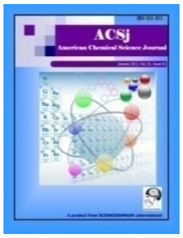

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Modeling of Advanced Photo Oxidation of Alizarin Red-S Dye Using Tio$_2$ as Photo Catalyst

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

The objective of this study was to investigate the experimental study and theoretical study of advanced photo oxidation using TiO_2 as photo catalyst and to compare between these two studies. This work contains two parts, the first part was removing efficiency of an industrially important dye Alizarin Red-S (ARS) from aqueous media using TiO_2 anatase as photo catalyst was studied in various conditions, such as initial concentration, temperature, pH, photo catalyst dosage.
The second part deals with the theoretical study of the TiO_2 surface and the pollutant substance (ARS) using the program (Spartan '08 V1.2.0). we used two kinds of calculations, the first was the Equilibrium Geometry optimization at ground state by Density Functional Theory/B3LYP method and Semi-empirical/PM3 method to predict the most stable geometrical formula for TiO_2 anatase (001),(101) and (ARS) pollutant in different medium (neutral, acidic, basic). The program showed that the method DFT/B3LYP give the best results compared with DFT/PM3 and that the basic medium was better than acidic and neutral medium which means that the highest rate of (ARS) degradation was in basic medium. The second calculation was the energy geometry at ground state by density functional theory/EDF2 method to calculate standard thermodynamic quantities for (ARS) pollutant and TiO_2 anatase (001), (101) surface that showed the highest stability for them in the basic medium.
The results from theoretical study agreed with the results obtained in the experimental study. Results from the experimental study showed Thermodynamic properties was

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calculated for the photo degradation of (ARS) as (ΔH , ΔG , ΔS) which is showed an exothermic heterogeneous reaction with pseudo first order reaction and optimum parameters for removal of this dye from aqueous medium were (0.16 g/l, 20ppm, temp.30ºc, pH9). Theoretical study DFT/B3LYP method showed better results than DFT/PM3 to predict the most stable geometrical formula, and TiO_2 anatase (001) surface was more active than TiO_2 anatase (101) surface.

Keywords: Molecular modeling; Alizarin Red-S degradation; TiO_2 anatase (001) (101) surface; DFT Methods; equilibrium geometry optimization; energy geometry.

1. INTRODUCTION

Textile dyeing process is a significant source of contamination responsible for the environmental pollution. To meet the demand of textile industry, a large variety of dyes are annually produced in tremendous quantities (7×10^5 Tones) in the world. Thus the volume of wastewater containing processed textile dyes is on steady increase [1].

Most of the dyes used in the textiles industries are stable to light and non biodegradable [2]. In order to reduce the risk of environmental pollution from such wastewater, it is necessary to treat them before discharging into the environment [3]. Today more than 10,000 dyes have been incorporated in color index [4], as being the derivatives of aromatic compounds, with halo, nitro, and sylph grouping in their structures most of these are toxic and carcinogenic in nature and pose serious environment threats to human beings as well as aquatic life when present in industrial effluents. Many physical, chemical, and biological methods are employed to eliminate dyes from the wastewater. Physical methods are preferred over chemical and biological methods, because firstly they are simple and inexpensive and secondly do not produce byproducts in water bodies [5,6].

Alizarin Red-S (1,2-dihydroxy-9,10-anthra- quinine sulfonic acid sodium salt, Fig. 1) is a water- soluble, widely used anthraquinone dye in woven fabrics, wool,cotton textiles [7,8]. It is synthesized by sulfonation of alizarin which is a neutral dye obtained from madder (Rubia tinctorum L. Rubiaceae). Anthraquinone dyes like ARS are durable pollutants, released especially by textile industries in the aquatic ecosystems.

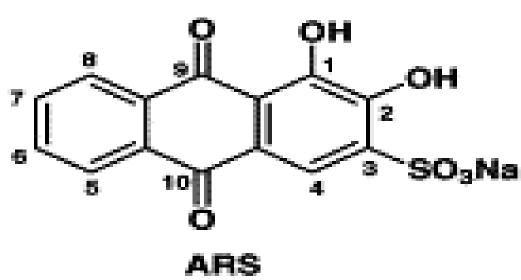


Fig. 1. Molecular structure of Alizarin Red-S

Removal these dyes from industrial wastewaters is a crucial process, from both economical and environmental points of view [9].

In this study, TiO_2 is used as a photo catalyst. K. M. Joshi et al. [10] indicated that TiO_2 is a good photo catalyst for removal ~~of~~ Alizarin Red-S from the aqueous medium at pH 8. The aqueous phase photochemical degradation of dyes like Alizarin red-S has been studied in the presence of semiconducting oxide like TiO_2 and ZnO [11,12]. In recent years, photo catalytic oxidation technology has been advanced for capable of effectively removing pollutants [13], Anatase TiO_2 is in the focus of photo catalytic research because of its strong oxidizing property, high catalytic ability, etc. [11]. The anatase TiO_2 surface has an important impact on photo catalytic activity, photovoltaic properties, and gas sensor characteristics. Hence, an intensive study of the anatase TiO_2 surface is very significant. The most stable surface of anatase TiO_2 is the (101), followed (001) surfaces [14,15].

Experimental work aims to evaluate photo degradation of Alizarin Red-S (ARS) as pollutant substance using TiO_2 anatase as an absorbance surface and photo catalyst with UV-light. Influence of initial concentration of ARS in the solution, the pH, and the temperature are studied on the rate of photodecomposition of (ARS).

The theoretical study consists of two parts. The first is Equilibrium Geometry optimization at ground state using Density Functional Theory/B3LYP method and Semi-empirical/PM3 method to predict the most stable geometrical formula of TiO_2 surface and ARS, and the second is calculation of Standard Thermodynamic quantities for the pollutant and TiO_2 surface from the energy at ground state by using Density Functional Theory/EDF2 method. And then, the theoretical results were compared to the experimental results.

Quantum chemical calculations employing DFT [16] are conducted to investigate the energetic of TiO_2 anatase (101) and (001) surfaces and ARS in different mediums (basic, natural, acidic). (101) face represents the most probable anatase surface [17] and (001) face is considered to be the most stable surface of TiO_2 anatase [18]. The anatase TiO_2 cluster contains two Ti atoms and nine O atoms. This cluster approach is a well known and successful approach applied in quantum chemical calculations [19,20]. However, since there may be limitations to the use of small cluster models to represent oxide surfaces where the peripheral oxygen atoms are saturated with hydrogen atoms, the effect of cluster size is also tested by use of semi empirical PM3 calculations. The basis set employed in the DFT calculations was 6-31G** provided in SPARTAN' 08 (Wave function Inc.). SPARTAN'08 was used for all the semi empirical and DFT calculations reported, Neutral cluster models of(101) and (001) TiO_2 anatase surfaces represented by $Ti_2O_9H_{10}$ but basic cluster models was represented by $Ti_2O_9H_9$ and acidic cluster models represented by $Ti_2O_9H_{12}$ for (101) surface whereas (001) surface acidic cluster models was represented by $Ti_2O_9H_{11}$ [21]. These clusters geometries were then energetically optimized. A. Cordoba et al. [22] investigated the possibility of use of enzymatic treatment by experimental and theoretical study involve molecular modeling through MM2–PM6 by used MOPAC. 2009, Vittadini et al. [23] indicated that the adsorption of formic acid and sodium format on the dry and hydrated TiO_2 anatase (101) surfaces, in which HCOOH is a molecular monodentate species, hydrogen bonded to a surface two-fold coordinated oxygen on the dry surface, but HCOOH and HCOONa preferentially form an inner-sphere adsorption complex on the hydrated surface. Opera et al. [24] showed that the Ti–O bond lengths for NKX-2398 dye are shorter than NKX-2311 and C343 dyes, suggesting a strong binding. Selloni et al. [25] indicated by Molecular Dynamics (MD) calculations adsorption of water is more favorable on TiO_2 anatase (101) surface these results are agree with the findings of the Red Fevn [26]. But using Ab-initio Molecular Orbital Theory Density Functional Theory, Gong et al. [27] explained TiO_2 anatase (001) surface with a lot of Ti5c atoms contributes for highly efficient adsorption of molecules such as formic acid, which is agree with results of high activity on TiO_2 anatase (001) surface due to the Ti5c atoms and the large value of Ti-O-Ti bond angles reported by M. Vittoria & E. Selli [28].

2. EXPERIMENTAL DETAILS

2.1 Chemicals

All chemicals used during experimental work were of analytical grade and were used as such without purification. Alizarin Red-S (Riedel de Haèn) and HCl (EDH 37%). NaOH (Fluka 99%) were used. Double distilled water was used for the preparation of all types of solution and dilution when required.

2.2 Instrumentation

Balance METTLER AE240 and Uv-vis spectrophotometer (PG Instruments Limited U.V- T80) were used in this study.

2.3 Standard Solutions

The stock solution of the dye was prepared by dissolving 0.1g/l of dye in water and made up a stock solution in volumetric flask. The concentration of the dye solution was determined spectrophotometericaly. Standard solutions of dye were prepared by successive dilution of stock solution.

2.4 Experimental Procedure

The photo catalytic degradation of Alizarin red-S for both initial concentration and irradiation sample was determined by Uv-Visible Spectrophotometer (PG Instruments Limited U.V-T80). The calibration curve was obtained at λ_{max} = 260 nm. The reaction mixture was irradiated with light source Uv lamp (PHILIPS-125Watt) at a distance of 15cm from the reaction vessel. Double distilled water was used throughout the experiment. Kinetics of adsorption was determined by analyzing adsorptive uptake of dye from aqueous solution at different time intervals for 15 minutes. In each experiment an accurately weighted amount of TiO_2 was taken in flask in 25 ml dye solution by adjusting pH of the Alizarin red-S dye solution**.**

3. RESULTS AND DISCUSSION

In order to find the appropriate conditions of photo catalyst dose, concentration of dye, pH, and temperature for the adsorption of Alizarin Red-S on TiO_2 anatase, various experiments were conducted .The results of these experiments were as follow.

3.1 Effect of Photo Catalyst Dose

The effect of variation in the photo catalyst amount on the process adsorption of Alizarin Red-S was studied, with different photo catalyst amount (Adsorbent dose) in the range of (0.1, 0.3, 0.4) g. The results are shown in Fig. 2.

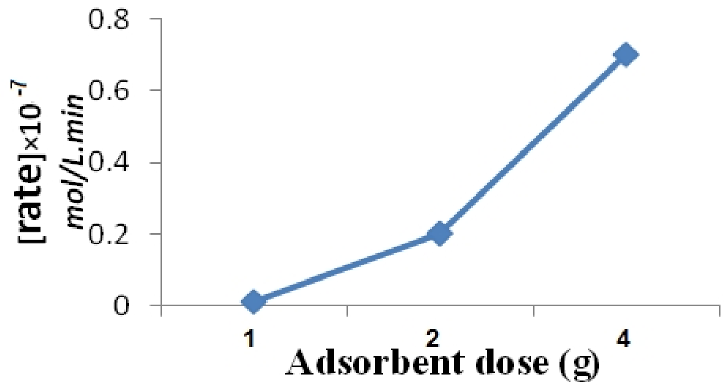


Fig. 2. Effect of photo catalyst dose on ARS degradation rate. experimental parameters: contact time, t (15 min), initial concentration of dye (20 ppm), temp. (30ºC) and solution volume 25 ml

From Fig. 2, an increase in photo catalyst dose leads to increase in the percentage of the removed of alizarin. This is caused by an increased in number of available active points with increase in photo catalyst dose which mean increase of (h^+ e^-) pair number which caused increase in degradation rate [12]. On the other side when photo catalyst dose increase the absorbate photons number well increase that caused increase in degradation rate [29].

3.2 Effect of Initial Dye Concentration

Initial dye concentration was one of the effective factors on the rate of degradation reaction. The rate of Alizarin Red-S degradation was studied as a function initial dye concentration of in the range of 10-30ppm. The results obtained are present in Fig. 3. The rate of (ARS) degradation increases with increasing the initial concentration of the dye TiO_2. It was observed that adsorption yield increased with increase in initial concentration of the dye. Minimum rate was 1 x10^{-7} mol/l.min for 10ppm concentration to maximum rate value 1.3 x10^{-7}mol/L.min for 30ppm concentration of dye solution. This may be due to available active sites and increase in the adsorbed molecules which mean molecules involved in the interaction, as an increase in the high initial concentration of the dye [10].

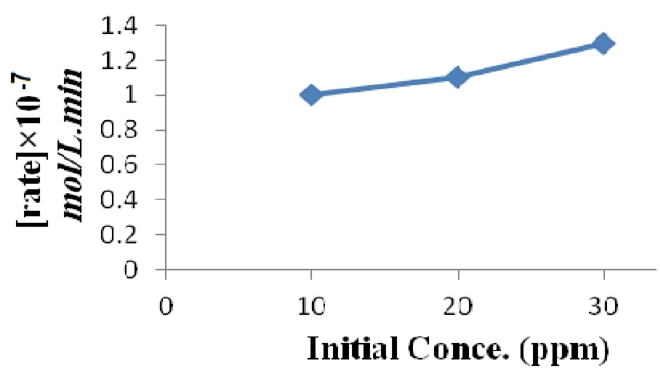


Fig. 3. Effect of initial concentration of dye on (ARS) degradation rate. Experimental parameters: t(15 min) ,temperature (30ºC) and solution volume (V) 25ml

3.3 Effect of pH

The pH of the aqueous solution was clearly an important parameter that controls the degradation process. The rate of Alizarin Red-S degradation was studied as a function of pH in three mediums. The results obtained were shown in Fig. 4. The minimum degradation rate was 0.3 $x10^{-7}$ at pH 5.0 and maximum degradation rate was 0.9 $x10^{-7}$ at pH 9 was followed the consequences basic > neutral > acidic.

Because ARS as pollutants, which are hydrolyzed under alkaline conditions may show an increase of reaction rate with increase of pH [30]. Finally, the presence of ionic species could affect the degradation process via adsorption of the pollutants, absorption of UV light and reaction with hydroxyl radicals that is leads to increase in degradation rate [31,32].

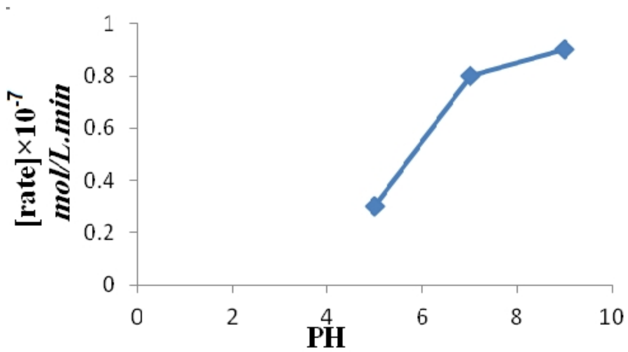


Fig. 4. Effect of pH on (ARS) degradation rate. Experimental parameters: t(15 min), initial concentration of dye (20ppm), temperature (30ºC) and solution volume (V) 25 ml

3.4 Effect of Temperature

Temperature has an important effect on the rate of adsorption. The rate of Alizarin Red-S degradation was studied as a function of temperature in the range of 25-40ºC. The results obtained were present in Fig. 5. It was observed that the ARS degradation rate decreases with increase in temperature. The minimum degradation rate was at 40ºC and maximum degradation was at 30ºC for 20ppm initial concentration of dye solution. The decrease in adsorption was obtained at high temperature because molecules move with great speed and less time of interaction was available for dye anions with photo catalyst material [33,34].

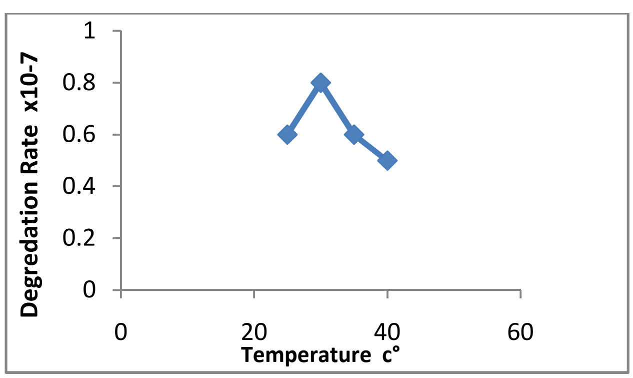


Fig. 5. Effect of temperature on (ARS) degradation rate of Alizarin Red-S. experimental parameters: t (15 min), initial concentration of dye (20ppm), and solution volume (V) 25 ml

3.5 Thermodynamic Parameters

Thermodynamic parameters such as standard Gibbs free energy *(ΔG*), Enthalpy (*ΔH*) and entropy (*Δ*S) were also calculated using equations 1,2 and 3 and the results obtained are illustrated in Table 1.

$$\Delta G = -RT \ln K \quad \text{---------------} \qquad (1)$$

$$\frac{\Delta H^*}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] = \ln \frac{K_2}{K_1} \quad \text{----------} \qquad (2)$$

$$\Delta G = \Delta H - T\,\Delta S \quad \text{-------------} \qquad (3)$$

T is the absolute temperature in Kelvin.

Table 1. Adsorption of alizarin Red S

Adsorbent	**Temperature K**	***ΔG*** **kJ.mol^{-1}**	***ΔH*** **kJ.mol^{-1}**	***ΔS*** **kJ.mol^{-1}. K^{-1}**
TiO_2	303	-12.250	-20.9	0.028

The negative value of the ΔG at the studied temperature range indicated that the sorption of alizarin Red S on sorbent was thermodynamically feasible and spontaneous. The negative value of ΔH showed that the sorption was exothermic. The positive value of ΔS showed an increased randomness at the solid alizarin Red S solution interface during the adsorption of alizarin Red S [12] as Table 1 showed.

3.6 Geometrical Optimization

After selection of the final model for each (ARS) pollutant and TiO_2 surface Anatase (101), (001) the equilibrium geometry was calculated for ground state by (Density Functional Theory/B3LYP) and (PM3 /Semi-Empirical) in the three different mediums (natural, basic, acidic), calculate the bonds length and angles for the result optimized structure which give us idea of surface stability and reactivity that is resulted from the most stable structure and least reactivity in this mediums. Surface reactivity increase with increase titanium atoms (Ti_{5C}) in the surface and from large value of bond angle (Ti-O-Ti) which from reactivity of O atoms Figs. 6,7,8.

From Table (2) value of (θ) angle showed that the (001) surface has most value from others that is mean highest reactivity in basic medium and showed that the method DFT/B3LYP give the best results and confirmed with The practical methods that the basic medium give the highest rate of decomposition of (ARS) fallowed the consequences:

basic > neutral > acidic

Whereas (Ti_{5C} -O_{2C}) bond lengths in acidic medium has most value from others that is mean non favorite medium for TiO_2 anatase (001) surface.

TiO_2 anatase (001) Surface Geometrical Optimization

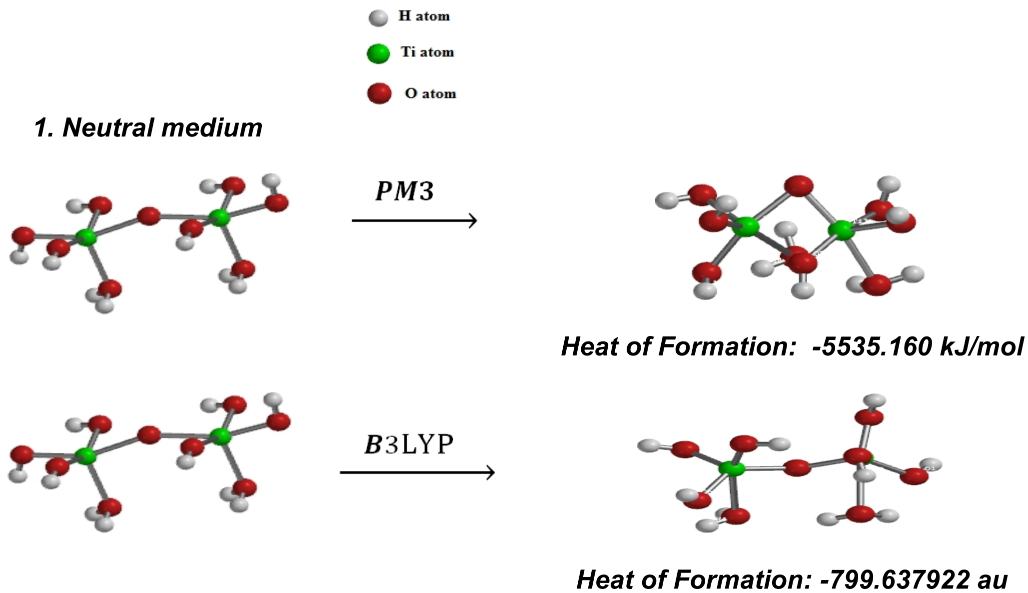


Fig. 6. (001) surface Optimized geometrical formula in neutral medium

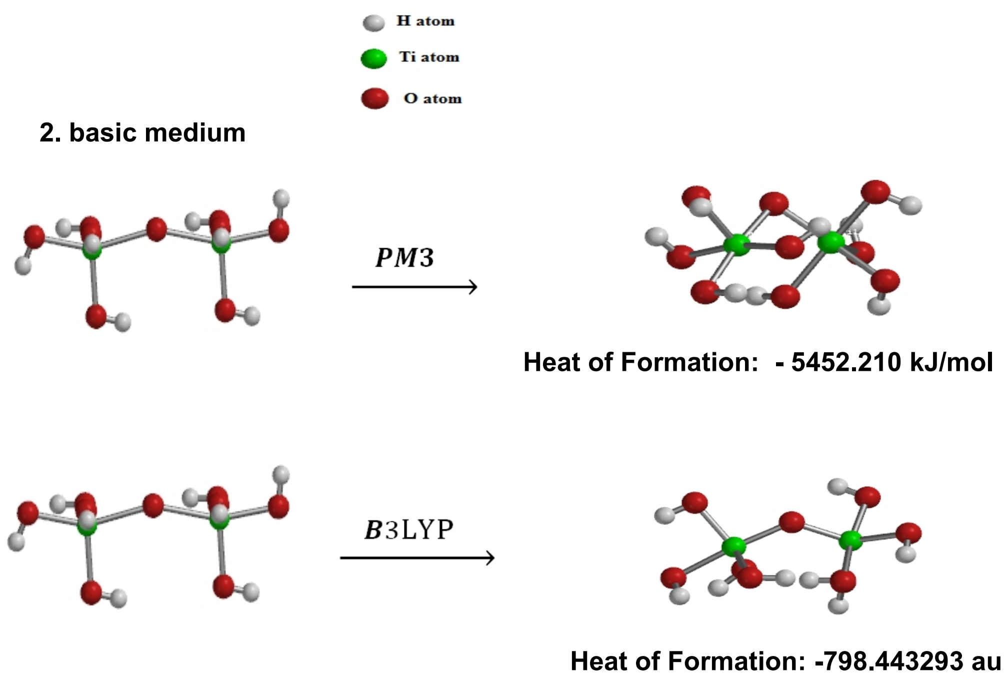


Fig. 7. (001) surface Optimized geometrical formula in basic medium

3. Acidic medium

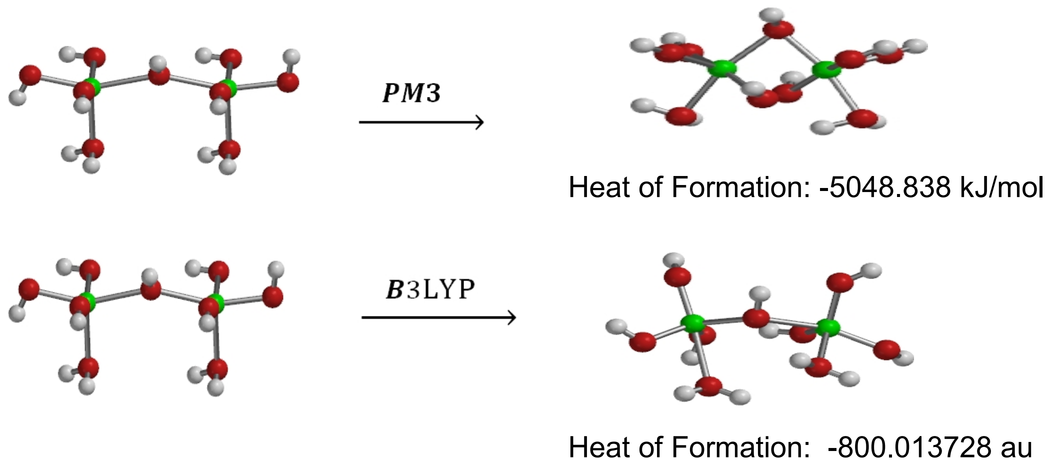


Fig. 8. (001) surface Optimized geometrical formula in acidic medium

Table 2. Bonds length and angle value for (001) surface

	Medium	Method	Ti_{5C} -O_{2C}(a°)	θ
Calculated	Basic	B3LYP	1.831	131.73°
		PM3	1.949	80.70°
Calculated	Natural	B3LYP	1.738	129.73°
		PM3	1.950	81.22°
Calculated	Acidic	B3LYP	2.138	128.28°
		PM3	2.010	76.78
Ref.35		B3LYP	1.857	-
Ref.37		PBE	-	146°

θ : *value of (Ti-O-Ti) bond*
Ti_{5C}*: fivefold Titanium atom*
O_{2C}: *twofold oxygen atom*

Figs. 9,10,11 shows the surface geometrical optimization of TiO_2 anatase in different medium.

Both methods PM3 and B3LYP showed that the θ value for TiO_2 anatase (101) surface in the basic medium is more than that's in neutral medium which refers to high reactivity for (101) surface in basic medium but in acidic medium values varied where(B3LYP) method give large value of θ which refers to high reactivity from the basic and neutral mediums that doesn't agree with the experimental results while PM3 method showed small value of θ which refers to low reactivity less than in basic and neutral mediums which agree with the experimental results Table 3.

Comparing between TiO_2 anatase (001) and (101) surfaces by bonds length and angle value, we find that the (001) surface was more reactive than (101) surface. Our results agree with the previous findings reported in different studies [39,40,27].

PM3 methods in Table 4 showed that both TiO2 anatase (001) and (101) surfaces has less heat of formation in neutral medium which means each of them had highest stability and lowest reactivity in neutral medium, whereas in acidic medium both surfaces have high heat of formation which means lowest stability and highest reactivity in acidic medium.

<u>TiO_2 anatase (101) Surface Geometrical Optimization</u>

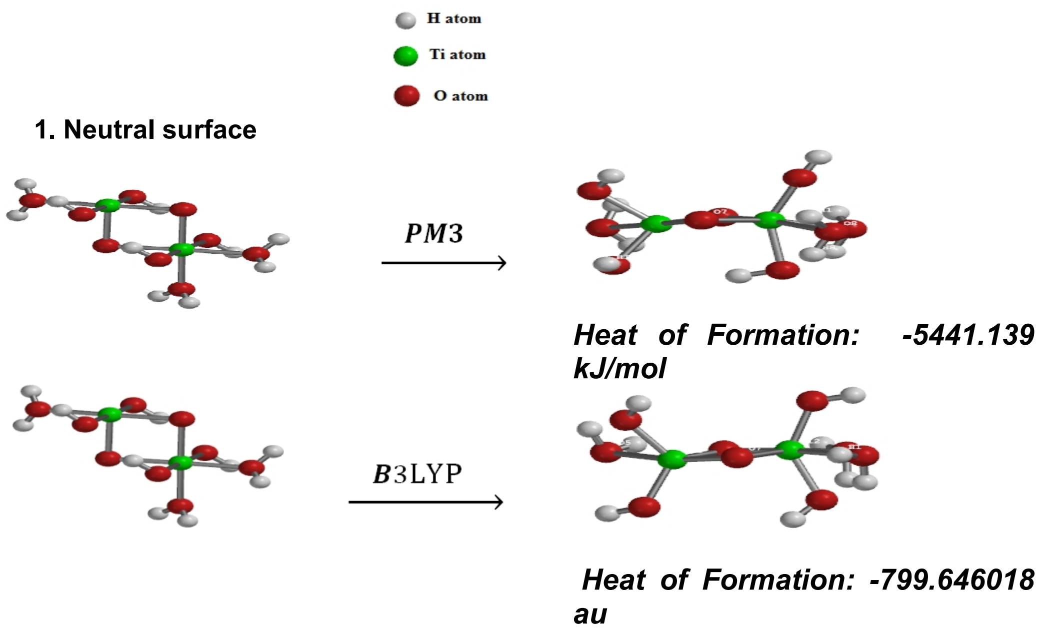


Fig. 9. (101) surface Optimized geometrical formula in neutral medium

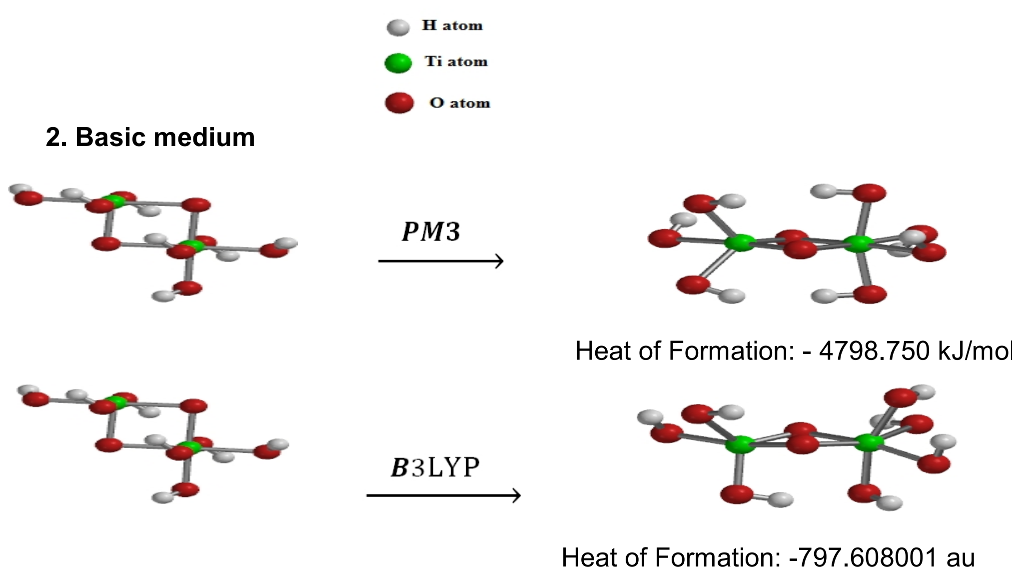
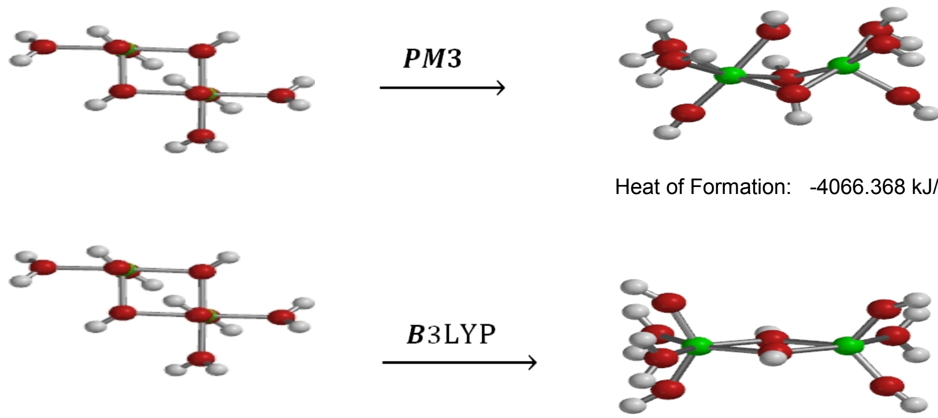


Fig. 10. (101) surface Optimized geometrical formula in basic medium

3. acidic medium



Heat of Formation: -4066.368 kJ/mol

Heat of Formation: -800.256054 au

Fig. 11. (101) surface Optimized geometrical formula in acidic medium

Table 3. Bonds length and angle value for (101) surface

	Medium	Method	Ti_{5C} -O_{2C}	Ti_{6C} -O_{2C}	θ
Calculated	Basic	B3LYP	1.953	1.831	99.13
		PM3	1.896	1.981	83.09
Calculated	Natural	B3LYP	1.873	1.823	96.71
		PM3	1.917	1.938	80.36
Calculated	Acidic	B3LYP	2.004	1.979	109.38°
		PM3	2.014	2.027	75.70°
Ref.35		B3LYP	1.966	1.937	-
Ref.36		B3LYP	1.830	1.850	-
Ref.38		GGA	1.836	1.849	-
Ref.37		PBE	1.942	-	102

***θ*:** *Value of (Ti-O-Ti) bond*
Ti_{5C} *: Fivefold Titanium atom*
Ti_{6C}: *sixfold Titanium atom*
O_{2C} *: twofold oxygen atom*

Table 4. Heat of formation for (001),(101) surface in different medium

	Method	Basic	Neutral	Acidic	Energy unit
001	PM3	-5452.21	-5535.16	-5089.44	kJ/mol
	B3LYP	-798.443	-799.639	-800.013	au
101	PM3	4798.750-	-5441.139	-4066.36	kJ/mol
	B3LYP	-797.6	-799.646	-800.256	au

B3LYP methods showed that both TiO_2 anatase (001) and (101) surfaces have high heat of formation in basic medium which means each of them had lowest stability and highest reactivity in basic medium, whereas in acidic medium both surface have lowest heat of formation which means highest stability and lowest reactivity ,that's agree with the experimental results which indicate ARS degradation rate is the most in basic medium and this was very clear in 101 surface where the highest heat of formation was observed.

On the other hand comparing between calculated heat of formation by B3LYP method for both TiO_2 surfaces showed that (101) surface has highest heat of formation which means low stability and high reactivity than (001) surface. This result agree with previous studies [25,26].

Heat of formation values in Table 5 was calculated by B3LYP showed that's ARS pollutant has highest heat of formation in basic medium fallowed the consequences basic > neutral > acidic whereas PM3 method showed that's highest heat of formation in acidic medium fallowed the consequences acidic > basic > neutral that's indicate B3LYP methods give good results which is agree with the experimental results Figs. 12,13,14.

Table 5. Heat of formation for ARS pollutant in different medium

	Method	Basic	Natural	Acidic	Energy Unit
ARS	PM3	996.948-	-1081.805	-902.387	**kJ/mol**
	B3LYP	-1461.857	-1462.497	-1462.995	**au**

***Geometrical Optimization*) Alizarin Red-S (ARS)**

1. Neutral medium

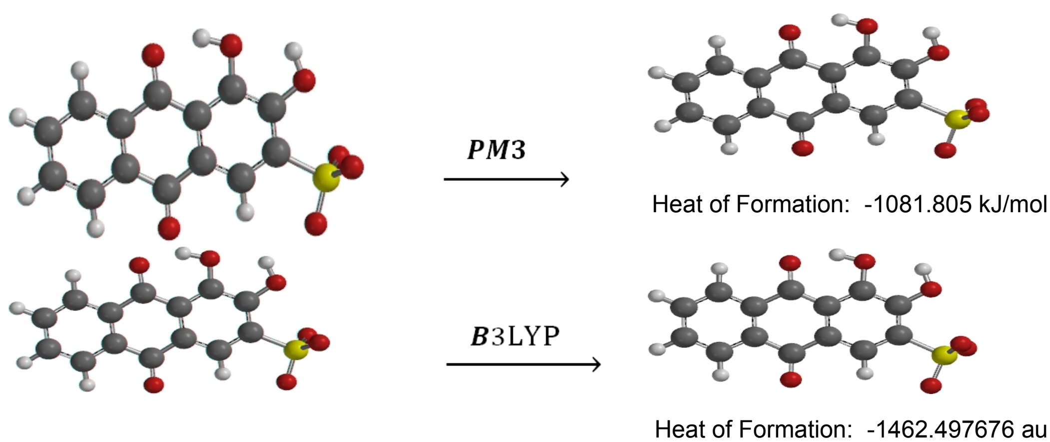


Fig. 12. ARS pollutant Optimized structure in neutral medium by (PM3)(B3LYP)

3.7 Theoretical Calculations for Surface and Pollutant

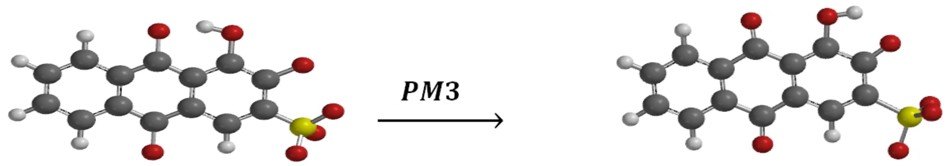
The thermodynamic calculation was performed depending on the energy calculations at ground state by using Density Functional Theory/EDF2 method to calculate Standard Thermodynamic quantities for pollutant and TiO_2 surface.

The theoretical thermodynamic values for both (101),(001) surfaces and ARS pollutant in different mediums in Tables 6 and 7 the increase of this values Means an increase of stability and decrease of reactivity fallowed the consequences:

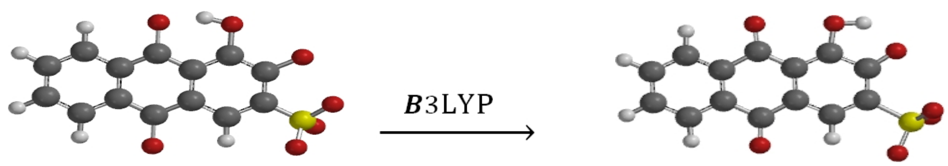
Increase reactivity ← basic > neutral > acidic → Increase stability

This results agreed with the experimental results that showed the highest reactivity and lowest stability for each pollutant (ARS) and TiO_2 surface in the basic medium.

2. Basic medium



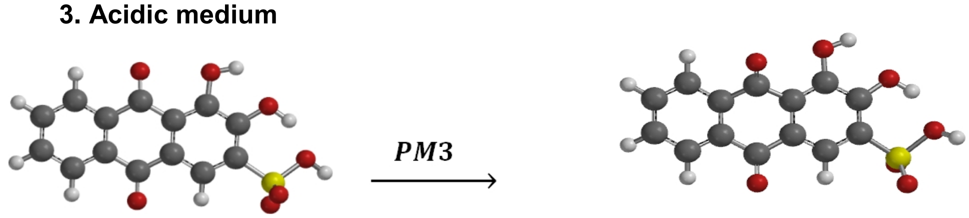
Heat of Formation: -996.948 kJ/mol



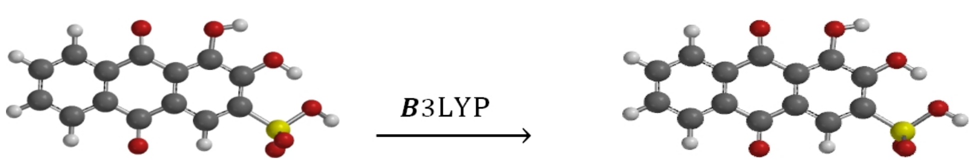
Heat of Formation: -1461.857569 au

Fig. 13. ARS pollutant Optimized structure in basic medium by (PM3) (B3LYP)

3. Acidic medium



Heat of Formation: -902.387 kJ/mol



Heat of Formation: -1462.995253 au

Fig. 14. ARS pollutant Optimized structure in acidic medium by (PM3) (B3LYP)

Tabel 6. Standard Thermodynamic quantities for surface at 298.15 K and 1 atm

Surface	Medium	ZPE kJ/mol	Enthalpy kJ/mol	Entropy J/mol.K	Cv J/mol.K	Gibbs free energy G (kJ/mol)
	Basic	254.6410	344.2600	528.5494	254.6410	186.916
001	Natural	361.9670	409.9561	537.8440	266.3754	249.924
	Acidic	388.7331	434.5602	522.5073	257.6182	279.004
	Basic	268.0738	313.1480	517.0250	250.3672	159.082
101	Natural	361.6021	414.0866	574.2387	284.7062	243.028
	Acidic	412.2940	470.5403	606.5702	317.5846	289.952

***C_V**: heat capacity*
***ZPE:** Zero point energy*

Tabel 7. Standard Thermodynamic quantities for ARS pollutant at 298.15 K and 1 atm

	system	ZPE kJ/mol	Enthalpy kJ/mol	Entropy J/mol.K	Cv J/mol.K	Gibbs free energy G kJ/mol
ARS/EDF2	Basic	467.4259	511.7977	527.8044	268.1554	354.4328
ARS/EDF2	Natural	502.9677	549.7038	546.4649	279.8043	386.7753
ARS/EDF2	Acidic	532.9485	577.9819	532.0865	274.4549	419.3403

4. CONCLUSION

Results from the experimental study showed that the photodegradation reaction from pseudo first order and exothermic reaction and optimum parameters for removal of this dye from aqueous medium were (0.16 g/l, 20ppm, temp. 30ºC, pH9).

Theoretical study DFT/B3LYP method showed better results than DFT/PM3 to predict the most stable geometrical formula, and TiO_2 anatase (001) surface was more active than TiO_2 anatase (101) surface.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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