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PHOTOCATALYTIC DEGRADATION OF PHENOL RED BY ZnO-Co (II) TETRAAMINOPHTHALOCYANINE UNDER NATURAL SOLAR RADIATION

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ABSTRACT

In this study, Co (II) Tetraaminophthalocyanine (Co (II)TAPc) have been resynthesized and characterized by UV-Visible, FT-IR Spectrophotometer. The photocatalytic activity of the ZnO-Co (II) TAPc catalysts was evaluated for the degradation of the Phenol Red. The results revealed that UV-Visible absorption edge of ZnO-Co (II)TAPc is slightly moved towards the red shift. The photocatalytic activity of ZnO-Co (II) Tetraaminophthalocyanine was studied on Phenol Red and it was observed that ZnO-Co (II)TAPc was superior to that of ZnO. Besides the photocatalyst ZnO-Co (II) TAPc is stable and is reused for several times.

Keywords: Co (II) Tetraaminophthalocyanine, Photocatalyst, Degradation, Phenol Red.

1. INTRODUCTION

Water is essential for life on the planet. There are limited water resources in the universe and due to an increase in global population, water consumption increases. Growth of surface and groundwater pollution is a big issue in the world. An increasing number of pollutants come from industry. Pollutants i.e., toxic chemicals, bacteria, viruses enter into water resources, and even low concentration affect the human health and environment. Color dyes have been extensively used in textile industries and up to 15% is released to wastewater during their production and application [1-7]. Various methods have used to remediate contaminated water. Advanced oxidation processes (AOPs) have been effective methods for oxidizing these substances. but these are quite costly. Its cost can reduce by using renewable energy resources i.e., solar energy as the source for AOPS. Visible light photocatalysis used for the degradation of organic pollutants and elimination of pathogenic bacteria over semiconductors showed effective results towards environmental remediation using abundant solar energy. Semiconductors like TiO₂, Al₂O₃, SiO₂, ZnO etc. have large bandgap and absorb radiation in the U.V. region. To make it in the visible region, it is necessary to doped with photosensitizers. Photosensitizers have proven to be able, when electronically excited, to inject electrons in the conduction band of semiconductors [8-10].

Porphyrins, complexes, Metal phthalocyanines were used as photosensitizers in photocatalysis processes. Among these metal phthalocyanines (MPc), as typical organic semiconductors, have been extensively studied for this purpose [11]. In this study, ZnO sensitized with cobalt phthalocyanine is used for photocatalytic degradation of Phenol Red dye. ZnO is an n-type semiconductor possessing alternating arrangement of zinc and oxygen atoms in the crystalline planes. Due to the wide bandgap, this oxide possesses optical, electrical properties. Because of high quantum efficiency, Nontoxicity and low make cost this oxide more attention than other semiconductors. Metal phthalocyanines are synthetic color dye having structural similarity with natural pigments of life, like porphyrin such as chlorophyll and hemoglobin possessing a conjugated system of 18 pi-electrons. The presence of a pi-electron system is essential for charge-carrier transport, so MPcs exhibit several unique properties. Many studies proved that MPcs as a sensitizer to enhance the photocatalytic activity of the semiconductors [12-15].

In this work, Co (II) Tetraaminophthalocyanine (Co (II) TAPc) has been synthesized and ZnO was pasted on a strip of Whatman filter. Then these strips were dipped in solution of Co (II) TAPc for 24 hrs. And its photocatalytic activity was tested on phenol red under solar radiation.

2. MATERIAL AND METHODS

4-Nitrophthalimide was synthesized from phthalic anhydride as per literature [16]. Urea, Cobalt sulphate, ammonium molybdate. zinc oxide was used without further purification.

2.1. Synthesis of Cobalt Tetraaminophthalocyanine

Co (II) Tetraaminophthalocyanine has been resynthesized by following the scheme given below [17-19].

2.1.1. Synthesis of Cobalt Tetranitrophthalocyanine (CoTNPc)

A 0.05 mol Nitrophthalimide, 0.025 mol urea, 0.0125mol Cobalt sulphate and 0.00013 mol of ammonium molybdate were finely grounded and placed in a 250 ml beaker with a glass rod. The temperature

was maintained between 180-200°C for 1 h. The product formed was treated with HCl (1.0 M) and NaOH (1.0 M) respectively. After filtration, the product was washed to neutralization with water and dried in vacuum.

2.1.2. Synthesis of Co (II) Tetraaminophthalocyanine (Co (II) TAPc)

A 0.005 mol of finely ground cobalt (II) tetranitro phthalocyanine was transferred to 250ml beaker containing 100 ml water. To this 0.20 mol of Na_2S was added and stirred at 50°C for 5 Hr. The solid product was separated and purified using 1.0 M Hydrochloric acid and 1.0 M sodium hydroxide. Finally, the complex was washed with water until free from sodium hydroxide. The dark bluish-green product was dried in the oven.



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2.2. Instrumentation

Chemical structure was characterized with FTIR spectrophotometer, The UV-visible spectra were obtained using Shimadzu spectrophotometer in DMF for Pc.

2.3. Degradation of Phenol red by ZnO-Co (II) Tetraaminophthalocyanine photocatalyst

The photocatalytic experiments were carried out at room temperature. Strips were prepared by immersing strip of Whatman filter paper in the suspension of ZnO. The strips were dried by 60 min on a hot plate at 50°C. For CoTAPc/ZnO strip, the ZnO pasted strip was immersed in a solution of Co (II) TAPc (0.5g/100ml) for 24 Hrs. [19-20] after that, the sensitized strip was dried at 50°C by 60 mins. 20mL of Aqueous Phenol red solution (15 ppm) was used as a reaction solution. The concentration of dye was determined spectrophotometry at λ max = 560 nm by using the calibration curve and law of Beer. The content of the solution during irradiation was determined at intervals of illumination by spectrophotometry. We prepared five photocatalytic tests to study the effect of different experimental conditions to confirm the presence of a photocatalytic effect. Table 1 is listed the experimental conditions of tests; all measurements in each test were recorded three times to ensure the confidence of results.



Table 1: Experimental conditions to different photocatalytic tests

No of test	Test	Experimental Condition
1	Aqueous Phenol red/ O_2	Sunlight
2	Aqueous Phenol red/ H_2O_2/O_2	Sunlight, H_2O_2 (1ml of 30% H_2O_2), $O_{2(g)}$
3	Aqueous Phenol red/ ZnO/O_2	Sunlight, ZnO strip and $O_{2(g)}$
4	Aqueous Phenol red/ CoTAPc	Sunlight, CoTAPc and $O_{2(g)}$
5	Aqueous Phenol red/ CoTAPc -ZnO/O ₂	Sunlight, CoTAPc -ZnO strip and $O_{2(g)}$

3. RESULTS AND DISCUSSION

In this method conversion of phthalic anhydride to phthalimide was carried out by following scheme 1.4nitro phthalimide was prepared from the nitration of phthalimide by following scheme 1.4-nitro phthalimide was used to prepared Cobalt tetranitro phthalocyanine (CoTNPc). And then CoTNPc was converted to CoTAPc. The yield of CoTNPc was 82% and Åmax in DMF obtained at 690,640 and 280 nm respectively. The yield of CoTAPc was 88% and Åmax in DMF obtained at 775 nm and 350 nm respectively. The IR spectra of CoTAPc showed absorption peaks around 720-745, 830-889 and 1114-1135 cm⁻¹. which may be assigned to phthalocyanine skeletal vibrations. Two weak absorption peaks are observed at 3370 and 3230 cm⁻¹ in the IR spectrum of CoTAPc complex due to the asymmetric and symmetric stretching of the amino group.

3.1. Photocatalytic analysis

The solution was taken from the reaction mixture at a regular time span of 60 minutes and absorbance was measure at Amax = 560 nm. It was found that the value of absorbance decreased with increasing time, which shows that the concentration of Phenol Red decreased with increasing time of exposure to solar light. A plot of 2+log A vs. time was linear. In several studies, to characterize the effect of different experimental condition on the degradation rate, the assumption of the pseudo-first-order model was used.

The pseudo first-order model was applied to kinetic data and the rate constant of the photodegradation reaction, k, was determined using the following expression [20]:

 $k = 2.303 \times \text{slope}$

(1)The photocatalytic degradation did not show substantial degradation for test 1 and 2 when phenol red was exposed with solar light, these results are possible because they confirm that O_2 or H_2O_2 was not effective in the photocatalytic degradation under the given condition, these results are expected because H₂O₂ cannot absorb visible light. Whereas under the condition of test 3 and 4 considerable degradation take place, this result shows ZnO absorbs visible light with a small extent. Co-Phthalocyanine is paramagnetic with unpaired electrons and shows photocatalytic activity for dye degradation under the condition of test 4. When phenol red was exposed to visible radiation under the condition of test 5, the photodegradation of phenol red was increased. Test 1 and Test 2 have those are the lowest k values and, it confirms that these tests had not effective in the degradation of phenol red. The values of k for test 4 and test 5 had found to be considered as compared to test 1 and test 2. The value of k indicated that the sensitization of ZnO with metal phthalocyanine improved the photocatalytic properties of ZnO and useful result to future engineering design and applications [21].

Table 2 Kinetic and photocatalytic results of different tests

No. Test	k (min ⁻¹) x 10 ⁻⁴	% Degradation
1	0.069	1.54
2	0.11	2.38
3	43.75	64.58
4	59.80	75.24
5	78.34	83.51

3.2. Mechanism

On the basis above results and the studies on the dyesensitized photocatalytic oxidation of phenol red, a proposed mechanism for photodegradation with the ZnO-CoTAPc catalyst is illustrated below. The conduction and valence band of the electronic structure of ZnO are at - 4.5 and - 7.7 eV below vacuum level, respectively. CoTAPc when loaded into ZnO, it may act as a hole capturer, resulting in the effective transfer of the hole from the valence band of ZnO to the HOMO of CoTAPc. This mechanism can potentially delay the recombination of photogenerated electronhole pairs, leading to the effective interface charge separation. Hence, an unpaired electron of ZnO can react with the oxygen group, leads to the higher photocatalytic reaction rate due to the decrease in electron-hole pair recombination, thus improving the photocatalytic process [21].

$$ZnO + h\nu \rightarrow ZnO \ (e^{-} + h^{+})$$
 (2)

 $ZnO(e^{-}) + 1/2O_2 + H_2O \rightarrow OH + ZnO + OH^{-}$ (3)

$$ZnO (h+) + H_2O \rightarrow OH + ZnO + H^+$$
(4)

 $CoTAPc + ZnO (e^{-} + h^{+}) \rightarrow CoTAPc^{+} + ZnO (e^{-})$ (5) From the above process it is confirmed that the electrons and holes are separated effectively on the interface of ZnO and CuPc and finally, the following occurs:

 $CoTAPc^+ + e^- \rightarrow CoTAPc$ (6)

4. CONCLUSION

The rate of the photocatalytic process was enhanced by Metal phthalocyanine (MPc). The photocatalytic activity of ZnO was improved under visible light due to charge injection from the excited state of the dye into the conduction band of the ZnO. The ZnO sensitized with CoTAPc enhanced the photocatalytic degradation of phenol red compared to ZnO and CoTAPc. Hence it is a better option in photocatalytic degradation processes of harmful and toxic dyes and in water purification method.

5. ACKOWLEDGMENTS

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Conflict of interest

The authors declare that they have no conflict of interest.

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