

Table 3-F. 2: Photoreduction Data of  $Hg^{+2}$  on Various  $TiO_2$  Samples.

Sample	Photoreduced percentages of $Hg^{-2}$
T	40
T <sub>CTAB</sub>	51
T <sub>CTAB v</sub>	11
T <sub>CPB v</sub>	27
T <sub>SDS (pH=2.0)</sub>	7.5
T <sub>SDS (pH=4.8) at 623 K</sub>	33
T <sub>SDS (pH=4.8) at 773 K</sub>	19
T <sub>SDS (pH=7.0) at 623 K, (0.1gm), pH=5.5</sub>	94
T <sub>SDS (pH=7.0) at 773 K</sub>	21.5
T <sub>SDS (pH=9.0) at 623 K</sub>	24
T <sub>SDS (pH=7.0) at 623 K, (0.1gm), pH=3.2</sub>	19
T <sub>SDS (pH=7.0) at 623 K, (0.1gm), pH=7.0</sub>	100 after 45 min.
T <sub>SDS (pH=7.0) at 623 K, (0.05gm), pH=5.5</sub>	28
T <sub>SDS (pH=7.0) at 623 K, (0.15gm), pH=5.5</sub>	33
T <sub>SDS (pH=7.0) at 623 K, (0.2gm), pH=5.5</sub>	25
T <sub>SDS (pH=7.0) at 623 K, (0.1gm), SDS</sub>	43
T <sub>SDS (pH=7.0) at 623 K, (0.1gm), Triton</sub>	44
T <sub>SDS v at 623 K</sub>	20
T <sub>SDS v at 773 K</sub>	70
T <sub>NY at 623 K</sub>	20
T <sub>NY(C) at 623 K</sub>	50.2
T <sub>NY(C) at 773 K</sub>	46
T <sub>G at 623 K</sub>	84
T <sub>G at 773 K</sub>	66
T <sub>G v at 773 K</sub>	18

not found a relation between photoreduction efficiency and surface area of the prepared samples.

iv) The initial rates of sorption are estimated from the initial slopes of the kinetic curves in Fig. 3-F.1, assuming a linear dependence of the Hg(II) sorbed with time in the first 10 minute. This may indicate that the sorption/photoreduction process follows a first-order kinetics.

v) Enhancing the photoreduction efficiency on TiO<sub>2</sub> samples synthesized using SDS surfactant (at 623 K) and glucose (at 623 K) was in part due to the decreased particles size of the produced TiO<sub>2</sub> species, which were sharply distributed from ~ 8.0 to 12 nm. This suggests that adjusting the particles size of TiO<sub>2</sub> to be in the nanorange (>10 nm) will enhance the reduction of metal ions.

### 3-F.3. Effect of pH

The previous series of experiments conducted signified that the most active catalyst was T<sub>SDS</sub> at pH=7.0 heated at 623 K. Thus, the rest of experiments were carried out using this catalyst. The efficiency of photoreduction process strongly depend upon the pH of the reaction solution. This is due to the amphoteric behaviour of semiconducting TiO<sub>2</sub>. The surface charge properties of TiO<sub>2</sub> change with the changes of pH values. As has been explained previously that increasing the pH value increases the amount of Hg(II) sorbed and consequently the photoreduced. The examined range of pH was from 2.5 to 6.5. The results are presented in Fig. 3-F.6(a,b). The best results were obtained at pH=5.5 (94%) and pH=6.5 (100 %). At this latter pH the sorption rate was terribly higher and after 10 min. of illumination a complete vanishing of Hg<sup>+2</sup> was accomplished. Thus, pH = 6.5 was chosen for the sorption/photoreduction process of Hg<sup>+2</sup> into Hg<sup>0</sup>.

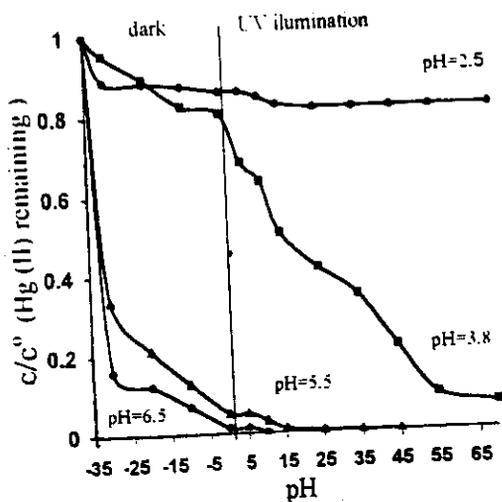


Fig.3-F. 6a: Sorption (dark) and photoreduction of Hg(II) [50 ppm] on the TSDS (pH=7.0, 623 K) as photocatalyst as a function of varying pH values: a) 2.5 b) 3.8 c) 5.5 d) 6.5  
 Experimental conditions: The illumination time 70 min., the photocatalyst (4g per dm<sup>3</sup> of solution). at 298 K.

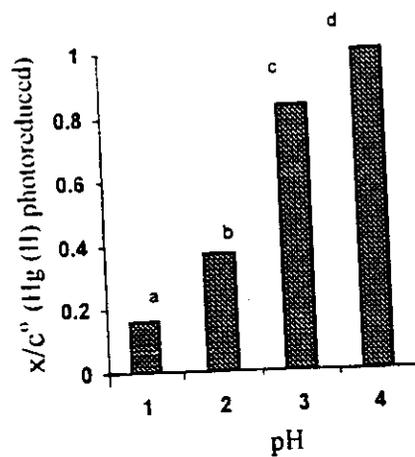


Fig. 3-F. 6b: Effect of pH on the photoreduction of Hg(II) on the TSDS (pH=7.0) as photocatalyst: a) 2.5 b) 3.8 c) 5.5 d) 6.5  
 Experimental conditions: The illumination time 70 min., the photocatalyst (4g per dm<sup>3</sup> of solution). at 298K.

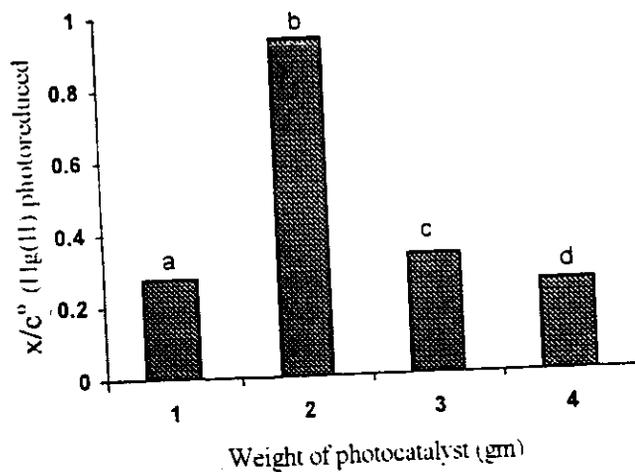


Fig. 3-F.7: Effect of photocatalyst weight on the photo-reduction of Hg(II) on TSDS (pH=7.0) samples : a) 0.05 g b) 0.1g c) 0.15g d) 0.2 g  
 Experimental conditions: The illumination time 70 min., the initial concentration of Hg(II) [50 ppm], pH=5.5 at 298 K.

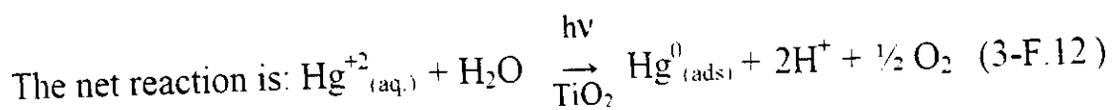
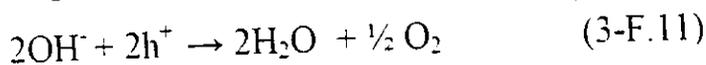
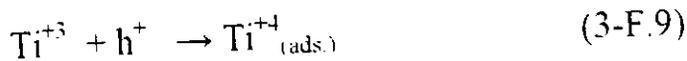
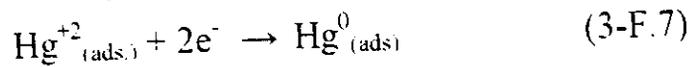
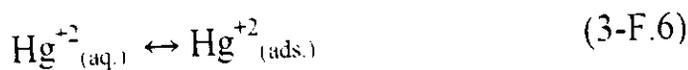
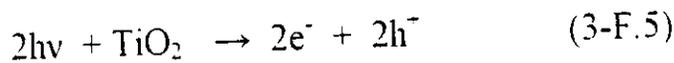
### 3-F.4. Effect of Photocatalyst Content

In order to determine the optimal amount of photocatalyst, a series of experiments with varied amount of photocatalyst have been conducted. The amount of the photocatalyst was varied between 0.05g (2 g/dm<sup>3</sup>) and 0.2g (8 g/dm<sup>3</sup>). The results of these experiments are shown in Fig. 4.7. The degree of photoreduction of Hg<sup>+2</sup> reaches the higher value (93 %) at catalyst loading = 0.1g (4 g/dm<sup>3</sup>) and then decreases markedly at catalyst amount 0.2 g (8 g/dm<sup>3</sup>). This behaviour is caused by the so called shielding effect after exceeding the optimal amount, the suspended TiO<sub>2</sub> reduces the penetration of the light in the solution. Thus, one can conclude that at low amounts of TiO<sub>2</sub> the sorption process is predominate while at high amounts the photoreduction process becomes more conspicuous. C. S. Turchi and D. F. Ollis,<sup>(162)</sup> on the other hand, explained that at a higher weight of the catalyst (> 0.1g), the actual photon absorption by TiO<sub>2</sub> slurries would be less due to scattering of some incident light, where at a lower weight of the catalyst (0.05g) a less active sites for photoreduction of Hg<sup>+2</sup> can be expected. The results in Fig. 3-F.7 that showed that the optimum catalyst weight was found to be 4 g/dm<sup>3</sup> of solution reflect the maximum attained light absorption by TiO<sub>2</sub>.

### 3-F.5. Effect of Initial Concentration of Hg<sup>+2</sup>

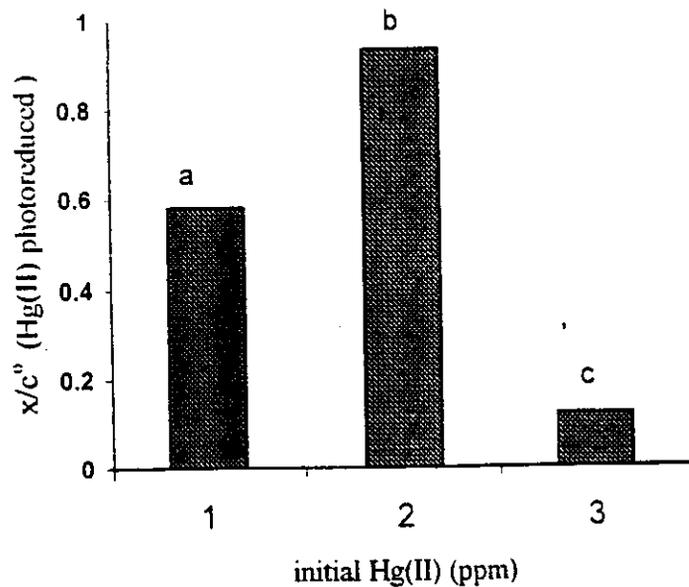
The effect of initial Hg<sup>+2</sup> concentration in water on the photoreduction process has also been examined. The results of these experiments are depicted in Fig. 3-F.8. For the concentration 50 ppm reduction was almost complete (93 %) after 70 min. of illumination, but for the higher concentration (100 ppm) the photoreduction process runs with markedly lower efficiency at similar illumination time (70 min). This could be related to the formation of several layers of adsorbed Hg<sup>+2</sup>

on the photocatalyst surface, which are higher at higher  $\text{Hg}^{+2}$  concentrations. Thus, the large amount of adsorbed  $\text{Hg}^{+2}$  inhibits the reaction of  $\text{Hg}^{+2}$  ions with photogenerated electrons (or holes) because there is no direct contact of photocatalyst with them. On the other hand, increasing concentration of  $\text{Hg}^{+2}$  also causes the  $\text{Hg}^{+2}$  ions to adsorb light and the photons never reach the photocatalyst surface. The stoichiometry of the photocatalysed reduction of  $\text{Hg}^{+2}$  using  $\text{TiO}_2$  may be summarized in the following.<sup>(80)</sup>

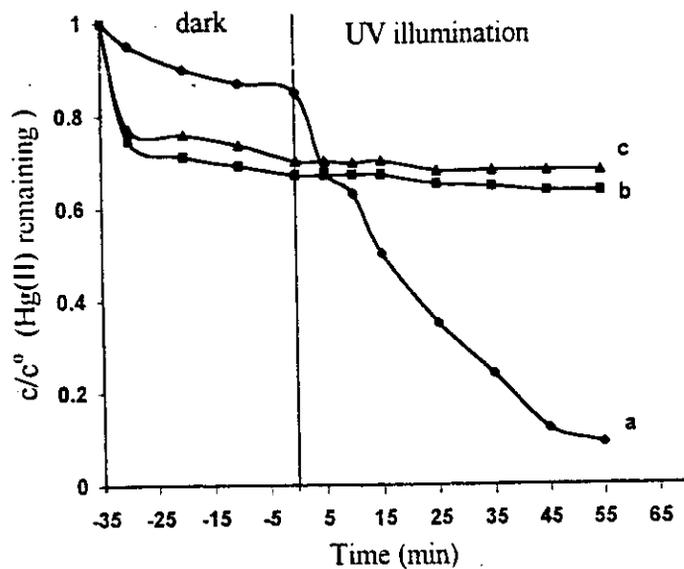


### 3-F.6. Effect of Different Illumination Sources

Figure 3-F.9 compares the photoreduction of  $\text{Hg}^{+2}$  in solution on the  $\text{T}_{\text{SDS}}$  (pH=7.0) catalyst using either UV or visible light or sunlight, under identical experimental conditions. The results show that using UV illumination was superior to the other sources. In addition, no any improvement in the reduction process of  $\text{Hg}^{+2}$  was revealed at the time exposing the sample to either visible or sunlight sources i.e. no revealed changes upon illumination signifying that the decreased amount in  $\text{Hg}^{+2}$  measured was a factor in the sorption process that takes place at the first 35 min. This indicates that UV illumination releases photons with an energy of  $h\nu$  exceeds the energy of band gap in  $\text{TiO}_2$  (3.2 eV) (the



**Fig. 3-F. 8: Effect of initial Hg(II) concentration on the photoreduction of Hg(II) using the T<sub>SDS</sub> (pH=7.0, 623 K) as photocatalyst: a) 25 ppm b) 50 ppm c) 100 ppm**  
**Experimental condition: The illumination time 70min., pH=5.5 and at 298 K.**



**Fig. 3-F. 9: Sorption (dark) and photoreduction of Hg(II) [50 ppm] on T<sub>SDS</sub> (pH=7.0, 623 K) as photocatalyst with various illumination sources: a) UV b) Visible light (Flourecent) c) Sun light**  
**Experimental conditions: The illumination time 70 min., the photocatalyst (4g per dm<sup>3</sup> of solution), pH=5.5 and at 298 K**

minimum energy of light required to make the material electrically conductive). Thus freeing electron ( $e^-$ ), which promoted from the valence band to the conduction band leaving a hole ( $h^+$ ) behind.<sup>(163)</sup> Portion of this photo-excited electron-hole pairs diffuse to the surface of the catalytic particle and take part in the chemical reaction with the adsorbed donor or acceptor molecules. In our case, the energy of electrons in conduction band that is high enough to reduce  $Hg^{+2}$  acceptor ions. Thus, one may conclude that illumination with visible light or sunlight is insufficient to photogenerate electron-hole pair that responsible for the reduction process. It must be mentioned that the range of solar light is large and indeed include UV but it seems that the rate of photons or the amount of photons per unit area striking the catalyst are not enough to proceed to reduce metal ions.

### 3-F.7. Effect of Vanadia Loaded Titania

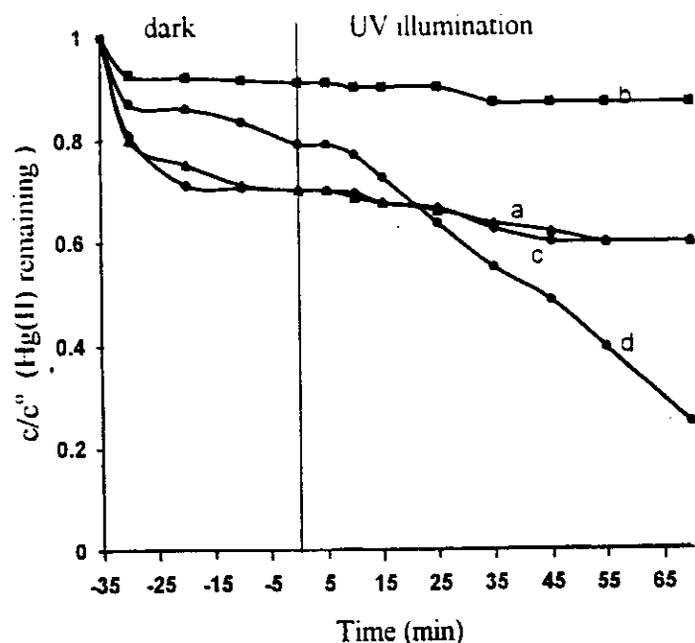
Figure 3-F.10 shows the effect of vanadia loading (6 wt%) on the photoreduction behaviour of the  $TiO_2$  sample synthesized using SDS at  $pH = 7.0$ . As it can be seen, the optimal rate for  $Hg^{+2}$  photoreduction was achieved on the  $T_{SDS/V}$  sample calcined at 773 K. On the other hand, the  $T_{SDS/V}$  sample heated at 623 K indicates a typical activity as that of base  $TiO_2(T)$  sample.

In a semiconductor photocatalyst, band-gap photoabsorption generates electrons and holes which can migrate to the surface to drive redox reactions with adsorbed molecules, competing with their disappearance due to mutual recombination. Certain surface sites can trap the photoexcited electrons before their recombination with the holes. The life time of trapped electrons has been related to the photocatalytic activity of base and metal-loaded  $TiO_2$  powders.<sup>(164)</sup>

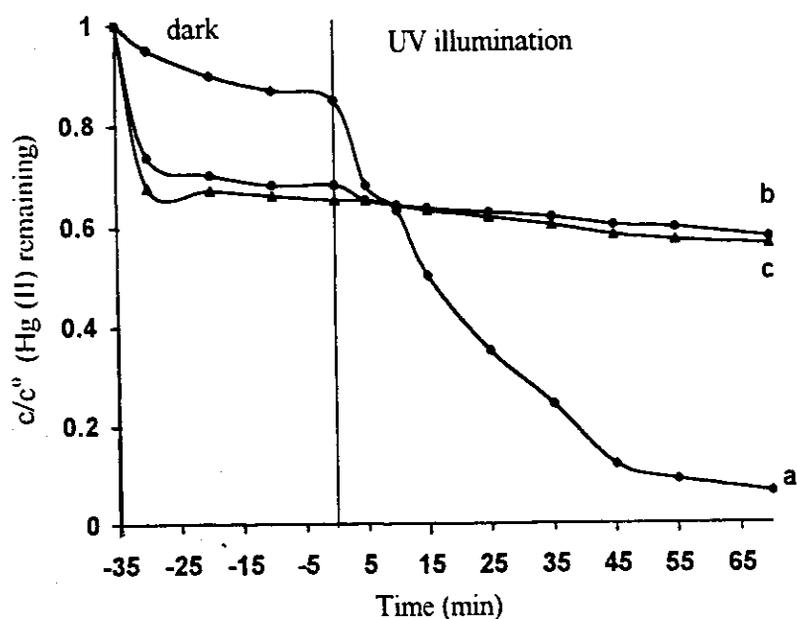
Thus as a general trend, the lower the electron-hole recombination rate, the higher the photocatalytic activity of the samples. Indeed, we expect that doping  $\text{TiO}_2$  with vanadia reduces the  $e^-h^+$  recombination and thus gives a chance for the reduction reaction to take place. However, the encountered varied activity of  $T_{\text{SDS/V}}$  following heating at 623 and 773 K might originally correlated, with surface characteristics of the samples following heat treatment. For example, the  $T_{\text{SDS/V}}$  sample calcined at 773 K presented higher nanocrystalline anatase phase (37%) than that heated at 623 K (31 %). In addition, the former sample presented higher pore radius (34.9 Å) than that of the latter (25.0 Å). The particle size of  $\text{TiO}_2$  particles after calcination (773 K) was larger (15 nm) than when heated at 623 K (10 nm), implying that such particles size (15 nm) could also enhance the catalytic activity not only because of the appreciable surface area ( $335 \text{ m}^2\text{g}^{-1}$ ) of the sample but also because of defects sites might be produced following the calcination process.

### 3-F.8. Effect of Surfactant

Figure 3-F.11 shows that the addition of either anionic (SDS) or neutral (triton X-100) surfactants to water contaminated with  $\text{Hg}^{+2}$  does not improve the activity during UV illumination if they compared with the surfactant free samples. This confirms that such surfactant molecules lower the rate of the photoreduction process. This could be due to absorption of some protons by surfactant molecules, which suppose to disperse or surround the suspended  $\text{TiO}_2$  particles. On the other hand, some free electrons are used to oxidize such bulky organic molecules through the availability to form hydroxide (OH) or radicals ( $\text{OH}^\cdot$ ).



**Fig. 3-F.10 :** Sorption (dark) and photoreduction of Hg(II) [50 ppm] on:  
 a)T b) T<sub>SDS</sub> c) T<sub>SDSΛ</sub> (623 K) d) T<sub>SDSΛ</sub> (773 K)  
 Experimental conditions: The illumination time 70 min., the photocatalyst  
 (4g per dm<sup>3</sup> of solution), pH=5.5 and at 298 K



**Fig. 3-F.11:** Effect of adding surfactant; either anionic (SDS) or non-ionic  
 (triton X-100), on sorption (dark) and photoreduction of Hg(II)  
 [50 ppm] on the T<sub>SDS</sub> (pH=7) as photocatalyst:  
 a) without adding surfactant b) 0.025 M of SDS c) 0.025 M of triton  
 Experimental conditions: The illumination time 70 min., the photocatalyst (4g per  
 dm<sup>3</sup> of solution), pH=5.5, at 298 K.

### 3-F.9. Catalyst Durability

In order to check the durability of the  $T_G$  catalyst, it was recycled three times under the same experimental conditions, i.e. by adding fresh molar amounts of  $Hg^{+2}$  ions for each run. As can be seen in Fig. 3-F.12, the photoreduction activity of the catalyst was neither decreased nor influenced on going from the first cycle till the third one, i.e. the performance of the catalyst was almost same in all three runs in achieving complete photoreduction of  $Hg^{+2}$  in about 80 min. illumination time. This indicates that the successive illumination by UV on the  $T_G$  sample during all the three runs dose not influence the  $TiO_2$  surface properties and thus retain the photoreduction efficiency of the  $T_G$  sample following each run. One can indeed relate the higher photoreduction rate of  $Hg^{+2}$  on nanosized  $TiO_2$ , modified by surfactant or poly-ol groups rather than non modified ones to:

- i) The modifier promote sorption of the metal ions to the semiconductor  $TiO_2$  crystal surface .
- ii) They create new trapping sites on the crystal, thus allowing a two electron transfer to occur to the sorbed metal upon illumination.
- iii) They physically separate photogenerated electrons/holes preventing their recombination.

In order to reveal to what extent the surface functional groups (active sites) of the  $T_G$  sample are affected following the successive UV illumination, IR spectra of the  $T_G$  sample taken following carrying out each run are presented in Fig. 3-F.13, in comparison with the spectrum of  $T_G$  taken prior exposing to the reaction.

The spectra were obtained after performing the photoreaction for the  $T_G$  sample in two regions, namely the low frequency and hydroxyl groups, in comparison with the fresh sample. The bands displayed at 667, 598 and 468  $cm^{-1}$ , in the low frequency region, in the fresh sample and

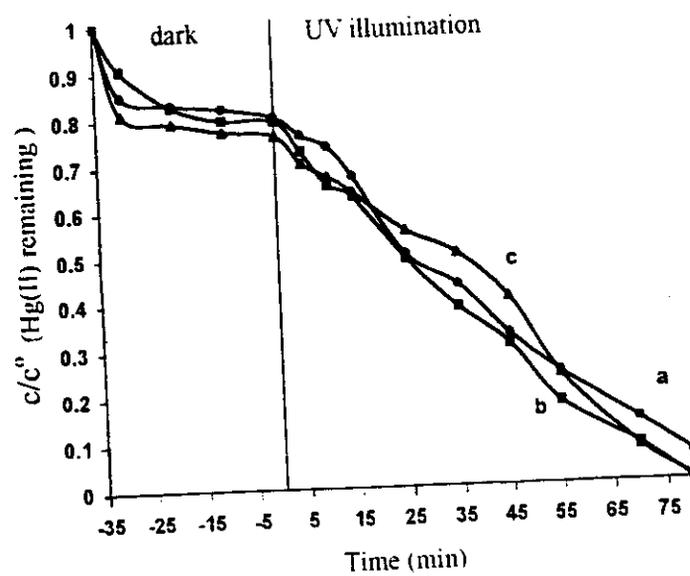


Fig. 3-F.12: Durability of the  $T_G$  catalyst during Sorption (dark) and photoreduction of  $Hg(II)$  [50 ppm] using 0.1 gm amount of the catalyst for the three run cycles: a) First run      b) second run      c) third run  
 Experimental conditions: The illumination time 80 min., pH=5.5 and at 298 K.