EE-4

GAMMA-RAY INDUCED CATALYTIC DEGRADATION OF METHYLENE BLUE IN AQUEOUS SUSPENSION OF TITANIA

Ahmed F. Twfik[*], Ahmad A. Baraka[*], Mohamed A. El-Sayed[*]and Ahmad M. Omar[*]

ABSTRACT

Gamma radiation-induced degradation of methylene blue (MB) in aqueous solution was studied for two groups: one with suspension of Titania, TiO_2, photo-catalyst and the other without it. Degradation of methylene blue by gamma-rays (doses range: 200-1000 Gy) was investigated by measuring the change of absorbance spectrophotometrically at λ_{max}= 661 nm. Initial pH of solution (values 5, 7 and 9) was considered as a basic factor to study. The changes of pH values for irradiated methylene blue solutions with respect to gamma dose were recorded. Post irradiation effect was determined by measuring absorbance after 24 hours. For both groups, the color of methylene blue was bleached gradually with dose indicating its degradation. It was found that presence of TiO_2 causes more bleaching. Also, as initial pH increases, the degradation increases. Methylene blue IR spectra, before and after irradiation, were recorded to investigate the effect of gamma radiation on MB.

Keywords

Gamma radiation, catalytic degradation, Methylene Blue, Titania.

[*] Egyptian Armed Forces

1. INTRODUCTION

Nowadays, several activities produces large amounts of organic wastes, most of which have a harmful effect on human, and find its way to water mass such as rivers, lakes and even underground water resources. Specifically, textile industries are known to discharge considerable amounts of non fixed dyes. About 15% of the total world's production of dyes leaks during the process of dyeing and is released in effluents. It is well known that some of these dyes are highly carcinogenic [1,2]

Methylene blue is as an organic pollutant because of its wide use in many industrial applications as well as many uses in a biology and chemistry [3]. It is a heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}N_3SCl$, Figure 1. At room temperature, it appears as a solid, odorless, dark green powder, that yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per molecule of methylene blue. In present study, this compound was selected for decontamination as a good representative for organic dye pollutants. [4]

Gamma irradiation of solutions containing organic pollutants is a very promising technique for decontamination by degradation [5]. A considerable number of researches on application of radiation have shown that ionizing radiation, such as gamma radiation and electron beam, is effective for the degradation of many organic pollutants which are biologically resistant in water [6]. Practically, an industrial plant for treating 10000 m^3 per day of textile dyeing wastewater with electron beam (1 MeV, 400 kW) has been constructed in the city of Daegu (Korea) with the support of International Atomic Energy Agency and Korean government [7].

Photocatalysis is another effective well established technique to remediate water by degrading organic pollutant and it is of interest because of its rapid increasing applications over the last 20 years [8]. Its effectiveness stems from strong redox chemical reactions. This technique deploys the use of sun light or different wave lengths of ultra-violet sources.

Semiconductor materials are typical photocatalysts for this type of reactions. The commonly used photocatalysts are TiO_2, ZnO, CdS, ZnS, $SrTiO_3$ and Fe_2O_3. There are many photocatalysts beside these mentioned; however, TiO_2 (or Titania) is the most active for organic compounds degradation processes as frequently reported and applied [9]. In water treatment processes, TiO_2 shows non-toxicity and insolubility, both in the dark and on illumination, which are important considerations. [10]. Figure 2 shows the principle of photo-degradation of organic compounds using a photocatalyst.

In this work, coupling of ionizing radiation, other than ultra-violet, such as gamma and semiconductor material (TiO_2) was investigated to claim its powerful effect in organic pollutant degradation. Gamma-rays source (Co^{60}) was used instead of ultra-violet sources as TiO_2-activating electromagnetic radiation. Gamma rays of 1.1732 and 1.3325 MeV, (from Co^{60} source) are highly ionizing and it is thought that it can activate TiO_2 in the same way as ultra-violet does. To our knowledge and after thorough search, this coupling (gamma radiation and a semiconductor (TiO_2) for such applications has not been investigated yet.

To elucidate this decontamination power, the degradation and mineralization of methylene blue in aqueous solutions were investigated using gamma-irradiation in two different reaction groups; one in the presence of TiO_2 and the other without it. The change of absorption spectra

of methylene blue with gamma-dose, i.e. degradation efficiency, for each group was investigated with respect to solution initial pH change.

2. Experimental
2.1 Sample preparation
Methylene blue (BDH chemicals ltd poole England), bi-distilled water as a solvent, diluted HCl acid and diluted NaOH to adjust pH (Hanna instrument) and TiO_2 powder (El-Nasr Co.) were materials used to prepare samples. For the first group of samples: each sample was a plastic vial that contains (40 ml) of methylene blue aqueous solution (of concentration 0.5×10^{-4} M). The vial was then introduced into gamma cell (Indian type (Gamma Chamber 5000), rate= 2.1 kGy/hr) to expose to steady state radiolysis. For the second group of samples: samples were prepared as before and, 0.25 g of TiO_2-powder was added (6.25 g/l). The vial containing Titania suspension was then stirred in the dark for about 30 minutes before gamma-irradiation exposure to ensure equilibration and homogenous distribution. The used Titania has the following properties: average particle size, d_{ave} = 30 nm, specific surface area, S_{BET} = 55 m^2/g and percentage of anatase = 70%. (El-Nasr Co.data)

2.2 degradation measurement
Methylene blue degradation was detected by measuring the absorbance of irradiated samples at λ_{max}=661 nm, using UV-Vis (Shimatzu UV-160) spectrophotometer. All spectrophotometrically measurements were carried out at ambient temperature using quartz cells with 1 cm optical path length. A calibration curve was previously determined to calculate the concentration of methylene blue residue in solutions. The pH value for each sample was also determined after gamma irradiation using (Hanna instrument).

2.3 FTIR Analysis
For a preliminary investigation of the radiolytic products, selected irradiated samples (with and without TiO_2) and a non-irradiated sample of methylene blue were analyzed using FTIR technique employing (Shimatzu FTIR 8400). The spectra were compared to determine the change in structure and the produced groups.

3. Results and discussion
3.1 Degradation of methylene blue in the absence of TiO_2
3.1.1 Bleaching with dose
The absorbance against dose for samples prepared at pH 5, 7 and 9 are shown in Figure 3. It is clear that absorbance decreased, i.e. bleaching increased, as dose increased from 200 – 1000 Gy for the three pH values. This bleaching is due to degradation and mineralization of methylene blue. Also, as initial pH increases each dose value, the absorbance at λ_{max} decreases indicating more degradation. Table 1 elucidates this numerically.

Since MB is a dilute aqueous solution, it is expected that the chemistry of water may control the degradation process. The radiolysis of water is very well documented and it has been known that it produces (H_2), (H_2O_2), (H^+), (OH^-) besides hydrated electron (e_{aq}^-), hydroxyl radical ($^.OH$) and hydrogen atom ($^.H$) as intermediate species in varying amounts depending upon the linear energy transfer value of the radiation.[10] In dilute solutions the yield of these species are as follows: $G(e_{aq}^-) = G(^.OH) = 0.28$ and $G(^.H) = 0.06$ µmol/J. These intermediates can then take part in many different reactions with the solute molecule (in our case MB) thereby causing a change in its composition [11]

The hydrated electron (e_{aq}^-) and the hydrogen radical ($\cdot$H) are the main reductive species produced in irradiated aqueous solution, whereas, the hydroxyl radicals ($\cdot$OH) and perhydroxyl radicals ($\cdot$HO$_2$, produced in subsequent reactions) are the main oxidizing species produced in water radiolysis. One of the consequences of radiolysis in aqueous solutions is that the charged species become hydrated within a very short interval of time (10^{-11} seconds), e.g. formation of e_{aq}^-.[11]
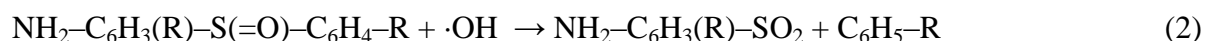
In dilute aqueous solutions, most of radiation energy is practically absorbed by water molecules. Accordingly, the change in solute composition would essentially results from the secondary reactions of radiation induced species from water and solute molecules rather than the direct effect of radiation on the solute molecules. These secondary reactions arise from the reactions of solutes with the oxidizing and reducing species initially produced during water radiolysis [12]

As all solutions in this study were not de-aerated, irreversible oxidative degradation mechanism could be suggested [13,14].
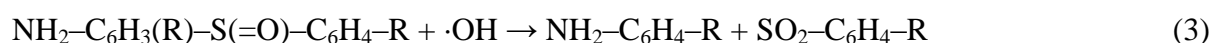
The $\cdot$OH radical is the active oxidizing radical in this mechanism according to the degradation pathway of methylene blue provided by Houas *et al* [15] i.e. $\cdot$OH radical makes the main contribution to degradation of methylene blue and its intermediates. Since MB is cationic and not electron donor, the initial step of MB degradation could be ascribed to the cleavage of C–S$^+$=C bonds in the functional group in MB:

$$R–S^+=R' + \cdot OH \rightarrow R–S(=O)–R'+H^+ \tag{1}$$

The sulfoxide group can undergo a second attack by an $\cdot$OH radical producing the sulfone and causing the definitive dissociation of two benzenic rings:
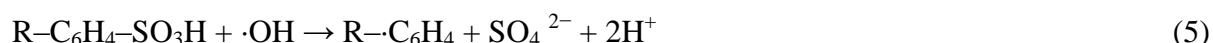
$$NH_2–C_6H_3(R)–S(=O)–C_6H_4–R + \cdot OH \rightarrow NH_2–C_6H_3(R)–SO_2 + C_6H_5–R \tag{2}$$

and/or

$$NH_2–C_6H_3(R)–S(=O)–C_6H_4–R + \cdot OH \rightarrow NH_2–C_6H_4–R + SO_2–C_6H_4–R \tag{3}$$

Subsequently, the sulfone may be attacked by a third $\cdot$OH radical giving a sulfonic acid:

$$SO_2–C_6H_4–R + \cdot OH \rightarrow R–C_6H_4–SO_3H. \tag{4}$$

Finally release of SO_4^{2-} ions may be attributed to a fourth attack by $\cdot$OH:

$$R–C_6H_4–SO_3H + \cdot OH \rightarrow R–\cdot C_6H_4 + SO_4^{2-} + 2H^+ \tag{5}$$

The amino group in MB could be substituted by an $\cdot$OH radical, forming the corresponding phenol and releasing a $\cdot$NH$_2$ radical which generates ammonia and ammonium ions, estimated to be primary products.

$$R–C_6H_4–NH_2+\cdot OH \rightarrow R–C_6H_4–OH+\cdot NH_2 \tag{6}$$
$$\cdot NH_2+\cdot H \rightarrow NH_3 \tag{7}$$

$$NH_3+H^+\rightarrow NH_4^+ \tag{8}$$

This mechanism shows production of H^+ in steps (1) and (5) which causes acidity. However, steps (7) and (8) show production of alkalinity sources. It could be suggested that the overall change in pH is null and this can be determined stichiometerically by balancing the products with S and N atoms present in MB structure.

3.1.2 Effect of gamma dose on pH value
After irradiation of different samples of different initial pH values, the pH was measured. It was found that pH did not change significantly after irradiation for all studied doses. Figure 4.

We may conclude that degradation did not produce any net pH-affecting ions such as OH^- or H^+ or any other similar moieties, which consides with the suggested mechanism fulfills this behavior.

3.2 Methylene blue at different pH values in the presence of TiO₂
3.2.1 Bleaching with dose
The irradiation results of MB in the presence of TiO₂ for the three different initial pH values 5, 7, and 9 are shown in Figure 5 and Table 2. All samples showed bleaching the alkaline sample (pH 9) was more bleached than the other two pH values (5 and 7). This is similar to the results without TiO₂. On the other hand bleaching of pH values 5 and 7 samples showed some crossings.

Table 3 showed that the Δabs. values for samples with TiO₂ are higher than without it .this means that coupling of gamma ionizing radiation with semiconductor material positively affected the degradation process.

3.2. 2 Effect of gamma dose on (pH values)
After irradiation of different samples of different initial pH values, in the presence of TiO₂ the pH was measured. The alkaline and acidic samples showed a change to neutrality for all studied doses. The neutral samples remain almost within the same values. [Table 4 and clearly depicted in Figure 6]. This phenomenon is in marked contrast to degradation of methylene blue without presence of TiO₂.
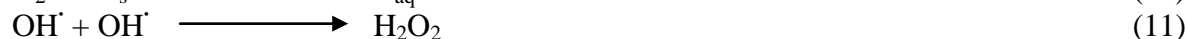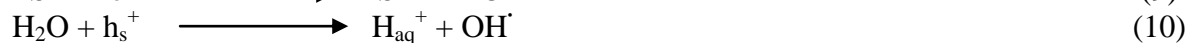
This result is opposite to the results obtained in the absence of TiO₂, which indicates the contribution of TiO₂ thus the behavior in dilute solutions must be considered. The point of zero charge of TiO₂ is $pH_{pzc}= 6.0$ to 6.8 and this property controls the degree of adsorption of pollutant on TiO₂ surface, especially when it has ionic (cationic or anionic structure). In aqueous media, the surface of TiO₂ is charged according to pH of media as follows;

Case 1: At $pH > pH_{pzc}$: $Ti\text{-}OH + OH^- \leftrightarrow TiO^- + H_2O$
Case 2: At $pH < pH_{pzc}$: $Ti\text{-}OH + H^+ \leftrightarrow TiOH_2^+$
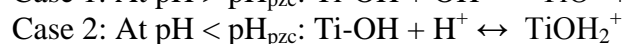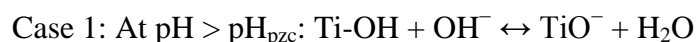
Since MB is a cationic dye, it is conceivable that at $pH > pH_{pzc}$, its adsorption is favored on a negatively charged surface. On the contrary; for $pH < pH_{pzc}$, adsorption is hindered.

Consequently, the degradation mechanism could be suggested to differ according to pH as follows:

For Case 1, $pH > pH_{pzc}$, MB is adsorbed on TiO_2-surface. The photo-ejected e^- has the direct opportunity to react with the main colur centre of methylene blue, $=S^+-$ of MB (instead of being captured by O_2 present in water), which led to initial reductive destruction of this group and consequently colur bleaches.thus The suggested reaction is as follows;

$$=S^+- + e^- \longrightarrow = S^{\cdot}-H + OH^{\cdot} \tag{9}$$
$$H_2O + h_s^+ \longrightarrow H_{aq}^+ + OH^{\cdot} \tag{10}$$
$$OH^{\cdot} + OH^{\cdot} \longrightarrow H_2O_2 \tag{11}$$

The produced H_2O_2 has oxidative degradation effect on MB. The overall consequence is initial reductive destruction by e^-, subsequent oxidative destruction by H_2O_2, and release of H_{aq}^+ which decreases the pH as observed. Generally in this case, the destruction is reductive / oxidative one.

In this case we may suggest that bleaching is a two step process, adsorption of MB on TiO_2 followed by degradation reaction with activation products of TiO_2 while the contribution of radiolytic products of water is limited.

For Case 2, $pH < pH_{pzc}$, adsorption of MB on TiO_2-surface is hindered. The effect of gamma radiation on TiO_2 would be similar to that of ultra-violet:

$$TiO_2 \xrightarrow{\text{gamma}} h_\gamma^+ + e_{aq}^- \tag{12}$$

As the solution was not de-aerated, then;

$$e_{aq}^- + O_2 \longrightarrow O_2^- \tag{14}$$

The previous two steps prevent the recombination of h_γ^+ and e_{aq}^-, enabling h_γ^+ to oxidize the dye molecule. Furthermore, the produced O_2^- moluclar ion are powerful oxidants [12,13], and can also oxidatively degrade the dye. The oxidative degradation by h_γ^+ and O_2^- originates from TiO_2 surface. As MB in this case is not adsorbed on TiO_2 surface, further degradation occurs by radiolytic product of water. In this case, it is more difficult to trace the origin of pH increase to neutrality.

In general, it is essential to take into account that water radiolysis-products may play relative role in the degradation of MB and in affecting the solution pH for the different conditions (with and without TiO_2). This picture makes it difficult to assign exactly the mechanisms for each set of conditions present in this work (irradiation: without TiO_2, with TiO_2 with alkaline media, with TiO_2 with acidic media and with TiO_2 with neutral media). The previous suggested mechanisms are primary ones depending on pH and absorbance and IR data collected. To get a more idea about the 2 suggested mechanisms, more analysis is required during radiolysis. Pulse radiolysis is seems too precise to be suitable tool and this will be considered in a future work.

3.3 Degradation of methylene blue in the absence of TiO_2 (after 24 hrs of Irradiation)
Absorbance against doses for the different pH values, are shown in Figure 7. MB at pH 9 is more bleached than at pH 7 and 5. Form Table 5, more bleaching was observed when compared with samples measured just after irradiation, [Table 1]. This is a positive result form the decontamination point of view.

3.4 Degradation of the methylene blue in the presence of TiO$_2$ (after 24 hrs of irradiation)

Absorbance against doses for the different pH values, are shown in Figure 8. Again, as for without TiO$_2$ (section 3-3), MB suffers bleaching at pH 9 more than at pH 7 and 5. Compared with similar samples measured just after irradiation, there is more bleaching was recorded. [Table 6 when compared with Table 2], this gives more effectiveness. For the decontamination process

3.5 FTIR analysis

Figure 9 shows the IR spectra of MB, MB without TiO$_2$ irradiated at 1000 Gy and MB with TiO$_2$ irradiated at 1000 Gy. In the figure, the spectra of MB without TiO$_2$ irradiated by 1000 Gy and MB with TiO$_2$ irradiated by 1000 Gy are very similar indicating the same degradation effects and products. while They are markedly different from that of MB. The main bands and peaks of MB are as follows: the absorption band at 1600.8 and 1357 cm^{-1} correspond to the vibration of the aromatic ring. The bands observed at about 2920–2850 cm^{-1} could be assigned to the aliphatic C–H groups. C-N stretch is present at 1357.8 cm^{-1}. From the other two spectra it can be deduced that gamma-degradation (with and without TiO$_2$) have, qualitatively, the same effect. Some functional groups either disappeared or diminished such as at 1253.6, 1141.8, 887.2 and 833.2 cm^{-1}. [16-17].

4. Conclusion

It was found that the pH adjustment is very important in the degradation of Methylene blue as the more degradable samples were the ones prepared at pH 9, also the presence of TiO$_2$ was great importance as it catalyses the degradation of Methylene blue using gamma radiation at pH 9 more than the samples without TiO$_2$, as Methylene blue was completely degradated at 1000 Gy. Finally the presence of TiO$_2$caused the degradation of MB using gamma radiation to be complete

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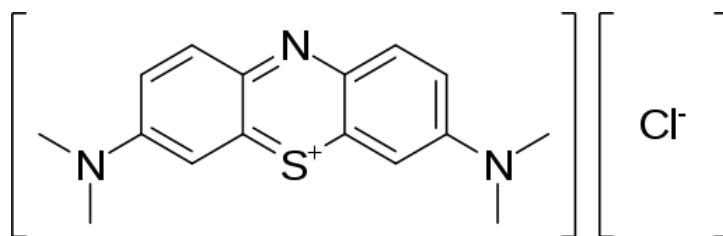
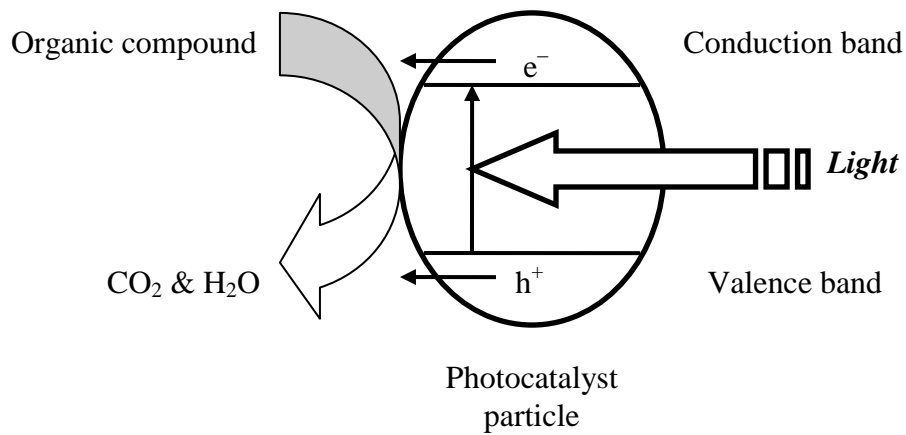Figure 1: Chemical structure of methylene blue

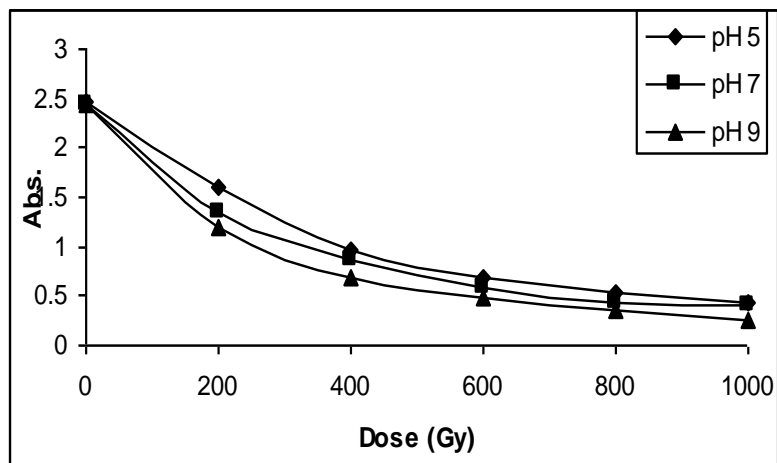Figure 2: General mechanism of photocatalytic degradation of organic compounds

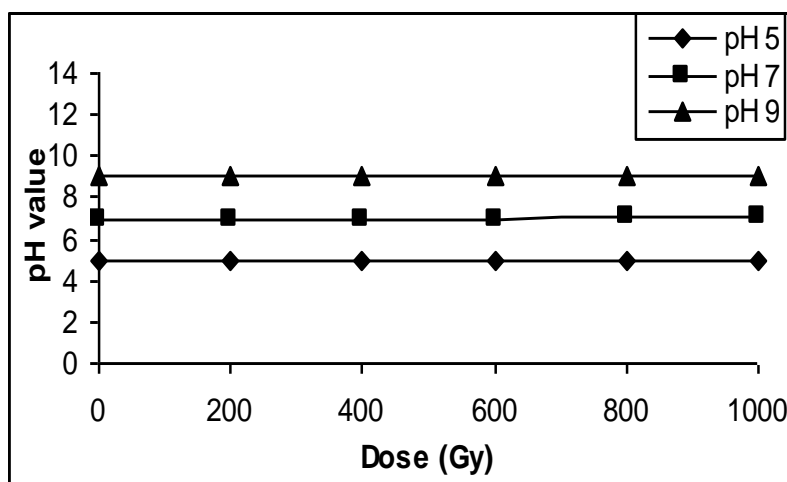Figure 3: Change of MB absorbance with gamma dose at pH 5, 7 and 9 (without TiO_2).

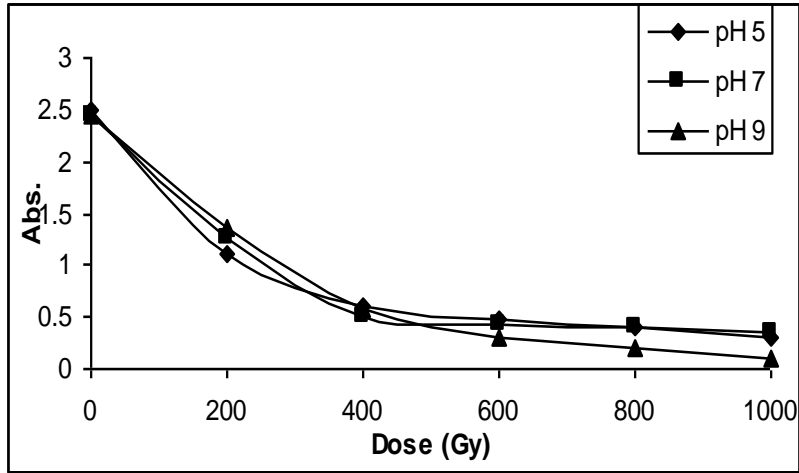Figure 4: Change in pH values with gamma dose (without TiO_2).

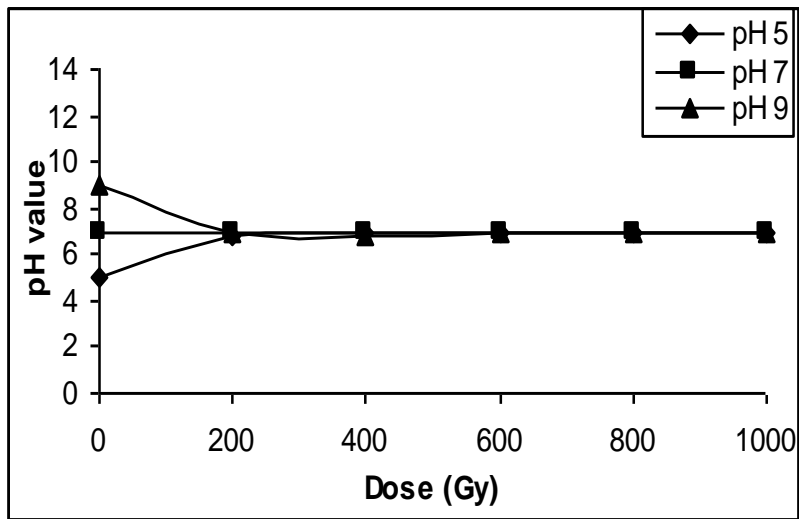Figure 5: Change of MB absorbance with gamma dose at pH 5, 7 and 9 (with TiO_2).

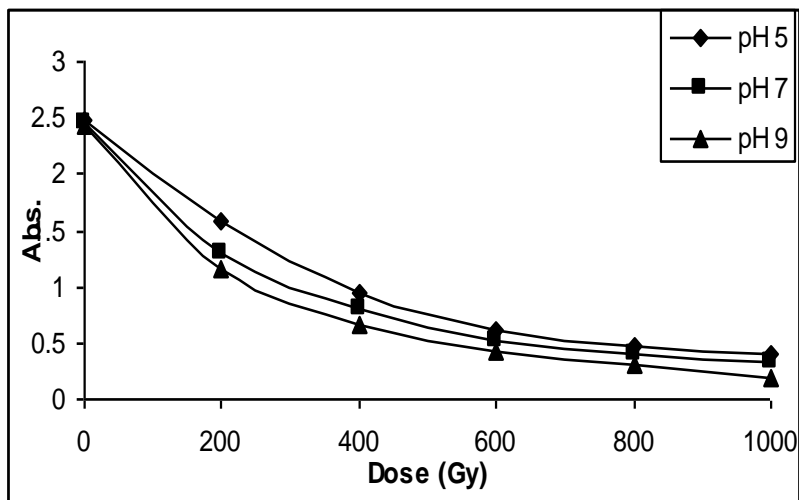Figure 6: Change in pH values with gamma dose (with TiO_2).

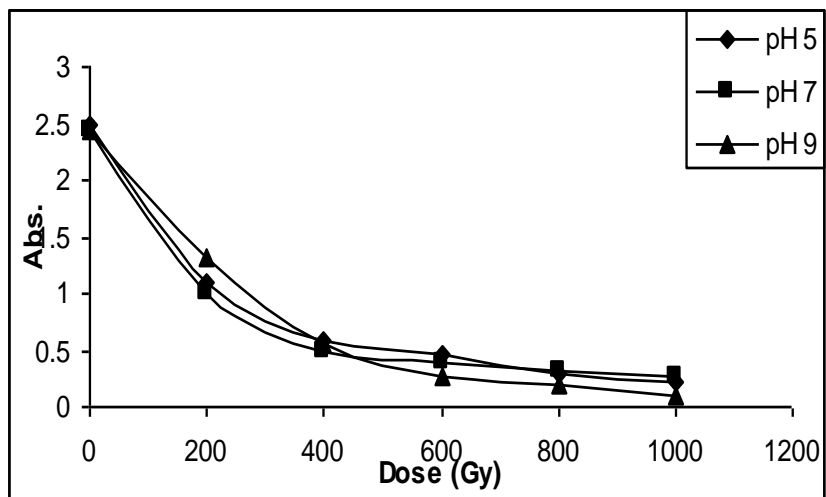Figure 7: variation of MB absorbance after 24 hours of gamma irradiation (without TiO_2)

Figure 8: variation of MB absorbance after 24 hours of gamma irradiation (with TiO_2)
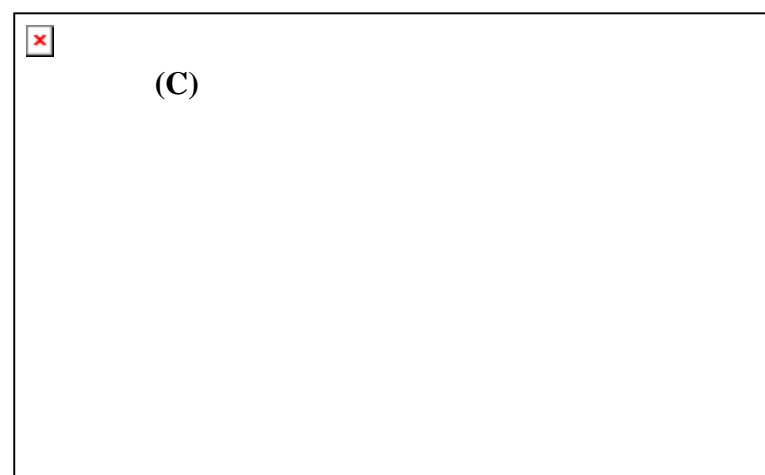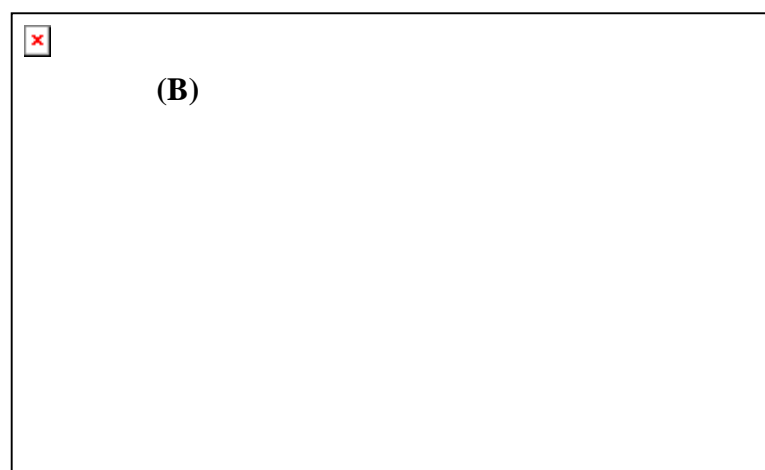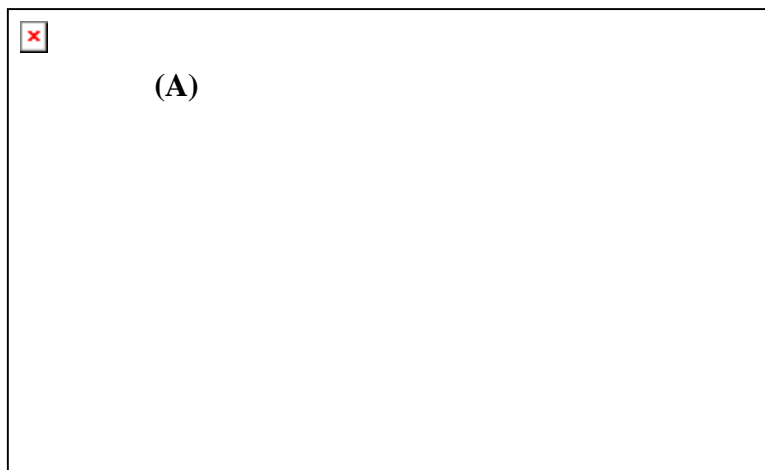
(A)

(B)

(C)

Figure 9: IR spectra of (A) MB, (B) MB without TiO2 irradiated at 1000 Gy and (C) MB with TiO$_2$ irradiated at 1000 Gy.

Table 1: Absorbance of methylene blue against gamma doses

Dose (Gy)	pH 5	pH 7	pH 9
0	2.478	2.453	2.429
200	1.602	1.348	1.200
400	0.973	0.854	0.680
600	0.679	0.587	0.480
800	0.546	0.435	0.355
1000	0.444	0.401	0.252

Table 2: Absorbance of methylene blue (with 0.25 g of TiO_2) against gamma doses

Dose (Gy)	pH 5	pH 7	pH 9
0	2.496	2.445	2.440
200	1.106	1.271	1.353
400	0.615	0.500	0.586
600	0.474	0.420	0.295
800	0.400	0.410	0.200
1000	0.303	0.350	0.090

Table 3: comparison between ΔAbs. values for samples at different pH values and doses

Dose (Gy)	pH 5		pH 7		pH 9	
	Δ Abs.					
	Without TiO_2	With TiO_2	Without TiO_2	With TiO_2	Without TiO_2	With TiO_2
200	0.876	1.39	1.105	1.174	1.229	1.087
400	1.505	1.881	1.599	1.945	1.749	1.854
600	1.799	2.022	1.866	2.025	1.949	2.154
800	1.932	2.096	2.018	2.035	2.074	2.24
1000	2.034	2.193	2.025	2.093	2.177	2.35

Table 4: pH values after irradiation at different gamma doses

Dose, Gy	Initial pH 5	Initial pH 7	Initial pH 9
	pH After irradiation		
200	6.86	6.96	6.93
400	6.90	6.93	6.86
600	6.89	6.98	6.95
800	6.91	6.99	6.91
1000	6.92	6.94	6.89

Table 5: Absorbance of methylene blue for post irradiation after 24 hours without TiO_2

Dose (Gy)	pH 5	pH 7	pH 9
0	2.478	2.453	2.429
200	1.589	1.3	1.15
400	0.952	0.811	0.653
600	0.62	0.51	0.43
800	0.48	0.39	0.3
1000	0.4	0.32	0.2

Table 6: Absorbance of methylene blue for post irradiation after 24 hours with TiO_2

Dose (Gy)	pH 5	pH 7	pH 9
0	2.496	2.445	2.44
200	1.086	1	1.307
400	0.58	0.48	0.562
600	0.452	0.4	0.264
800	0.303	0.31	0.2
1000	0.21	0.266	0.09

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