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Visible light driven photocatalytic degradation of organic pollutant: Cleaning the environment by novel $ZrCdPbO_4$

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Heterogeneous photocatalysis is found an effective technique for degradation of organic pollutants in wastewater breaking them into smaller fragment of molecules that can easily be biodegraded further. Present work comprises of photocatalytic degradation of Crystal Violet dye (CV) which is found more resistant and more stable and so generates toxicity in the environment. A novel quaternary metal oxide is synthesized for this purpose and is characterized by various analytical techniques. XRD is carried out to obtain the crystal structure, EDX is carried to know about the elements present in the material, XPS is carried to know the oxidation states of the elements, FE-SEM is done for getting the crystal arrangements and morphology of the material. Combined results of these analyses suggest the formula of prepared material to be $ZrCdPbO_4$. Further UV-Vis analysis is used to calculate the band gap which comes out to be 5eV. This material is then used as photocatalyst for degradation of CV in heterogeneous conditions. A kinetic study is carried and it is observed that the reaction follows pseudo first order rate law. Optical density is recorded and different factors are varied to obtain optimum conditions for maximum degradation.

Keywords: Crystal violet, Degradation, Kinetic study, Photocatalysis, Quaternary

Water is one of most important resource for living entity. In this present era, we are experiencing consequences of mess done with natural resources like water and are suffering with various diseases such as allergy, skin infection, damages in internal system of human body etc. Chemical based materials are used at huge level in scientific, agricultural, textile, paper, printing, and other industries and when not consumed, these are released in water polluting it. These pollutants require extra work to be done on them for their removal from natural resources. Photocatalyst is a material that does that extra work by absorbing photons of light of desired wavelength to start a reaction and helps by reducing activation energy. Oshida[1] stated that “A photocatalyst is a material which absorbs light to bring it to higher energy level and provides such energy to a reacting substance to make a chemical reaction occur”.

A good photocatalyst must possess the following properties:

- ✓ It should have proper band gap to absorb desired wavelength of light
- ✓ It should have greater surface area for proper absorption of light
- ✓ It should be capable in creating electron-hole pairs that participates in the reaction
- ✓ It should lower the thresh hold energy required for any reaction to occur.

Photocatalyst can be oxides, sulfides, nitrides, iodides or any other material. Most of the photocatalysts have transition metal ions with configuration varying from d^0 and d^{10}. Their conduction bands are usually composed of d and sp orbitals. The valence bands of metal oxysulfides are formed by 3p orbital of sulphur and 2p orbital of oxygen. Similarly valance bands of oxynitrides are formed of 2p orbitals of nitrogen and 2p orbitals of oxygen. 3d orbitals of Cu^+, 4d orbitals of Ag^+, 6s of Pb^{2+}can also form valence bands in some oxide and sulfide photocatalysts[2].

Different types of photocatalysts, nanocomposites, nanomaterials have been prepared by narrowing their band gap by mixing of other metal ion as well as doping processes. Some of them are $BiVO_4/FeVO_4$ heterojunction composite, AgBr-ZnO nanocomposite, ZnO material, bismuth titanate mixed oxide, nano-sized novel fluorite structure $Ga_2Zr_{2-x}W_xO_7$ etc[3-7]. These are effectively used for degradation purpose.

Some doped materials used for degradation are Mn doped and PVP capped ZnO nanoparticles, Iridium doped ZnO, 3D flower like F-doped titanium dioxide bronze (F-TiO_2(B)), F-doped titanium dioxide bronze fullerene (F-TiO_2(B)/fullerene), cobalt doped nano-titania photocatalytic system etc[8-11]. Vijay *et al.*[12] studied degradation of coloured pollutant Azure-B using barium yttrium tungsten oxide while Nihalani *et al.*[13] carried-out degradation of P-Rosaniline hydrochloride using barium tungstate as photocatalyst.

Crystal violet (CV), ($C_{25}N_3H_{30}Cl$, Tris(4-(dimethylamino) phenyl) methylium chloride) belongs to triarylmethane group of dyes and is also named as gentian violet. Mani and Bharagava[14] reported that crystal violet is used in biological staining, providing deep violet color to paints, printing and textile processing industries etc. CV is also used to prevent the fungal growth in poultry feed. Lennard[15] studied that crystal violet or Sudan black, can be used for the detection of the fatty components in latent fingermark deposits. Besides its many uses, CV is reported as a recalcitrant compound which stays in environment for a long period. It has toxic effects, acts as a mitotic poison, potent carcinogen and a potent clastogene which can promote tumor growth as examined in some fish species. Thus, it is considered as a biohazard. Hashimoto *et al.*[16] reported a case of chemical cystitis due to intravesical instillation of CV. Study carried out by John[17] reports the cases of two infants who had a severe mucosal reaction to local crystal violet.

Number of adsorbentsare used for removal of dye molecules from environment. Sagaun sawdust and coniferous pinus bark powder (CPBP) were used as adsorbents[18,19]. Bentonite–alginate composite was effectively used as a sorbent for dye removal and was synthesized by microwave rapid heating method[20]. Visible light photocatalytic degradation of crystal violet dye and electrochemical detection of ascorbic acid & glucose using $BaWO_4$ nanorods was also studied[21].

Present work comprises of a facile method of preparation of a novel and excellent quaternary photocatalyst $ZrCdPbO_4$ and it is further used for complete degradation of Crystal Violet. Kinetic study has been carried out and maximum degradation conditions are drawn by varying different factors like pH, dye concentration, amount of photocatalyst, intensity of light etc. Rate constant is calculated as well.

Experimental Section

Preparation of $ZrCdPbO_4$ photocatalyst

The photocatalyst $ZrCdPbO_4$ is synthesized by co-precipitation method. Nitrates of Zr, Cd and Pb were taken 2.49 g, 3.08 g and 3.31 g (0.1 mole/ Litre each) respectively and were dissolved in doubly distilled water. The solutions were stirred individually, mixed and then stirred for 2 h. The mixture was then filtered and to this, NaOH solution (5N) was added dropwise with continuous stirring. Off white Crystalline solid precipitate was obtained. The precipitate was allowed to settle for half an hour after a rigorous stirring of two hours, supernatant liquid was checked for further precipitation and was then filtered, washed with distilled water and dried in a microwave oven for 2 h at 90°C. Dried powder was grounded and calcined at 500°C for 5 h to obtain crystalline powder of $ZrCdPbO_4$. The yield was 71%.

Solution of Crystal Violet

Stock solution of Crystal Violet (CV- 1.0×10^{-3} M concentration) was prepared in doubly distilled water. It was used as stock solution and was diluted as required. The solution was then tested for photocatalytic activity and complete mineralization of the dye was observed.

Photocatalytic study

The desired concentration of CV solution was taken in a beaker and photocatalyst $ZrCdPbO_4$ was added to it. The *p*H of the solution was adjusted by adding pre-standardized HCl or NaOH solutions and measured by *p*H meter (Hena pen type *p*H meter). The solution was then exposed to a 200 watt tungsten lamp as the light source and the progress of photocatalytic reaction was monitored by recording the decrease in optical density with time at λ_{max} 576 nm by a visible spectrophotometer (CHINO). Water filter was used to avoid thermal side reactions. The intensity of light was measured by solarimeter (CEL 201). It was observed that optical density does not show any change in presence of sun light or in presence of photocatalyst individually. The solution showed decrease in its optical density and change in colour as well, when it was exposed to light in presence of photocatalyst. The experiment suggested that the reaction is photocatalytic degradation. Participation of $^{\bullet}OH$ free radicals in the reaction is identified by scavenger test. It was observed that addition of iso propyl alcohol (IPA), which is OH free radical scavenger, ceased the reaction completely.

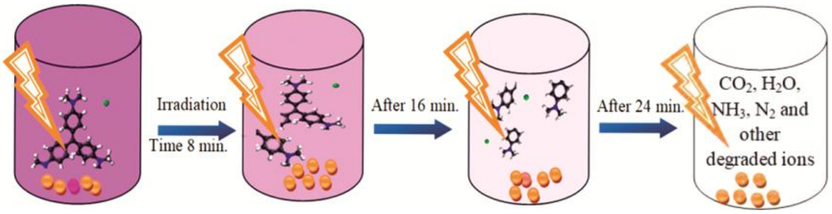

Fig. 1 ─ Photocatalytic degradation of Crystal Violet (Beakers containing CV solution and $ZrCdPbO_4$ exposed to light)

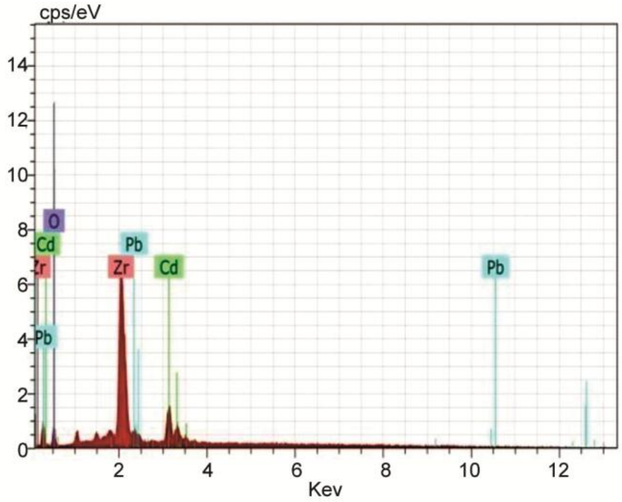

Fig. 2 ─ EDS analysis of $ZrCdPbO_4$

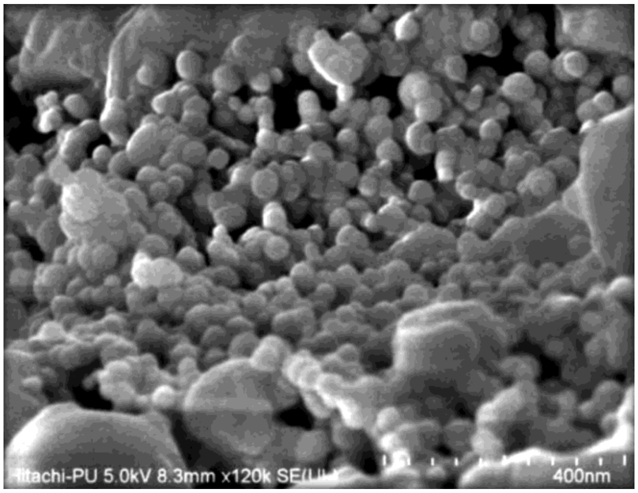

Fig. 3 ─ FESEM image of $ZrCdPbO_4$

These free radicals were found strong enough to break different bonds of dye (N=N, C=N, C-N, C=C, C-C etc) thus breaking the conjugation resulting into complete degradation of the pollutant. Figure 1 explains the setup and photocatalytic degradation of Crystal Violet at different time intervals.

Results and Discussion

Characterization

Characterization of the synthesized $ZrCdPbO_4$ photocatalyst was carried out by EDS, FESEM and UV-VIS spectral techniques. The morphology of the prepared nanoparticles was examined by field emission scanning electron microscope (FESEM) with an accelerating voltage of 5 kV equipped with Energy Dispersive X-ray Spectroscopic analyser (EDS model Hitachi PU8010 image analyser) and results are given in Fig. 2. The y-axis in the Fig. 2 denotes peak intensity (cps/eV) and x-axis denotes energy (KeV). Various peaks obtained in the figure clearly suggest the presence of Zr, Cd, Pb and O elements. The intensity ratio of these peaks suggests the formula of prepared material to be $ZrCdPbO_4$. Figure 3 shows FESEM image of prepared material. It is evident from the figure that the crystals of the prepared catalyst are arranged in homogeneous cluster form and in an organized manner. The grains are present in round shape. Figure 4 shows absorption spectra and graph is plotted between hν and $(\alpha h\nu)^2$. Band gap of $ZrCdPbO_4$ was determined by Tauc relation[22]:

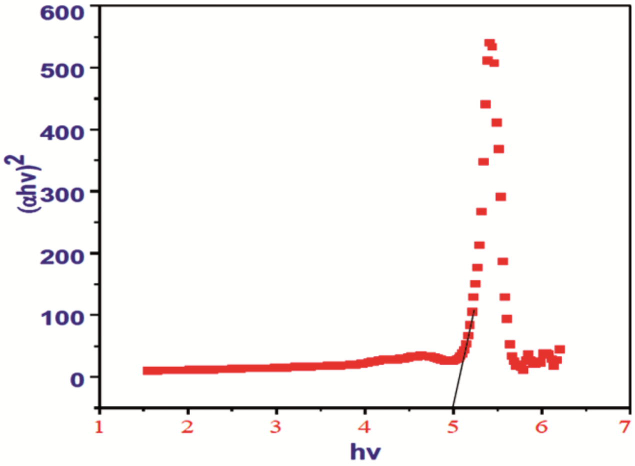

Fig. 4 ─ Band gap determination plot

$$\alpha h\nu = A\,(h\nu - E_g)^n$$

Where α is absorption coefficient, E_g is optical band gap, A is constant, hν photon energy and n=1/2 for direct transitions.

The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ gives the value of optical band gap of prepared

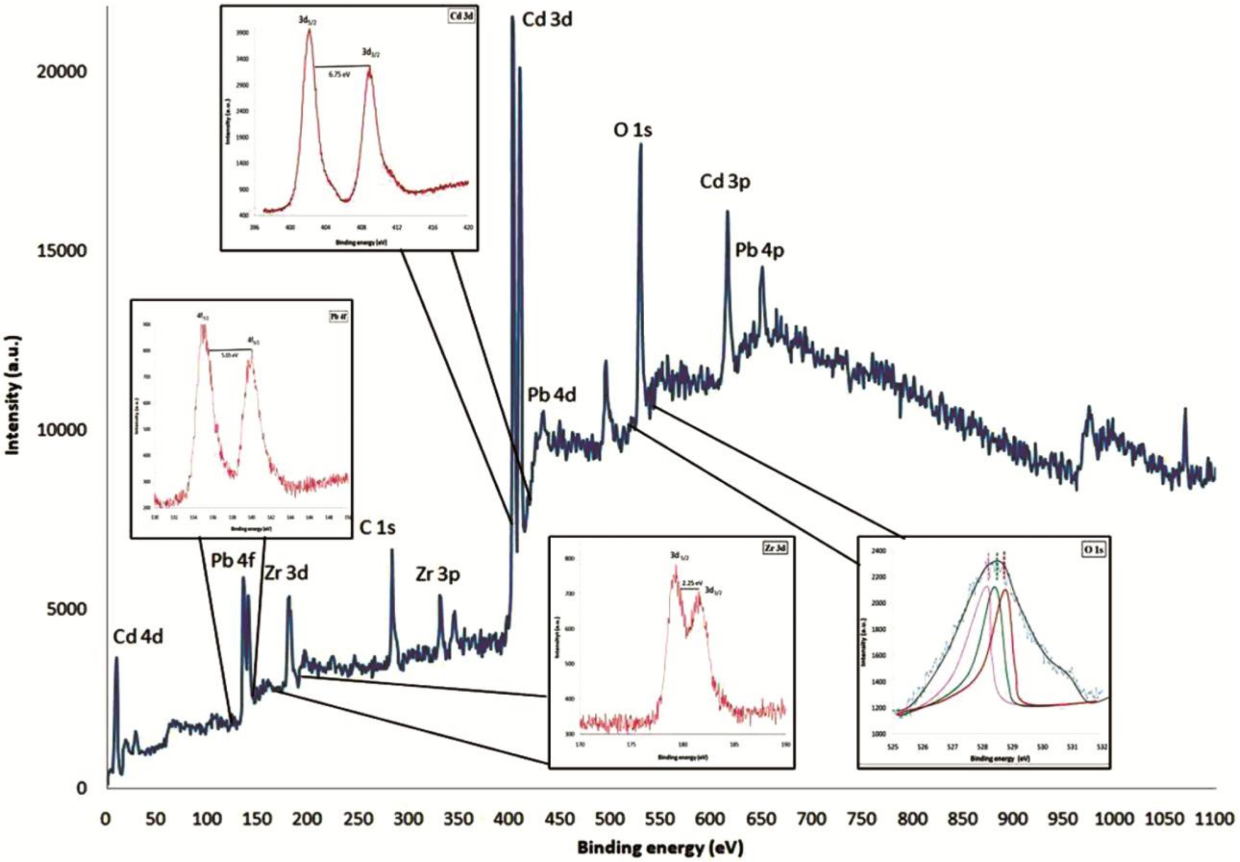

Fig. 5 — Full XPS spectrum of prepared material

Table 1 — Observation data of XPS spectrum for prepared material

Elements	Spin-orbit components	Observed binding energy (eV)
Zr	$3d_{5/2}$	179.30
	$3d_{3/2}$	181.55
Cd	$3d_{5/2}$	402.15
	$3d_{3/2}$	408.90
Pb	$4f_{7/2}$	135.05
	$4f_{5/2}$	140.10
O	1S	528.2-528.7

Table 2 — A typical run

pH =9.5, Amount of $ZrCdPbO_4$ = 0.18 g, [CV] = 4.8×10^{-4} M, Light intensity = 74.0 mW/cm^2
K = 1.08×10^{-3} (s^{-1})

Time (min.)	Optical Density	1+log O.D.
0	0.796	0.9009
4	0.659	0.8188
8	0.505	0.7032
12	0.408	0.6106
16	0.312	0.4941
20	0.236	0.3729
24	0.183	0.2624
28	0.140	0.1461
32	0.112	0.0492

photocatalyst. Band gap energy calculated with the help of above equation, comes out to be 5 eV.

X-ray Photoelectron Spectroscopy (XPS) is employed for the estimation of electronic and chemical states of prepared material. The analysis is carried out on an instrument model SOFH PHI versa probe III. A monochromatic X-ray source Al Kα (1486.6 eV) is used. The result shown in Fig. 5 represents the full XPS spectrum of prepared material and confirms the presence of relevant elements. The peaks observed for Cd3p, Cd3d, Cd4d, Pb4p, Pb4d, Pb4f, Zr3p, Zr3d, C1s and O1s reveal the presence of Zr, Cd, Pb and O. Observed data are summarized in Table 1 showing relative core level splitting and their binding energy. The analysis data favors the presence of Zr^{4+}, Cd^{2+}, Pb^{2+} cations and oxygen anions O^{2-} bonded to metal cations.

A typical run

A graph for typical run in between time and 1+log O.D. was plotted (Table 2). A straight-line plot suggests the reaction to follow pseudo first order kinetics. Different rate affecting operational parameters were varied to obtain the optimum conditions for maximum degradation. The rate constant was found to be 1.08 × 10^{-3}(s^{-1}), at values *p*H=9.5, amount of catalyst=0.18 g, concentration of Crystal Violet= 4.8×10^{-4} M and light intensity = 74.0 mW/cm^2.

Effect of *p*H

*p*H of the solution is major factor affecting the degradation. Thus it was considered as a factor and was varied from 5.5 to 10.5 by intervals of 0.5, in acidic as well as basic medium and all other factors were kept constant. Results are given in Figure 6a and Table 3. It was observed that rate of photocatalytic degradation increases with increase in *p*H (up to 9.5) which is attributed to the fact that addition of NaOH adds more number of OH^- ions to the solution. These are converted to OH. Holes generated at photocatalyst surface abstract electrons from these ions producing OH free radicals that are the responsible species causing degradation. After *p*H 9.5, repulsion becomes more effective amongst OH^- ions and electrons on semiconductor surface. This repulsion causes the recombination of electrons and holes, which were generated by light irradiation, besides abstracting electrons from OH^- species. Thus, a decrease in the rate is observed.

Effect of amount of photocatalyst

The amount of photocatalyst $ZrCdPbO_4$ was varied with keeping all other factors constant and the results are summarized in Fig. 6b and Table 4. The increase in rate of degradation with increase in amount of photocatalyst is due to the fact that more surface area of the photocatalyst is available for exposure to light which generates more hole-electron pairs. After attaining maximum value (at 0.18 g of $ZrCdPbO_4$), rate of reaction decreases because of formation of multilayers of catalyst in the solution. This promotes the recombination of electrons and holes at the surface of photocatalyst. Thus rate of degradation reduces.

Effect of concentration of Crystal Violet

The effect of concentration of CV on degradation was studied, that is represented in Figure 6c and data are given in Table 5. All other factors were kept constant. It is evident from the observations that with increase in concentration of CV, rate of reaction increased (up to 4.8 × 10^{-4} M) because more dye molecules are available for excitation and so for degradation when exposed to light. Further increase in concentration of the dye decreases the rate of degradation because dye molecules themselves now start acting as a filter to the incident light. Thus, the incident light is not able to reach the photocatalyst surface, as a result the rate of reaction decreases.

Effect of Intensity of Light

The intensity of light was varied and its effect on degradation was studied. All other factors were kept constant and the data are given in figure 6d and Table 6. It is observed that rate of photocatalytic degradation increases with increase in intensity of light as number of photons striking per unit area per unit time increases. Rate of photodegradation was observed maximum at light intensity 74.0 mW/cm^2 for Crystal Violet. Higher light intensities were found to cause thermal side reactions and so were avoided.

Table 3 — Effect of *p*H

$ZrCdPbO_4$= 0.18 g, [CV] = 4.8×10^{-4} M, Light intensity = 74.0 mW/cm^2

pH	$k\times10^3$ (s^{-1})
5.5	0.156
6.0	0.336
6.5	0.344
7.0	0.373
7.5	0.450
8.0	0.450
8.5	0.804
9.0	0.847
9.5	1.087
10.0	1.044
10.5	0.960

Table 4 — Effect of amount of $ZrCdPbO_4$

*p*H =9.5, [CV] = 4.8×10^{-4} M, Light intensity = 74.0 mW/cm^2

Amount of $ZrCdPbO_4$ (g)	$k\times10^3$ (s^{-1})
0.06	0.222
0.08	0.261
0.10	0.607
0.12	0.667
0.14	0.614
0.16	0.886
0.18	1.087
0.20	0.921
0.22	0.900

Table 5 — Effect of concentration of Crystal Violet

*p*H =9.5, $ZrCdPbO_4$ = 0.18 g, Light intensity = 74.0 mW/cm^2

[CV] × 10^{-4}M	$k\times10^3$ (s^{-1})
4.2	0.430
4.4	0.632
4.6	0.737
4.8	1.087
5.0	0.725
5.2	0.687
5.4	0.615
5.6	0.560

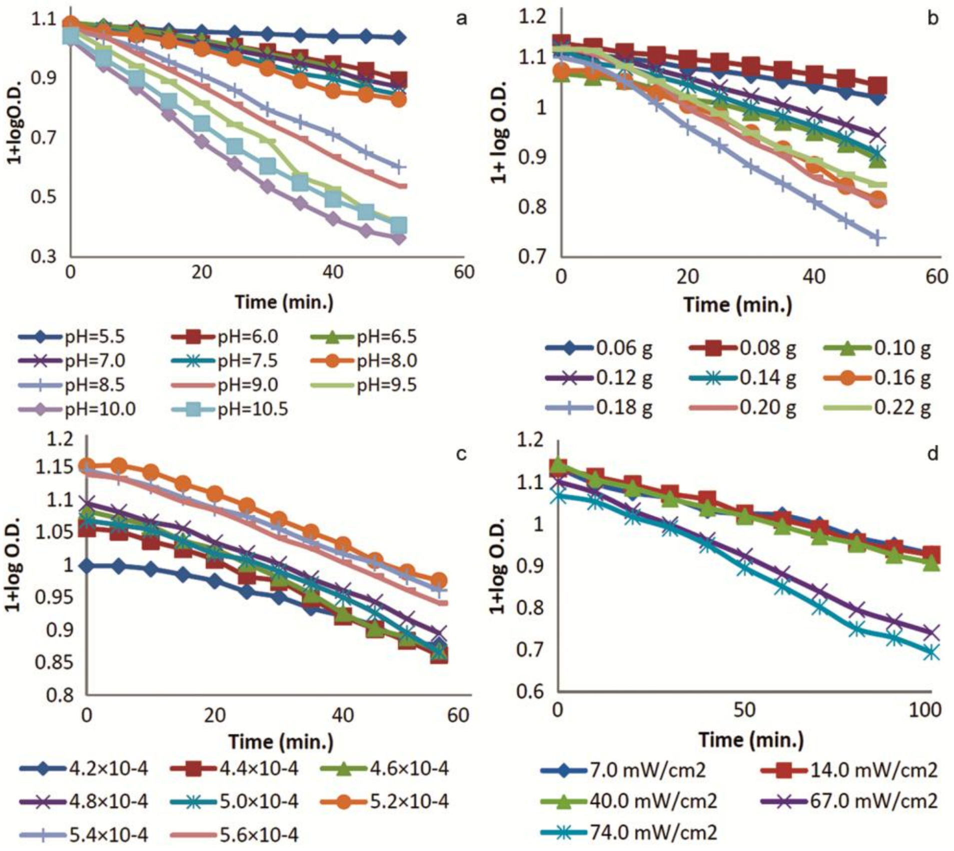

Fig. 6 ─ (a) Effect of *p*H; (b) Effect of amount of photocatalyst; (c) Effect of concentration of CV (in moles/Litre) and (d) Effect of light intensity

Table 6 ─ Effect of light intensity

*p*H =9.5, $ZrCdPbO_4$ = 0.18 g, [CV] = 4.8×10^{-4} M

Light intensity (mW/cm^2)	$k\times10^3$ (s^{-1})
7.0	0.392
14.0	0.506
40.0	0.594
67.0	0.942
74.0	1.087

Mechanism

A tentative mechanism for photocatalytic degradation of Crystal Violet in presence of $ZrCdPbO_4$ photocatalyst and light is proposed and is given in Figure 7. Initially the dye molecules in presence of light get excited from ground state to singlet state.

$$CV^0 \xrightarrow{h\nu} CV^1 \text{ (Singlet excited state)} \quad \text{... (1)}$$

(Here hν is photon from light)

In next step these dye molecules from singlet state get converted to triplet state by releasing energy through inter system crossing.

$$CV^1 \xrightarrow{ISC} CV^3 \text{ (Triplet excited state)} \quad \text{… (2)}$$

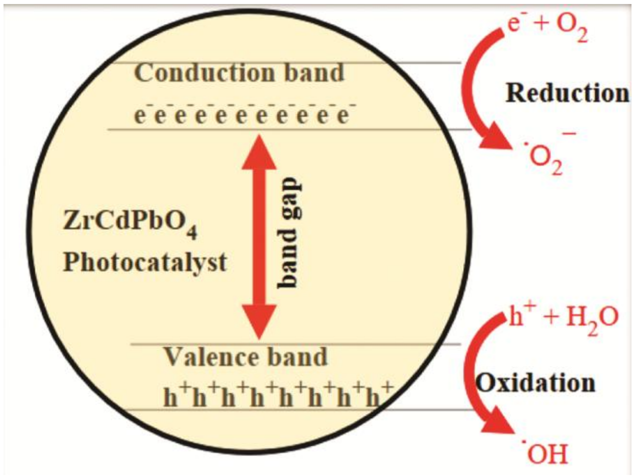

Fig. 7 ─ $ZrCdPbO_4$ photocatalytic system

(Here ISC is inter system crossing)

On the other hand, electrons present at the valence band of the photocatalyst surface get excited to the conduction band by absorbing light radiations. This phenomenon leaves behind hole at the valence band. These holes cause oxidation and electrons cause reduction of the pollutant.

$$ZrCdPbO_4 + h\nu \rightarrow [e^-(CB) + h^+(VB)] \qquad \ldots (3)$$

These holes abstract electrons from base or OH^- ions generating OH free radicals.

$$h^+ (VB) + OH^- \rightarrow {}^{\bullet}OH \text{ (oxidation)} \qquad \ldots (4)$$

In next step, these free radicals attack the weaker conjugated site of the dye molecules, breaking it and a reaction is initiated.

$$^{\bullet}OH + {}^3CV_1 \rightarrow \text{Leuco CV} \qquad \ldots (5)$$

This causes break down of the dye molecules into smaller fragments like CO_2, H_2O etc.

$$\text{Leuco CV} \rightarrow \text{Oxidized Products} \qquad \ldots (6)$$

The participation of $^{\bullet}OH$ radicals as active oxidizing species was confirmed by using hydroxyl radical scavengers (2-propanol), addition of which reduced the degradation rate drastically.

Conclusion

A novel photocatalyst $ZrCdPbO_4$ is synthesized and characterized by EDS, FESEM etc techniques. This is further used for removal of organic, carcinogenic pollutant Crystal Violet dye in a heterogeneous manner. The dye is degraded completely in presence of $ZrCdPbO_4$ and solar light. Factors are varied and maximum degradation conditions are extracted. Participation of OH free radicals in oxidation of the dye is confirmed by scavenger study as addition of scavenger ceases the reaction completely. The process if found environment friendly as:

- ✓ It uses solar energy as the driving force
- ✓ No harmful chemical is added to the environment while the process as it is heterogeneous in nature
- ✓ It removes pollutant from water making water chemical free, that is the need of the hour
- ✓ A small amount of photocatalyst can be reused for the same purpose, several times and so is economic too

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