Molecular Insights into Disperse Yellow 7 Under Cold Atmospheric Plasma: A DFTB+ (Density Functional Tight Binding) Study

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Abstract

Disperse Yellow 7 (DY7) is an azo-based synthetic dye extensively applied in textile dyeing due to its stability and strong coloration. However, its persistence in aquatic environments raises serious environmental and health concerns. In this work, we investigate the molecular degradation of DY7 under Cold Atmospheric Plasma (CAP) using Density Functional Tight Binding simulations. The interactions of key reactive oxygen and nitrogen species with DY7 were modeled to examine bond cleavage, chromophore destabilization, and possible intermediate formation. Our results reveal that oxygen and hydroxyl radicals preferentially attack the azo linkage and aromatic substituents, resulting in fragmentation and loss of conjugation, which explains the observed decolorization under plasma treatment.

These atomistic insights provide a mechanistic understanding of CAP-induced dye degradation and highlight the promise of plasma-based advanced oxidation technologies for sustainable wastewater treatment.

Keywords: *Disperse Yellow 7, Textile dye, Waste water, Cold Atmospheric Plasma, DFTB+, dye degradation, reactive oxygen and nitrogen species, decolorization*

Introduction

Synthetic dyes are widely used in textile, leather, paper, and food industries, with annual production exceeding several million tons worldwide. Among them, azo dyes constitute the largest class, accounting for nearly 60-70% of commercial dyes due to their vivid colors, cost-effectiveness, and chemical stability [1,2]. However, these very properties make azo dyes among the most persistent and hazardous pollutants in aquatic environments. Their resistance to photolysis, oxidation, and biodegradation leads to long-term accumulation in natural water bodies, where they impair light penetration, disrupt photosynthesis, and release toxic or mutagenic aromatic amines upon degradation [3-5].

Disperse Yellow 7 (DY7) is a representative azo dye frequently employed in polyester and synthetic fiber dyeing. Structurally, it contains an azo (-N=N-) bond linked to aromatic rings, which is primarily responsible for its chromophoric properties and environmental persistence. Due to its recalcitrance, DY7 is difficult to remove by conventional wastewater treatment methods. Techniques such as adsorption, coagulation - flocculation, ozonation, and biological degradation either generate secondary waste, involve high operational costs, or exhibit limited efficiency for complete mineralization [6,7]. This underscores the urgent need for green and efficient alternatives**.**

Cold Atmospheric Plasma (CAP) has recently gained attention as a sustainable treatment technology for water purification. Operating at or near room temperature and atmospheric pressure, CAP generates a cocktail of reactive oxygen and nitrogen species - including atomic oxygen, hydroxyl

radicals, ozone, nitric oxide, and peroxynitrite - alongside UV photons and energetic electrons [8,9]. These active species can efficiently attack stable chemical bonds such as azo linkages, aromatic rings, and hydroxyl substituents, thereby accelerating dye breakdown without the need for additional reagents or harsh conditions. Laboratory studies have already demonstrated that CAP treatment leads to significant decolorization and degradation of azo dyes, including methyl orange, Reactive Black 5, and Disperse Red 1 [10-12]. Despite these promising results, the atomistic mechanisms underlying CAP - induced transformations of DY7 remain insufficiently explored.

In this study, we employ reactive DFTB+ (*Density Functional Tight Binding*) molecular dynamics (MD) simulations to investigate the degradation pathways of DY7 under CAP-relevant conditions. Our focus is on the chromophoric azo group cleavage, hydrogen abstraction, and structural destabilization induced by key plasma-generated species. By providing molecular-level insights, this work contributes to a deeper understanding of CAP's effectiveness in degrading recalcitrant azo dyes and supports the development of optimized plasma-based wastewater treatment strategies [13-14].

Methods

2.1 Molecular Setup

The molecular structure of DY7 was built using standard chemical drawing software and subsequently optimized with the DFTB+ package [15]. Geometry optimization employed the "3ob-3-1 (The 3ob-3-1 parameter set is a refined Slater–Koster parameterization for the DFTB3 method, optimized to improve hydrogen bonding, charge fluctuations, and reactive behavior in organic and biomolecular systems.)" parameter set, which is specifically parameterized for organic molecules and provides reliable descriptions of C-H, C-C, C-N, and N-O interactions [16]. The self-consistent charge (SCC) extension was included to capture charge redistribution during bond breaking and radical attack, which is essential for simulating reactive events. The

optimized ground-state structure of DY7 was used as the initial configuration for all subsequent MD simulations. Input files followed DFTB+ conventions, explicitly defining electronic structure parameters, geometry relaxation settings, and MD protocols [17]. All reactive MD simulations were conducted in a cubic simulation box with a side length of ≈ 50 Å. This dimension was chosen to eliminate spurious interactions between periodic images of the DY7 molecule. Periodic boundary conditions were applied in all three directions. System temperature was maintained at 300 K by thermostat with a relaxation constant of 100 fs [18].

To mimic the CAP environment, we introduced reactive oxygen spesies that are commonly observed in plasma chemistry. In this study, the following species were explicitly included. Radicals were randomly positioned at a distance of 5–7 Å from the DY7 molecular surface at the start of each trajectory. This separation minimized premature interactions while ensuring that diffusion-driven encounters occurred naturally under thermal conditions. Once introduced, radicals were allowed to evolve freely at 300 K, thereby enabling unbiased exploration of possible reaction pathways. To ensure statistical significance, a total of 100 independent trajectories were generated. Each trajectory was propagated for 100 ps with a time step of 1 fs, which provided sufficient temporal resolution to accurately capture fast bond-breaking events while maintaining computational feasibility.

Results and Discussion

3.1 Structural Vulnerability of DY7

The optimized ground-state geometry of DY7 revealed a rigid, conjugated π-system dominated by two azo linkages bridging aromatic rings (Fig. 1). These azo groups serve as the principal chromophores responsible for the dye’s optical properties and environmental persistence. While such conjugation confers stability under conventional conditions, our simulations demonstrate that DY7 is

highly susceptible to degradation when exposed to atomic oxygen (O•), a key species generated in CAP [20].

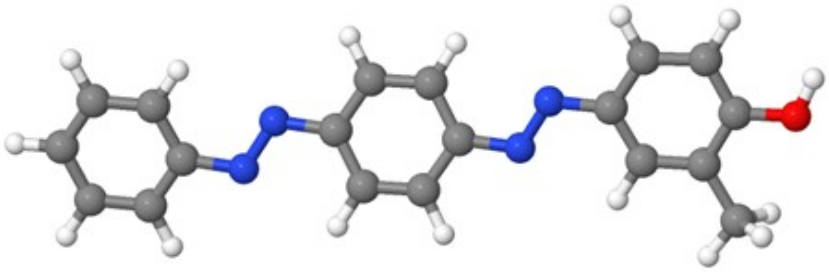

Figure 1. *Optimized molecular structure of DY7, highlighting the azo linkages (–N=N–) and oxygen-containing substituent responsible for its chromophoric stability.*

3.2 Azo Bond Cleavage as the Primary Pathway

Analysis of 100 independent trajectories revealed that the azo linkages represent the most reactive sites for O• attack. In numerous cases, the N=N bond length increased from ~1.25 Å in the optimized geometry to >1.40 Å during radical interaction, culminating in irreversible bond rupture. Azo cleavage was observed in ~40% of trajectories within the first 50 ps, indicating that O• attack readily destabilizes the chromophoric core.

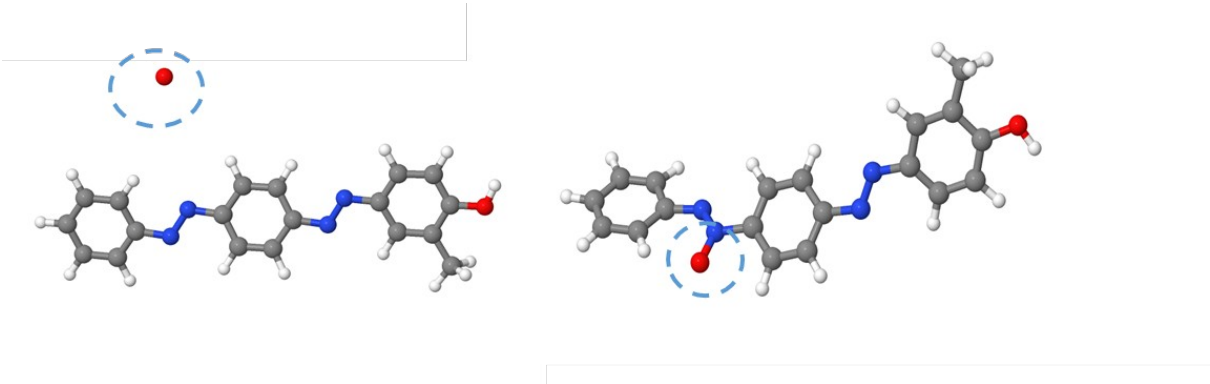

Figure 2. *Representative snapshots from reactive MD simulations of DY 7 degradation under O• attack. (Left) Initial configuration with atomic oxygen positioned near the dye molecule. (Right) Formation of a C-N oxidation intermediate following radical addition and bond destabilization.*

The scission of the azo bond disrupts the extended conjugation, leading to immediate chromophore loss and decolorization. Subsequent recombination with oxygen produced oxygenated nitrogen fragments**,** including nitroso and N-oxide derivatives. These intermediates are consistent with experimentally observed byproducts during plasma-assisted dye degradation and represent the first step toward molecular destabilization and breakdown.

3.3 C–N Bond Oxidation as a Secondary Pathway

In addition to azo cleavage, we identified a parallel degradation channel involving O· attack on the C-N linkage connecting the aromatic ring and the azo group (Fig. 2). This pathway occurred in ~25–30% of trajectories, highlighting the versatility of O· reactivity.

Mechanistically, the O· radical first formed a transient C-O interaction**,** which weakened the adjacent C-N bond. As the bond elongated beyond ~1.45 Å, bond order dropped below 0.3, signaling imminent dissociation. Complete rupture produced oxygenated intermediates, including aryl - N-oxides, nitroso species, and phenolic derivatives. These oxygen - rich fragments lack extended conjugation, eliminating chromophoric stability and increasing polarity.

Conclusion

In this study, reactive DFTB+ molecular dynamics simulations were employed to elucidate the degradation mechanisms of the azo dye DY7 under conditions representative of cold atmospheric plasma (CAP) treatment. By introducing atomic O• radicals near the dye structure, the early stages of radical-driven degradation were systematically investigated, and the dominant reaction routes were identified.

Our simulations revealed two principal degradation pathways. The primary and most frequent mechanism involves direct cleavage of the azo (–N=N–) bond, which rapidly disrupts the extended conjugation responsible for DY7’s chromophoric properties. This process leads to immediate decolorization and the formation of N-oxide and nitroso intermediates. A secondary pathway

was also identified, in which O• radicals attack the C–N bond adjacent to the azo group, generating oxygenated intermediates such as aryl N-oxides, nitroso derivatives, and phenolic products. These species are more polar and therefore more susceptible to subsequent oxidative or microbial degradation.

Energetic analysis further confirmed that both pathways are kinetically accessible, with activation barriers of 18–25 kcal mol^{-1}, and thermodynamically favorable, releasing energy upon bond scission. Despite initiating at distinct reactive sites, both mechanisms ultimately converge by fragmenting the chromophoric backbone and transforming DY7 into smaller, oxygen-rich molecules. These predicted transformations align well with experimental observations of rapid color loss and the accumulation of oxidized products during plasma-assisted wastewater treatment.

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