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Electronic and Optical Properties of Reactive Orange 16 azo dye

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ABSTRACT: Azo dyes constitute the largest family of synthetic dyes. They are widely used in the textile, dye stuff and pharmaceutical industries. The uncontrolled and undesirable discharge of the azo dyes into the environment may represent a serious ecological problems and health effects. The oxidation of azo dyes (e.g., Photo-oxidation, Oxidation by ozone) leads to its degradation. To determine the reactivity and the active sites of azo dye reactive Orange 16 (RO16) , we calculated its electronic and optical properties by using DFT and TD-DFT methods at B3LYP/6-311+G(,p) level in solvent (IEF-PCM model). The results showed that RO16 is polar and high soluble compounds in water. The Fukui indices showed that the N11 is the favoured site of nucleophilic attack (e.g, ozone). A good correlation was obtained between the predicted and experimental absorption bands of RO16 (R2=97%).

KEYWORDS: Reactive Orange 16, DFT, TD-DFT, UV/vis, PCM.

1 INTRODUCTION

Azo dyes constitute the largest group of synthetic dyes. They are widely used in the textile dye and pharmaceutical industries ([1],[2],[3],[4],[5],[6],[7],[8]). The azo dyes' chemical structure contains at least an azo group (–N=N-), and substituted aromatic rings by different group, which make them recalcitrant and xenobiotic [9, 10]. The poor fixation of azo dyes to the fibre or the discharge of the coloured textile wastewater lead to its loss into the environment, which may represent a serious ecological problem and impact on health, in addition to the generation of degradation products [1, 7].Various physical, chemical and biological techniques were employed for wastewater remediation. The combination of biological treatment (bioremediation) with advanced oxidation processes (e.g, ozonation, advanced oxidation process by using OH radical) is one of the most known efficient techniques for azo dyes degradation or colour removal[11, 12].

In most cases the oxidation reaction is selective and proceeds through electrophilic attack on double bond of azo chromophoric group or on double bonds of the connecting aromatic rings [13],[14],15]. The biodegradation of dyes, or other pollutant by liquid fungal cultures and/or purified ligninolytic enzymes has been extensively studied, and it proved the capacity of white rot fungi to degrade synthetic dyes as well as other types of organic pollutants ([7],[16][17],[18],[19]]. Reactive orange 16 (RO16) dye belongs to the group of vinylsulfone dyes and it is used for dyeing cellulose fibres. Svobodovà et al. reported the degradation mechanism of RO16 by the fungus Irpex lacteus cultures and they observed that no re-colorization effect appeared during azo dye degradation [20]. Tauber et al. used Laccase enzyme and ultrasound treatments to degrade azo dyes and they reported that a simultaneous treatment with both processes showed synergistic effects for dye degradation compared with individual treatments[21].

The computational chemistry is an important tool for the investigation and the understanding of the reactivity and optical properties of natural or synthetic organic compounds. Density functional theory (DFT) is a convenient method to determine the electronic properties and reactivity of azo dyes. It has great importance to help understand the mechanism by means the azo dyes operate and with this to potentially obtain application for the protection of the environment. Hihara et al. used a semi empirical approach (PM5 method) to study the reactivity of azo dyes with singlet oxygen by using molecular orbital theory and they obtained a linear correlation between the second-order rate constants and the sum of electrophilic frontier density of the reactivity of azo dyes with singlet oxygen [22]. Time dependent density functional theory (TDDFT) appears the most reliable method to predict UV/vis spectra of azo dyes with an intermediate size [23-26]. Jacquemin et al. reported the methodology choice and reproduction of the UV/visible spectra of a large series of dyes by using PBE0 and B3LYP hybrid functionals in polarisable continuum model (PCM) [23, 24, 27, 28].

In this paper, focus is on determining the electronic and optical properties of RO16 azo dye by using DFT and TDDFT methods. First, the electronic properties and Fukui indices of the titled azo dyes were calculated by means of DFT, with the purpose of generating accurate information such as polarity, solubility, reactivity and nucleophilic, electrophilic and radical attack sites which enables a better understanding of its degradation. Secondly, by using TD-DFT calculations, an attempt is made to predict the UV/vis spectra of RO16, with the aim of rationalizing the differences observed in its experimental spectra.

2 MATERIALS AND METHODS

Materials

- RO16 azo dye was obtained from hight school of textiles, Casablanca, Morocco.

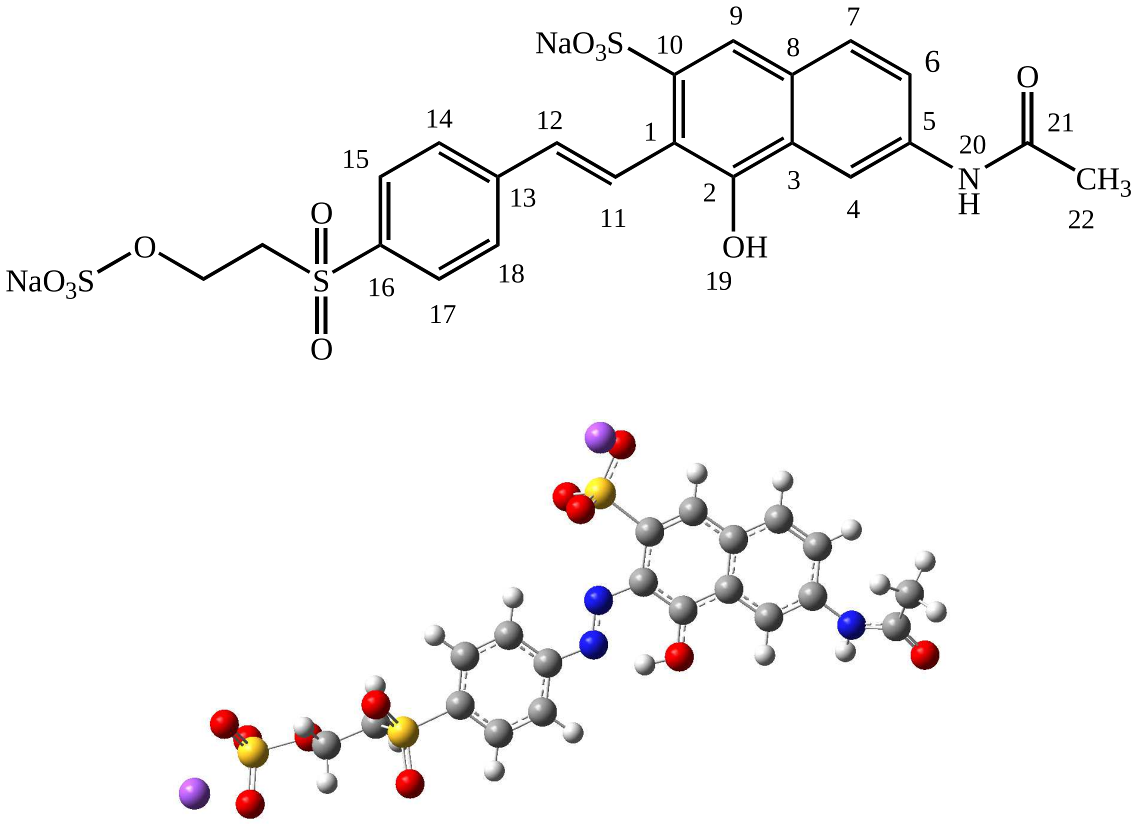


Fig.1. Chemical and optimized structures of RO16 obtained at B3LYP/6-31+G(d,p) level

Table.1 Orange 16 molecul

Name	Reactive Orange 16	
Synonyms	6-(Acetylamino)-4-hydroxy-3-[[4-[[2-(sulfooxy)ethyl]sulfonyl]phenyl]azo]-2-naphthalenesulfonic acid disodium salt	
Molecular Structure	Molecular Formula:	C20H17N3O11S3.2Na
	Molecular Weight:	617.53
	CAS Registry Number:	20262-58-2 (12225-88-6)

- Experimental UV/visible spectra for reactive RO16 azo dye was recorded on a *spectrometer in our laboratory* in water solvent.

3 THEORETICAL DETAILS

Geometry optimization and frequency calculations for colorants RO16 have been carried out at B3LYP/6-31+G(d,p) level (DFT method) as implemented in Gaussian 09[29]. The minima of ground states (GSs) were confirmed by the absence of imaginary frequencies. To determine the reactivity of the titled colorants, the electronic properties such as energy of solvation, the dipole moment (μ'), the isotropic polarizability (α), total energy, HOMO and LUMO energies, energy gap, electronic affinity (EA), ionization potential (IP), electronegativity (χ), chemical hardness (η), softness (S), electrophilicity (ω) and a Fukui functions analysis were calculated at the same level of theory (B3LYP/6-31+G(d,p)). The values of EA, IP,χ, η were calculated in two different ways. One, by using Koopman's theorem, which states that IP=-E_{HOMO} and EA=-E_{LUMO}. The other, by taking the differences of total energies when adding/removing an electron from/to the neutral molecule EA=E_0 –E_{-1} and IP=E_{+1}-E_0 where E_0, E_{-1} and E_{+1} are the electronic energies of neutral molecule, neutral molecule when adding an electron and neutral molecule when removing an electron, respectively. χ, η and ω are calculating using the following formula:

$$\chi = \frac{IP + EA}{2} = -\mu$$ (μ is the chemical potential)

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v = \left(\frac{IP - EA}{2}\right)$$

$$S = \frac{1}{\eta}$$

$$\omega = \frac{\mu^2}{2\eta}$$

$$\mu' = \sqrt{\mu_x'^2 + \mu_y'^2 + \mu_z'^2}$$

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

In the hardness formula, N is the number of electrons, υ the external potential, and E the electronic energy. To identify the most likely reactive atoms for titled colorants to react with electrophile or nucleophiles, Fukui indices were calculated. In DFT, the Fukui functions are the key of region selectivity indicators for electron-transfer controlled reactions [Reference Fukui book]. The condensed Fukui functions were computed using Mulliken population analysis method [30].The Fukui indices are obtained by the following formula:

$$F_k^+ = q_k(N+1) - q_k(N)$$: For nucleophilic attack

$$F_k^- = q_k(N) - q_k(N-1)$$: For electrophilic attack

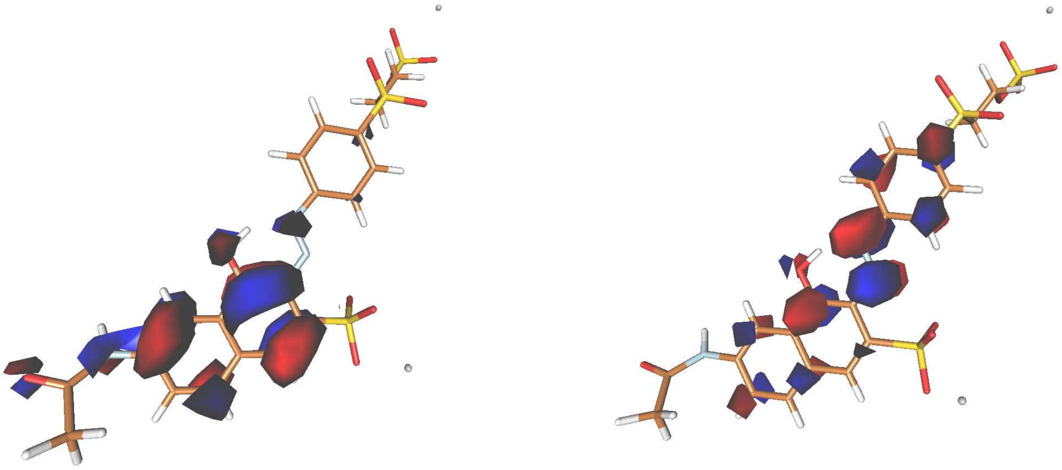
$$F_k^0 = \frac{[q_k(N+1) - q_k(N)]}{2}$$: For radical attack

Excited singlet state (ES) energies were calculated from the optimized geometries at B3LYP/6-31+G(d,p)level (TDDFT method)[31]. The allowed vertical electronic excitation energies were thus obtained, which consequently give the absorption energies in the UV/vis range with their configuration interaction(CI) description as well as their oscillator strength (*f*>0.1). The solvent effects are taken into account implicitly by using the polarisable continuum model with the integral equation formalism variant (IEFPCM). In PCM model, the solute is embedded into a cavity surrounded by a dielectric continuum characterized by its dielectric constant (ε_{CH3OH}=32.613)[32]. The molecular orbitals and the optimized geometries were visualized by using Molden software (http://www.cmbi.ru.nl/molden/) and Gaussian View 5, respectively.

4 RESULTS AND DISCUSSION

4.1 ELECTRONIC PROPERTIES OF OR 16

The free solvation energie for RO16 is -86 kcal/mol. This indicates that the azo dye is highly soluble in water, so it don't transfer to sludge. It has an amphipathic behaviour i.e. its chemical structure containing hydrophobic (phenyl rings) and hydrophilic (hydroxyl groups) parts. The high polarity of RO16 is corroborated by the high values of permanent dipole moments of RO16 18Debye, which confirm its high solubility in water. The dipole moment is considered an important parameter to determine the reactivity in molecular systems (*i.e.* it represents a measurement of charge distribution in a molecule as we can see in Fig.2.



HOMO *LUMO*

Fig.2. HOMO and LUMO charge distribution of RO16 obtained at B3LYP/6-31+G(d,p) level.

The high polarisability values of RO16 (613 Boh^3 for RO16) indicate that the azo dye has the capacity to polarize other neighbouring systems. The low energy of the LUMO orbital indicates that this azo dye can behave as soft electrophiles. The ionization potential (IP) is the energy required to remove an electron from the outer shell of a molecule system. High IP values indicate that the molecular system does not lose its electrons with facility. While, adding an electron to a molecular system is defined as electronic affinity (EA). High E.A values indicate that molecular systems tend to take electrons easily. The gap energy values (difference energy between HOMO and LUMO energies) are an indication of the reactivity and stability of molecular systems. A low gap energy value indicates the molecular system is less stable and more reactive, while high values indicates that the molecular system is more stable and less reactive. In case of RO16, azo dye has small gap energie (2.94 eV), which indicates that the azo dye is less stable and more reactive systems. Table 2 reports the electronic properties associated with the chemical potential for RO16.

To determine the active sites through Fukui indices for RO16, two types of charge distribution are calculated (i) electrostatic potential(ESP) and (ii) natural population (NPA) charges. In accordance with Fukui indices showed in Table 2, nitrogen atom N11 of the double N11=N12 for RO16. This result is confirmed by the charge distribution in the LUMO orbitals of RO16 (Fig.2), in which a high electronic density in nitrogen atoms of the double N11=N12 is present. In a recent study, Tizaoui and Grima reported that the oxidation of azo dyes by ozone proceed through electrophilic attack, and the attack occurs on sites possessing high negative charge density including multiply bonded species such –C=C- or –N=N- double bonds [4].

Table.2. Fukui indices of RO16 calculated at IEF-PCM/B3LYP/6-31+G(d,p) level.

	Orange 16		
	Nucleophilic Attack	Electrophilic Attack	Radical Attack
C1	-0.008	-0.142	-0.075
C2	-0.018	-0.002	-0.010
C3	-0.048	-0.026	-0.037
C4	-0.005	-0.099	-0.052
C5	-0.017	-0.050	-0.034
C6	-0.049	-0.017	-0.033
C7	-0.013	-0.098	-0.056
C8	-0.006	0.083	0.039
C9	-0.063	-0.203	-0.133
C10	0.010	0.024	0.017
N11	-0.142	0.054	-0.044
N12	-0.173	-0.090	-0.131
C13	0.077	0.019	0.048
C14	-0.088	-0.035	-0.061
C15	-0.022	-0.001	-0.012
C16	-0.052	-0.039	-0.046
C17	-0.018	0.005	-0.007
C18	-0.087	-0.043	-0.065
O19	-0.096	-0.095	-0.095
N20	-0.010	-0.042	-0.026
C21	0.014	0.016	0.015
C22	-0.004	0.010	0.003
O23	-	-	-

Several studies reported that the mechanism responsible for the partial oxidation of azo dyes by ozone (first stage of decolourization) occurs through the ozone reaction with the double bond of azo (-N=N-) group [14, 15, 33]. These results appear in accordance with the results obtained here regarding the favoured sites of nucleophilic attack (i.e, ozone). Electrophilic attack can be in different sites e.g. C1 and C9 sites for RO16. The charges distribution in HOMO orbitals for RO16 confirmed that the mentioned positions are sites of electrophilic attack (Fig.3). Hihara et *al,* showed that C1=C2, C4=C5, C6=C7, C13=C14, C13=C18 and N11=N12 are almost all possible double bonds that can react with the single oxygen ($^1O_2$)[22]. The authors excluded the reactivity of C3=C4 and N11=N12 with the $^1O_2$ due to the low electron density, d_{HOMO} of the HOMO orbitals (See Fig. 2).

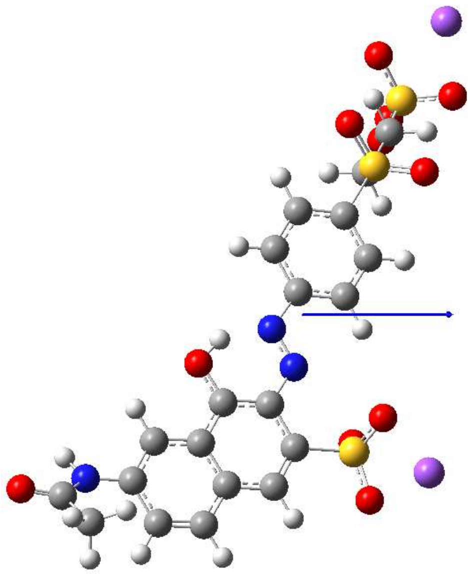


Fig.3. Dipole moment orientations of RO16 obtained at B3LYP/6-31+G(d,p) level.

The electrophilic site obtained by using NPA or ESP are in good agreement with the results obtained by Hihara et al [22]. Regarding the radical attack, different active sites can be suggested. The C9 and N12 are the favoured sites for radical attack in RO16.

4.2 UV/VIS SPECTRA OF OR 16

The experimental UV/vis spectra of RO16 were obtained in water solvent. The calculated electronic excited states are performed in gas and in PCM by using TD-DFT method at B3LYP/6-31+G(d,p) level (Table 3). The maximum absorption bands at 490 nm for RO16 (Fig.4), correspond to HOMO→LUMO electronic transition. The electronic transition induces a charge transfer from one side to another site in the azo dye (Fig. 5).

Table.3. Electronic properties of RO16 calculated at IEF-PCM/B3LYP/6-31+G(d,p) level.

	IA (eV)	EA (eV)	χ (eV)	η (eV)	S (eV)	ω (eV)	α (Bohr^{3})	μ' (Debye)
Orbital consideration	6.17	3.23	4.70	2.94	0.17	3.76	613.47	18.46
Energy consideration	6.05	3.37	4.71	2.68	1.34	4.14	613.47	18.46

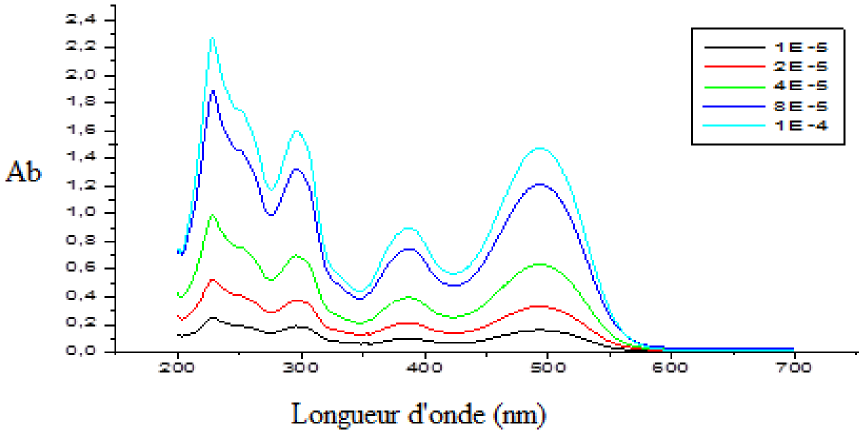


Fig.4 . OR16 absorption

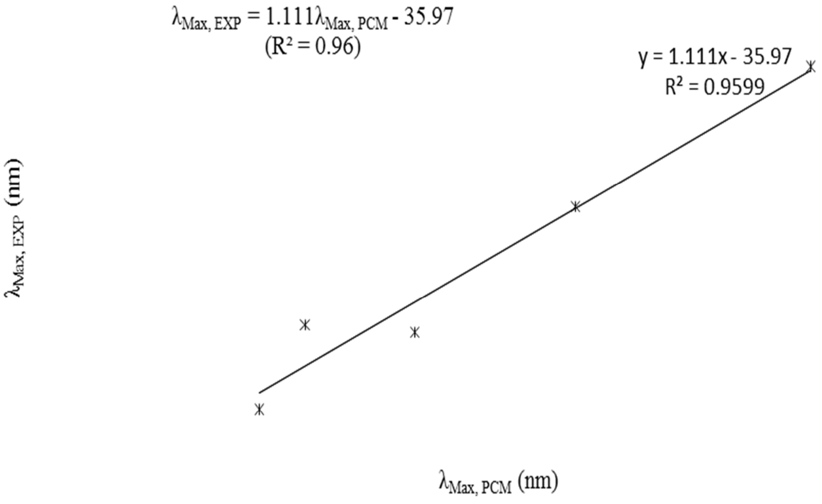


Fig.5. Linear correlation between calculated and experimental absorption bands for RO16 obtained at B3LYP/6-31+G(d,p) level.

The calculated absorption bands were underestimated in the gas phase. The PCM solvent induces a bathochromic shift of the absorption bands. A good correlation was obtained between the calculated and experimental absorption band values of RO16 (R^2= 96 %).

5 CONCLUSION

In the present study, by using DFT method we showed that RO16 is polar and high soluble azo dye in water, and N11 is the most active site involved in the degradation process (by ozone for example). The UV/vis spectra of RO16 is well reproduced using TDDFT method (R^2=97%). The perspectives of this study are the determination of the degradation products, and density functional study of the oxidation process.

REFERENCES

[1] A. Lopez-Lopez, J. Pic, H. Debellefontaine, Ozonation of azo dye in a semi-batch reactor: a determination of the molecular and radical contributions, Chemosphere, 66 (2007) 2120-2126.

[2] W. Jing, L. Lihua, Z. Jiti, L. Hong, L. Guangfei, J. Ruofei, Y. Fenglin, Enhanced biodecolorization of azo dyes by electropolymerization-immobilized redox mediator, Journal of hazardous materials, 168 (2009) 1098-1104.

[3] C. Tizaoui, N. Karodia, M. Aburowais, Kinetic study of the manganese-based catalytic hydrogen peroxide oxidation of a persistent azo-dye, Journal of Chemical Technology and Biotechnology, 85 (2010) 234-242.

[4] C. Tizaoui, N. Grima, Kinetics of the ozone oxidation of Reactive Orange 16 azo-dye in aqueous solution, Chemical Engineering Journal, 173 (2011) 463-473.

[5] A. Telke, D. Kalyani, J. Jadhav, S. Govindwar, Kinetics and mechanism of Reactive Red 141 degradation by a bacterial isolate Rhizobium radiobacter MTCC 8161, Acta Chimica Slovenica, 55 (2008) 320.

[6] D. Çetin, G. Dönmez, Decolorization of reactive dyes by mixed cultures isolated from textile effluent under anaerobic conditions, Enzyme and Microbial Technology, 38 (2006) 926-930.

[7] G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I. Banat, R. Marchant, W. Smyth, Microbial decolourisation and degradation of textile dyes, Applied Microbiology and Biotechnology, 56 (2001) 81-87.

[8] K. Jain, V. Shah, D. Chapla, D. Madamwar, Decolorization and degradation of azo dye–Reactive Violet 5R by an acclimatized indigenous bacterial mixed cultures-SB4 isolated from anthropogenic dye contaminated soil, Journal of hazardous materials, 213 (2012) 378-386.

[9] G. Liu, J. Zhou, J. Wang, X. Wang, R. Jin, H. Lv, Decolorization of azo dyes by Shewanella oneidensis MR-1 in the presence of humic acids, Applied Microbiology and Biotechnology, 91 (2011) 417-424.

[10] K. Kumar, S. Saravana Devi, K. Krishnamurthi, S. Gampawar, N. Mishra, G. Pandya, T. Chakrabarti, Decolorisation, biodegradation and detoxification of benzidine based azo dye, Bioresource technology, 97 (2006) 407-413.

[11] X. Wang, S. Chen, X. Gu, K. Wang, Y. Qian, Biological aerated filter treated textile washing wastewater for reuse after ozonation pre-treatment, (2008).

[12] S. Ledakowicz, M. Solecka, Influence of ozone and advanced oxidation processes on biological treatment of textile wastewater, Ozone Science and Engineering, 23 (2001) 327-332.

[13] G. Bablon, W. Bellamy, M. Bourbigot, B. Langlais, D. Reckhow, D. Brink, Ozone in Water Treatment: Application and Engineering, Fundamental Aspect, 22 (1991).

[14] P. Ball, C. Nicholls, Azo-hydrazone tautomerism of hydroxyazo compounds—a review, Dyes and pigments, 3 (1982) 5-26.

[15] A. Lopez, H. Benbelkacem, J.S. Pic, H. Debellefontaine, Oxidation pathways for ozonation of azo dyes in a semi-batch reactor: A kinetic parameters approach, Environmental technology, 25 (2004) 311-321.

[16] M. Rabinovich, A. Bolobova, L. Vasil'chenko, Fungal decomposition of natural aromatic structures and xenobiotics: a review, Applied Biochemistry and Microbiology, 40 (2004) 1-17.

[17] A.A. Dias, R.M. Bezerra, P.M. Lemos, A.N. Pereira, In vivo and laccase-catalysed decolourization of xenobiotic azo dyes by a basidiomycetous fungus: characterization of its ligninolytic system, World Journal of Microbiology and Biotechnology, 19 (2003) 969-975.

[18] H. Claus, G. Faber, H. König, Redox-mediated decolorization of synthetic dyes by fungal laccases, Applied Microbiology and Biotechnology, 59 (2002) 672-678.

[19] S. Pointing, L. Vrijmoed, Decolorization of azo and triphenylmethane dyes by Pycnoporus sanguineus producing laccase as the sole phenoloxidase, World Journal of Microbiology and Biotechnology, 16 (2000) 317-318.

[20] K. Svobodová, M. Senholdt, Č. Novotný, A. Rehorek, Mechanism of Reactive Orange 16 degradation with the white rot fungus Irpex lacteus, Process Biochemistry, 42 (2007) 1279-1284.

[21] M.M. Tauber, G.M. Gübitz, A. Rehorek, Degradation of azo dyes by oxidative processes–laccase and ultrasound treatment, Bioresource technology, 99 (2008) 4213-4220.

[22] T. Hihara, Y. Okada, Z. Morita, A semiempirical molecular orbital study of the photo-reactivity of monoazo reactive dyes derived from γ-and J-acids, Dyes and pigments, 73 (2007) 141-161.

[23] D. Jacquemin, J. Preat, M. Charlot, V. Wathelet, J.-M. Andre, E.A. Perpete, Theoretical investigation of substituted anthraquinone dyes, The Journal of Chemical Physics, 121 (2004) 1736-1743.

[24] D. Jacquemin, V. Wathelet, J. Preat, E.A. Perpète, Ab initio tools for the accurate prediction of the visible spectra of anthraquinones, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 67 (2007) 334-341.

[25] E.H. Anouar, J. Gierschner, J.-L. Duroux, P. Trouillas, UV/Visible spectra of natural polyphenols: A time-dependent density functional theory study, Food Chemistry, 131 (2012) 79-89.

[26] J. Gierschner, J. Cornil, H.J. Egelhaaf, Optical Bandgaps of π-Conjugated Organic Materials at the Polymer Limit: Experiment and Theory, Advanced Materials, 19 (2007) 173-191.

[27] D. Jacquemin, X. Assfeld, J. Preat, E.A. Perpète, Comparison of theoretical approaches for predicting the UV/Vis spectra of anthraquinones, Molecular Physics, 105 (2007) 325-331.

[28] E.A. Perpète, V. Wathelet, J. Preat, C. Lambert, D. Jacquemin, Toward a theoretical quantitative estimation of the λmax of anthraquinones-based dyes, Journal of Chemical Theory and Computation, 2 (2006) 434-440.

[29] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Wallingford CT, 2004.

[30] R.G. Parr, W. Yang, Density functional approach to the frontier-electron theory of chemical reactivity, Journal of the American Chemical Society, 106 (1984) 4049-4050.

[31] M.E. Casida, C. Jamorski, K.C. Casida, D.R. Salahub, Molecular excitation energies to high-lying bound states from time-dependent density-functional response theory: Characterization and correction of the time-dependent local density approximation ionization threshold, The Journal of Chemical Physics, 108 (1998) 4439-4449.

[32] J. Tomasi, B. Mennucci, R. Cammi, Quantum Mechanical Continuum Solvation Models, Chem. Rev. (Washington, DC, U. S.), 105 (2005) 2999-3093.

[33] B. Langlais, D.A. Reckhow, D.R. Brink, Ozone in water treatment: Application and engineering: Cooperative research report, CRC Press, 1991.