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Experimental and Computational Investigations of Decolourization of Rhodamine B in Aqueous Solution

Sulu Çözeltide Rodamin B'nin Renk Gideriminin Deneysel ve Hesaplamalı Araştırılması

Research Article

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ABSTRACT

The aim of the study was comparatively to investigate decolourization of Rhodamine B (RhB) in aqueous solution using photocatalytic and ultrasonic processes. Also, computational investigations of RhB^0 and RhB^{+-} compounds were performed at HF/6-31G level in gas phase. Photocatalytic decolourization of RhB was studied using TiO_2 and silver-loaded TiO_2 (Ag-TiO_2) as catalyst. It was found that decolourization by photocatalytic process of RhB increased with decreasing pH, and decolourization rate also increased in the presence of TiO_2/UV when compared to UV irradiation alone. Moreover, Ag-loading to TiO_2 dramatically reduced decolourization time. The decolourization by ultrasonic process of RhB was also studied by using various salts and initial dye concentrations at various pHs and amplitudes. The decolourization by ultrasonic process of RhB was found to increase with decreasing pH, increasing amplitudes and addition of various salts to aqueous solution. It was observed that the decolourization decreased with increasing initial RhB concentration. The decolourization rate of the dye was monitored spectrophotometrically at 554 nm.

Key Words
Dye, photocatalytic decolourization, ultrasonic decolourization, silver, titanium dioxide, Ab-initio study.

ÖZ

Bu çalışmanın amacı fotokatalitik ve ultrasonik yöntem ile sulu çözeltideki Rodamin B (RhB)'nin renk gideriminin karşılaştırmalı olarak araştırılmasıdır. Ayrıca, RhB^0 and RhB^{+-} nin gaz fazında HF/6-31G seviyesindeki hesaplamalı araştırılması da yapılmıştır. RhB'nin fotokatalitik renk gideriminde TiO_2 ve gümüş yüklü TiO_2 (Ag-TiO_2) katalit olarak kullanılmıştır. RhB nin fotokatalitik yöntemle renk gideriminin azalan pH ile arttığı, ayrıca renk giderim oranının sadece UV ışığı ile ışınlamayla kıyaslandığında TiO_2/UV varlığında daha da arttığı gözlenmiştir. Ag-yüklü TiO_2 in kullanılması ise renk giderme zamanını önemli ölçüde azaltmıştır. RhB nin renk gideriminde çeşitli tuzların, farklı pH'larda boya başlangıç derişiminin ve ses dalgası şiddetinin etkisinin de araştırıldığı ultrasonik yöntemle de çalışılmıştır. RhB nin ultrasonik yöntemle renk gideriminin azalan pH, artan ses şiddeti ve sulu çözeltiye eklenilen çeşitli tuzların etkisiyle arttığı gözlenmiştir. Renk gideriminin RhB başlangıç derişiminin artmasıyla azaldığı gözlenmiştir. Boyanın renk giderim oranı 554 nm'de spektrofotometrik olarak izlenmiştir.

Anahtar Kelimeler
Boya, fotokatalitik renk giderimi, ultrasonik renk giderimi, gümüş, titanyum dioksit, Ab-initio çalışma.

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INTRODUCTION

Synthetic dyes are widely used in the textile, cosmetic, paper dyeing, drug and food processing industries. The industry wastewater is heavily charged with unconsumed dyes, surfactants and sometimes traces of metals. These effluents cause a lot of damage to the environment [1]. RhB is one of the most important dyes of the xanthene group and is used in many industrial processes, such as paper dyeing and the production of dye laser [2]. Advanced oxidation processes (AOPs) are quite appropriate for the remediation of wastewater as a pre- or post-treatment step. The AOPs are mainly based on the generation of the hydroxyl radical ($OH^{\cdot}$), which has a great oxidation power and is able to oxidize almost all organic compounds to carbon dioxide and water. Heterogeneous photocatalysis through illumination of UV on semiconductor surface is an attractive AOP [3]. Titanium dioxide (TiO_2), as a chemically stable, non-toxic, highly efficient, and relatively inexpensive photocatalyst, has been widely used for water and air purification since many environmental pollutants can be degraded by oxidation and reduction processes on TiO_2 surface [4,5]. Photocatalytic oxidation processes are usually referred to as advanced oxidation processes (AOP). When a photon with an energy which matches or exceeds the band gap energy of the semi-conductor is incident on a semiconductor surface, a conductive band electron will jump to its valence band leaving a positively charged hole behind. The initial step in this type of photo-oxidation process is believed to be the formation of free hydroxyl radicals [6-8]. Hydroxyl radicals are generated by the oxidation of water (OH^- ions) at the valence band positively charged holes.

$$TiO_{2(s)}TiO_{2(s)} + h\nu \rightarrow e^-_{CB} + h^+_{VB} \tag{1}$$

$$h^+_{VB} + OH^-_{(TiO_2 surface)} \rightarrow OH^{\bullet} \tag{2}$$

$$h^+_{VB} + H_2O_{(adsorbed\ on\ surface)} \rightarrow OH^{\bullet} + H^+ \tag{3}$$

$$OH^{\bullet} + Organic\ Molecule \rightarrow Degradation\ products \tag{4}$$

On the other hand, the dissolved O_2 molecules are transformed to anionic superoxide ($O_2^{-\bullet}$) radicals via electrons from conductive band.

$$e^-_{CB} + O_{2\ (adsorbed\ on\ surface)} \rightarrow O_2^{-\bullet} \tag{5}$$

The most commonly studied photocatalysts are TiO_2, ZnO, ZnS and CdS. Additionally, In_2O_3, $SrTiO_3$, SnO_2 and WO_3 have been used as photocatalysts but all showed lower levels of photo-activity [9], and SiO_2 and MgO are found to be inactive. Since most metal oxides and sulphides can undergo irreversible photo-corrosion on the surface [10], these types of semiconductor are not suitable for long term treatment processes. Transition metal doping with silver which enhances the interfacial charge-transfer reactions of TiO_2 bulk phase and colloidal particles, can increase the photocatalytic activity of TiO_2 [11].

In recent years considerable interest has been shown on the application of ultrasonic decolourization for the removal of hazardous contaminants from water [12,13]. Ultrasonic decomposition of organic compounds is resulted from the formation, growth and collapse of high-energy cavitation bubbles, which releasing large quantities of energy over a small location [14]. When water is sonicated, $H^{\cdot}$ and $OH^{\cdot}$ are produced. A simple mechanism for radical formation and depletion, during sonication of water is given below [13]:

$$H_2O \xrightarrow{)))} OH^{\bullet} + H^{\bullet} \tag{6}$$

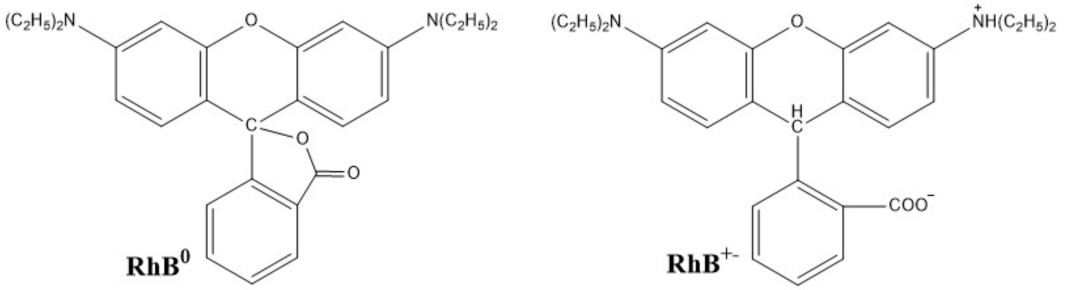
$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \tag{7}$$

$$OH^{\bullet} + H^{\bullet} \rightarrow H_2O \tag{8}$$

$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \tag{9}$$

There is an equilibrium in RhB^0 and RhB^{+-} which their color are colorless and violet, respectively [15]. Shematic diagram of RhB^0 and RhB^{+-} are represented in Scheme 1.

Optimized structures of RhB^0 and RhB^{+-} are calculated at HF/6-31G level in gas phase. Additionally, chemical reactivity of these compounds are examined in detail by using some quantum chemical descriptors which are energy of the highest occupied molecular orbital (E_{HOMO}),



Scheme 1. Schematic representation of RhB^0 and RhB^{+-}.

energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap between LUMO and HOMO (E_{GAP}), softness (σ), chemical potential (CP), nucleophilicity index (N) and dipole moment (μ).

MATERIAL and METHODS

Experimental Method

Reagents and Solutions

RhB was obtained from Merck (Darmstad, Germany). The stock solution of RhB was prepared in deionised water in all experiments. H_2SO_4 and NaOH solutions at 1.0 mol L^{-1} were used to adjust the pH of the studied dye samples. Solid reagents of Na_2CO_3, $NaHCO_3$, NaCl, Na_2SO_3 and $NaIO_3$ were supplied from Merck. Titanium dioxide (anatase 99.9%) was supplied by Aldrich (surface area 9.35 m^2 g^{-1}). The Ag-loaded titanium dioxide containing 1% (w/w) silver was prepared following the method described previously [16]. Initially, 9.2 mL of a 0.1 mol L^{-1} solution of $AgNO_3$ was added to a aqueous TiO_2 slurry (which contained 10.0 g of TiO_2), followed by about 10 mL of a 1% (w/w) solution of Na_2CO_3. The aqueous suspension was dried at room temperature and then baked for 6 h at 600°C (surface area 8.49 m^2 g^{-1}).

Photocatalytic Decolourization Experiments

100 mL of an aqueous dye sample and 0.1 g TiO_2 (neat TiO_2 or Ag-loaded TiO_2) were initially placed in a 500 mL pyrex flask (which with covered with aluminium foil) with a condenser. The pH of dye sample solution was adjusted. The stirred suspension was illuminated by an OSRAM-Ultra Vitalux 300 W low pressure mercury lamp (no cut off filters) with a flux output of approximately 5.8 W near the 254 nm wavelength. At regular intervals, 5 mL of aliquots of irradiated sample was withdrawn and centrifuged twice at 4000 rpm for 5 min to separate TiO_2 for residual dye analysis. Concentrations of the residual dye in the supernatant were spectrophotometrically monitored for 60 min at 554 nm.

Ultrasonic Decolourization Experiments

Sonolyses were performed with an ultrasonic processor (Cole Parmer Instruments, Vernon Hills, Illinois, USA) operating at 20 kHz and 25 °C. In each experiment, 250 mL of aqueous dye sample with desired concentration was placed in to a 500 mL pyrex flask and its pH was adjusted. The solution was poured into ultrasonic processor and mechanical stirrer was used to stir the solution. At certain reaction intervals, 5 mL of sample was withdrawn. Concentrations of the residual dye in the supernatant were spectrophotometrically monitored for 60 min at 554 nm. Also, by adding Na_2CO_3, $NaHCO_3$, NaCl as well as reducing and oxidizing salts such as Na_2SO_3 and $NaIO_3$ to the solution, their effects on degradation of RhB were investigated.

Computational Method

All computational processes were made by Gaussian package program [17,18]. Fully optimizations were performed at HF/6-31G level in gas phase and in these calculation results no imaginary frequencies were observed. Mentioned some quantum chemical parameters of RhB^0 and RhB^{+-} were calculated by using Equations (9)– (18):

$$E_{GAP} = E_{LUMO} - E_{HOMO} \tag{10}$$

$$I = -E_{HOMO} \tag{11}$$

$$A = -E_{LUMO} \tag{12}$$

$$\eta = \frac{I - A}{2} \quad (13)$$

$$\sigma = \frac{1}{\eta} \quad (14)$$

$$\chi = \frac{\left| E_{HOMO} + E_{LUMO} \right|}{2} \quad (15)$$

$$CP = -\chi \quad (16)$$

$$\omega = \frac{CP^2}{2\eta} \quad (17)$$

$$N = \frac{1}{\omega} \quad (18)$$

RESULTS and DISCUSSION

Photocatalytic Decolourization

Effect of TiO_2 and UV on the Photocatalytic Decolourization of RhB

A series of experiments using RhB dye was carried out in the presence of TiO_2 particles with and without UV illumination. The same procedure was repeated with Ag-loaded TiO_2 and the results are given in Figure 1. Each data point shown in all figures represents the mean of three replications.

It is seen that Ag-loading dramatically reduced decolourization time for the RhB dye. While the undoped TiO_2 decolorized about 47% of the initial amount within 10 min, Ag-loaded TiO_2 decolorized 88% of the initial amount during the same time period. As seen from Figure 1, decolourization of the dye was very slow in the absence of TiO_2 with UV irradiation and the decolourization with only TiO_2 without UV irradiation (in dark) is also very slow. The time required for complete decolourization is about 35-60 min with TiO_2 and UV irradiation. With the Ag-loaded catalyst, the complete decolourization of dye took a short time of 20 min.

As mentioned above, Ag-loading dramatically reduced decolourization time for the RhB dye. However, as seen in Figure 2, the increase in the amount of Ag-TiO_2 steadily affected the decolourization.

XRD pattern (as indicated in our first study, Figure 2) exhibited strong diffraction peaks at 25° and 48° indicating TiO_2 in the anatase phase and Ag loading did not greatly affected the structure [16-18]. The formation of silver islands in TiO_2 can be clearly seen in SEM image (Figure 4b, blue regions, in referred our study) [19] .

The enhancement of removal rate is due to: (i) the increase in the amount of catalyst increasing the number of dye molecule adsorbed and (ii) the increase in the density of particles in the area of illumination [20]. At TiO_2 concentrations less than about 1.0 g L^{-1}, the decolourization rate is proportional to the TiO_2 concentration. The decolourization rate has probably been limited over 2.0 g L^{-1} of TiO_2 because UV light can be blocked by catalyst itself.

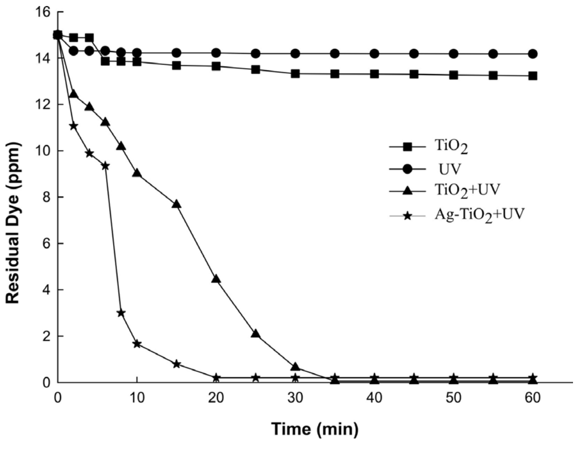


Figure 1. Photocatalytic decolourization of RhB versus irradiation time for several systems.

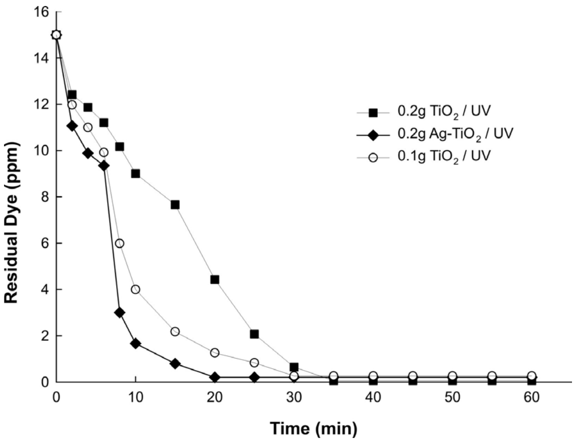


Figure 2. Photocatalytic decolourization of RhB versus irradiation time in TiO_2/UV and different amount of Ag-TiO_2/UV systems.

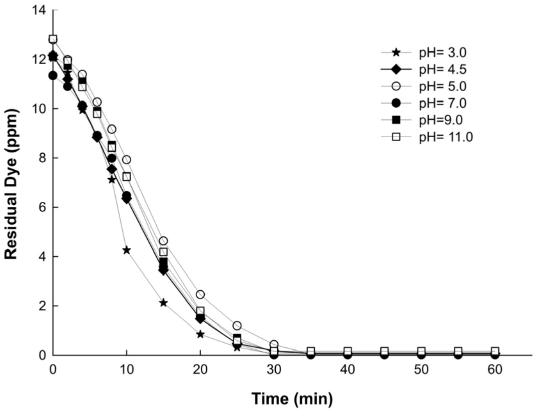


Figure 3. Effect of pH on the photocatalytic decolourization of RhB.

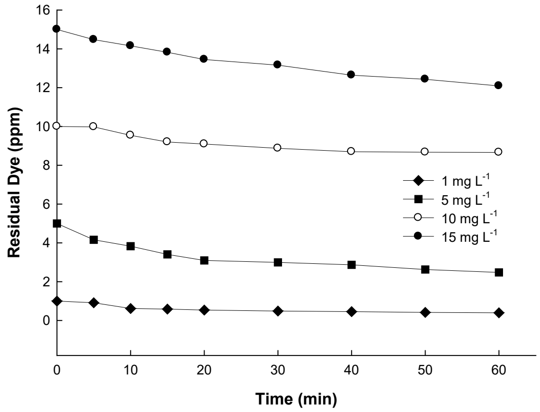


Figure 4. Effect of initial RhB concentration on the ultrasonic decolourization of RhB.

Effect of pH on the Photocatalytic Decolourization of RhB

Photocatalytic decolourization process is also known to be affected by pH. The effect of the initial pH of the aqueous medium on the degradation of RhB by the TiO_2/UV process was also studied at different pHs in the range of 3.0-11.0. The results were showed in Figure 3. The photocatalytic decolourization of RhB was maximum at pH 3.0. It was found that decolourization rate of RhB continuated with decreasing slope at pH 4.5. But, the decolourization of dye increase from pH 4.5 to 3.0, and there is almost no decolourization in dye at higher pHs. At higher pH values than pK_a (3.7) of RhB [19], the carboxyl group of cationic form (RhB^{+}) is deprotonated, thus the dye is transformed into zwitterionic form ($RhB^{\pm}$) [15-21]. The RhB molecule has two diethylamine groups, that can be protonated at acidic pHs. Therefore, with decreasing pH, the protonation of RB increases. In addition, the increasing of the oxidation potential of $OH^{\cdot}$ radical in the acidic medium might be another reason for the increase in decolourization rate [22]. Photocatalytic decolourization process has previously been studied [23]. In this study, it was observed that decolourization rate of dye increased with decreasing pH from 5.5 to 4.0.

Ultrasonic Decolourization

Effect of Initial Concentration of RhB on the Ultrasonic Decolourization

One important factor influencing the efficiencies of the ultrasonic decolourization is the initial concentration of RhB. In this work, effect of the initial concentration of RhB on the ultrasonic decolourization was investigated in the values ranging from 1 to 15 mg L^{-1}. The results were shown in Figure 4. As can be seen from this figure, decolourization rate decreases with increasing initial concentration of RhB. An explanation to this behaviour is the fact that as the initial concentration of RhB increases, intermediates form at higher concentrations [24]. Assuming most of the reactions take place at the bubble–liquid interface, with increasing initial concentrations of RB and correspondingly intermediates, the RB decolourization has been limited by the available interfacial area [24].

Effect of Amplitude on the Ultrasonic Decolourization of RhB

Another important factor influencing the efficiencies of the ultrasonic decolourization is the amplitude. The effect of amplitude was studied

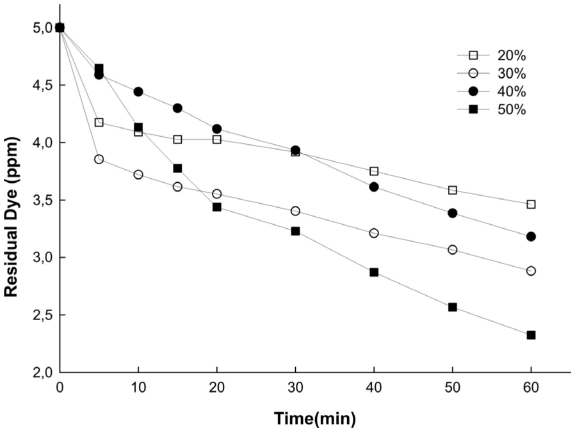


Figure 5. Effect of amplitude on the ultrasonic decolourization of RhB.

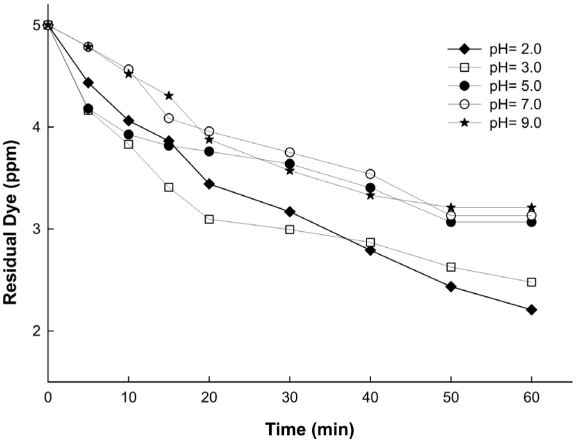


Figure 6. Effect of pH on the ultrasonic decolourization of RhB.

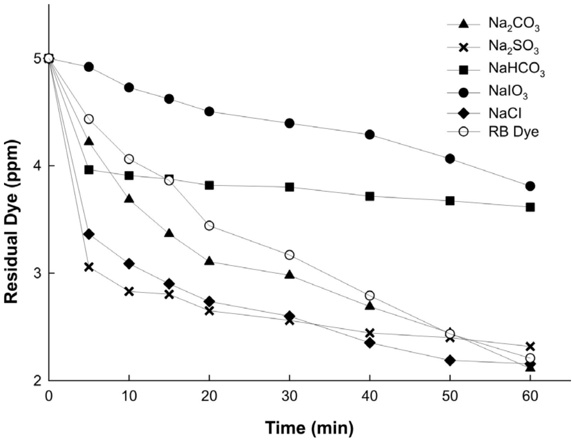


Figure 7. Effect of Na_2CO_3, Na_2SO_3, $NaHCO_3$, NaCl and $NaIO_3$ on the ultrasonic degradation of RhB.

in the range of 20-50%. Results were showed in Figure 5. As can be seen in the figure, final concentration of RhB decreases with increasing the amplitude. In this case, it is due to higher energy dissipated to the system with decreasing volume at the same energy input [25].

Effect of pH on the Ultrasonic Decolourization of RhB

The effect of pH on the ultrasonic decolourization of RhB was studied in the pH range of 2.0-9.0. The results were showed in Figure 6. It was found that the decolourization activity of RhB increased with decreasing pH values. Decrease of decolourization rate with increase in pH is due to dissociation of -COOH sites of dye, so that retards to diffuse into the reactive zone (bubble-liquid interface) in which uncombined •OH concentration is maximum [12].

The ultrasonic decolourization of RhB was maximum at pH 2.0. It was found that rate of decolourization of RhB gradually preceded with decreasing slope up to pH 3.0, but ah higher pHs there was almost no change in decolourization rate. The RhB molecule has amine groups that can be protonated at acidic pH. Therefore with decreasing pH, the protonation of RhB increases. In addition, the increasing of the oxidation potential of OH· radical in the acidic medium might be another reason for the increase in decolourization rate [16]. Decreasing of decolourization rate by increase of pH is due to dissociation of –COOH sites of dye, so that retards it to diffuse into the reactive zone (bubble–liquid interface), where uncombined •OH concentration is maximum [12].

At high pHs dye solutions undergo sonolytic decolourization at a much slower rate. At higher pHs, RhB is present in its zwitterion form and does not readily accumulate at the bubble interface. In strong acidic pHs, RhB exists in higher concentrations at the bubble interface and thus, is more readily subjected to the OH radical attack. The enhancement of decolorization rate in strong basic conditions (pH 11–13) may be caused by the change of hydrophobic property of the dye [24].

Effect of Na_2CO_3, $NaHCO_3$, NaCl, Na_2SO_3 and $NaIO_3$ on the Ultrasonic Decolorization of RhB

One of the aims of the study was also to investigate the effect of salts such as Na_2CO_3, $NaHCO_3$, NaCl, Na_2SO_3 and $NaIO_3$ on the ultrasonic decolorization of RhB. The salt effect on the decolorization process was investigated with the same way. The results were showed in Figure 7. As can be seen from the figures, the ultrasonic decolorization of RhB was significantly decreased in the presence of IO_3^- and HCO_3^- ions whereas its effectiveness increased significantly in the presence SO_3^{2-}, Cl^- ions and partly in the presence CO_3^{2-} ion. Addition of NaCl can increase the hydrophilicity, the surface tension and ionic strength of the aqueous phase and decrease the vapour pressure [26]. Addition of salt to aqueous solution of dye pushes RhB molecules from the bulk aqueous phase to the bulk-bubble interface [26,27].

The enhancement of RhB decolorization is due to the formation of carbonate radical, which

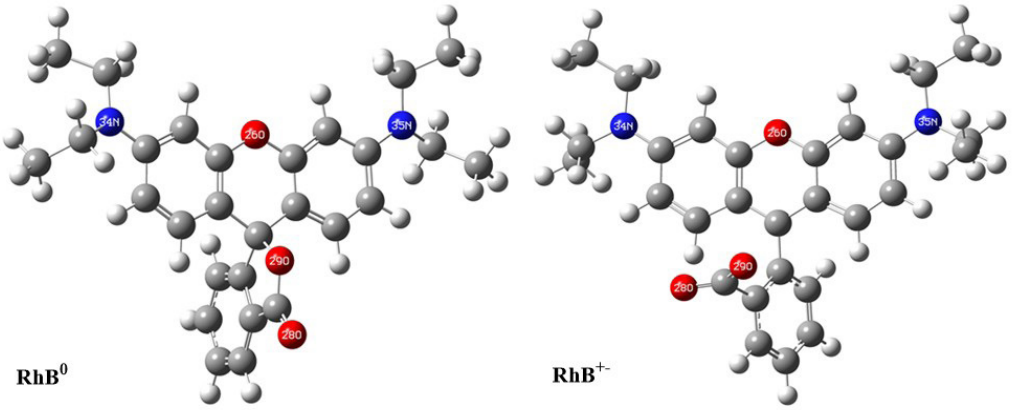


Figure 8. Optimized structures of RhB^0 and RhB^{+-} with atomic labelling.

may react more effectively than OH$^\cdot$ radical with dye molecules [28]. The addition of bicarbonate had a negative effect on the decolorization rate for higher RhB concentrations (3 and 5mg L^{-1}) [28]. Additionally, Na_2CO_3 and Na_2SO_3 have alkaline character; therefore such salts neutralize the RB having acidic character. As a result, it may be said that decomposition increased to change the load distribution.

Computational Results

Optimized structures of RhB^0 and RhB^{+-} compounds are obtained at HF/6-31G level and represented in Figure 8.

Thermodynamic parameters which are total energy (E_{TOTAL}), enthalpy (H) and Gibbs free energy (G) are calculated as -1410.102451, -1410.101507 and -1410.190419 a.u. for RhB^0 while -1410.084832, -1410.054342 and -1410.149451 a.u. for RhB^{+-}. According to these results, RhB^0 is more stable than RhB^{+-}. The equilibrium between these compounds has been mentioned in "Introduction section". Equilibrium constant of its is calculated as 0.999 and it is too close to equilibrium.

Chemical reactivity of mentioned compounds are investigated by computational method. For this goal, some quantum chemical parameters which are E_{HOMO}, E_{LUMO}, E_{GAP}, σ, CP, N and μ are calculated and given in Table 1.

Energy of HOMO is significant parameters to determine the chemical reactivity ranking. E_{HOMO} is associated with electron donating ability and chemical reactivity of molecules increases with the increasing of E_{HOMO} [29,30]. According to E_{HOMO}, chemical reactivity ranking should be as follow:

RhB^0 > RhB^{+-}

One of the other important parameter is LUMO energy. E_{LUMO} is related with electron accepting from appropriate molecule. If E_{LUMO} is decisive parameter, chemical reactivity ranking should be as follow:

Table 1. Calculated quantum chemical descriptors for mentioned compounds in gas phase.

Compounds	EHOMO^a	ELUMO^a	EGAP^a	I^a	A^a	η^a
RhB^0	-7.654	2.395	10.049	7.654	-2.395	5.025
RhB^{+-}	-7.913	0.313	8.226	7.913	-0.313	4.113
Compounds	σ^b	χ^a	CP^a	ω^a	Nb	μc
RhB^0	0.199	2.629	-2.629	0.688	1.453	6.838
RhB^{+-}	0.243	3.800	-3.800	1.755	0.570	15.949

^{a} in eV, ^{b} in eV-1, ^{c} in Debye.

$RhB^{+-} > RhB^0$

Other important parameter is E_{GAP} and chemical reactivity increases with the decreasing of E_{GAP} value [30]. According to E_{GAP}, the ranking is given as follow.

$RhB^{+-} > RhB^0$

The other important parameters are hardness and softness to explain the chemical reactivity ranking. The rule is that hard species prefer to coordinate to hard species and soft molecules to soft molecule. Big molecules are mainly accepted as soft species. The softness of mentioned tautomer ranking should be:

$RhB^{+-} > RhB^0$

According to softness values, RhB^{+-} is found as the most reactive. Chemical potential is other important parameters to determine the chemical reactivity ranking. Chemical potential is directly proportional with gibbs free energy and these parameters can be related with spontaneity. The chemical reactivity increases with decreasing of chemical potential and reactivity ranking should be as follow:

$RhB^{+-} > RhB^0$

Other important parameter is nucleophilicity index. The nucleophilicity index shows the ability of electron donating. The chemical reactivity ranking increases with increasing the N value. According to the N value, chemical reactivity ranking should be:
$RhB^0 > RhB^{+-}$

Azo-enol tautomer is the most reactive in gas phase than other areas. The last parameter is dipole moment. Chemical reactivity of molecules increases with increasing of this parameter. If dipole moment is decisive to determine the chemical reactivity ranking, ranking should be as follow.

$RhB^{+-} > RhB^0$

According to whole results, RhB^{+-} is more reactive than RhB^0. This result implies that reactivity of solutions decreases after the decolorization.

CONCLUSION

In this work, decolorization of RhB was investigated by using photocatalytic and ultrasonic processes. Among these methods, Ag-loading/UV photocatalytic process was found to be the most effective method. In this process approximately 100% decolorization was observed at treatment of 20 min. TiO_2/UV photocatalytic process was found to be secondly an effective process for decolorization of RhB. While the amount of decolorization obtained by ultrasonic process are 31% and 56%, the amount of decolorization obtained by photocatalytic process for treatments of 20 and 60 min are 70% and 100%, respectively. As a result, Ag-loading/UV photocatalytic process of dye reported in here is more advantageous than those of the other oxidation processes since it takes a few minutes, and moreover it requires less energy, and the catalyst can be reused for several times, and does not require further treatment. Optimized structures of RhB^0 and RhB^{+-} are calculated at HF/6-31G level in gas phase. RhB^0 is determined as more stable than RhB^{+-} by using thermodynamic parameters. The equilibrium constant between RhB^{+-} and RhB^0 is calculated as 0.999. Additionally, chemical reactivity of mentioned compounds examined in detail by using quantum chemical parameters and RhB^{+-} is defined as more reactive than RhB^0.

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