PHOTOCATALYTIC DEGRADATION OF BISMARK BROWN-R USING BARIUM CHROMATE AS PHOTOCATALYST

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Abstract: The photocatalytic degradation of bismark brown–R dye has been carried out in the presence of semiconductor barium chromate powder as a photocatalyst. The photocatalyst was prepared by precipitation method and further characterized by different techniques like XRD, SEM-EDS and FT-IR. Barium chromate absorbs major portion of visible light due to its yellow color and acts as an efficient photocatalyst. The progress of the reaction was monitored spectrophotometrically. The effects of various operating variables like pH, concentration of dye, amount of semiconductor and light intensity were studied. A tentative mechanism for the photocatalytic degradation of dye has been proposed.

Keywords: Photocatalytic degradation, Semiconductor, Bismark brown-R.

1. INTRODUCTION

The entire world has so many environmental problems at present. Water pollution is one of them, which is caused in different manners. Dye effluents from different textile, dyeing, printing and chemical industries are one type of pollutant as they are discharged by different industries into near-by water system without proper treatment. Dyes are very useful, but toxic and carcinogenic in nature. Hence, there is a pressing demand to search for alternate methods to remove effluents from wastewater, which are eco-friendly in nature. Photochemistry is considered as a promising technology for wastewater treatment.

Sacco et al.[1] used N-doped TiO_2 photocatalyst for photocatalytic degradation of organic dyes under visible light. Composite nanofibers system containing cellulose acetate, multiwall carbon nanotubes and TiO_2 nanoparticles was prepared by Salama et al.[2] and photocatalytic activity of as-prepared semiconductor was studied on degradation of organic dyes such as methylene blue and idigo carmine. Chen et al.[3] synthesized Zinc oxide photocatalyst by sol-gel method using Zinc acetate and used the synthesized photocatalyst for the degradation of azo dye such as methyl orange. Reddy[4] prepared Ag-TiO_2 nanomaterials and observed the photocatalytic efficiency of as-prepared materials on photocatalytic degradation of organic dyes where as photocatalytic degradation of textile dye procion yellow was investigated by Ram et al.[5] using TiO_2 nanocatalyst.

Pamecha et al.[6] used semiconductor $CeFeO_3$ as photocatalyst for the degradation of commercial azo dye Ractive blue 160. Photodegradation of rhodamine B (RB) was investigated by Byrappa et al.[7] using hydrothermally prepared ZnO where as Houas et al.[8] used TiO_2/UV-based photocatalyst to study the photocatalytic degradation pathway of methylene blue in aqueous solution. Girija et al.[9] prepared photocatalyst β-Ga_2O_3 using surfactant assisted hydrothermal process and observed the photocatalytic efficiency of as- prepared photocatalyst on photodegradation of organic pollutants while photocatalytic degradation of phenol was investigated by Tiyawarakul et al.[10] using mesoporous-assembled $SrTi_xZn_{1-x}O_3$ nanostructure photocatalysts.

Hernandez et al.[11] synthesized $Ba_3Li_2Ti_8O_{20}$ samples through sol-gel method and used for photocatalytic degradation of 2,4–dinitroaniline whereas Borja-Urby et al.[12] prepared nanocrystals of bismuth doped barium zirconate ($BaZrO_3$:Bi) using a facile hydrothermal method at $600°C$ and used for the degradation of methylene blue under UV and visible irradiation. $SrTiO_3$ composites of noble-metal like Ag, Pt and Au were synthesized by Subramanian et al.[13] and the photocatalytic property of $SrTiO_3$ composites was examined for the photodegradation of textile dye victoria blue while Eyasu et al.[14] reported the study of photocatalytic degradation of methyl orange dye using Cr-doped ZnS nanoparticles in presence of visible radiation.

Santhanalakshmi and Komalavalli[15] synthesized TiO_2 nano crystallites and photocatalytic efficiency of as-prepared nonoparticles was investigated on the photocatalytic degradation of four different dyes, that is, acid blue ffs, reactive yellow 1, acid green 3GM and methyl orange whereas Abdollahi et al.[16] investigated photocatalytic degradation of p-cresol by ZnO under UV irradiation. Ag_3PO_4 nanoparticles/TiO_2 nanobelts heterostructures were synthesized by Liu et al.[17] using co-precipitation method and photocatalytic activity of as-synthesized samples was examined on the degradation of methyl orange under UV irradiation while nanocrystalline $ZnTa_2O_6$ photocatalysts having different structures were synthesized by Ding et al.[18] through a simple and facile sol-gel method at a temperature range of 650-950°C and photocatalytic degradation of methyl orange was carried out using as-prepared sample. In the present study, barium chromate has been selected for photocatalytic degradation of bismark brown-R. It was found an excellent photocatalyst in the visible region due to its yellow colour.

2. EXPERIMENTAL

2.1 Reagents and Apparatus

K_2CrO_4, $BaCl_2$, bismark brown-R, NaOH and H_2SO_4 (Himedia) were used as received.

The molecular formula of bismark brown-R is $C_{21}H_{26}Cl_2N_8$ and its mol. wt. is 461.39 g mol^{-1}.
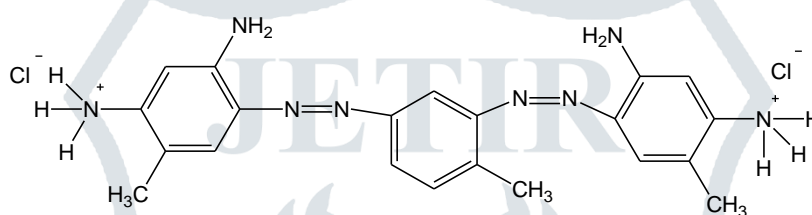
Figure 1: Chemical structure of bismark brown-R

2.2 Preparation of nano-sized barium chromate semiconductor

Barium chromate photocatalyst was prepared using K_2CrO_4 and $BaCl_2$ through precipitation method. 100 mL 5 % aqueous solution of $BaCl_2$ was mixed with 100 mL 5 % aqueous solution of K_2CrO_4 with constant stirring. The resulting precipitate of $BaCrO_4$ was allowed to settle down. The product was filtered, washed with double distilled water several times and dried at 60°C in oven.

2.3 Procedures

A 1.0×10^{-3} M solution of bismark brown-R was prepared as a stock solution in doubly distilled water, which was diluted further as and when required. The absorbance of bismark brown-R solution was determined with the help of a spectrophotometer (Systronics Model 106) at $\lambda_{max} = 445$ nm. In the present study, bismark brown-R dye has been selected as a model system to investigate the photocatalytic activity of barium chromate as a photocatalyst.

The dye solution was divided into four beakers and control experiments were carried out to confirm the use of barium chromate ($BaCrO_4$) as a photocatalyst. The first beaker containing bismark brown-R solution was kept in dark; the second beaker containing bismark brown-R solution was exposed to the light of a 200 W tungsten lamp; the third beaker containing bismark brown-R solution and 0.10 g $BaCrO_4$ was kept in dark, and the fourth beaker containing bismark brown-R solution and 0.10 g $BaCrO_4$ was exposed to light.

After keeping all these beakers for few hours, the absorbance of the solution in each beaker was measured with the help of a spectrophotometer. It was observed that the absorbance of solutions of first three beakers was remained almost constant, while there was a decrease in absorbance of solution of fourth beaker as compared to its initial value. From these observations, it becomes clear that this reaction requires presence of both light and the semiconductor $BaCrO_4$. Hence, this reaction is photocatalytic in nature.

2.4 Characterization

2.4.1 XRD

X-ray diffraction studies of the sample were conducted using PANalytical, Singapore make, XPERT-PRO model with Cu K_α radiation (λ = 1.54060 A°, 2Θ = 10 to 80° with generator setting 40 mA, 45 kV). Diffraction pattern was taken over the 2θ range 10º-70º. Fig. 2 shows the XRD pattern of synthesized nano-particles of $BaCrO_4$. It was observed that all the diffraction peaks were similar to that of orthorhombic phase of $BaCrO_4$ (JCPDS-15-376, lattice constants, a = 8.2026°, b = 8.2026°, c = 13.6302° A).

The particle size of the synthesized barium chromate was calculated using Sherrer formula (Eq. 1) and it was found as 14.71 nm.

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad \qquad \dots(1)$$

Where K is a constant, which depends on the shape of the crystal and its value is 0.9 assuming spherical shape; λ is the wavelength; D is the crystallite size; β is full width of half maxima (FWHM) value (calculated for the XRD pattern) and θ is Bragg's angle.
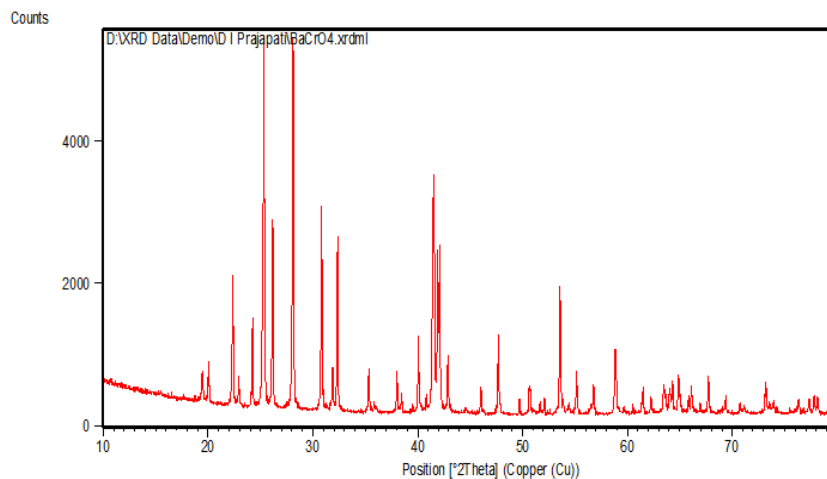

Figure 2: XRD of barium chromate semiconductor

2.4.2 SEM-EDS analysis

Scanning electron microscopy studies of the sample were conducted using JEOL, Japan make, 5610LV model. It was operated at 15 kV. SEM-EDS of barium chromate is given in Fig. 3.
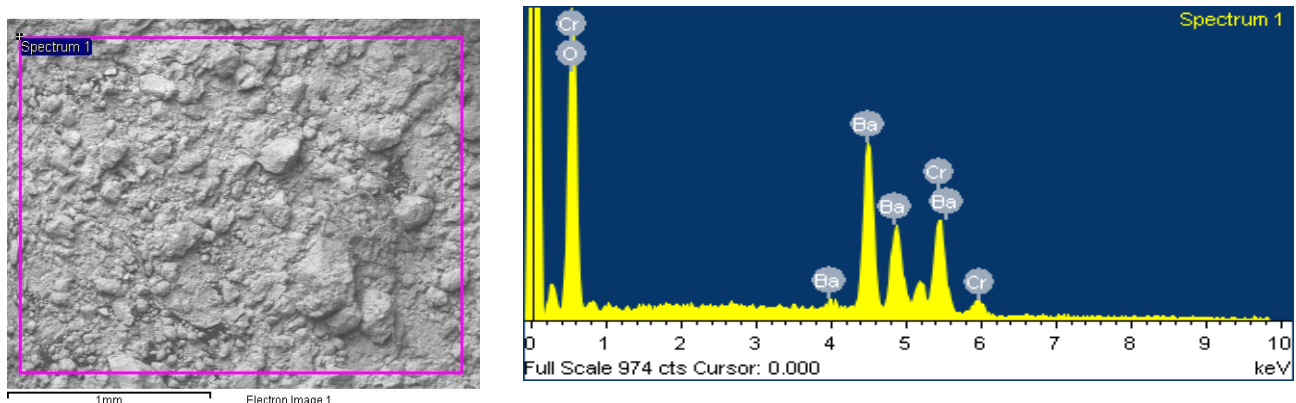

Figure 3: SEM-EDS of barium chromate

SEM of the synthesized semiconductor indicates that particles are unevenly distributed in size and EDS gives clearly that the catalyst contains only barium, chromium and oxygen only and it does not have any impurity.

2.4.3 FT-IR

Fourier transform-infrared (FT-IR) spectroscopy of the sample was carried out on a Shimadzu, IR Affinity, using KBr disk method and it shown in Fig. 4.
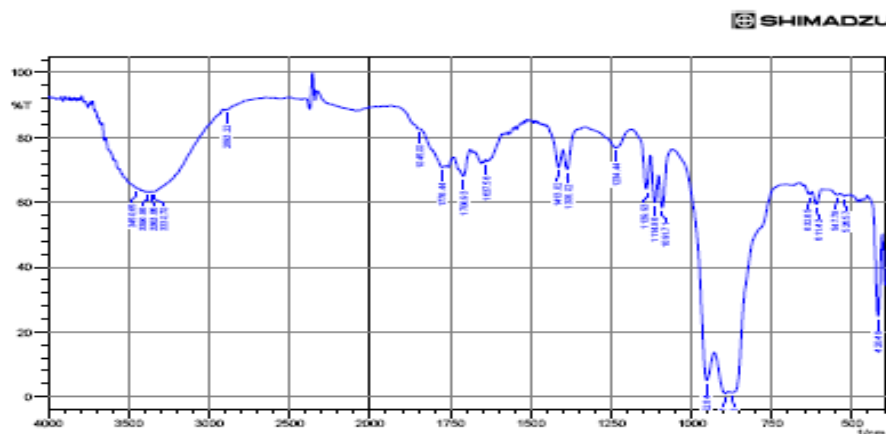

Figure 4: FT-IR of barium chromate

FT-IR spectra of $BaCrO_4$ nano-particles shows the characteristic absorption bands of chromate group located at 875, 894 and 952 cm^{-1}.

3. RESULTS AND DISCUSSION

A solution of 2.40×10^{-4} M of bismark brown-R was prepared in doubly distilled water and 0.08 g of $BaCrO_4$ was added to it. The pH of the reaction mixture was adjusted to 6.5 with the help of previously standardized sodium hydroxide and sulphuric acid solutions. Then the solution was exposed to the light of a 200 W tungsten lamp at light intensity 80.0 $mWcm^{-2}$. An aliquot of 2.0 mL was taken out from the reaction mixture and its absorbance was observed at 445 nm at regular time intervals. A decrease in absorbance of bismark brown-R solution was observed with increasing time of exposure. The typical run for the photocatalytic degradation of bismark brown-R in presence of barium chromate semiconductor has been presented in Table 1 and graphically represented in Fig. 5.

Table 1: A typical run

pH = 6.5, [Bismark brown-R] = 2.40×10^{-4} M, $BaCrO_4$ = 0.08 g, Light intensity = 80.0 $mWcm^{-2}$		
Time (min.)	Absorbance (A)	1 + log A
0.0	0.73	0.8633
5.0	0.66	0.8195
10.0	0.58	0.7634
15.0	0.50	0.6990
20.0	0.44	0.6435
25.0	0.39	0.5911
30.0	0.34	0.5315
35.0	0.30	0.4771
40.0	0.26	0.4150

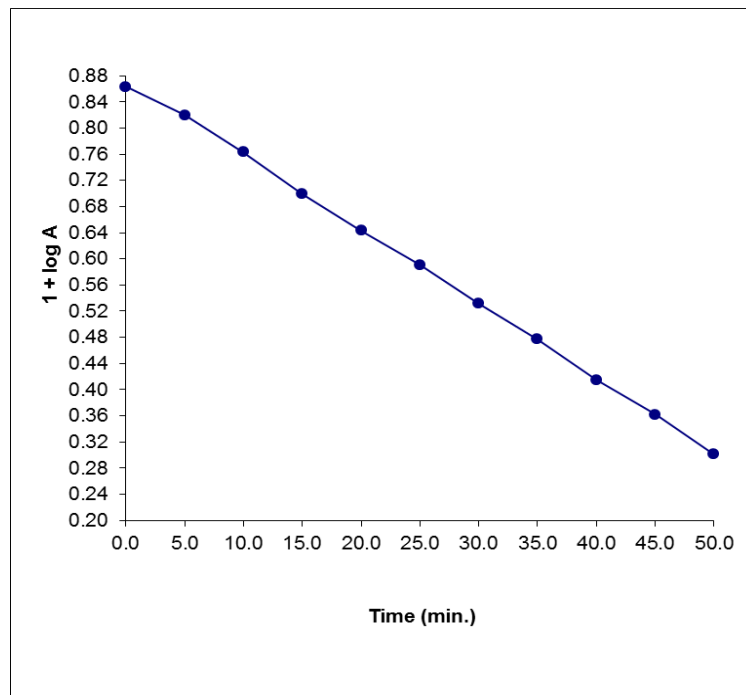| 45.0	0.23	0.3617
50.0	0.20	0.3010
		Rate constant (k) = 4.37×10^{-4} sec^{-1}

Figure 5: Typical run for degradation of bismark brown-R

The plot between 1 + log A and time was found to be linear. Hence, It has been concluded that the photocatalytic degradation of bismark brown-R follows pseudo-first order kinetics. The rate constant of this reaction was determined using the expression, (k = 2.303 × slope).

3.1 Effect of pH

The effect of pH on the rate of degradation of bismark brown-R was studied in the pH range 3.0-7.0, as degradation was found reasonably fast in this range. The results are reported in Table 2.

Table 2: Effect of pH

[Bismark brown-R] = 2.40×10^{-4} M, Light intensity = 80.0 mWcm^{-2}, BaCrO$_4$ = 0.08 g	
pH	**Rate constant (k) $\times 10^4$ (sec^{-1})**
3.0	0.22
3.5	0.25
4.0	0.28
4.5	0.46
5.0	0.72
5.5	1.56
6.0	3.43
6.5	**4.37**
7.0	2.97

It is evident from these data that the rate of photocatalytic degradation of bismark brown-R increases with increase in pH. The increase in the rate of photocatalytic degradation may be due to availability of more OH^- ions at higher pH values. OH^- ions will generate more $^{\bullet}OH$ radicals by combining with the holes (h^+) of semiconductor and these hydroxyl radicals are considered responsible for this photocatalytic degradation. But after a certain value of pH i.e. 6.5, a further increase in pH of the medium decreased the rate of photocatalytic degradation. It may be due to the fact that bismark brown-R does not remain in its cationic form due to greater concentration of OH^- ions and as such, the force of attraction between dye and negatively charged semiconductor surface decreases. As a result, the reaction rate decreases. It means that for efficient photocatalytic degradation of bismark brown-R, it should remain either in its neutral form or in partially cationic form.

3.2 Effect of bismark brown-R concentration

The effect of dye concentration on the rate of degradation was studied by taking different concentration of bismark brown-R. The results are reported in Table 3.

Table 3: Effect bismark brown-R concentration

pH = 6.5, $BaCrO_4$ = 0.08 g, Light intensity = 80.0 mWcm^{-2}	
[Bismark brown-R] $\times$ 10^4 M	Rate constant (k) $\times 10^4$ (sec^{-1})
2.10	3.43
2.20	3.68
2.30	4.02
2.40	**4.37**
2.50	3.35
2.60	2.70
2.70	2.34

It has been observed that there was an increase in rate of degradation on increasing the concentration of the bismark brown-R up to 2.40 x 10^{-4} M. It may be due to the fact that as the concentration of bismark brown-R was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate was observed. The rate of photocatalytic degradation was found to decrease with a further increase in the concentration of the dye. This may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles; thus, decreasing the rate of photocatalytic degradation of bismark brown-R.

3.3 Effect of amount of photocatalyst

The rate of degradation of dye was also affected by the amount of semiconductor and therefore, different amounts of semiconductor barium chromate were taken. The results are reported in Table 4.

Table 4: Effect of amount of photocatalyst

pH = 6.5, [Bismark Brown-R] = 2.4 $\times$ 10^{-4} M, Light intensity = 80.0 mWcm^{-2}	
$BaCrO_4$ (g)	Rate constant (k) $\times 10^4$ (sec^{-1})
0.02	2.34
0.04	2.68
0.06	3.42
0.08	**4.37**
0.10	4.35

| 0.12 | 4.35 |
| 0.14 | 4.37 |

It was observed that there was increase in the rate of photocatalytic degradation on increasing the amount of semiconductor up to 0.08 g, but after the amount 0.08 g of semiconductor, it becomes almost constant. This may be attributed to the fact that as the amount of semiconductor was increased, the exposed surface area of semiconductor also increased, but after a certain limit i.e. 0.08 g, if the amount of semiconductor was further increased, then there will be no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point; above which, any increase in the amount of semiconductor had negligible or no effect on the rate of photocatalytic degradation of dye, as any increase in the amount of semiconductor after this saturation point would only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifted to higher range for larger vessels, while reverse was true for smaller vessels.

3.4 Effect of light intensity

The effect of light intensity on the rate of photocatalytic degradation of bismark brown-R was also stidied. For this, the distance between the light source and the exposed surface area was varied. The intensity of light at each distance was measured using Suryamapi (CEL Model SM201). The results are reported in Table 5.
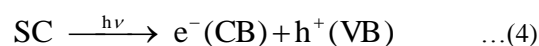
Table 5: Effect of light intensity

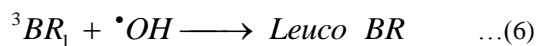| pH = 6.5, [Bismark Brown-R] = 2.4×10^{-4} M, BaCrO$_4$ = 0.08 g	
Light intensity (mWcm^{-2})	**Rate constant (k) $\times 10^4$ (sec^{-1})**
20.0	1.41
30.0	1.90
40.0	2.60
50.0	3.37
60.0	3.66
70.0	3.96
80.0	**4.37**

The results indicated that degradation of dye was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder.

Mechanism

On the basis of the experimental observations a tentative mechanism of photocatalytic degradation of bismark brown-R may be proposed as-

Bismark brown-R (BR) molecules absorb radiation of suitable wavelength and excited to its first singlet state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting barium chromate nanoparticles also utilizes the incident light energy to excite its electron from valence band to conducting band; thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to less harmful products.

$$^1BR_o \xrightarrow{h\nu} {}^1BR_1 \qquad\qquad \dots(2)$$

$$^1BR_1 \xrightarrow{ISC} {}^3BR_1 \qquad\qquad \dots(3)$$

$$SC \xrightarrow{h\nu} e^-(CB) + h^+(VB) \qquad \dots(4)$$

$$h^+ + OH^- \longrightarrow {}^\bullet OH \qquad\qquad \dots(5)$$

$$^3BR_1 + {}^\bullet OH \longrightarrow Leuco \; BR \qquad ...(6)$$

$$Leuco \; BR \longrightarrow Products \qquad ...(7)$$

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

Table 6: A comparative study for some physico-chemical parameters of aqueous solution of bismark brown-R (before and after treatment)

Parameters	Before treatment	After treatment
pH	4.55	6.62
Conductance (μS)	219.0	260.0
TDS (ppm)	122.0	145.0
DO (ppm)	5.58	6.42
COD (ppm)	52 .0	36.0
BOD (ppm)	14.0	8.0

pH of the dye solution was 4.55 before treatment and it was found almost neutral after photocatalytic degradation of the dye. TDS and conductance were also increased from 122 to 145 ppm and 219 to 260 μS, respectively in treated water. Dissolved oxygen (DO) analysis measures the amount of gaseous oxygen dissolved in an aqueous solution and in the present case it was increased from 5.58 to 6.42 ppm. Enhancement in pH, conductivity, TDS and DO confirms the mineralization of dye to a significant extent.

The value of chemical oxygen demand (COD) shows the oxidizability of a substance and it is expressed as the equivalent amount in oxygen of an oxidizing reagent consumed by the substance under fixed laboratory conditions. The chemical oxygen demand of reaction mixture before and after treatment has been determined by redox method. The photodegradation efficiency of the catalyst was calculated from the following expression:

$$\eta = \frac{COD_{before} - COD_{after}}{COD_{before}} \times 100$$

η = Photodegradation efficiency (%),

COD_{before} = COD of dye solution before illumination, and

COD_{after} = COD of dye solution after illumination

In the present case, COD was decreased from 52 to 36 ppm, which is a notable change. The photodegradation efficiency after 4 hours of illumination has been found to be 30.77%.

Biological Oxygen Demand (BOD) is a measure of the oxygen used by microorganisms to decompose waste. BOD of the dye solution before and after treatment was decreased from 14.0 to 8.0 ppm, which shows that photocatalytic treatment increases the biodegradability.

4. CONCLUSION

Nano-sized barium chromate photocatalyst was synthesized and characterized in the present work, which was used for the photocatalytic degradation of bismark brown-R. The results showed that dye was completely degraded using this photocatalyst and use of the photocatalyst can be explored for the degradation of different pollutants.

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