Investigation of oxygen vacancies in Ce coupled TiO$_2$ nanocomposites by Raman and PL spectra

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Abstract
CeO$_2$–TiO$_2$ nanocomposites with different Ce weight percentages (2, 4, 6 and 8%) were synthesized by sol-gel method. The influence of cerium inclusion on the structural, morphological, optical properties and elemental composition has been analyzed via XRD, BET surface area analysis, UV-DRS, HR-SEM, EDAX, TEM, Raman and photoluminescence spectra. The structural study showed that all the CeO$_2$–TiO$_2$ nanocomposites crystallized in tetragonal structure with anatase phase. Morphological study revealed that the nanocomposites are in spherical shape with size between 13–15 nm. Raman and PL spectra confirmed the presence and influence of oxygen vacancy defects. The adsorption ability of the CeO$_2$–TiO$_2$ nanocomposites was investigated for congo red dye under dark condition. CeO$_2$–TiO$_2$ nanocomposites have enhanced adsorptive performance in comparison with bare TiO$_2$ nanoparticles. The enhanced adsorptive activity of CeO$_2$–TiO$_2$ nanocomposites is due to the higher surface area of the nanocomposites and oxygen vacancies present in the surface of the nanocomposites. The pseudo second order kinetic equation fits well with higher correlation coefficient compared to the pseudo first order in explaining the reaction kinetics.

Keywords: sol-gel method, nanocomposites, anatase, absorption
Classification numbers: 4.00, 5.01, 5.06

1. Introduction

Among the various applications of nanoscience and nanotechnology, catalysis has been very much attracted and significant amount of research was done during the past decade. The research on the plasmonic enhancement of photocatalytic activity of nanostructures consisting of various metals and oxide semiconductors is reviewed in [1]. The photocatalytic activity of titania coupled with nanocarbons of different types including single-walled carbon nanotubes, multi-walled carbon nanotubes and graphene oxide are recently reviewed in [2]. Dyes are used in many industries such as textile, paper, plastics, cosmetics, leather etc., among them congo red (CR) is the most used one [3]. It is a benzidine based diazo carcinogenic dye which is mostly used in cotton textiles, paper and plastic industries [4–6]. It is difficult to biodegrade because of its complex aromatic structures. The wastes from these industries pollute the water resources and affect aquatic life [7, 8]. It is potentially harmful to human beings since it causes skin, eye and gastrointestinal irritations [9]. Several methods are used to remove the organic dyes and convert them into less harmful chemicals using semiconductor
materials. Commercially, electrochemical coagulation [10], photocatalytic degradation [11], ozonation [12], electrochemical oxidation [13], nano filtration [14], reverse osmosis [15], adsorption [16] methods, etc are used to remove the toxic dyes from industrial wastes. Among these, adsorption method is the most effective one since it is fast, inexpensive and sludge free method to remove the organic dyes [5, 17].

Semiconductor oxide nanoparticles have been used to complete mineralization of organic pollutant. Finding out a good catalyst is the greatest challenge in the field of catalysis. Several semiconductors, like TiO₂, Fe₂O₃, ZnO, and WO₃, are recognized to have higher photocatalytic properties. Among all the various semiconductor oxides, TiO₂ is widely used because of its high stability, adsorption capability, non-toxicity, and low cost [18–20]. It has been studied for environmental problems, solar energy applications and hydrogen production [21].

The performance of TiO₂ can be improved by coupling it with other non-metal or metal oxides like SnO₂, CeO₂, ZnO, Bi₂O₃, etc. Among them CeO₂ is one of the most interesting rare earth material for researchers in the field of catalysis. The coupling of CeO₂ boosts the performance of TiO₂ because it has some special properties such as the UV absorbing ability, high oxygen storage capacity, better electrical conductivity and good thermal stability [22]. It has high oxygen mobility since cerium exists in both Ce³⁺ and Ce⁴⁺ forms which leads to strong catalytic activity. There are several numbers of oxygen vacancies generated on the surface of the nanocomposites which promotes the number of active sites [23]. The CeO₂–TiO₂ nanocomposites are mostly used in gas sensors, waste water treatment and water purification in the presence of light [24–27].

In the literature, the degradation of CR was mostly done using TiO₂ under light illumination. Thomas et al [28] prepared two different sized (50 and 200 nm) TiO₂ nanoparticles by sol-gel method, used them as photocatalyst for the degradation of CR under 10 h of UV illumination and the degradation efficiency of 56.20 and 27.78% was reported. Guo et al [29] obtained titania/sulphonic acid nanocomposites through hydrothermal method and they reported that the degradation of CR was completed in 210 min of visible light illumination. Narayan et al [30] synthesized rare earth ion doped TiO₂ nanocomposites (Y, Yb and Gd doped TiO₂) through co-precipitation/hydrolysis. 275 mg of photocatalyst was added in 850 ml of CR (25 mg l⁻¹) and allowed for 180 min of visible light illumination. The degradation efficiency of 91, 85 and 80% was obtained for Y, Yb and Gd doped TiO₂ nanocomposites, respectively. However, pure TiO₂ took 120 min to degrade half the initial concentration of CR. Farbod et al [31] synthesized TiO₂ nanoparticle by sol-gel process and they achieved 70% degradation of CR in 60 min for the sample annealed at 400 °C and 50% for sample annealed at 800 °C. Li et al [32] prepared TiO₂/PCNF heterostructures through hydrothermal method and reported photocatalytic degradation efficiency of 60% and 80% in 170 min of visible light illumination for TiO₂/PCNFs-1 and TiO₂/PCNFs-2, respectively. Djellabi et al [33] prepared TiO₂–montmorillonite composite (TiO₂-M) through impregnation method and the removal of 6.2% of congo red dye was achieved under 6 h dark condition and 22.64% under 6 h of UV light illumination.

In the present study Ce coupled TiO₂ with various weight % of Ce were synthesized by the sol-gel method and used as an adsorbent to mineralize the congo red dye in the absence of light source. With increasing Ce content, reduction in crystallite size, particle size and increase of surface area of TiO₂ nanoparticles were observed which facilitate the larger number of active sites on the surface of the nanocomposites. The role of oxygen vacancies in TiO₂ on adsorption process has been investigated. The effect of cerium inclusion on adsorption of congo red was determined using pseudo first and second order kinetic models.

2. Experimental

2.1. Materials

All chemicals used in this work were of analytic grade and used without additional purification. Titanium (IV) isopropoxide (purity 97%, Sigma Aldrich, India), cerium (III) nitrate hexahydrate (purity 99%, Sigma Aldrich, USA), ethanol, glacial acetic acid (purity 99 to 100% Merck, India), congo red powder (Nice, Cochin) were purchased with analytical grade and used without purification. Double distilled water was used for all processes.

2.2. Preparation of the adsorbent

CeO₂–TiO₂ nanocomposites were prepared by sol-gel method using titanium tetraisoopropoxide (TTIP) as the precursor. 5 ml of TTIP solution was added drop by drop with 5 ml of ethanol. Then 10 ml of double distilled water was added drop wise and the pH of the solution was adjusted to 3 by adding glacial acetic acid. After 30 min of stirring, the resultant sol was allowed to gel for one day and then dried at 80 °C for 6 h. The resultant material was milled with mortar and pestle and annealed at 450 °C for 2 h to obtain TiO₂ nanoparticles. To prepare Ce coupled TiO₂ nanocomposites, 2 wt% of cerium nitrate were added to the titanium isopropoxide solution and the same method of preparation was followed. The weight percentage of Ce content in the composition was varied as 2%, 4%, 6% and 8% and named as 2CT, 4CT, 6CT and 8CT, respectively.

2.3. Characterization

The powder x-ray diffraction (XRD) patterns of the prepared CeO₂–TiO₂ nanocomposites were obtained from PANalytical XPERT PRO x-ray diffractometer using Cu Kα radiation with λ = 1.5405 Å. The Brunauer–Emmett–Teller (BET) surface area measurement and pore size analysis were carried out for samples previously outgassed at 150 °C, by N₂ sorption on a quantachrome autosorbe IQ instrument. UV–Vis diffuse reflectance spectra were measured in the wavelength range of 220–850 nm using UV–Vis diffuse reflectance spectrometer (Shimadzu UV-2700). The morphology and composition of the CeO₂–TiO₂ nanocomposites were examined using high resolution scanning electron microscope (FEI Quanta FEG 200HR-SEM) equipped with energy dispersive x-ray (EDAX)
analysis. Transmission electron microscopic (TEM) images were examined using TEM, JEOL/JEM 2100. Raman spectra were recorded using Bruker RFS27 FT-Raman spectrometer with an excitation wavelength of 1064 nm from Nd:YAG laser source. The Cary Eclipse EL08083851 fluorescence spectrophotometer was used to record the photoluminescence (PL) spectra with an excitation wavelength of 390 nm.

2.4. Adsorption studies

Congo red (CR) dye with 10 ppm concentration was prepared by adding 10 mg of CR in 1 l of double distilled water. 25 mg of CeO$_2$–TiO$_2$ nanocomposite was dispersed in 25 ml of congo red dye solution (10 mg l$^{-1}$) and allowed to adsorb CR in dark condition with continuous stirring. The decrease in dye concentration was analyzed for every 15 min using UV–Vis spectrophotometer (Techcomb UV 2301). To determine the dye concentration, the solution was separated from the adsorbent by centrifugation.

3. Results and discussion

3.1. X-ray diffraction analysis

Figure 1 shows the XRD patterns of annealed CeO$_2$–TiO$_2$ nanocomposites. The observed 2$\theta$ values at 25.25°, 37.75°, 47.97°, 53.87°, 55.07°, 62.81°, 68.72°, 70.30° and 75.04° are indexed to (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0) and (2 1 5) planes, respectively. All these peaks belong to anatase phase of TiO$_2$ which crystallized in the tetragonal (2 2 0) and (2 1 5) planes, respectively. All these peaks belong to anatase phase of TiO$_2$ which crystallized in the tetragonal structure and matches well with the standard JCPDS card no.84-1285. The diffraction peaks corresponding to CeO$_2$ are not present in the XRD pattern which clearly shows that Ce might have entered into the interstitial position of Ti. The ionic radius of Ce$^{4+}$ (0.97 Å) and Ce$^{3+}$ (1.14 Å) are much greater than Ti$^{4+}$ (0.64 Å) and hence the substitution of Ce$^{3+}$/Ti$^{4+}$ in the TiO$_2$ lattice is not viable. Moreover, when the Ce content is increased, the higher angle x-ray peaks slightly broadened, indicating lattice distortion. The average crystal size was calculated using Scherrer’s formula.

$$D = \frac{0.9\lambda}{\beta\cos \theta},$$  \hspace{1cm} (1)

where $D$ is the average crystallite size, $\lambda$ is the wavelength of incident radiation, $\beta$ is the full-width at half-maximum (FWHM) and $\theta$ is the Bragg angle.

The average crystal size for TiO$_2$, 2CT, 4CT, 6CT and 8CT are 18.60, 18.51, 14.22, 13.78 and 13.15 nm, respectively. This shows that the crystallite size decreases as the Ce content increases. It is inferred that the inclusion of higher concentration of Ce in the TiO$_2$ matrix yields lower crystallite size. The lattice constants and the cell volume were calculated using Unitcell software and the unit cell parameters are given in table 1. The cell volume values obtained indicate that there is no shrinkage or expansion of crystal lattice supporting the interstitial substitution of Ce in TiO$_2$ lattice. The cerium cation may be placed at the surface and grain boundaries of TiO$_2$ crystal lattice due to the mismatch of the ionic size [34].

The effect of the specific surface area and porosity of TiO$_2$ is very important in catalysis. Table 2 shows that the nanocomposites are having higher specific surface area than bare TiO$_2$. The 8% Ce:TiO$_2$ exhibit a higher pore volume (0.1427 cm$^3$ g$^{-1}$) and surface area (29.227 m$^2$ g$^{-1}$) which enhance the surface reaction of TiO$_2$ and lead to the high adsorptive capacity [35, 36].

3.2. UV–Vis diffuse reflectance spectrum study

Figure 2 shows the reflectance of all the nanocomposites recorded using diffuse reflectance spectrum (DRS) at room temperature. The optical band gap of CeO$_2$–TiO$_2$ nanocomposites is determined by Kubelka–Munk function [37, 38].

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where \( K \) and \( S \) are the absorbance and scattering co-efficients, respectively, \( R_{\infty} = \frac{R_{\text{sample}}}{R_{\text{standard}}} \) is the reflectance of the reference BaSO\(_4\) and \( R_{\text{sample}} \) is the reflectance of nanocomposites. The indirect band gap energy of the sample is calculated by extrapolating the linear portion of \([F(R_{\infty})h\nu]^{1/2}\) at \( F(R_{\infty}) = 0 \) and the obtained band gap values are 3.151(2), 3.077(3), 3.055(4), 3.032(4) and 2.968(1) eV for TiO\(_2\), 2CT, 4CT, 6CT and 8CT, respectively. Compared to TiO\(_2\), the absorption edge (reflectance dip) of CeO\(_2\)–TiO\(_2\) nanocomposites is red shifted to higher wavelength due to the incorporation of Ce content. With the increase in the concentration of Ce, the absorption edge is shifted towards longer wavelength. The bandgap energy also decreases with the increase in the concentration of Ce content. Cerium can store/release oxygen through the redox shift between Ce\(^{4+}\) and Ce\(^{3+}\) under oxidizing and reduction conditions respectively. On including cerium into TiO\(_2\), the 4f oxygen defect states are formed and create an impurity band below the minimum of the conduction band [39, 40]. This has caused the red shift of band edge and narrowing of bandgap. The oxygen vacancies in nanocomposite are considered to be major reasons for the observed enhancement of adsorption, which could play a role as electron acceptor in improving charge transport and shift the Fermi level of composite toward the conduction band. Such a shift of the Fermi level can facilitate the charge separation.

3.3. HR-SEM and EDAX analysis

The high resolution scanning electron microscopy (HR-SEM) images of TiO\(_2\) and CeO\(_2\)–TiO\(_2\) nanocomposites are shown in figure 3 give information about the microstructure. It reveals that all the nanoparticles are homogeneous, agglomerated and spherical in shape. The agglomeration may be the result of the preparation condition. Figure 3(a) shows that the pure TiO\(_2\) nanoparticles have the size between 18–21 nm. Figures 3(b)–(e) show that the CeO\(_2\)–TiO\(_2\) nanocomposites with different weight percentage (2, 4, 6 and 8\%) are also homogeneous and have agglomerated particles. However, the size of the nanoparticles is reduced when Ce enters into TiO\(_2\) matrix. The addition of cerium reduces the agglomeration and forms nearly uniform particles whose sizes ranges between 13–15 nm in CeO\(_2\)–TiO\(_2\) nanocomposites. Several voids are seen at the surface of nanocomposites which may be due to low temperature annealing and low atomic diffusion [41].

Figure 4 shows EDAX spectra of all the samples and it gives the information about the chemical composition. This confirms the presence of oxygen, titanium and cerium elements and also the absence of any impurities.

3.4. TEM analysis

Further information on microstructure of CeO\(_2\)–TiO\(_2\) nanocomposites is obtained from transmission electron microscopic images (TEM) and selected area electron diffraction (SAED) patterns depicted in figure 5. All the nanoparticles are nearly spherical in shape with moderate aggregation. The particle size of the nanocomposites sample is in the range of 13–18 nm. It clearly shows that the inclusion of cerium decreases the particle size of the CeO\(_2\)–TiO\(_2\) nanocomposites. Both the pure TiO\(_2\) nanoparticles and CeO\(_2\)–TiO\(_2\) nanocomposites have uniform and well crystalline nature.

The SAED patterns of anatase TiO\(_2\) nanoparticles show a set of rings instead of spots due to the smaller crystallite size. The interplanar spacing of the lattice was obtained from the radius of the circular ring. The observed interplanar spacing of 0.35 nm corresponds to the (1 0 1) facet of tetragonal TiO\(_2\). The lattice spacing calculated through SAED patterns of the selected area of the corresponding HR-TEM image indicates the presence of TiO\(_2\) anatase phase nanocomposites. The obtained results are good agreement with XRD studies and SEM morphology.

3.5. Raman spectral analysis

Raman spectra of TiO\(_2\), 2CT, 4CT, 6CT and 8CT are displayed in figure 6. The anatase phase of the nanocomposites is further confirmed by Raman spectroscopy. The Raman lines at 144 (\( E_g \)), 197 (\( E_g \)), 396 (\( B_{1g} \)), 514 (\( B_{1g} \)) and 639 (\( E_g \)) cm\(^{-1}\) are assigned to the anatase crystalline phase. The strongest peak at 144 cm\(^{-1}\) and the weaker one at 197 cm\(^{-1}\) are the \( E_g \) modes.
which are caused by symmetric stretching vibrations of oxygen atoms in O–Ti–O bond. \(B_{1g}\) and \(A_{1g}\) modes are due to symmetric and anti-symmetric bending vibrations of O–Ti–O bond in anatase phase of TiO\(_2\) [42, 43]. As the weight percentage of Ce increases, the intensity of all the peaks decreases and the high intense Raman peak (\(E_{g}\)) slightly shifted towards the higher wavenumber side and are 143.12, 144.13, 144.57, 144.58 and 144.68 cm\(^{-1}\) for TiO\(_2\), 2CT, 4CT, 6CT and 8CT, respectively. Due to the mismatch of ionic radius of Ce and Ti, the inclusion of Ce distorts the lattice structure of TiO\(_2\) by entering into interstitial site. When Ce\(^{3+}\) enters into the TiO\(_2\) matrix, it generates oxygen vacancies and in turn distorts the lattice. The oxygen vacancies could be produced by the electron transformation between Ce\(^{3+}\) and Ce\(^{4+}\), and the higher concentration of Ce\(^{3+}\) could form more oxygen vacancies. The generation of these oxygen vacancies shifted the Raman peak to the higher wavenumber side [44, 45]. The broadening and shifting of Raman active modes are due to the presence of oxygen vacancies (lattice defects) occurred by the displacement of oxide ions from their normal lattice. As the crystallite size decreases, the change in vibrational properties of nanocomposites occurs. Due to the size-induced radial pressure, volume contraction occurs within the nanocomposites. The decrease in the interatomic distances leads to an increase in the
Figure 5. TEM micrographs of TiO$_2$ ((a) and (b)), 4CT ((d) and (e)) and 8CT ((g) and (h)) with two different magnifications and SAED patterns of TiO$_2$ (c), 4CT (f) and 8CT (i) nanocomposites.

Figure 6. (a) Raman spectra of TiO$_2$, 2CT, 4CT, 6CT and 8CT nanocomposites, and (b) enlarged view of high intense peak in the Raman spectra.
3.6. Photoluminescence spectral study

Figure 7 shows the photoluminescence (PL) spectra of the prepared TiO$_2$ and Ce:TiO$_2$ nanocomposites. In general, PL spectra of anatase TiO$_2$ are attributed to three kinds of physical origins: self-trapped excitons, oxygen vacancies and surface states [48, 49]. According to the self-trapping theory of Toyozawa [50], two competing processes follow the excitation. One is localization process in which the excited state generates a local distortion and localized at the distorted site, thus lowering its energy equal to lattice relaxation energy. Second one is delocalization process in which the excited state lowers its energy by transferring from one site to a neighboring site. Then the energy level of the excitons is lowered by extrinsic or defect-assisted self-trapping. In the PL spectra, six emission peaks are noticed; among them the peak at 409 nm is strongest. The near band gap emission (NBE) occurs at 409 nm and the deep level emissions (DLE) are observed at 422, 447, 460, 485 and 531 nm. All the peaks are observed in the visible region 400–600 nm. The PL emissions in the visible region are due to the surface defects and oxygen vacancies. The violet emission at 422 nm, blue emission at 447 nm and 460 nm and blue-green emission at 485 nm are attributed to the band-edge free excitons and bound excitons. The blue emission arises due to the intrinsic defects resulting from non-stoichiometric TiO$_2$ or oxygen vacancy defects. The blue-green emission observed at 485 nm can be attributed to the charge transfer from Ti$^{3+}$ to oxygen anion in a (TiO$_6$)$^{8-}$ complex associated with oxygen vacancies at the surface, indicating that the band is originating from the intrinsic state rather than the surface state. The green emission at 531 nm is caused by the deep hole trap states created above the valance band of TiO$_2$. The green emission suggests that excitons in anatase are in the self-trapped state which is due to the strong electron–phonon coupling and small exciton band width of anatase. The exciton band width is narrower in anatase TiO$_2$ because of the coordination number of neighboring octahedra is smaller in anatase (=8). In anatase structure, each octahedron is in contact with 8 neighbors and Ti–Ti interionic distances are larger in anatase. The TiO$_6$ octahedra are distorted to lower symmetry in anatase which leads degeneracies and creates band splitting. In anatase TiO$_2$, the conduction band has mainly Ti 3d and the valence band has O 2p, the oxygen related defects can be expected to introduce electronic states above the valence band. Here, most of the surface states are oxygen vacancies or the Ti$^{4+}$ ions adjacent to oxygen vacancies. The bands are separated by a wide gap (3.2 eV), so that these materials absorb only UV radiation. The optical absorption corresponds to an O$^{2-} \rightarrow$ Ti$^{3+}$ charge transfer transition. The intensity variation in the PL emission is attributed to the formation of different defect states in between the band gap of nanocomposites [51–53].

3.7. Adsorption study

The dye removal efficiency of each sample was evaluated in terms of its ability to adsorb the congo red dye. The UV–Vis spectrum of adsorption for CR using Ce:TiO$_2$ nanocomposites measured at various interval of time is shown in figure 8. As the time increases the absorption peak ($\lambda_{\text{max}}$) intensity decreases. Two peaks are observed: one at 498 nm corresponds to the azo bond (–N=N–) while the other peak at 338 nm belongs to naphthalene ring present in the CR dye [4, 54]. The percentage of dye removal efficiency is calculated using

$$\text{Removal efficiency} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100,$$

where $C_0$ is the initial dye concentration and $C_t$ is the final concentration of the dye after time $t$ [55]. The removal of 80%, 94.99%, 96.67%, 97.98% and 99.65% of CR dye in 75 min is achieved for TiO$_2$, 2CT, 4CT, 6CT and 8CT, respectively. The 8% CeO$_2$–TiO$_2$ composite efficiently remove the dye and CR was totally decolorized within 75 min. It is to be noted that 95% of CR was removed in first 15 min itself using 8CT nanocomposites.
sites. The formation of Ce$_3^+$ some time, adsorption decreases due to saturation of active sites. The adsorbent has lots of free sites. After 15 min, the increase in adsorption is very rapid because the adsorbent is very active and have a very high affinity toward CR dye molecules.

The adsorption rate decreases when the dye molecules are saturated at the surface due to an increase in diffusion resistance. Adsorption is followed by desorption which regenerates the adsorbents. The aggregation of molecules on the surface continues until the rate of adsorption is equal to the rate of desorption. After this there occurs no accumulation [56–58]. The mechanism of adsorption is shown in figure 8 as inset. Adsorption of molecules can be represented as

$$A + B \rightarrow A \cdot B,$$

(4)

where A is the adsorbate, B is the adsorbent and A · B is the adsorbed compound. Adsorption increases with increase in contact time. Initially, within 15 min, the increase in adsorption is very rapid because the adsorbent has lots of free sites. After some time, adsorption decreases due to saturation of active sites. The formation of Ce$_3^+$ plays a main role in the adsorption process. The inclusion of Ce reduces the bandgap of the nanocomposites by forming localized impurity levels which increases the vacancies in the TiO$_2$ lattice and hence provides larger active sites. The charge difference between Ce$_3^+$ and Ti$^{4+}$ provides oxygen vacancies in the TiO$_2$ lattice [59].

3.72. Reusability. After adsorption treatment, the adsorbent was collected separately by centrifugation, dried and reused. The adsorbent exhibited 98, 97 and 96% removal efficiency in three successive cycles under dark condition. XRD taken for the collected adsorbents after three cycles of CR dye removal is shown in the figure 9. XRD patterns indicate that the intensity of the adsorbent varies slightly only after the adsorption treatment. These results clearly showed that the CeO$_2$-TiO$_2$ adsorbent remains effective and reusable for number of times.

### 3.7.3. Adsorption kinetics

The kinetics for the removal of congo red is studied using both the pseudo first and second order kinetic models. The pseudo first order equation is the simple kinetic analysis, which is suitable for lower concentrations of dye solution. The Langmuir Hinselwood equation is used to describe the rate of removal of dye in the presence of adsorbent as a function of time

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC},$$

(5)

where $r$ is the oxidation rate of congo red dye, $C$ is the concentration at time $t$, $k_1$ is the reaction rate constant and $K$ is the adsorption coefficient of the reactant. At lower concentrations of the dye, $KC$ is negligible ($KC \ll 1$) and the equation becomes first order

$$\ln \frac{C_0}{C} = k_1 t,$$

(6)

where $k_1$ is the apparent first order rate constant and $C_0$ is the initial concentration of the dye [60, 61].

The slope of the plot $\ln(C_0/C)$ versus $t$ has been tabulated in table 3 and it gives the apparent first order rate constant ($k_1$) and correlation coefficient ($R^2$). The experimental points are deviating from the linear fit and also the correlation coefficient is not nearly equal to 1, which indicates the poor fit. Hence, the Blanchard’s second order equation is tried to determine the kinetic parameters.

The pseudo second order kinetic equation is expressed as

$$q_t = \frac{k_2q_0^2}{1 + k_2q_0t},$$

(7)

where $q_t$ and $q_0$ are the amount of dye adsorbed at time $t$ and at equilibrium (mg g$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) is the pseudo second order rate constant. The linear form of the above equation is

$$\frac{t}{q_t} = \frac{k_2q_0^2}{q_e} + \frac{t}{q_e}.$$

(8)

The pseudo second order rate constants are determined experimentally by plotting $t/q_t$ against $t$. The plot of $t/q_t$ and $t$ gives a linear relationship and is shown in figure 10. The value of $q_e$ and $k_2$ are determined from the slope and intercept of the plot $t/q_t$ versus $t$, respectively [62, 63] and given

| Sample   | $k_1$         | $R^2$  |
|----------|---------------|--------|
| TiO$_2$  | 0.016(7)      | 0.7383 |
| 2CT      | 0.036(7)      | 0.9321 |
| 4CT      | 0.03(1)       | 0.8054 |
| 6CT      | 0.04(1)       | 0.7793 |
| 8CT      | 0.05(2)       | 0.8288 |

Table 3. Pseudo first order rate constant ($k_1$) and the corresponding correlation coefficient ($R^2$).
The amount of CR adsorbed per unit adsorbent at equilibrium firms that the adsorption obeys pseudo second order kinetics. The calculated maximum adsorption capacity \( q_e \) and the corresponding correlation coefficient \( R^2 \) with \( q_e \) are presented in Table 4. The observed correlation coefficient of \( R^2 \) confirms that the adsorption obeys pseudo second order kinetics. The amount of CR adsorbed per unit adsorbent at equilibrium (mg g\(^{-1}\)) is calculated using
\[
q_e = \frac{V(C_i - C_f)}{m},
\]

where \( C_i \) and \( C_f \) are initial and final concentrations of CR (mg l\(^{-1}\)), \( V \) is volume of the dye solution (ml), \( m \) is mass of adsorbent used (mg). The calculated maximum adsorption capacity \( q_e \) (mg g\(^{-1}\)) of sample TiO\(_2\), 2CT, 4CT, 6CT and 8CT is found to match well with experimentally determined values.

### 4. Conclusion

Ce coupled TiO\(_2\) nanocomposites were successfully obtained by sol-gel method. The change in weight percentage of Ce in TiO\(_2\) matrix brings out a change in crystallite size along with the bandgap. The decrease in the Raman intensity along with the peak shift in Ce coupled TiO\(_2\) confirms the generation of oxygen vacancies in these nanocomposites. The generation of oxygen vacancies is further confirmed by the peaks observed in the visible region of PL spectra. The presence of enriched oxygen vacancies could facilitate the formation active sites. The dye removal abilities of the nanocomposites were investigated using congo red as a model pollutant. It is found that the kinetics of dye adsorption fitted well with the pseudo second order model rather the first order. The adsorption studies showed that the maximum removal efficiency of 99.65% was achieved in 75 min for 8% Ce:TiO\(_2\) nanocomposites because of its high adsorption capacity, lower band gap, high surface area and high pore volume.

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