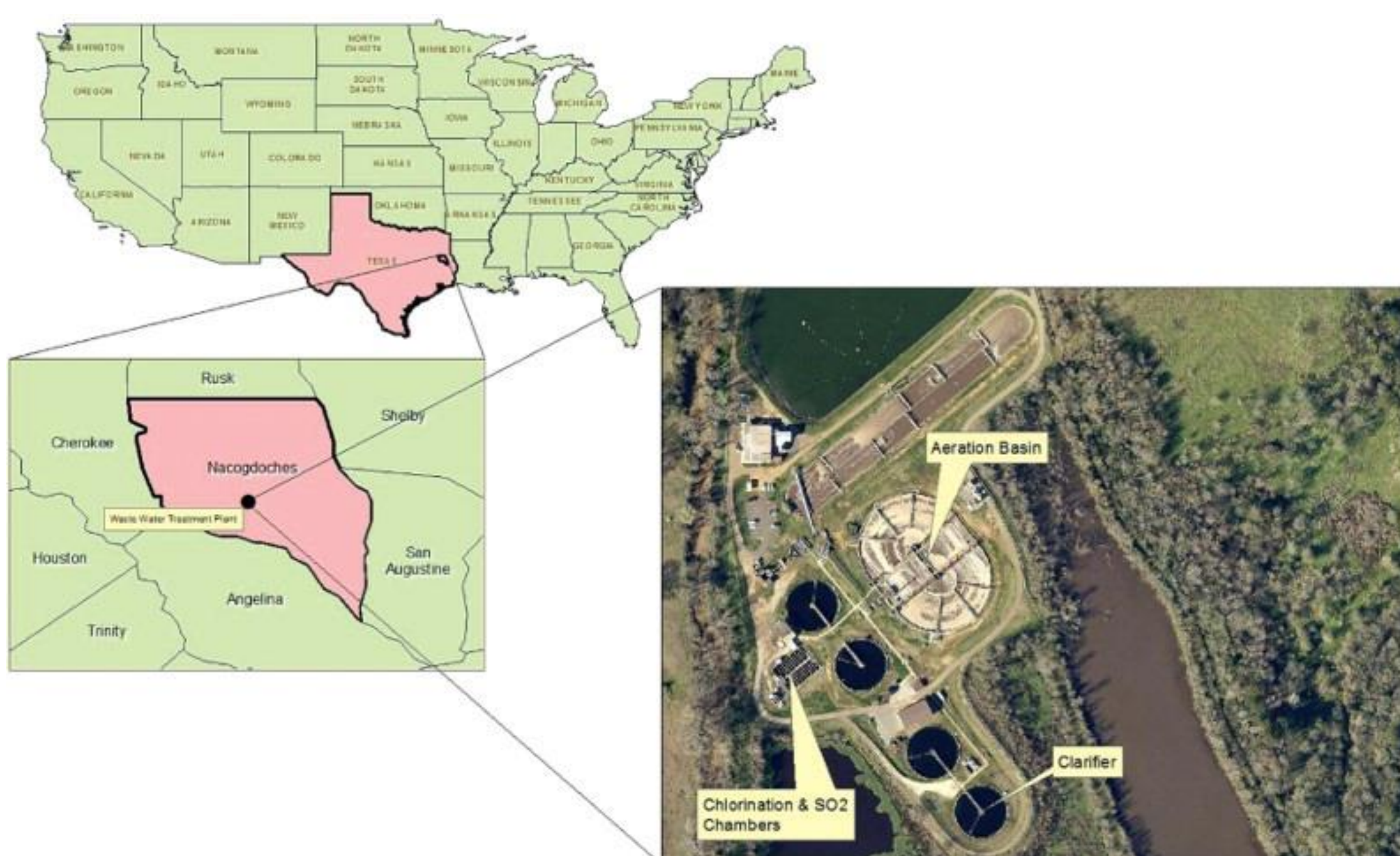
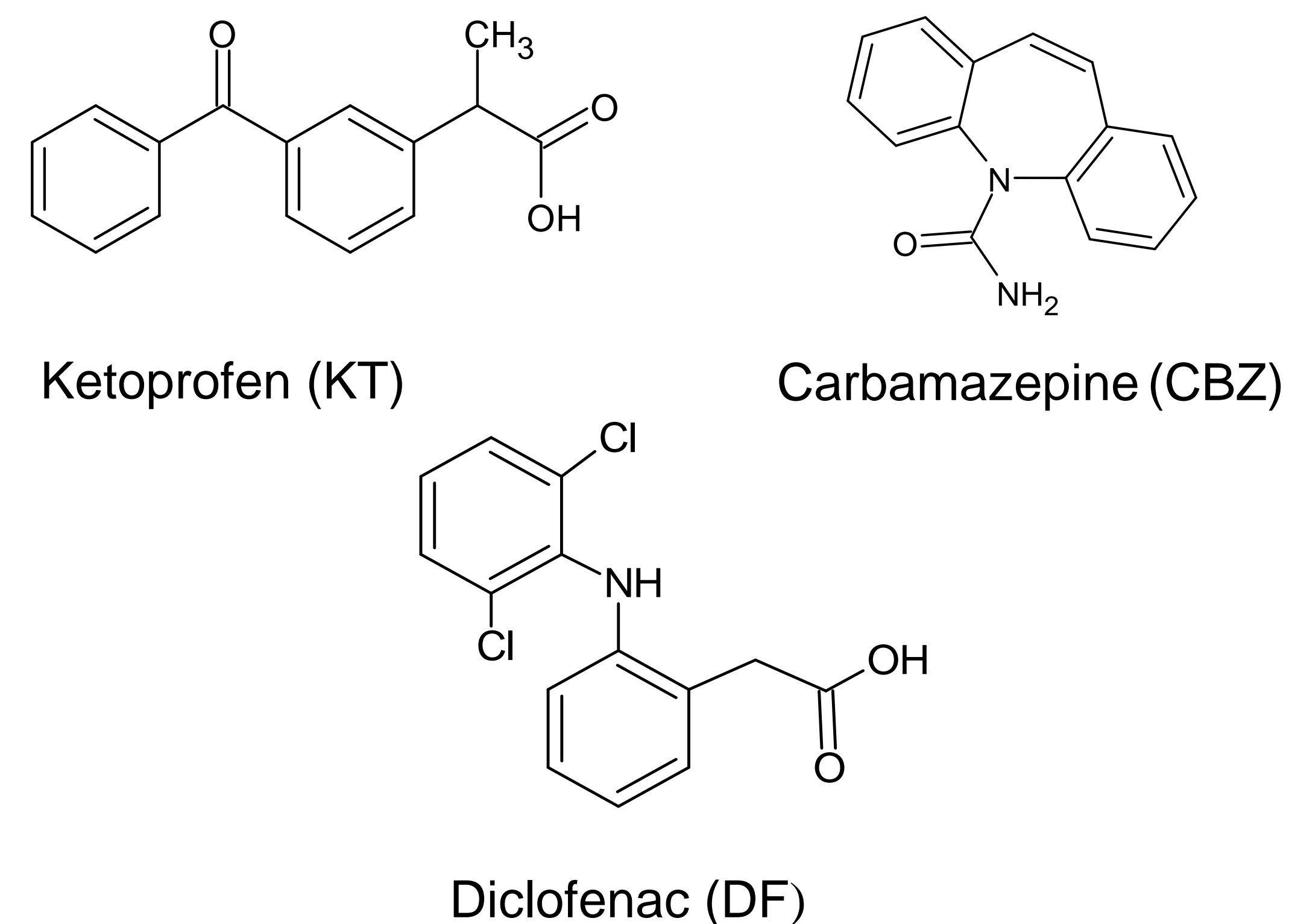


Figure 1. Map of USA, Texas and Nacogdoches County in East Texas. An aerial diagram showing the series of the four treatment stages at the NWWTP – four clarifiers are shown in parallel to the aeration stage of treatment.

4. Structures of Pharmaceuticals



5. Materials and Methods

Standard Dilution solutions

- 2 – 3 mg mg of CBZ, DF, KT were dissolved in methanol/nanopure water solution of (70:30 v/v)
- A series of six standard dilutions were prepared with the (70:30 v/v) solution @ pH = 2.

Instrumentation

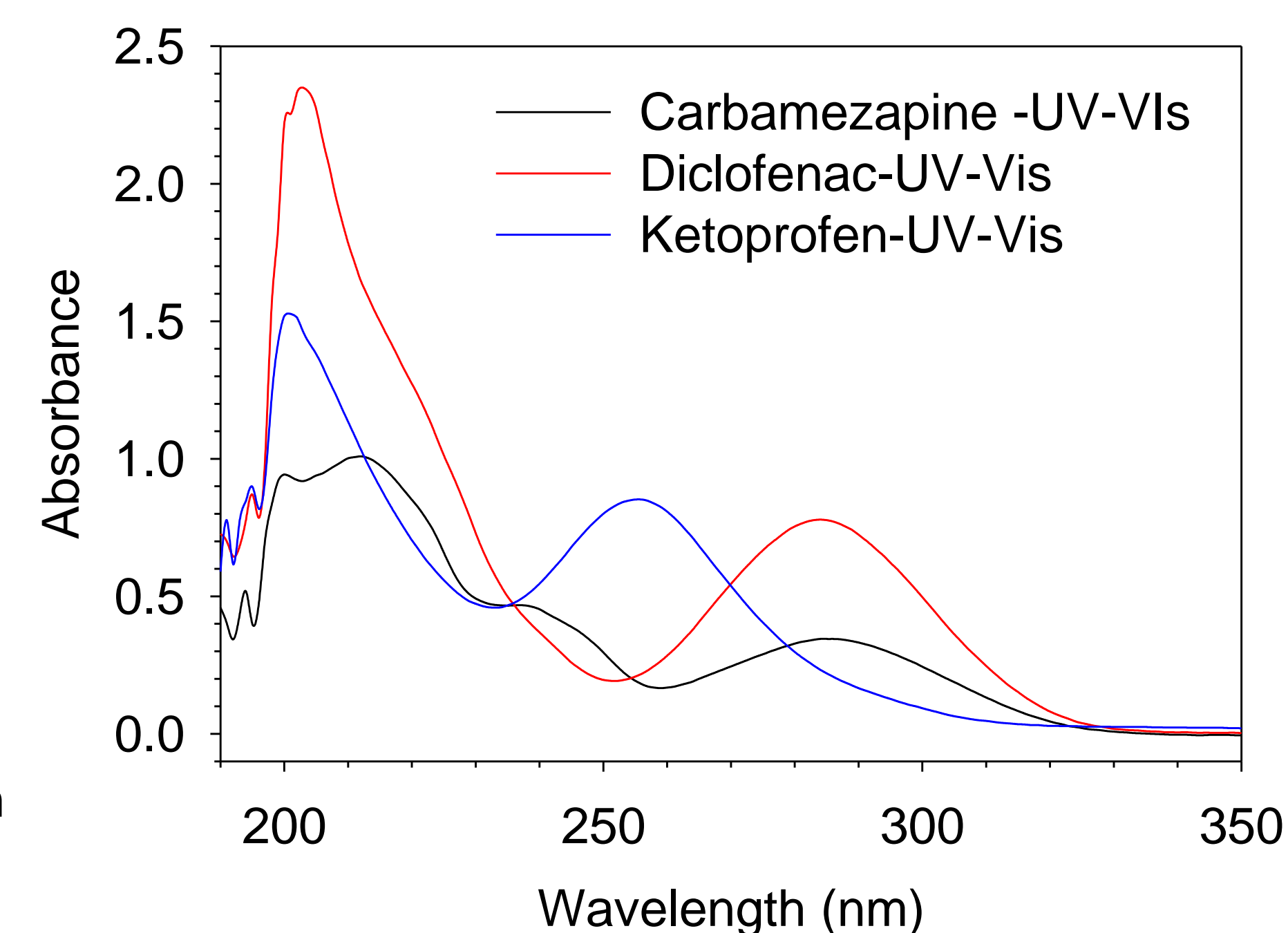
- JASCO high-performance liquid chromatograph.
- Shimadzu 2550 PC UV-Vis Spectrophotometer.
- Perkin Elmer FL6500 fluorometer
- C18 SPE cartridge Hypersep (Thermoscientific)

Run Conditions:

- Isocratic elution with MeOH/Water (70:30 v/v)
- C18 Waters Spherisorb LC Column 250 x 4.6 mm, ODS (5 μ m, 100 \AA)
- 35 $^{\circ}$ C column oven temperature; Flow rate (1.00 mL/min)

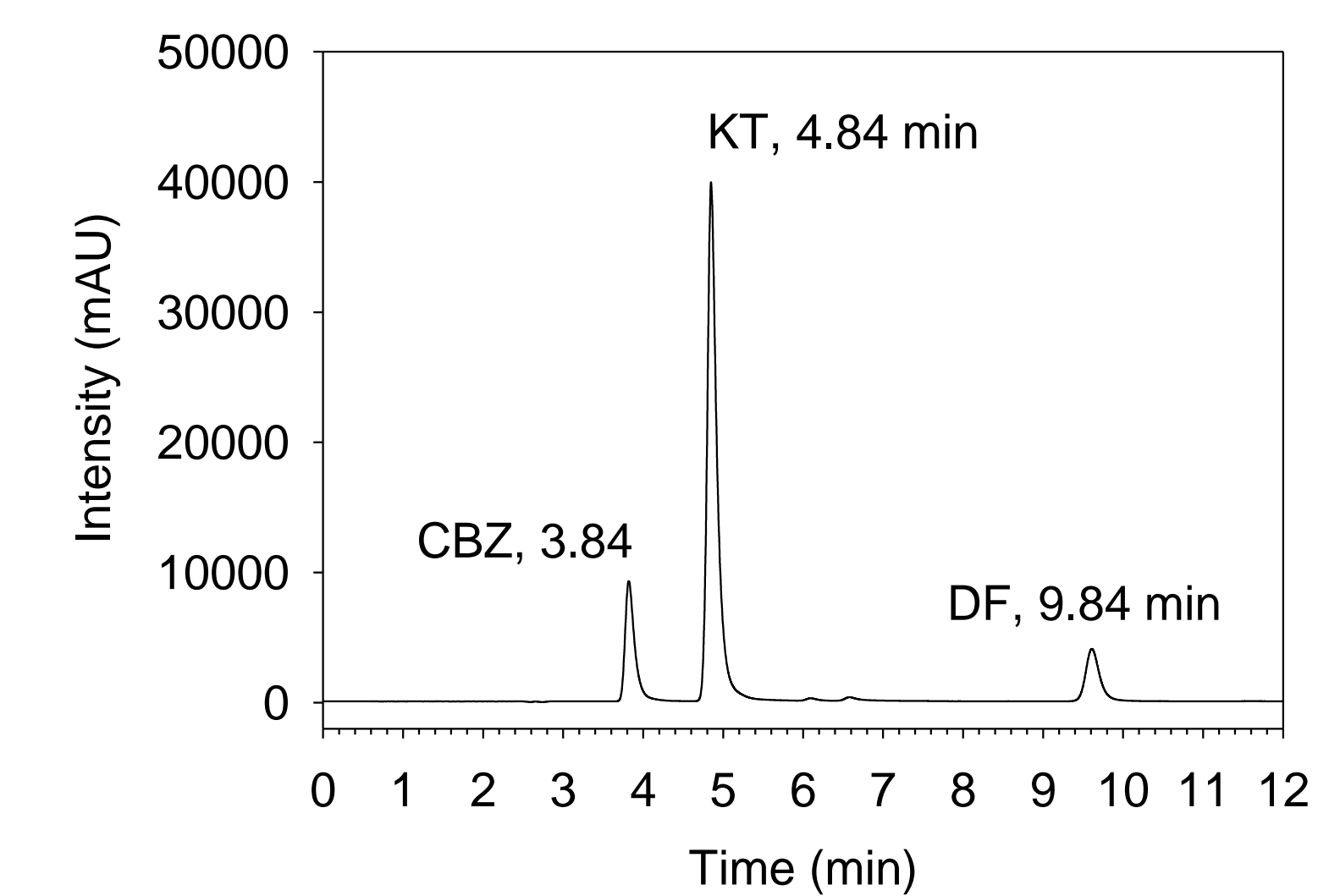
6. Results (UV-Vis)

i) UV-vis spectra of CBZ, KT, and DF

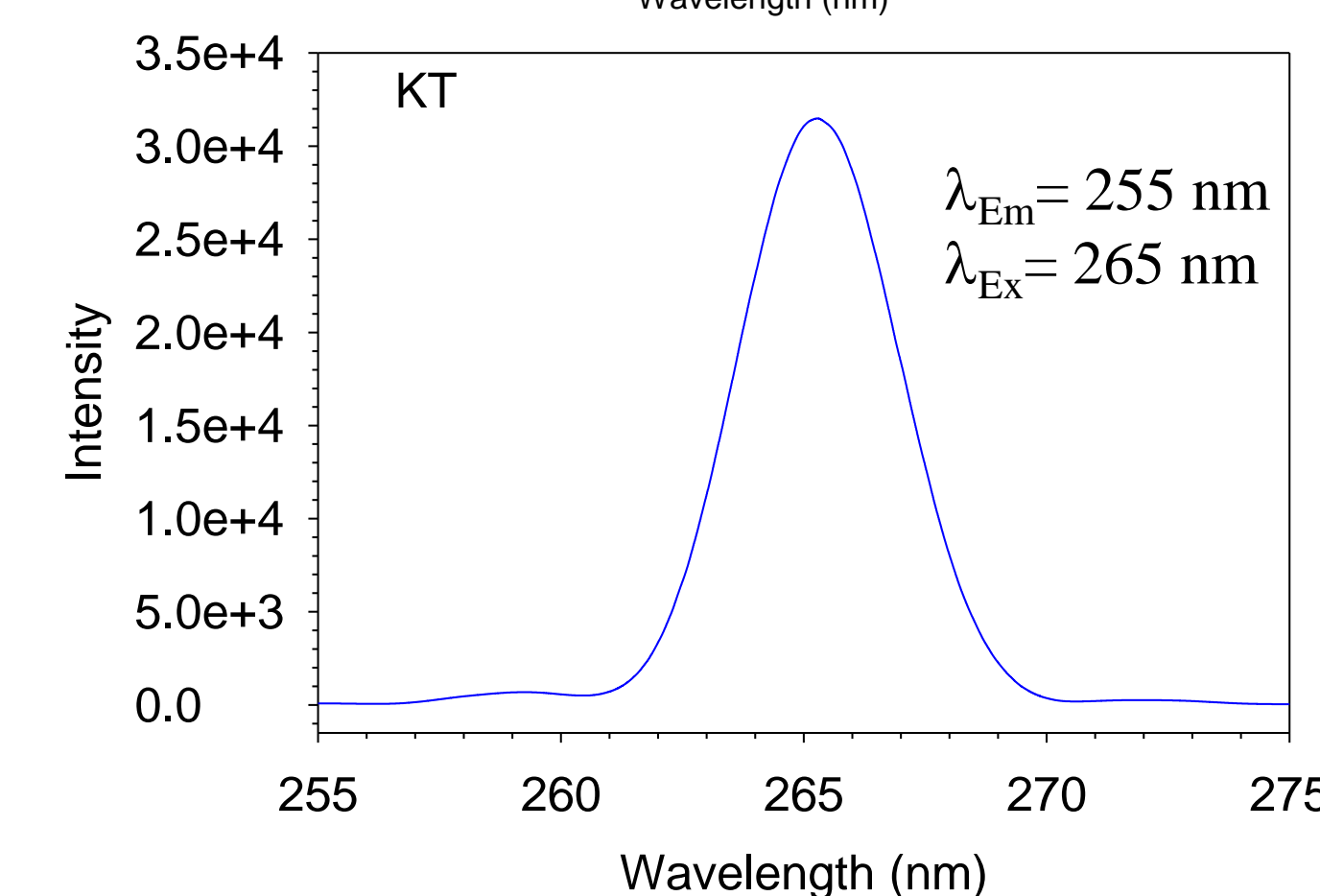
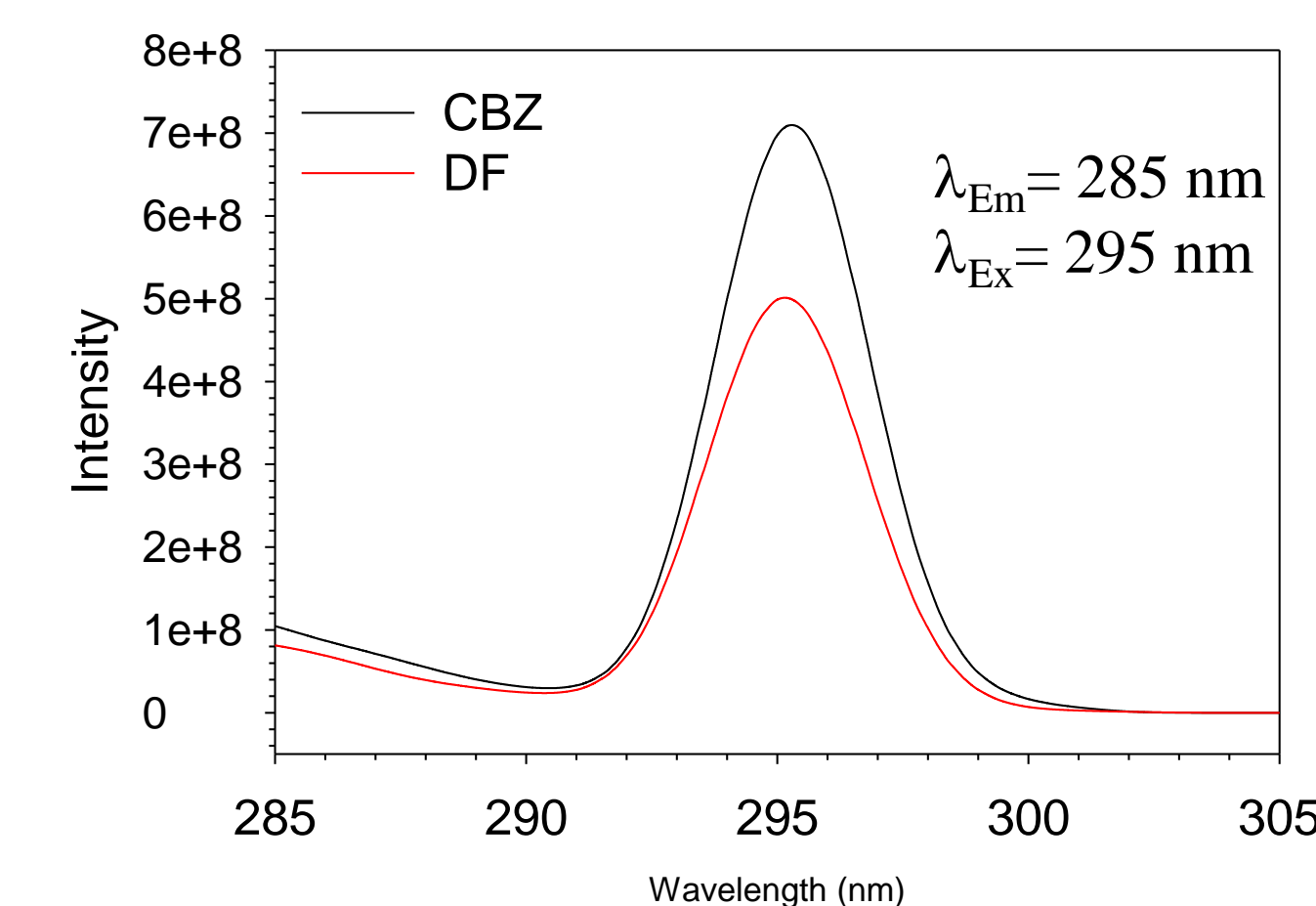


6. Results (HPLC, Cont'd)

ii) HPLC Chromatogram of Carbamazepine (CBZ) Ketoprofen (KT) and Diclofenac (DF)



iii) Fluorescence Emission $\lambda_{em} = 285$ nm, $\lambda_{exc} = 295$ nm, slit widths= 2.5, 2.5 nm, abs< 0.10



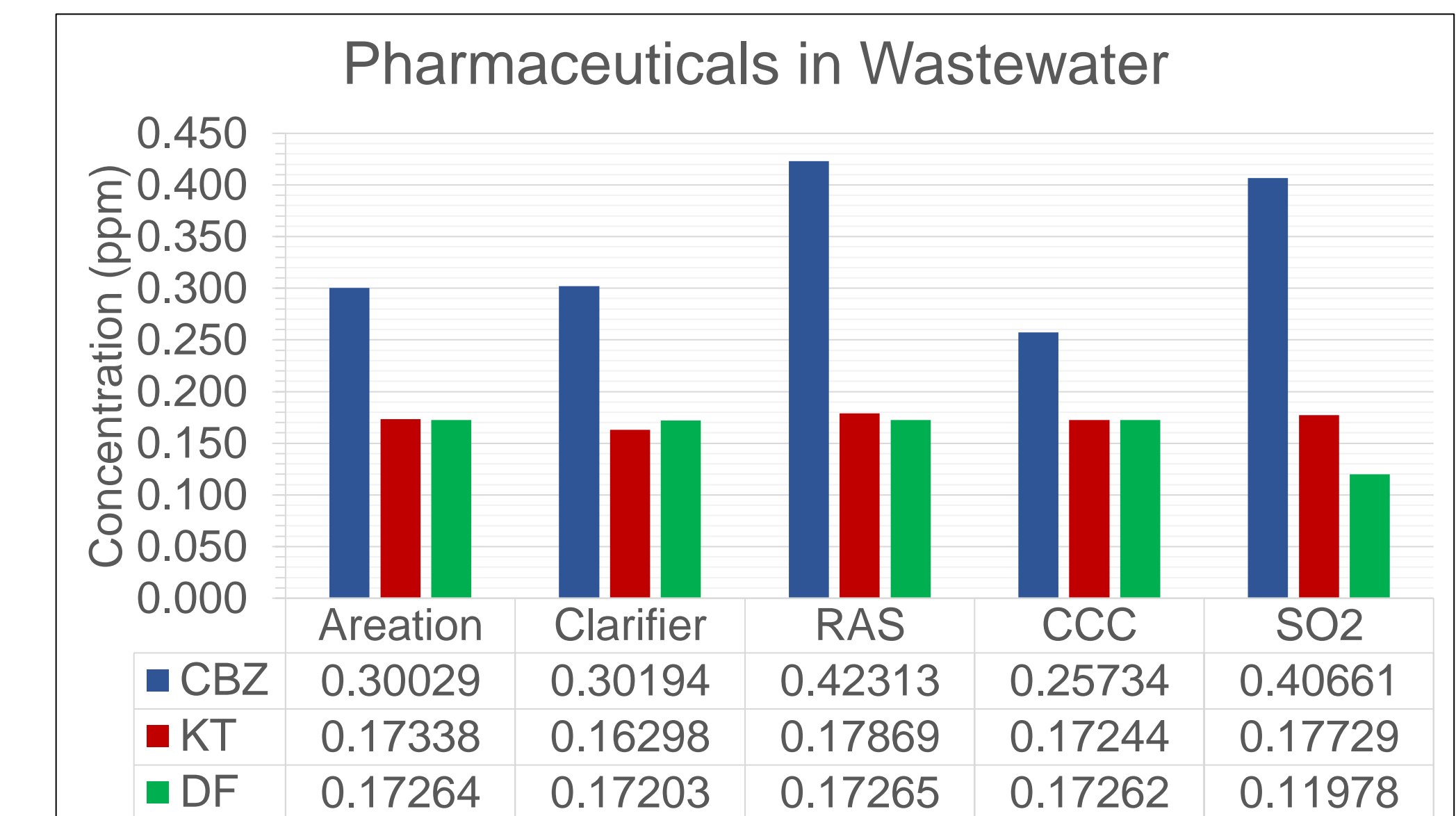
7. Experimental Quantum Yields

Name	Absorbance	λ_{Ex}	λ_{Em}	Start λ	End λ	Φ_f
KT	0.0970	255.6	265.6	260.2	270.5	0.327
DF	0.0810	285.0	295.0	290.4	300.0	0.287
CBZ	0.0800	285.0	295.0	300.4	300.4	0.226

$$\phi_f = \frac{A_s F_u \eta_u^2}{A_u F_s \eta_s^2} \phi_s = \frac{\text{emitted photons}}{\text{absorbed photons}}$$

A = absorbance
 F = integrated Area
 η = refractive index
 u = unknown
 s = standard
 ϕ_s = quantum yield of standard

8. Pharmaceuticals Concentrations



9. Conclusions

- The quantum yields trend follow the order: KT (0.327) > DF (0.287) > CBZ (0.227)
- KT, and DF show higher quantum yields (F_f) vis-à-vis CBZ
- The concentration % removals of pharmaceuticals are in the order;
 - CBZ: RAS > SO₂ > Clarifier \approx Aeration > CCC
 - KT: RAS > SO₂ > Aeration > CCC > Clarifier
 - DF: RAS \approx Aeration \approx CCC > Clarifier > SO₂

Removal Efficiencies

Carbamazepine ~ 39.2%
 Ketoprofen ~ 8.8%
 Diclofenac ~ 30.6%

References

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