TiO_2/CdS Photocatalytic Degradation of Carbamazepine

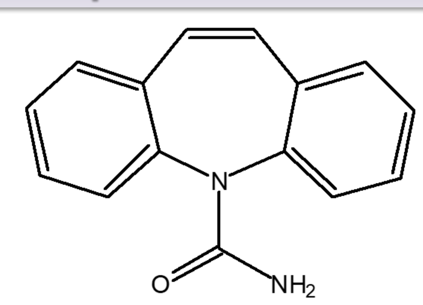
Rebekah Preshong, Kristina Jevtic, Nastasia Allred, Dr. Pedro Arce
Department of Chemical Engineering

Tennessee TECH

Introduction

Pharmaceuticals and personal care products (PPCPs) cannot be degraded by traditional methods of wastewater treatment, leading to contamination in groundwater and even drinking water and posing potential harm to people and to aquatic life. Photocatalytic degradation is an advanced oxidation process (AOP) that may provide an effective method for breaking down these substances. This research examines the degradation of carbamazepine (CBZ), a model PPCP, by titanium dioxide (TiO_2) and cadmium sulfide (CdS).

Carbamazepine, a Model PPCP



$C_{15}H_{12}N_2O$ • 236.269 g/mol
MP: 191-192ºC
Biological half-life: 25-65 hours (initial), 12-17 hours (repeated doses)

- Used to treat epilepsy, seizures, neuralgia, etc.
- Like other PPCPs, has high affinity for aqueous phase
- Detected in municipal wastewater, groundwater, seawater, and even drinking water
- For example, was found at concentrations up to 1075 ng/L in surface water in Berlin

Methodology

Generic Photocatalytic Process

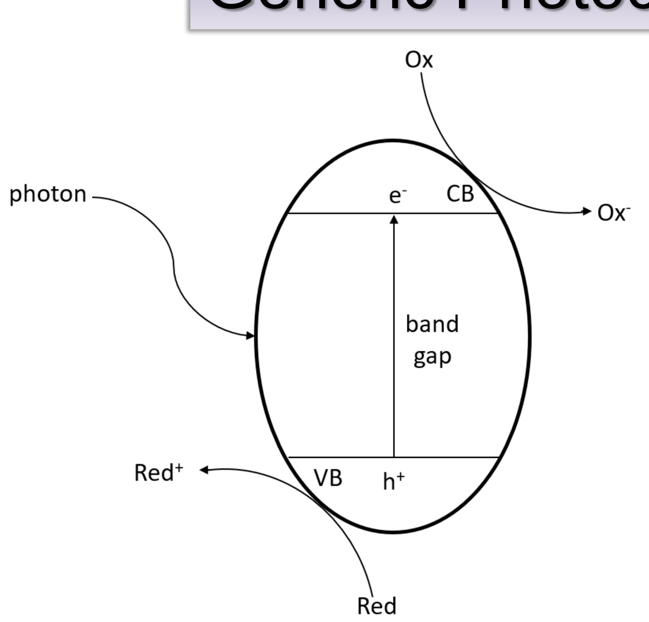


Figure 1: Generic Photocatalytic Mechanism (Rebekah Preshong)

- Can oxidize organic pollutants
- Photon of sufficient energy excites electron from valence band (VB) to conduction band (CB) of semiconductor
- Positive hole left behind in VB
- Charge recombination can occur rapidly
- Oxidizing agents reduced by CB electron
- Reducing agents oxidized by VB hole

Important Elements in Papers Reviewed

- Titanium dioxide photocatalysis
- Degradation mechanisms (esp. of CBZ with TiO_2)
- Modified TiO_2 photocatalysts (esp. TiO_2/CdS)
- Effect of UV vs. UV-Vis light
- Importance of hydroxyl radicals
- Kinetic analysis

Results

Dual Semiconductor

- Allows activation of photocatalyst by visible light
- Electrons migrate to CB of TiO_2 (lower than CdS CB)
- Holes migrate to VB of CdS (higher than TiO_2 VB)
- Creates charge separation that slows recombination of electron/hole pairs
- Water is oxidized, producing hydroxyl radicals that will oxidize CBZ
- Oxygen (most likely) is reduced; $O_2^{\bullet -}$ and $HO_2^{\bullet}$ will also oxidize CBZ
- Ideally, CBZ will reach complete mineralization

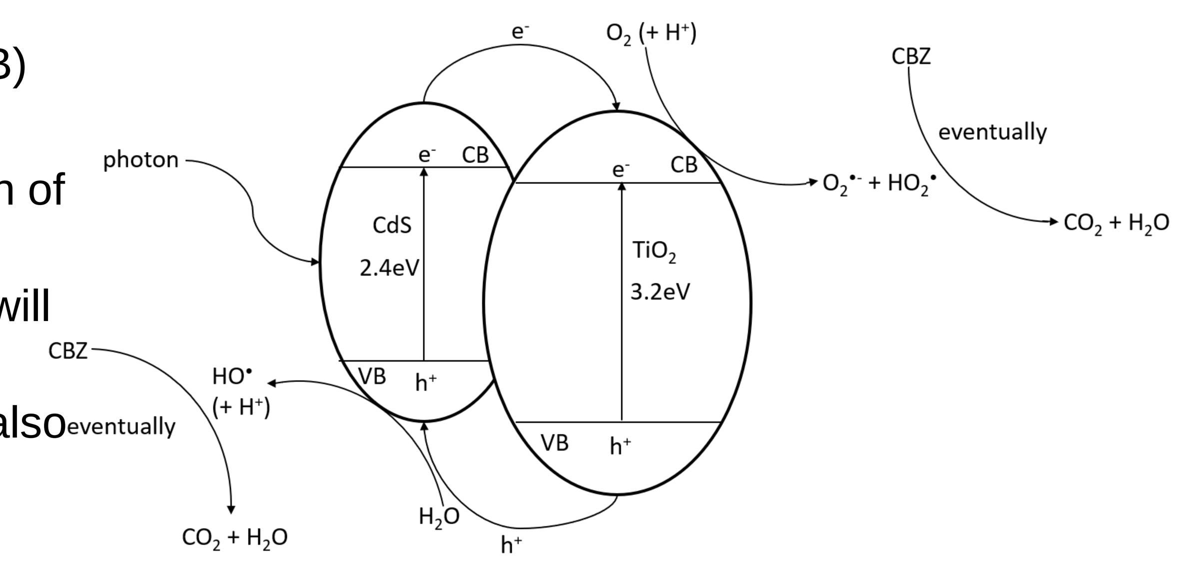


Figure 2: Dual Photocatalytic Mechanism (Rebekah Preshong)

Mechanism Proposed by Martínez *et al.*

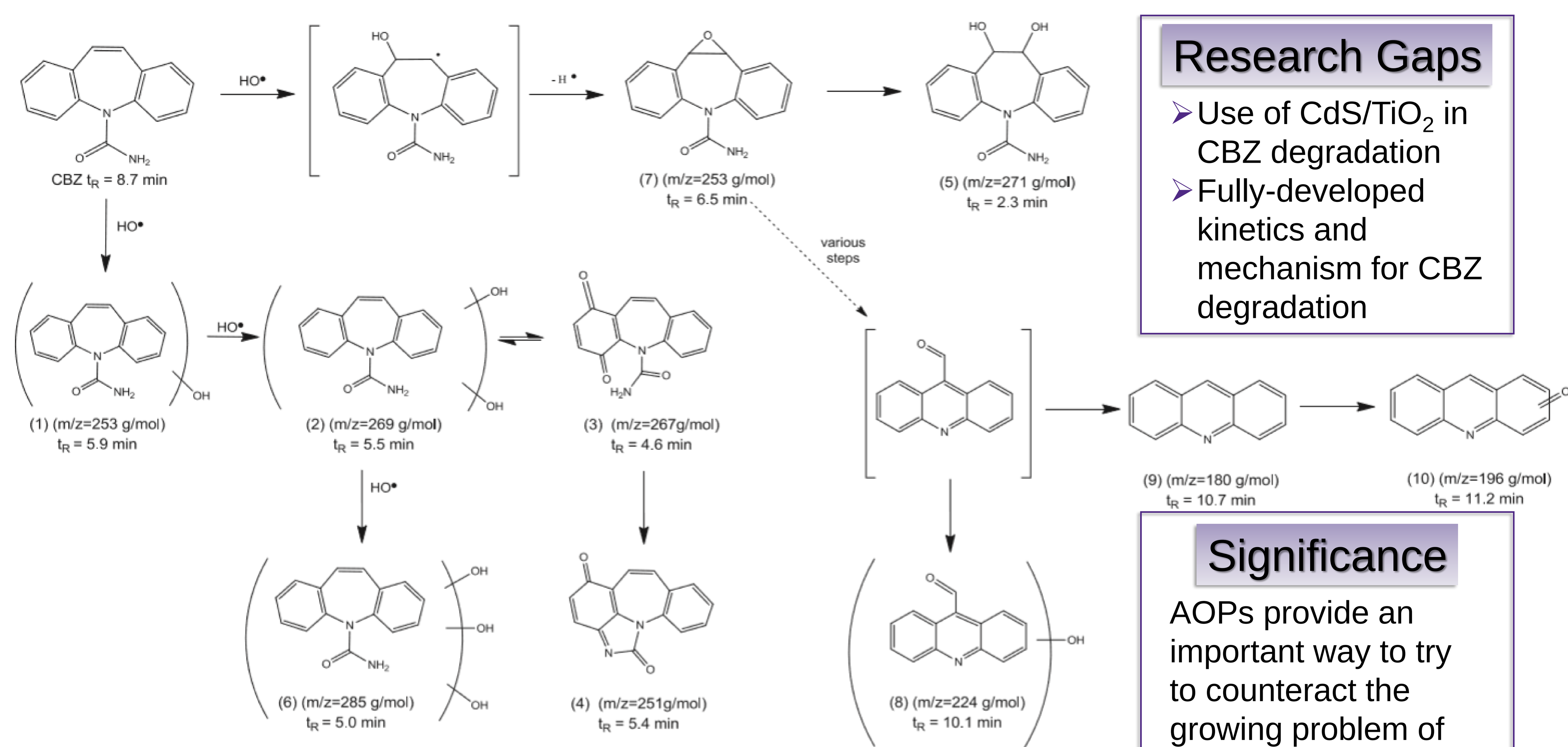


Figure 3: Martínez et al. Degradation Mechanism

Research Gaps

- Use of CdS/TiO_2 in CBZ degradation
- Fully-developed kinetics and mechanism for CBZ degradation

Significance

AOPs provide an important way to try to counteract the growing problem of PPCP contamination.

Variations Based on Reaction Conditions (from Martínez *et al.*)

Photoproducts (numbered according to Scheme 2) obtained upon degradation of CBZ after photocatalysis upon UV or NUV–Vis irradiation.

Reaction conditions			Photoproducts
Lamp	Catalyst	$\%O_2$/co-oxidant	
NUV–Vis	P25	0	1, 2, 3, 7, 9, 10
		50	1, 3, 4, 5, 7, 8, 9, 10
		50/H_2O_2	1, 3, 4, 5, 7
	Anatase	50	1, 3, 4, 5, 7, 8, 9
	Rutile	50	1, 3, 4, 5, 7, 8, 9, 10
	ZnO	50	1, 4, 7
	P25 + MWCNT	50	1, 2, 3, 5, 7, 9, 10
	10-MWCNT-TiO_2	50	1, 2, 3, 5, 7, 9
		50	1, 2, 5, 7
UV	P25	50	1,3, 4, 5, 6, 7, 8, 9, 10
	Anatase	50	1, 3, 4, 5, 6, 7, 8, 9
	Rutile	50	1, 3, 4, 5, 6, 7, 10
	10-MWCNT-TiO_2	50	1, 3, 7, 9, 10
		50	1, 3, 5, 6, 7, 8, 9

Table 1: Intermediates Detected Based on Varied Reaction Conditions (Martínez et al.)

Kinetics

- Langmuir-Hinshelwood kinetics model typically used:

$$r = -\frac{dC}{dt} = \frac{k_r K_{ad}}{1 + K_{ad} C}$$

  - r: degradation rate
  - C: concentration of reactant at time t
  - t: irradiation time
  - k_r: reaction rate constant
  - K_{ad}: adsorption coefficient

- Under many conditions can be simplified to a first-order rate equation:

$$\ln\left(\frac{C_0}{C}\right) = k_r K t = k_{app} t, \text{ or}$$

$$C = C_0 e^{-k_{app} t}$$

  - k_{app}: apparent first-order rate constant

Conclusions

Brief Summary

- Titanium dioxide (TiO_2): Inexpensive; non-toxic; effective; activated only by UV light
- Cadmium sulfide (CdS): Smaller bandgap; can be activated by visible light
- TiO_2/CdS: Use of effective TiO_2 ***and*** activation with visible light
- Hydroxyl radicals: essential in CBZ degradation
- Intermediates: vary with reaction conditions

Proposed Experiment

- Preparation of dual photocatalyst from Na_2S, $Cd(NO_3)_2$, and TiO_2
- Experiments run with various catalyst loadings, CBZ concentrations, and types of irradiation
- Samples collected every 5 minutes and analyzed with UV-Vis spectrophotometer at 284nm to determine CBZ degradation

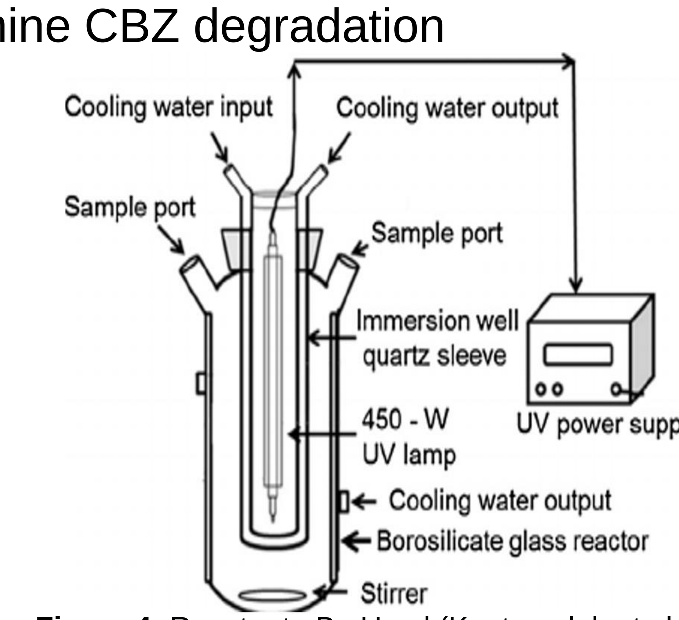


Figure 4: Reactor to Be Used (Koutazadeh et al.)

Sample Concentration	Amount of CBZ, ppm	PC Loading, mg/L	Irradiation Source	Irradiation Time, min
Low	5	50	UV, Vis	45
Low	5	250	UV	45
Low	5	500	UV, Vis	45
High	250	50	UV, Vis	45
High	250	250	UV	45
High	250	500	UV, Vis	45

Table 2: Proposed Experimental Conditions (Kristina Jevtic)

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