Fenton degradation of binary synthetic dyes mixture: Experimental and DFT studies

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Abstract

Fenton process is one of the efficiencies oxidation processes for destroying toxic organic compounds in aqueous solution. In this work, Fenton degradation of a solution mixture of Basic Yellow 28 (BY28) and Methylene Blue (MB) catalyzed by ferric ions was examined. Results showed that this system could degrade and mineralize the dye mixture. Therefore, degradation of MB is faster than BY28. Kinetic studies showed that the degradation followed a pseudo-first-order reaction.

However, the theoretical study using density functional theory (DFT) with the B3LYP (Three parameter local, non-local, Hartree-Fock) hybrid exchange functional (B3) with Lee-Yang-Parr correlation functional (LYP)) together with the 6–31+G(d,p) basis set was used to explain the experimental results.

Keywords: Fenton reaction, Degradation, Basic Yellow, Methylene Blue, Mixture, DFT.

Introduction

A total of 15% of the total world production of dyes is lost during the dyeing process and is released in textile effluents[1]. The release of those coloured waste waters in the ecosystem is a dramatic source of aesthetic pollution, of eutrophication and of perturbations in the aquatic life. As international environmental standards are becoming more stringent (ISO 14001), technological systems for the removal of organic pollutants such as dyes have been recently developed. We can use some techniques including biological, physical and chemical processes for treatment of textile wastewater. However, several biological and physicochemical methods showed low performance for removing dyes.

In the last fifteen years, numerous research studies have been addressed to a special class of oxidation techniques defined as Advanced Oxidation Process (AOP) pointing out its potential prominent role in the wastewater purification[2]. It was shown that AOP could successfully solve the problem of biorecalcitrant water pollutants working at or near ambient temperature and pressure[3-4].

All AOP are characterized by the same chemical feature: the production of hydroxyl radicals •OH. These radicals are extremely reactive species and attack mainly every organic molecule[5]. •OH radicals are also characterized by a low selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for •OH radicals production, thus allowing a better compliance with the specific treatment requirements.

Fenton's reagent consisting of Fe^{2+} and H_2O_2 is one of the most effective advanced oxidation agents for degradation of organic dyes compounds such as Methylene Blue (MB) and Basic Yellow 28 (BY28)[6-8].

Recently, the researchers have been using computation methods for molecular structure description, spectroscopic properties and molecular reactivity. Density functional theory (DFT) which is one of these methods, has been widely used in literature because of its efficiency and accuracy with respect to the evaluation of several molecular properties[9-12]. In this work, the comparison of the degradation of mixture of both dyes (BY28 and MB) was evaluated by using Fenton reaction. Then, this experimental comparison was compared with theoretical study using density functional theory (DFT) method.

Material and Methods

Materials: Methylene Blue (Thiazine dyes) was obtained from Loba Chemie, India, the molecular structure of it is displayed in fig. 1. The Basic Yellow 28 (azo dye) was prepared from a local textile factory in Casablanca (Morocco) and used without further purification. The structure of the dye is given in fig. 2.

The chemicals used for Fenton process are ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (30% w/w). The pH was adjusted with sodium hydroxide and sulfuric acid. All these chemicals are purchased from Loba Chemie,

India. All reagents were used without further purification. Distilled water was used throughout this study.

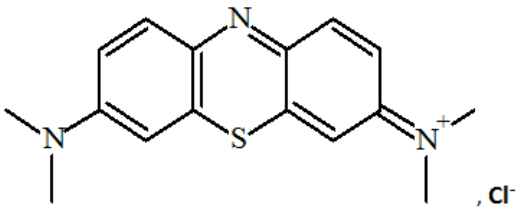

Fig. 1: Chemical structure of Methylene Blue

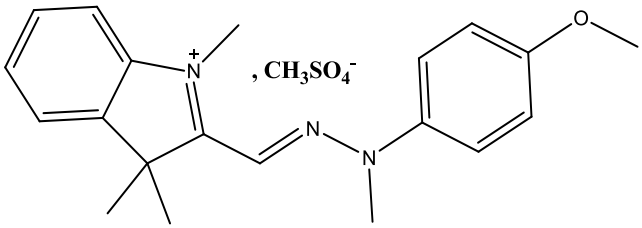

Fig. 2: Chemical structure of Basic Yellow 28

Analytical methods: The colour of solution was analysed using a Rayleigh spectrophotometer (Rayleigh UV-1800). Each dye solution was scanned from 300 to 800 nm and its maximum absorbance was determined in water solvent at acidic conditions. The colour removal was based on the change of the maximum absorbance.

Computational details: Theoretical study is performed by the Gaussian 09 program package[13] and displayed with Gauss View[14]. For the non-radical species, global reactivity indices such as chemical potentials (μ), chemical hardness (η) and global electrophilicity (ω) were used where $\mu=(\varepsilon_{HOMO}+\varepsilon_{LUMO})/2$, $\eta=\varepsilon_{LUMO}-\varepsilon_{HOMO}$ and $\omega=\mu^2/2\eta$[15,16]. Then, the global nucleophilicity *N* is expressed as $N=\varepsilon_{HOMO\ (nucleophile)} - \varepsilon_{HOMO\ (TCE)}$; it is referred to tetracyanoethylene (TCE) because it presents the lowest HOMO energy for a large molecular series.

For the radical species, chemical potential μ°, chemical hardness η°, global electrophilicity ω° are calculated by the following formulas: $\mu°=(\varepsilon^{\alpha,\circ}_{HOMO} + \varepsilon^{\beta,\circ}_{LUMO})/2$, $\eta°=(\varepsilon^{\beta,\circ}_{LUMO}-\varepsilon^{\alpha,\circ}_{HOMO})$ and $\omega°=\mu°^2/2\eta°$ where $\varepsilon^{\alpha,\circ}_{HOMO}$ is the energy of one electron in α spin state of the frontier molecular orbital HOMO and $\varepsilon^{\beta,\circ}_{LUMO}$ is the energy of one electron in β spin state of the frontier molecular orbital LUMO. On the other hand, the global nucleophilicity N° of the radical species is given as: $N°= \varepsilon^{\alpha,\circ}_{HOMO}$ (radical) - $\varepsilon^{\alpha,\circ}_{HOMO}$ (DCM) where DCM is dicyanomethyl radical. [(•CH(CN)$_2$] is applied as a reference radical because it leads to positively scale of global nucleophilicity of radicals.

Results and Discussion

Experimental results: After having determined the optimal degradation conditions of each dye by Fenton process in other studies[8,17], we have tried in this work to compare the degradation of a mixture of these two dyes (BY28 and MB). The results of degradation of mixture the both dyes are given in fig. 3 at the optimum pH value (pH 3) using Fenton reaction. We observed that the degradation of MB is important than that of BY28.

Several studies have demonstrated that the Fenton reaction for dye degradation follows pseudo-first-order kinetics[20,21].

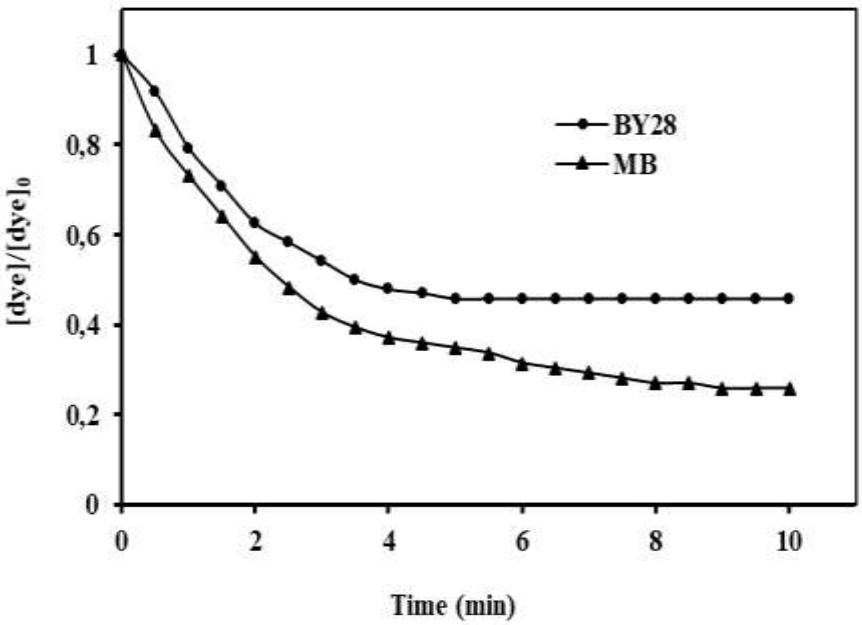

Fig. 3: Removal of an aqueous mixture of dyes MB and BY28 ($[dye]_0 = 10^{-5}$ M of each dye) during Fenton oxidation treatment in the presence of Fe^{2+} ions as catalyst. Reaction conditions: $[Fe^{2+}]_0 = 0.14$ mM, $[H_2O_2]_0 = 0.2$ mM pH = 3.00 and temperature = 25°C

Regression analysis based on the pseudo-first-order reaction kinetics for the decolorization of mixture of the both dyes (BY28 and MB) in Fenton oxidation process was conducted and the results were shown in table 1. Degradation rate constants k_{app} (in min^{-1}) were determined from the slope of $\ln([dye]/[dye]_0) = k_{app}.t$ plots where $[dye]_0$ and [dye] are the concentration of dye at times 0 and t. As illustrated in table 1, the degradation ate constant of MB is greater than that of BY28 indicating a faster reaction rate of MB dye.

Table 1
Rate constants k_{app} (min^{-1}) obtained from fitting of plots of $\ln([dye]/[dye]_0)$ *vs.* time. Reaction conditions: $[dye]_0 = 10^{-5}$ µM, $[Fe^{2+}]_0 = 0.14$ mM, $[H_2O_2]_0 = 0.2$ mM pH = 3.00 and temperature = 25°C

Dye	k_{app} (min^{-1})	R^2
Methylene Blue	0.27	0.99
Basic Yellow 28	0.20	0.99

Theoretical results: Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as frontier molecular orbitals are considered as very important molecular parameters for the stability and chemical reactivity of the species[20,21]. HOMO and LUMO energies and LUMO-HOMO energy gap (ΔE_{L-H}), in eV are reported in table 2. The lower is the HOMO energy, more ready is that orbital to participate in chemical reaction by donating electrons. LUMO energy, on the other hand, determine the ability to accept an electron in a chemical change. LUMO-HOMO energy gap reflects the chemical hardness-softness and polarizability of the molecule[22,23].

From the tables 2 and 3, the electrophilicity index of the •OH Radical (5.87eV) was greater than the MB and BY28: 4.80 and 3.32 eV respectively and implying that in this reaction, the •OH Radical behaved as an electrophile while MB and BY28 as nucleophiles. However, the nucleophilicity indices are 2.98, 2.94 for MB and BY28 respectively. Thus, MB is the nucleophile which will react quickly with •OH radical.

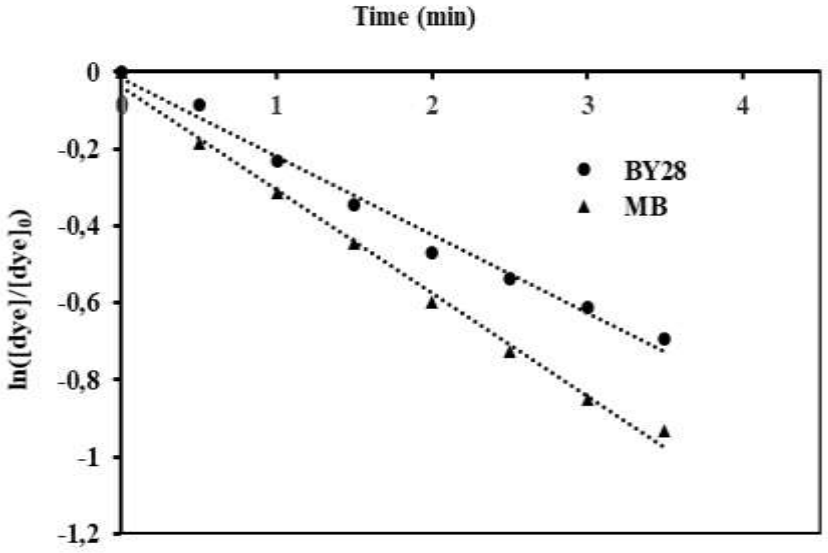

Fig. 4: Pseudo-first order the degradation of the both dyes using Fenton process

Table 2
Global chemical reactivity indices: HOMO and LUMO energies (eV), chemical potential (µ) (eV), chemical hardness(η) (eV), chemical softness (S) (eV^{-1}), electrophilicity index (ω) (eV) and nucleophilicity (N) (eV)for MB and BY28 dyes using B3LYP/6-31+G(d,p) level.

	E_{HOMO}	E_{LUMO}	µ	H	S	ω	N
MB	-6,01	-3,60	-4,81	2,41	0,42	4,80	2,98
BY28	-6,05	-2,98	-4,52	3,07	0,33	3,32	2,94

Table 3
$E^{\alpha,o}_{HOMO}$, $E^{\beta,o}{}_{HOMO}$, $E^{\alpha,o}_{LUMO}$ and $E^{\beta,o}{}_{LUMO}$ energies (eV), chemical potential µ (eV), absolute hardness η (eV), electrophilicity index (ω°) (eV) and dipole moment (Debye) of the •OH radical using B3LYP/6-31+G(d,p) level.

$E^{\alpha,o}_{HOMO}$	$E^{\beta,o}{}_{HOMO}$	$E^{\alpha,o}_{LUMO}$	$E^{\beta,o}{}_{LUMO}$	μ^o	η^o	S°	ω^o	N°
-9,7397	-8,9966	-1,2106	-5,0681	-7,4039	4,6716	0,2141	5,8672	-

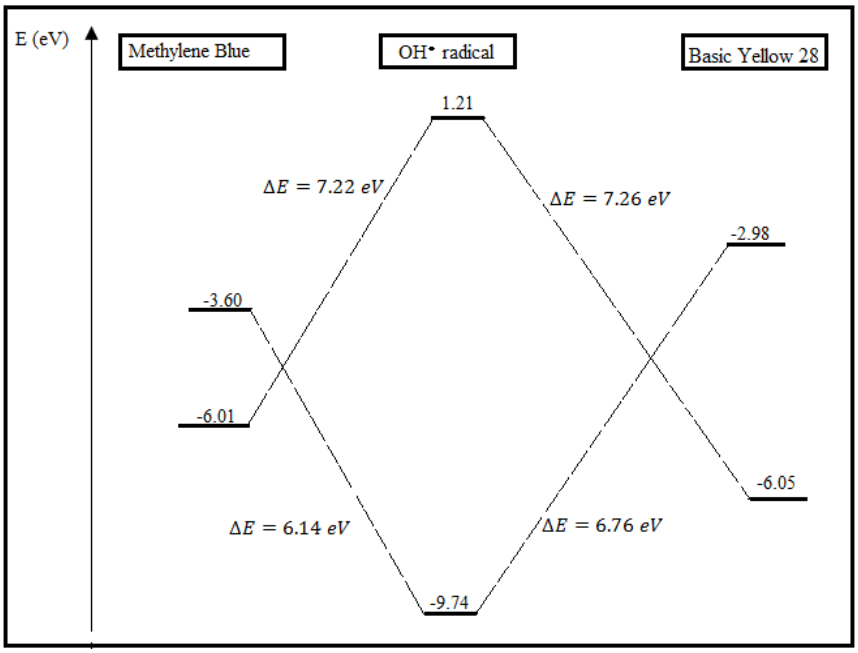

Fig. 5: The HOMO and LUMO energies and LUMO-HOMO energy gap (ΔE) of MB, BY28 and ˙OH radical.

The HOMO energies are computed as -6.01, -6.05 eV and 1.21 eV and LUMO are -3.60 and -2.98 eV and -9.74 eV for MB, BY28 and ˙OH radical respectively (Tables 2 and 3). On the other hand, we observed that the lower energy gap is between LUMO of ˙OH radical and HOMO of MB dye (6.14 eV). Therefore, computed values of energy gap (ΔE) show that MB is more reactive than BY28 (Fig. 5). This is in accord with the calculated chemical softness 0.42 and 0.33 for MB and BY28 respectively. This indicates that the experimental results are in accordance with the theoretical results.

Conclusion

Fenton process appears to have the capacity to mineralize the mixture of both dyes (MB and BY28) in aqueous solution in a short reaction time. Fenton degradation constant rate increased in the order of k_{app}(BY28) < k_{app}(MB), this is because MB dyes have a low energy gap (ΔE) and a great chemical softness according to the theoretical study investigated using density functional theory. We concluded that the experiment study is in good agreement with the theoretical study.

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