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Influence of surface metallic silver deposit and surface fluorination on the photocatalytic activity of rutile TiO$_2$ for the degradation of crystal violet a cationic dye under UV light irradiation

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Abstract

Silver metallization and fluorination on the surface of rutile TiO$_2$ (SRT and FRT) was carried out by photochemical reduction and wet impregnation methods respectively. TiO$_2$, SRT and FRT were characterized by various analytical techniques like PXRD, SEM, EDX, FTIR, PL, UV-visible absorbance and XPS. The photocatalytic degradation of crystal violet (CV) was carried out at three different pH conditions. Acidic pH was found to be more favorable for the degradation, in spite of low adsorption of cationic CV molecules on the Ti-OH$_2^+$ catalyst surface. The electrostatic repulsion at this pH drives the CV molecules into the bulk of the solution suggesting the involvement of bulk hydroxyl radicals rather than surface adsorbed hydroxyl radicals. The degradation efficiency can be represented by the following order SRT > FRT > TiO$_2$. The Ti-peroxo (Ti-OO-Ti) complex species formed in presence of H$_2$O$_2$ by the combination of two trapped holes (Ti-O$^-$) in aqueous medium is predicted to enhance the rate of generation of hydroxyl radicals. The exciton mobility is dependent on the polaron effective mass which is higher for rutile TiO$_2$ accounting for its lower activity. The bulk charge carrier transport which is less in bare rutile TiO$_2$ is enhanced in the surface modified TiO$_2$. Effective trapping of photogenerated excitons/electrons by F$^-$
/Ag\(^0\) can facilitate their migration and increase the activity by tenfolds. The rate of degradation of CV followed two reaction pathways, slower N-demethylation in basic conditions and rapid aromatic cleavage at the central carbon atom in the acidic pH conditions.

**Keywords:** Rutile TiO\(_2\), Surface modification, Silver metallization, Fluorination, Photocatalysis

1. Introduction

TiO\(_2\) is most popular photocatalyst for the decomposition of various organic pollutants [1-3]. The pure anatase phase is generally accepted as a better catalyst compared to the rutile TiO\(_2\). Different crystallographic orientations in these phases of the same material may exhibit different activities. The two crystal structure differs by the distortion of each octahedron and the assembly pattern of octahedral chains [4]. Each Ti\(^{4+}\) ion is surrounded by six O\(^2-\) ions in an octahedron. These octahedrons in rutile phase are not regular and show a slight orthorhombic distortion [5]. The octahedron in the case of anatase is significantly distorted and its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are greater (3.96 and 3.04 Å in anatase verses 3.57 and 2.96 Å in rutile) whereas the Ti-O distances are shorter than rutile (1.934 and 1.980 Å in anatase verses 1.949 and 1.980 Å in rutile). In the rutile structure each octahedron is in contact with ten neighboring octahedrons, two sharing edge oxygen pairs and eight sharing corner oxygen atoms whereas, in the case of anatase structure each octahedron is in contact with eight neighbors, four sharing an edge and four sharing a corner [6]. These differences in lattice structure cause different mass densities and variation in electronic band structure between the two forms of TiO\(_2\). The valence band (VB) is composed of oxygen 2p orbitals and the conduction band (CB) is composed of titanium 3d, 4s and 4p orbitals. The titanium 3d orbitals dominate the lower portion of the CB [7]. In general the photocatalytic activity of rutile is
reported to be less than the anatase. The anatase form is stable up to 650°C and is converted into rutile above 700°C temperature. As the annealing temperature increases the crystallite size increases leading to the increase in the particle size [8]. These differences in the crystal structure and particle size should be responsible for the lower activity of rutile. Anatase has larger band gap than rutile TiO₂ this may lead to the raise in the CB maximum to higher energy levels relative to redox potentials of adsorbed molecules [9]. This increases the oxidation potential of electrons and subsequent charge transfer process. The rate of transfer of electrons in anatase phase is faster and efficient compared to the rutile phase. They can more easily migrate and transfer to the surface from its place of origin due to smaller particle size [10].

In the present research, charge carrier dynamics of rutile polymorph is studied for different surface modifications like Ag metallization and surface fluorination by taking the model compound as crystal violet (CV). Such modifications are expected to change the electronic properties, co-ordination structure and may lead to the creation of defects and induced surface states which may actively participate in the charge separation and charge trapping at the surface. Charge transport characteristics are expected to change with these surface modifications. Exciton lifetime and exciton mobility is expected to get altered in such conditions [11-12]. The excited electron is expected to be easily trapped by F⁻ ions on the surface fluorinated sample or by Ag⁰ in the silver metallized sample. It is expected that the complex surface effects will mask the bulk properties of rutile TiO₂. The exciton diffusion length is higher for rutile due to its larger particle size and hence charge carrier recombination is predominant compared to anatase phase. Effective trapping of photogenerated excitons/electrons by F⁻/Ag⁰ can facilitate their migration and thereby increase the photocatalytic activity.

2. Experimental section

2.1. Materials
Titanium (IV) chloride (TiCl₄ ≥ 99.9%) is obtained from Merck Chemicals Limited, crystal violet (CV) and ter-Butanol (t-BuOH) from Qualigens fine chemicals, 30% w/v hydrogen peroxide (H₂O₂), ammonium per sulphate (APS), hydrogen fluoride (HF), silver nitrate were from Sisco-Chemical Industries, Bombay. Liquor ammonia, potassium iodide (KI) from SD Fine Chem limited. Double distilled water was used throughout all the experiments.

2.2.1 Preparation of Rutile TiO₂ photocatalyst

TiO₂ was prepared by sol-gel method by the hydrolysis of TiCl₄[13]. Diluted TiCl₄ solution (50ml) was taken along with 5ml concentrated H₂SO₄ in a beaker and it was diluted to 1L. It was further precipitated by the addition of liquor ammonia (~50ml to obtain pH 7-8). The titanium hydroxide sol-gel obtained was allowed to settle. This sol-gel precipitate obtained was washed several times with double distilled water to eliminate all the chloride and ammonium ions. The gel was filtered, oven dried at 120º C for 48 h to remove the water content and then ground to a fine powder. Anatase phase can be obtained in the present preparation methodology when this dried gel residue is calcined at 600ºC. The phase transformation from anatase to rutile takes place when the temperature of annealing is above 700ºC. In the present case the dried precipitate was directly heated to 1000ºC to obtain rutile phase [8]. The transformation in the titania polymorph involves both kinetic and thermodynamic aspects. The rutile configuration is thermodynamically favorable as its linearity allows the relaxation of the Ti–Ti bond. During the crystallization, anatase-type crystallite seems to form prior to rutile-type. Around the phase transition temperature, initiation of rutile crystallization takes place and the formation of anatase nucleation will either be inhibited or these crystallites get transformed to rutile structure. Anatase to rutile phase transformation occurs in a wide temperature range of 600-1100ºC and this transformation at room temperature is very slow and practically does not occur [8].

2.2.2 Preparation of fluorinated rutile TiO₂ (FRT) by wet impregnation method
Fluorinated TiO$_2$ was prepared by dispersing 0.5 g of TiO$_2$ in 5 ml of 1% HF solution. This solution was ultrasonicated for 30 minutes. The powder was filtered and dried overnight [14].

### 2.2.3 Preparation of silver deposited rutile TiO$_2$ (SRT) by photoreduction method.

SRT was obtained by photoreduction of AgNO$_3$ on TiO$_2$ surface in the presence of oxalic acid in aqueous suspension [15]. An aqueous solution of $2 \times 10^{-4}$ M AgNO$_3$ and $5 \times 10^{-3}$ M oxalic acid along with TiO$_2$ (1 g) was suspended in 1 L of distilled water and the solution was maintained at pH 6-7 by the addition of 0.1 N NaOH. The suspension is stirred continuously under UV irradiation for 40-50 min. The color of the reaction mixture changed under UV light indicating the reduction of Ag$^+$ to Ag$^0$ and confirming the deposition of Ag$^0$ on TiO$_2$ surface. After the irradiation the solution was allowed to stand for 6 h. The solid is filtered, washed and dried at 120$^\circ$C for 2 h. The color of the solid catalyst changes from light brown to greenish brown. The absence of silver in the aliquot sample was checked by chloride precipitation method and this confirms the complete deposition of silver.

### 2.3. Characterization of the catalyst

The powder X-ray diffractogram (PXRD) patterns were obtained using Panalytical X’pert Pro MPD diffractometer. FTIR spectra were obtained using the Thermo Avtar 370 spectrometer. The Diffuse Reflectance Spectra (DRS) of the photocatalyst were obtained using Schimadzu-UV 3101 PC UV-VIS-NIR UV-Visible spectrophotometer. The decrease in the concentration of substrate (CV) was measured by monitoring the absorbance using T80 UV/VIS UV-spectrometer, PG Instruments Ltd. The surface morphology was analyzed by scanning electron microscopic (SEM) and EDX analysis using ULTRA 55 microscope operating at 25 kV on the specimen upon which a thin layer of platinum had been evaporated. An electron microprobe is used in the EDX mode. The PL emission spectra were recorded using Hitachi F-7000 fluorescence spectrophotometer at 700 V PMT. The pH of the solutions was measured using Systronics digital pH meter 335.
2.4. Photochemical reactor

Experiments were carried out at room temperature using a circular glass reactor whose surface area is 176.6 cm². Medium pressure mercury vapour lamp (125 W) was used as the UV light source. Photon flux was found to be 7.8 mWcm⁻² by ferrioxalate actinometry whose wavelength peaks around 370nm. The irradiation was carried out by focusing the light directly into the reaction mixture in open air condition at a distance of 29cm. All the experiments were performed using double distilled water. The reaction mixture was stirred for 30min before irradiation to ensure the establishment of adsorption-desorption equilibrium between the substrate and catalyst. Test samples of 5 ml aliquots containing residual concentration of the CV were collected from the suspension at definite time intervals and were centrifuged to remove the suspended catalyst particles for the UV-visible spectrophotometric analysis in the wavelength range of 200-800 nm. In the experiments requiring hole scavengers or oxidizing agents, the calculated amount of the reagent was introduced into the reaction mixture at the beginning of the experiment.

3. Results and discussion

3.1. PXRD studies.

Fig.1 shows the PXRD patterns of TiO₂, FRT and SRT. All the samples show peaks corresponding to rutile phase at 2θ values of 27.45°(110), 36.08°(101), 39.20°(200), 41.25°(111), 44.07°(210), 54.33°(211), 56.64°(220), 62.74°(002), 64.06°(310), 65.53°(221), 69.02°(301), 69.80°(112), 72.47°(311), 72.72°(320), 76.54°(202) and 79.84°(212). The numbers in the parentheses represent hkl values. All the observed peaks can be indexed to pure tetragonal rutile phase and were consistent with the standard data (JCPDS 21-1276) [16]. No characteristic peak pertaining to anatase phase was observed, indicating the high purity of the rutile phase. No additional diffraction peaks were observed in the case of SRT and FRT, indicating that both Ag and F particles were well dispersed on the surface of rutile.
TiO$_2$ and below the PXRD detection limit. The average crystallite size was estimated using the Scherrer’s equation \( D = \frac{k\lambda}{\beta \cos \theta} \) based on the line broadening of (110) peak at \( 2\theta = 27.45^\circ \), where \( \lambda \) is the wavelength of the Cu K\( \alpha \) source used \( (\lambda = 1.541 \text{ Å}) \), \( \beta \) is the full width at half maximum (FWHM), \( k \) is a shape factor \( (0.94) \) and \( \theta \) is the angle of diffraction. The average crystallite size was found to be 53 nm, 39 nm and 48 nm for TiO$_2$, FRT and SRT respectively (Table 1). The grain size, phase content, phase stability and purity of the prepared photocatalyst powder are the most important parameters, especially in the nanometer scale region. Reports in the literature also show the stability of the rutile phase around this temperature of annealing and the reported crystallite size is usually greater than 35 nm [17]. Textural features that stabilize the rutile phase in the bulk form show low tolerance to defects. From Table 1 it is observed that crystallite size decreases gradually on surface modification either by Ag or by F which provides dissimilar boundaries and suppresses the mass transportation [18]. The decrease in crystallite size results in the increase in surface area of the FRT and SRT photocatalysts. The lattice strain was calculated from the following equation, \( \varepsilon = \frac{\beta}{4\tan \theta} \), where \( \varepsilon \) is the lattice strain, \( \beta \) is the FWHM of the (110) diffraction plane and \( \theta \) is the angle of diffraction. The lattice strain calculated using the above formula for TiO$_2$, SRT and FRT was found to be 0.00274, 0.00302 and 0.00375 respectively (Table 1). The observed increase in the lattice strain for SRT and FRT compared to TiO$_2$ confirms the successful deposition of metallic silver and fluorine on the TiO$_2$ surface. These surface modifications lead to very slight shift in the diffraction angle towards high \( 2\theta \) value in the PXRD patterns. Further it was also observed that the unit cell volume decreased on surface deposition of F$^-$ and Ag$^+$. 

3.2. UV-Visible Diffused Absorption Spectral studies
The optical absorption property of a semiconductor depends on its electronic structure which plays an important role in its photocatalytic performance [19]. Fig. 2 shows the UV-visible diffused absorption spectra of all the three catalysts. The TiO$_2$ sample shows a strong absorption band in the ultraviolet region at 409 nm, FRT at 414 nm and SRT at 449 nm. The band gap energies were calculated by using the formula $E_g = \frac{1240}{\lambda}$, where $\lambda$ is the absorption wavelength of the catalyst. The calculated band gap energy values of TiO$_2$, FRT and SRT were found to be 3.0 eV, 2.99 eV and 2.78 eV respectively. Lower band gap value observed for SRT can be accounted to the fact that the metallic Ag particles introduce localized energy levels with respect to the energy levels of TiO$_2$ [20]. The electrons can be excited from the VB of TiO$_2$ to the energy levels of silver rather than to the CB of the semiconductor with lower energy photons. Each collective oscillation with a different surface charge distribution leads to Surface Plasmon Resonance (SPR) effect. The frequencies and number of such modes are determined by the electron density, effective mass, dielectric function, particle size, shape, and its environment. Due to these oscillations, there is an enhancement of the electric near-field on the silver particle surface and it is observed collectively all around the silver nanoparticles. Magnification of electric field within the silver nanoparticle and also between the adjacent silver nanoparticles is the direct reason for the appearance of these optical effects [21-22]. The observed wide absorption in the range of 400 to 600 nm (Fig. 2 (inset)) by the SRT samples should be ascribed to the characteristic absorption of SPR effect. Normally, surface fluorination of TiO$_2$ photocatalyst does not affect the electronic structure but modifies mainly its surface characteristics [23]. Therefore optical properties were not significantly modified in the case of FRT except some small changes. Literature also shows several reports on the slight shift or variation of the absorption edge at $\lambda \sim 400$ nm for surface fluorine deposited TiO$_2$ samples[23].

3.3. FTIR analysis
Fig. 3 represents the FTIR spectra of TiO$_2$, FRT and SRT in the range 400-4000 cm$^{-1}$. The characteristic peaks observed around 475 to 527 cm$^{-1}$ can be assigned to O-Ti-O and Ti-O vibrations. A broad band observed around 3655 to 3250 cm$^{-1}$ can be assigned to the stretching vibrations of surface OH groups and adsorbed water. The peak corresponding to the O-H in-plane bending mode is observed at 1591 cm$^{-1}$, which is detected in all the samples [24-25]. In the case of FRT, the intensity of this band is reduced implying the efficient surface fluorination where surface OH groups are replaced by F$^-$ ions [26].

3.4. Scanning electron microscope (SEM) and Energy dispersive X-ray analysis (EDX)

SEM and EDX were recorded for all the samples in order to investigate the surface and bulk morphology. The images illustrate the particles to be large flakes (Fig. 4). Slight agglomeration is observed for all the samples and it is high for SRT. Literature also shows such agglomerations for rutile TiO$_2$ [27-29]. The metallic Ag$^0$ particles of irregular shape and sizes are unevenly distributed on the surface of rutile TiO$_2$. The higher magnification image shows the selective deposition of Ag particles mainly on the edges of the grains and such depositions on the grain boundaries lowers the energy of the system to a larger extent [30]. The average size of the Ag particles were in the range of 10-30 nm.

Qualitative and quantitative determination of elements in the prepared samples were obtained by EDX technique (Fig. 5) using grid supported carbon film of 15-25 nm thickness which is well known to give exceptionally low background. The atomic % and weight % values for the elements present in the samples are represented in Table 2 (The presence of fluorine in FRT was not detected by the EDX instrument as the concentration of fluorine ion was lower than detection limit).

3.5. XPS analysis.

The presence and the chemical state of Ag$^0$ and F$^-$ on the surface of SRT and FRT were confirmed by XPS analysis. The binding energy (BE) values of Ti 2p $3/2$ and Ti 2p $1/2$ of
pristine TiO$_2$ were observed at 458.61 eV and 464.32 eV respectively (Fig. 6 a) [31]. These peaks were found at 457.53 eV and 463.28 eV for SRT. Almost similar BE values were observed for FRT (457.5 eV and 463.2 eV). The BE of Ti 2p$_{3/2}$ is slightly lowered for both SRT and FRT compared to unmodified TiO$_2$. The extent of decrease in the BE was found to be 1.08 eV and 1.1 eV for SRT and FRT respectively suggesting the presence of titanium in Ti$^{3+}$ oxidation state [30]. The BE of O 1s was observed at 530 eV for TiO$_2$ corresponding to the lattice oxygen (Fig. 6 b) [31]. This BE peak was found at 529.8 eV and 529.7 eV for SRT and FRT. In addition to this major peak, a minor peak with BE of 532.3 eV was observed only for SRT and FRT which can be attributed to the presence of surface adsorbed hydroxyl groups/water molecules. These groups are invariantly present in all the catalysts, but to a higher extent in the modified samples. The Ag 3d$_{5/2}$ and 3d$_{3/2}$ peaks appeared at a BE of 367.2 eV and 373.1 eV for SRT (Fig. 6 c). The presence of surface metallic silver in the Ag$^0$ state is confirmed by the 3d doublet splitting energy of 5.9 eV [32]. The F 1s BE peak was found at 684.59 eV (Fig. 6 d) which can be assigned to the F$^-$ ions which are chemically adsorbed on the surface of TiO$_2$ in the case of FRT [33]. These XPS results indicate the successful surface modification of rutile TiO$_2$ by Ag$^0$ and F$^-$.

3.6. Photocatalytic Reactivity

3.5.1. Effect of initial pH

The pH of the reaction mixture is one of the crucial reaction parameter in the photocatalytic degradation reaction of organic contaminants, since it determines the surface charge of the photocatalyst and also the pollutant molecule. Electrostatic interaction between semiconductor surface with various entities like solvent molecules, substrate molecules and the charged radicals formed during photocatalytic oxidation strongly depends on the solution pH [34]. In addition, the process of protonation and deprotonation of the organic molecules takes place depending on the solution pH. Prior to the photocatalytic experiment,
adsorption/desorption equilibrium of CV molecules on the surface of the photocatalyst was achieved by stirring the solution with the calculated amount of catalyst. The experiments were performed in acidic (pH~2), neutral (pH~7) and basic (pH~9) pH conditions. The experiments using TiO₂, SRT and FRT showed that the cationic CV dye exhibited least adsorption (~5%) at all the three pH conditions. This is because of very few surface active sites on rutile TiO₂ surface due to the high temperature annealing. It is well known that rutile TiO₂ is the most thermodynamically stable allotropic form with best crystallized state obtained at higher temperature. There exists a higher degree of crystallinity in the bulk as well as at the surface, with very few structural defects. Hence observed adsorption is minimum at saturated surfaces. It is therefore concluded that major degradation process may take place in the bulk of the solution rather than on the surface of the catalyst. From Fig. 7 it was observed that acidic pH was more favorable for the degradation of CV compared to basic and neutral pH conditions. Fedkin et al. reported the isoelectric point of rutile TiO₂ to be around 5.26 (± 0.45) at 25ºC [35]. The surface electrical charge on the TiO₂ varies with the pH of the solution as shown below:

\[
\begin{align*}
\text{Ti}^\oplus & \quad \text{OH}^- \\
\text{Ti}^\oplus & \quad \text{OH}^- \\
\text{Ti}^\oplus & \quad \text{OH}^- \\
\end{align*}
\]

(1)

TiO₂ acquires positive charge below the pH of 5.26 and hence at this pH condition the electrostatic repulsion dominates between TiO₂ and CV molecules. If the pH value is too high (pH >9.5), CV molecules changes to leuco form and the solution becomes colorless leading to the disappearance of absorption peak implying the destruction of chromophore but not complete destruction of the molecule. At acidic pH, the hydroxyl groups on the TiO₂ surface attain positive charge (\(\text{OH}^+\)) as shown in the equation 1. Under these conditions, CV being a cationic dye doesn’t get adsorbed on the surface of the catalyst and thus it remains completely in the bulk of the solution. In general, it is obviously expected that degradation
rate of the cationic dye should decrease at acidic pH conditions due its poor adsorption on the catalyst surface [36]. However, in the present study the degradation rates increased at acidic pH in spite of low adsorption (Table 3) and the activity is attributed to the fact that the bulk hydroxyl radicals in the solution play a major role in the degradation process. This fact is further confirmed by addition of free radical scavengers during the process of photocatalytic degradation reaction (discussed in the further section). A new absorption peak is observed in the wavelength range of 325-403 nm in the UV-Visible absorption spectra recorded during the degradation of CV in acidic pH condition (inset of Fig.8a).The intensity of this peak increases with time as the concentration of intermediate increases. This intermediate formation does not take place in basic media (Fig.8b).

3.5.2. Comparison of Photocatalytic activities of SRT, FRT and TiO₂

All the experiments were carried out under the acidic pH (~ 2) conditions as it was more favorable for the degradation of CV [Fig. 9a, 9b & 9c]. The calculated rate constant values fitted well to the pseudo-first-order kinetic model. This model is more appropriate since the initial concentration of the pollutant was low:

\[ \log \frac{C_t}{C_0} = -kt \]  

(2)

Where \( C_0 \) is the initial dye concentration and \( C_t \) is the dye concentration at time \( t \) respectively and \( k \) is the pseudo-first-order rate constant. The plot of \( \log (C_t/C_0) \) as a function of irradiation time gives the rate constant value \( (k) \) from the slope of the well fitted straight line. It is observed that all the three catalysts performed better in acidic pH conditions (Table 3). The rate constant values for FRT and SRT is ~2 times greater than TiO₂. It is observed that SRT exhibits higher degradation rate and in general the rate constants for the reaction show the following decreasing order SRT>FRT>TiO₂ (Table 3). In the case of SRT, the photogenerated CB electrons migrate directly to the Fermi level of Ag[37].The metallic silver nanoparticles functioned as an electron sink to trap the photogenerated electrons from the
excited SRT due to the formation of Schottky barrier and thus preventing the electron-hole recombination. This vectorial transfer of electrons is due to the electrical barrier created at the interface between Ag deposit and TiO$_2$ semiconductor and these electrons further facilitate dioxygen reduction [38]. At the TiO$_2$/Ag interface a significant redistribution of charge occurs due to the overlap of the wave functions from the two sides, the extent of this overlap depends on the Ag work function and TiO$_2$ electron affinity [39]. This charge redistribution leads to the downward band bending of VB and CB edges of n-type semiconductor in relation to the Fermi level of Ag facilitating the transfer of photogenerated electrons. But the opposite scenario is prevented, from the so-called Schottky barrier [40]. These electrons trapped in the Ag nanoparticles are immediately detrapped to dissolved oxygen to generate the superoxide radical anion ($O_2^{-}$) which in turn produce hydroxyl radical by reacting with surrounding water molecules. Simultaneously the holes in VB react with the water or hydroxyl ions to produce hydroxyl free radicals. These hydroxyl and $O_2^{-}$ radicals are reactive species which are mainly responsible for the degradation of CV. The charge transfer mechanism taking place in the case of SRT is summarized as follows [41]:

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow e^- + h^+ \quad (3) \\
\text{Ag}^o + e^- & \rightarrow \text{Ag}^- \quad (4) \\
\text{Ag}^- + \text{O}_2 & \rightarrow \text{O}_2^{-} + \text{Ag}^o \quad (5) \\
\text{H}_2\text{O} + h^+ & \rightarrow \cdot\text{OH} + \text{H}^+ \quad (6) \\
\cdot\text{OH} + \text{CV} & \rightarrow \text{By products} \quad (7)
\end{align*}
\]

In the case of FRT, the interfacial charge transfer process and the quantum efficiency of photocatalytic redox reactions is greatly affected by the presence of surface fluorine. Several reaction parameters are influenced by surface fluorination like substrate adsorption, production of active radical/free radical species, surface charge, photogenerated charge carrier separation and transfer, and thus in turn influence the surface photocatalytic reaction kinetics and mechanism [42]. The existence of strong electronegative fluoride ions on the surface may
result in net negative surface charge on the FRT. The Ti-OH species on the surface could be replaced by Ti–F species by fluorination as depicted in the following reactions [43]:

\[
\begin{align*}
\text{Ti-OH} + H^+ & \rightarrow \text{Ti-OH}_2^+ \quad (8) \\
\text{Ti-OH}_2^+ + h_{vb}^+ + OH^- & \rightarrow \text{Ti-O}^+ + H_2O \quad (9) \\
\equiv \text{Ti-F} + h_{vb}^+ + H_2O & \rightarrow \text{Ti-F} + \cdot \text{OH} + H^+ \quad (10) \\
\equiv \text{Ti}^{4+}\cdot\text{F} + e^- & \rightarrow \equiv \text{Ti}^{3+}\cdot\text{F} \quad (11) \\
\equiv \text{Ti}^{3+}\cdot\text{F} + O_2 & \rightarrow \equiv \text{Ti}^{4+}\cdot\text{F} + O_2^- \quad \text{(electron release)} \quad (12)
\end{align*}
\]

The photocatalytic degradation reaction is initiated in the bulk of the solution rather than the surface of the catalyst, though the surface is dominated by negative charge and CV being a cationic dye. During the photocatalytic reaction, Ti-F\(^-\) species enhances the rate of generation of hydroxyl free radicals(equation 12). The higher electronegativity of F\(^-\) minimizes the formation of Ti–O\(^-\) traps (equation 9) [44]. Due to the high oxidation potential of the F\(^+\)/F\(^-\) couple (3.6 V) the VB holes will not be able to oxidize the F\(^-\) anion and they directly react with water molecules at the interface, producing 'OH radicals according to equation 13 [26].

It is well known that bulk free hydroxyl radicals are stronger oxidants than the surface adsorbed hydroxyl radicals. FRT produces higher concentration of bulk free hydroxyl radicals and increase the photodegradation rate [26].

\[
\begin{align*}
h_{vb}^+ + H_2O & \rightarrow \cdot \text{OH} + H^+ \quad (13) \\
\equiv \text{Ti}^{4+}\cdot\text{F} + e^- & \rightarrow \equiv \text{Ti}^{3+}\cdot\text{F} \quad (14) \\
\equiv \text{Ti}^{3+}\cdot\text{F} + O_2 & \rightarrow \equiv \text{Ti}^{4+}\cdot\text{F} + O_2^- \quad \text{(electron release)} \quad (15)
\end{align*}
\]

The surface \(\equiv\text{Ti-F}\) groups can act as electron trapping sites to reduce the electron hole recombination and it also increases the surface acidity of the photocatalyst which is ascribed to the strong electronegativity of the fluoride [45]. The photogenerated holes are trapped by surface lattice oxygen atoms in the TiO\(_2\), which results in the breaking of bond between oxygen and titanium atoms. Subsequently, water molecules dissociatively adsorb at these sites leading to the formation of hydroxylfree radicals. It has been found that fluorination can
increase the concentration of bulk hydroxyl free radicals in the aqueous solution since the fluorine atoms have much stronger affinity for electrons compared to the oxygen. Upon fluorination the original electron cloud distribution in Ti-O bond will deviate from its mean position and align towards the fluoride ion resulting in the weakening of Ti-O bond[46]. In this way, a more efficient charge separation is achieved, leading to the enhancement of photocatalytic efficiency of FRT. The lower activity of TiO₂ compared to SRT and FRT is due to the absence of electron traps on the surface. The photogenerated charge carriers in rutile TiO₂ on UV illumination readily undergo rapid recombination even before reaching the surface for interfacial charge transfer mechanism. Exciton mobility is dependent on the polaron effective mass [47]. Although contradicting values for effective masses are reported in the literature, generally a higher effective mass is reported for rutile (7–8 m₀, where m₀ is the electron mass) than for anatase [47-48]. Therefore the observed percentage degradation for unmodified rutile TiO₂ is comparatively lower than FRT and SRT. The bulk charge carrier transport which is less in bare rutile TiO₂ is enhanced in the surface modified TiO₂. The optimized fluorine content on the surface of TiO₂ is most essential for efficient photocatalytic activity of the catalyst. Trapping of photogenerated electrons takes place due to the strong electronegativity of fluoride ion and excess electrons gets simultaneously detrapped to the O₂ molecules to yield superoxide radicals [49-50]. Degradation experiments were performed by varying the percentage of HF in the range of 0.5% to 2% [Fig. S1a]. It was found that the photocatalytic degradation rate increased with the increase in HF content up to 1%. Further increase in HF concentration, the degradation efficiency decreased. The ≡Ti-F bond on the catalyst surface changes the original charge equilibrium by drawing the excess electrons out of bulk TiO₂ lattice and renders the surface with increased negative charge density leaving the semiconductor bulk with localized excess positive charge. The number of electrons passing through ≡Ti-F increases and the electron density within the TiO₂ lattice reduces
leading to the reduction in the recombination rate up to the optimum concentration of HF
[51]. In general, the existence of two electrical potential gradients can be visualized in the
surface fluorinated rutile TiO$_2$ (Fig. S1b): i) one within the semiconductor bulk lattice leading
to the higher upward band bending preventing further movement of electrons and increasing
the width of space charge region, ii) another electrical potential gradient is created on the
surface of the semiconductor particle due to the excess negative charges. As the concentration
of fluoride increases, mismatch of electrical potential gradients takes place influencing the
extent of band bending. The higher extent of upward band bending leads to the easier
transportation of holes rather than electrons. This situation favors recombination rather than
charge separation. Therefore 1% HF was found to be optimized fluorine concentration in the
present study. Fluorine in FRT and silver in SRT act as electron traps which reduce the
electron-hole recombination and enhance the interfacial charge transfer mechanism leading to
an increase in the photocatalytic activity.

**Photoluminescence (PL) studies:** The above predicted charge carrier dynamics can be well
supported by the PL technique. Fluorescence probing method is found to be more suitable
 technique which is based on the reaction of OH$^-$ radical with stable molecules [52-53]. The
rate of generation of hydroxyl radicals at the illuminated photocatalyst interface was detected
by the PL technique using coumarin as the probe molecule. The photogenerated hydroxyl
radicals react with coumarin to yield 7-hydroxycoumarin which exhibits strong fluorescence
and can be easily detected by this technique [52]. The peak intensities are the direct measure
of free hydroxyl radical concentration. Fluorescence of 7-hydroxycoumarin emission is
observed in the visible region with $\lambda_{\text{max}}$ around 456 nm [52-53]. The observed 7-
hydroxycoumarin PL intensities decrease in the following order: SRT > FRT > TiO$_2$ (Fig. 10).
These results imply the fact that extent of generation of OH$^-$ radicals are higher in the case of
SRT followed by FRT, compared to unmodified rutile TiO$_2$. 

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3.5.4. Effect of addition of H$_2$O$_2$ and APS as electron acceptors on the photocatalytic activity of TiO$_2$, SRT and FRT

The photogenerated charge carrier recombination in rutile TiO$_2$ is more predominant and is considered as one of its major limitation for efficient photocatalytic activity especially in the absence of suitable electron acceptors. Therefore it is necessary to prevent the charge carrier recombination to ensure efficient photocatalysis. It is well known that molecular oxygen itself in the aqueous suspension acts as an electron acceptor in heterogeneous photocatalytic reactions [54]. Further, addition of external oxidant/electron acceptors in the suspension improves the rate of photocatalytic degradation. Since superoxide and hydroxyl free radicals play an important role in the photocatalytic degradation process, the effect of addition of electron acceptors such as H$_2$O$_2$ and APS on the photocatalytic degradation process is investigated for all the three catalysts at pH 2 under UV light irradiation. The reactive species such as SO$_4^-$ and ’OH produced from APS and H$_2$O$_2$ by the reactions with photogenerated electrons is expected to serve as strong oxidant and also as an electron scavenger. There was 100% degradation of CV on addition of H$_2$O$_2$ with a rate constant of $7.2811 \times 10^{-2}$ min$^{-1}$ (in 60 min) compared to photocatalytic activity in the absence of H$_2$O$_2$ with a rate constant of $1.1562 \times 10^{-2}$ min$^{-1}$ (for 150 min) for TiO$_2$ catalyst (Fig. 9a and Table 4a). During the photocatalytic degradation photogenerated electrons will be accepted by H$_2$O$_2$ to form hydroxyl radicals as shown in the equations below and thus suppress the charge carrier recombination and leading to the direct formation of hydroxyl radicals [55].

\[
\begin{align*}
H_2O_2 + e_{cb}^- &\rightarrow OH^- + 'OH \\
H_2O_2 + O_2^- &\rightarrow OH^- + 'OH + O_2
\end{align*}
\]

However, H$_2$O$_2$ can also serve as hole scavenger at higher concentrations, leading to the formation of hydroperoxo radicals and these radicals adversely consume hydroxyl free radicals to certain extent as shown in the following reactions:
\[ \text{H}_2\text{O}_2 + \cdot\text{h}^+ \longrightarrow \text{HO}_2^* + \text{H}^+ \quad (18) \]
\[ \text{H}_2\text{O}_2 + \cdot\text{OH} \longrightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad (19) \]
\[ \text{HO}_2^* + \cdot\text{OH} \longrightarrow \text{H}_2\text{O} + \text{O}_2 \quad (20) \]

Therefore optimum amount of H\textsubscript{2}O\textsubscript{2} (10 ppm) is essential for sustaining the efficiency of the photocatalytic reaction. In addition to the externally added H\textsubscript{2}O\textsubscript{2} there is in situ formation of H\textsubscript{2}O\textsubscript{2} via reaction between CB electron and surface adsorbed oxygen.

In the case of APS as an electron scavenger the following reactions are expected to take place [56]:

\[ \text{S}_2\text{O}_8^{2-} + \text{e}_{cb} \longrightarrow \text{SO}_4^{2-} + \text{SO}_4^* \quad (21) \]
\[ \text{SO}_4^* + \text{H}_2\text{O} \longrightarrow \text{SO}_4^{2-} + \cdot\text{OH} + \text{H}^+ \quad (22) \]

But the addition of APS leads to the decrease in the rate constant from \(1.1562 \times 10^{-2} \text{ min}^{-1}\) to \(0.7302 \times 10^{-2} \text{ min}^{-1}\) (for 150 min). The sulphate anions generated in this illuminated system readily reacts with \(\cdot\text{OH}\) radicals/ VB holes in a faster rate rather than allowing sulphate anion radicals to react with water to liberate \(\cdot\text{OH}\) radicals (equations 23 and 24). This process indirectly leads to reduction in rate of degradation.

\[ \text{SO}_4^* + \text{h}_{vb}^+ \longrightarrow \text{SO}_4^* \quad (23) \]
\[ \text{SO}_4^* + \cdot\text{OH} \longrightarrow \text{SO}_4^{2-} + \text{OH}^- \quad (24) \]

**Mechanism of \(\cdot\text{OH}\) radical generation on the surface of rutile TiO\textsubscript{2}/ SRT/ FRT in the presence of H\textsubscript{2}O\textsubscript{2}:** As reported in the literature the rate of generation of \(\cdot\text{OH}\) free radicals is low in rutile TiO\textsubscript{2} compared to anatase TiO\textsubscript{2}. The stability and the life time of the surface trapped holes in rutile TiO\textsubscript{2} is different from that of anatase. In anatase TiO\textsubscript{2} the trapped holes readily react with hydroxyl anion to generate surface adsorbed \(\cdot\text{OH}\) radicals, while in the case of rutile TiO\textsubscript{2}, the Ti-peroxo (Ti-OO-Ti) complex species are produced on the surface by the combination of two trapped holes (Ti–O’) in aqueous medium [57-58]. Due to the short separation distance between two Ti atoms in rutile (3.57 and 2.96 Å) compared to anatase (3.79 and 3.04 Å), the trapped holes could easily form a dimer to generate a Ti-OO-Ti
structure [58]. Further the adsorbed H₂O₂ will serve as a catalyst for the •OH radical generation. In our studies the degradation rate constants increased drastically for pristine rutile TiO₂ itself (from 1.1562 x 10⁻² min⁻¹ in a time period of 150 mins to 7.2811 x 10⁻² min⁻¹ with a time period of 60 mins), SRT (from 2.827 x 10⁻² min⁻¹ in a time period of 150 mins to 11.614 x 10⁻² min⁻¹ with a time period of 60 mins) and FRT (from 2.541 x 10⁻² min⁻¹ in a time period of 150 mins to 11.89 x 10⁻² min⁻¹ with a time period of 45 mins) samples on addition of H₂O₂ to the reaction mixture. The oxidation of the intermediate [Ti-O-O-Ti] is a crucial step in the generation of •OH radicals. The hole attacks O atom of [Ti-O-O-Ti], accompanied with a nucleophilic attack of hydroxyl anion (OH⁻) resulting in a transient intermediate [Ti-O• HOO-Ti] which can revert to the original peroxo complex species [Ti-O-O-Ti], along with the production of •OH radical. Further the added H₂O₂ promotes the •OH radical generation under UV illumination. This proposed mechanism is similar to the mechanism given by Nakabayashi et.al [57-58]. Similar mechanism was observed in the case of SRT and FRT except the fact that these catalysts additionally had surface electron trapping centers. The addition of H₂O₂ as an electron acceptor has increased the rate constant values by tenfolds (Fig. 9b & 9c, Table 4b &4c).

3.5.5. Effect of addition of hole scavengers like KI and t-BuOH on the photocatalytic activity of TiO₂, SRT and FRT

Photocatalytic activity is affected by both surface and bulk hydroxyl radicals. In the present study, the acidic condition allows the dye molecules to diffuse more readily into the bulk of the solution. The degradation of CV was carried out in the presence of KI (surface hydroxyl radical scavenger) and t-BuOH (bulk hydroxyl radical scavenger) with TiO₂, FRT and SRT photocatalysts[55]. Iodide ion is an excellent scavenger of VB hole and thereby hinders the formation of surface hydroxyl radicals[59-60]. It was observed that the extent of degradation was not altered by the addition of KI implying that the surface hydroxyl radicals had a minor
role in the degradation mechanism (Fig.9a, 9b & 9c). Further it can be observed that the rate of degradation decreases on addition of t-BuOH, implying the major role of bulk hydroxyl radicals in the photodegradation process.

3.7 Photocatalytic degradation pathway.

The degradation of CV is highly affected by the pH conditions of the reaction medium. Three main absorption peaks were observed for CV at 580 nm, 300 nm and 250 nm. In acidic medium a new absorption peak at 360 nm is observed. The intensity of this peak is quite high and prominent in acidic pH and very low in basic pH conditions (Fig. 8a and b). The probable predicted reaction mechanism (Scheme 1) involves two competitive pathways for the photodegradation of CV involving OH free radicals (i) N-de-methylation of the chromophore skeleton and (ii) cleavage of the whole conjugated chromophore structure [61]. The prominent peak at 360 nm is because of the cleavage of bonds at the central carbon atom by the attack of OH free radical which is the major reaction pathway in the acidic conditions leading to the fragmentation of CV molecules. But in the basic pH condition, N-de-methylation of the chromophore skeleton is the major degradation pathway leading to the hypsochromic shift of maximal absorbance peak till complete N-demethylation occurs. This leads to the formation of an intermediate of the type fuchsin basic which further undergoes slow aromatic cleavage.

4.0 Conclusions

The reasons for lower activity of rutile TiO$_2$ were explored. The surface modification of rutile TiO$_2$ leads to the improvement of photocatalytic activity. The mechanism of bulk charge carrier transport is enhanced in the surface modified rutile TiO$_2$. Acidic pH was found to be more favorable for the degradation, in spite of low adsorption of cationic substrate CV molecules on the Ti-OH$_2$ catalyst surface. The electrostatic repulsion drives the CV molecules into the bulk of the solution. Despite the poor adsorption of substrate molecule, efficient degradation takes place due to the major involvement of bulk hydroxyl radicals in the
aqueous reaction medium rather than the surface hydroxyl radicals. The concentration of the bulk hydroxyl radicals was high in the case of FRT as confirmed by the addition of t-BuOH as bulk hydroxyl radical scavenger. All the catalysts showed better performance in the presence of an oxidizing agent like H₂O₂. But however FRT showed higher performance due to the synergistic effect between surface fluorine and the H₂O₂ oxidant. Two probable mechanisms for the degradation of CV were predicted: N-de-methylation of the chromophore skeleton and cleavage of the whole conjugated chromophore structure. The second pathway is more dominant at pH 2 leading to complete destruction of substrate molecule at a faster rate. N-de-methylation is more probable at basic pH condition which is a slow process.

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Fig.1. PXRD pattern of TiO$_2$, FRT and SRT photocatalysts
Fig. 2. UV-vis diffuse absorbance spectra of TiO$_2$, SRT and FRT photocatalysts
**Fig. 3.** FTIR Spectrum of TiO$_2$, FRT and SRT photocatalysts
Fig. 4. SEM images of TiO$_2$, SRT and FRT photocatalysts
Fig. 5. EDX spectra of TiO₂ and SRT photocatalysts
Fig. 6. XPS patterns of (a) Ti 2p peaks in TiO$_2$, FRT and SRT, (b) O 1s peaks in TiO$_2$, FRT and SRT, (c) Ag 3d peaks of SRT and (d) F 1s peak of FRT.
Fig. 7. Plot of $C/C_0$ for the degradation of CV in the presence of TiO$_2$ with varying pH under UV light illumination.
Fig. 8. Photocatalytic degradation of CV using Rutile TiO$_2$: (a) at pH 2, (b) at pH 9.
Fig. 9a. Effect of H$_2$O$_2$ and APS (as electron acceptors), KI and t-BuOH (surface and bulk hydroxyl radical scavengers) for the degradation of Crystal Violet in the presence of bare TiO$_2$ under UV light illumination (at pH 2)
**Fig. 9b.** Effect of H$_2$O$_2$ and APS (as electron acceptors), KI and t-BuOH (surface and bulk hydroxyl radical scavengers) for the degradation of Crystal Violet in the presence of SRT under UV light illumination (at pH 2)
Fig. 9c. Effect of H$_2$O$_2$ and APS (as electron acceptors), KI and t-BuOH (surface and bulk hydroxyl radical scavengers) for the degradation of Crystal Violet in the presence of FRT under UV light illumination (at pH 2)
Fig. 10. PL spectra of SRT, FRT and TiO₂ dispersed in aqueous coumarin solution (10⁻³ M) under UV light illumination for one hour (excitation wavelength: 332 nm, scan speed: 1200 nm/min and slit width: 2.5 nm)
Scheme 1. Probable reaction mechanism for the photocatalytic degradation of CV
Table 1. Phase composition, crystallite size, lattice parameters, cell volume and lattice strain of rutile TiO$_2$, FRT and SRT photocatalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase composition</th>
<th>D (nm)</th>
<th>A in Å</th>
<th>V(Å$^3$)</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare TiO$_2$</td>
<td>Rutile</td>
<td>53</td>
<td>a=b=4.594, c=2.961</td>
<td>62.49</td>
<td>0.00274</td>
</tr>
<tr>
<td>FRT</td>
<td>Rutile</td>
<td>39</td>
<td>a=b=4.566, c=2.957</td>
<td>61.65</td>
<td>0.00375</td>
</tr>
<tr>
<td>SRT</td>
<td>Rutile</td>
<td>48</td>
<td>a=b=4.584, c=2.959</td>
<td>62.18</td>
<td>0.00302</td>
</tr>
</tbody>
</table>

D = crystallite size; A = lattice parameters in Å; V = unit cell volume in (Å)$^3$; ε = lattice strain.

Table 2. EDX analysis of rutile TiO$_2$, SRT and FRT photocatalysts

<table>
<thead>
<tr>
<th>Element</th>
<th>TiO$_2$</th>
<th>FRT</th>
<th>SRT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic%</td>
<td>Atomic%</td>
<td>Atomic%</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>65.84</td>
<td>35.33</td>
<td>44.18</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>34.16</td>
<td>64.67</td>
<td>55.72</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3. Rate constants and percentage degradation values with various catalysts at different pH conditions in 150 minutes

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>pH</th>
<th>Rate constant (min$^{-1}$)</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>2</td>
<td>1.1562 x 10^{-2}</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.1799 x 10^{-2}</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.4682 x 10^{-2}</td>
<td>52</td>
</tr>
<tr>
<td>FRT</td>
<td>2</td>
<td>2.541 x 10^{-4}</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.848 x 10^{-2}</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.678 x 10^{-2}</td>
<td>74</td>
</tr>
<tr>
<td>SRT</td>
<td>2</td>
<td>2.827 x 10^{-2}</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.607 x 10^{-2}</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.502 x 10^{-2}</td>
<td>72</td>
</tr>
</tbody>
</table>
Table 4a. Rate constants and % degradation of CV with TiO$_2$ in presence of H$_2$O$_2$, APS, KI and t-BuOH at pH 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate constant (min$^{-1}$)</th>
<th>Time (min)</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>$1.1562 \times 10^{-2}$</td>
<td>150</td>
<td>84</td>
</tr>
<tr>
<td>TiO$_2$ + H$_2$O$_2$</td>
<td>$7.2811 \times 10^{-2}$</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>TiO$_2$ + APS</td>
<td>$0.7302 \times 10^{-2}$</td>
<td>150</td>
<td>70</td>
</tr>
<tr>
<td>TiO$_2$ + KI</td>
<td>$1.837 \times 10^{-2}$</td>
<td>150</td>
<td>94</td>
</tr>
<tr>
<td>TiO$_2$ + t-BuOH</td>
<td>$0.5175 \times 10^{-2}$</td>
<td>150</td>
<td>57</td>
</tr>
</tbody>
</table>

Table 4b. Rate constants and % degradation of CV using SRT photocatalyst in presence of H$_2$O$_2$, APS, KI and t-BuOH at pH 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate constant (min$^{-1}$)</th>
<th>Time (min)</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRT</td>
<td>$2.827 \times 10^{-2}$</td>
<td>150</td>
<td>99</td>
</tr>
<tr>
<td>SRT + H$_2$O$_2$</td>
<td>$11.614 \times 10^{-2}$</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>SRT + APS</td>
<td>$0.0962 \times 10^{-2}$</td>
<td>150</td>
<td>79</td>
</tr>
<tr>
<td>SRT + KI</td>
<td>$1.9092 \times 10^{-2}$</td>
<td>150</td>
<td>95</td>
</tr>
<tr>
<td>SRT + t-BuOH</td>
<td>$1.099 \times 10^{-2}$</td>
<td>150</td>
<td>83</td>
</tr>
</tbody>
</table>

Table 4c. Rate constants and % degradation of CV using FRT photocatalyst in presence of H$_2$O$_2$, APS, KI and t-BuOH for the illumination of a time period of 150 min at pH 2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate constant (min$^{-1}$)</th>
<th>Time (min)</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRT</td>
<td>$2.541 \times 10^{-2}$</td>
<td>150</td>
<td>99</td>
</tr>
<tr>
<td>FRT + H$_2$O$_2$</td>
<td>$11.89 \times 10^{-2}$</td>
<td>45</td>
<td>100</td>
</tr>
<tr>
<td>FRT + APS</td>
<td>$0.876 \times 10^{-2}$</td>
<td>150</td>
<td>74</td>
</tr>
<tr>
<td>FRT + KI</td>
<td>$1.696 \times 10^{-2}$</td>
<td>150</td>
<td>92</td>
</tr>
<tr>
<td>FRT + t-BuOH</td>
<td>$0.934 \times 10^{-2}$</td>
<td>150</td>
<td>77</td>
</tr>
</tbody>
</table>