A Novel Advanced Oxidation Process Using Palladium Based Catalyst and its Application to Waste Water Treatment

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Abstract: ***Due to the improper disposal system our environment is getting hazardous and toxic day by day because of Dyes and derivatives. This study focuses on the evaluation of a new process for the post treatment analysis waste water using selective Advance Oxidation Process (AOPs). So this AOPs method uses Immobilised Pd-CoO and Hydrogen peroxide etc., for the degradation of Methylene Blue which has been discussed and compared. Some guidelines for the future work required to facilitate the optimization of the processes have also been proposed.***

Keywords: Immobilised Pd-CoO, Bimetal Oxide, AOPs methods, methylene Blue, Waste-Water Treatment etc.

1. Introduction

Advanced oxidation processes (AOPs) are more efficient, cheap, and eco-friendly in the degradation of any kind of toxic pollutants. AOPs generate hydroxyl radical, a strong oxidant, which can completely degrade or mineralize the pollutants and can convert the toxic component into non-toxic one. The process includes degradation of dye by using a palladium based immobilised catalyst mainly transition metal oxides like cobalt oxide i.e. Pd-CoO and hydrogen peroxide addition. This AOPs technique for the degradation of dye is governed by parameter like pH, Time, Amount of catalyst and Hydrogen peroxide dosage. This technology can be used for industrial applications also.

2. Experimental

2.1 Synthesis of Pd-CoO

1.0gm of cobalt sulphate is mixed in 70ml dist. Water. Then in another beaker add 0.1gm of palladium acetate is mixed 30ml ethanol. Then both the solutions are mixed together and then 1gm pvp is add to the solution mixture then it is sonicated for 30 mins maintaining sonication parameter as ;

1. Pulse = 05on/02off
2. Probe temperature = 46c
3. Set point temperature = 70c
4. Amplitude = 30%
5. Timer = 30 mins.

After 30 mins of sonication the solution obtained is dried at 100c in hot air oven to get dry powder. And powder is then characterized under SEM and XRD for determining its size and morphology as shown by Fig. 1, Fig. 2, and Fig. 3 respectively.

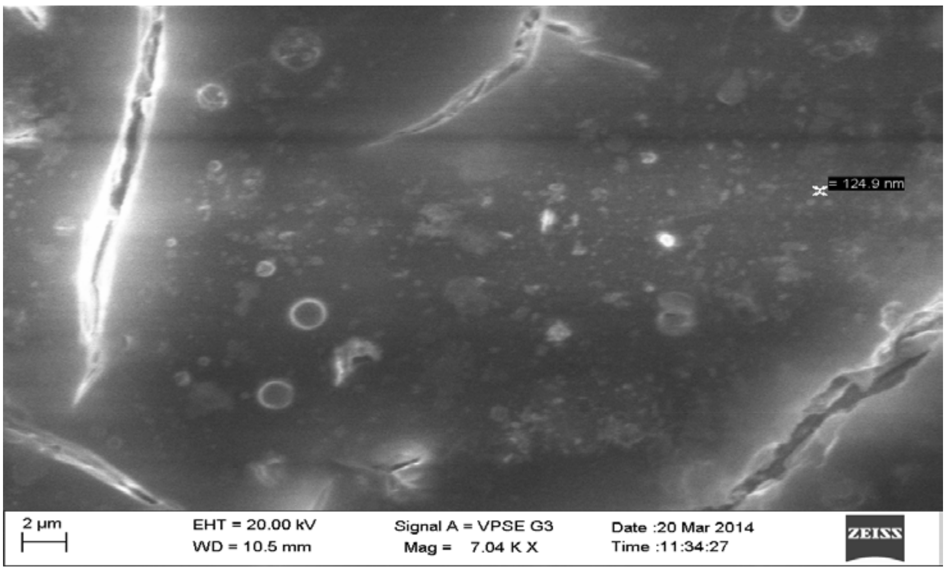


Figure 1: SEM image shows size of particle 124.9nm at 2µm

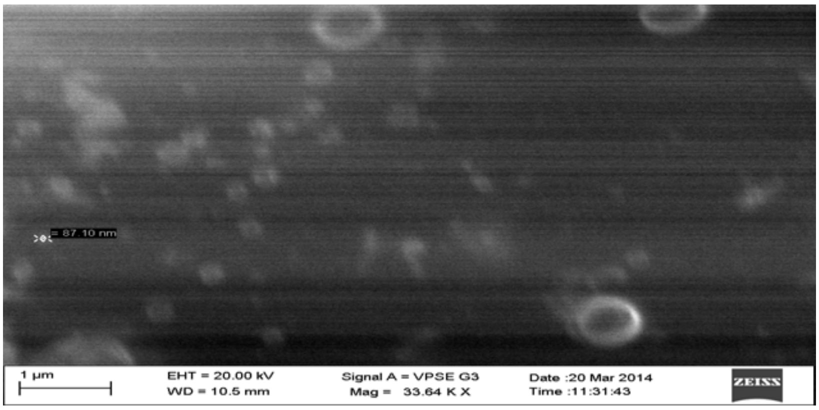


Figure 2: SEM image showing size of particle 87.10nm at 1µm

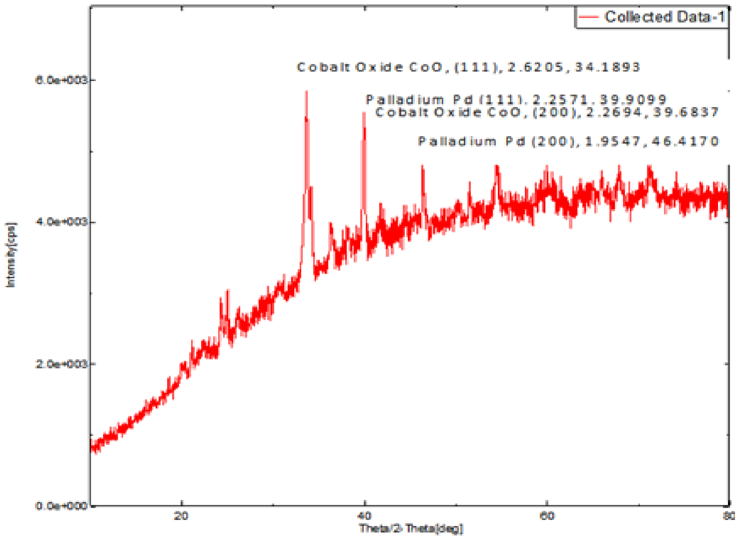


Figure 3: XRD image shows the presence of palladium and cobalt oxide at different peaks

2.2 Immobilisation Pd-CoO over Support

A thick layer of adhesive is spreaded over the ceramic filter. And then Pd-CoO slurry is spreaded over the layer of adhesive. Then it is kept for drying for 3-4 days, So that the catalyst will hold the surface firmly along with adhesive which is represented in Fig, 4.

Catalyst (Pd-CoO)
Adhesive
Substrate(Ceramic filter)

Figure 4: Immobilised Pd-CoO catalyst to support

3. Waste-Water Treatment

Most important concern over a decade is waste water because the handling and disposal of pollutant is not proper and hence it is polluting the water resources. There are several types of toxic pollutant present in the water resources which are mainly coming from the industries. Among these pollutants, Dye is one of the major pollutants. Textile industries are the major source of dye which when come in contact with water bodies under goes several chains of reactions and can form some non-degradable product which can affect the aquatic life. There are several methods have been applied to overcome this problem waste water treatment which includes biological treatment, chemical oxidation, electro-chemical decomposition, chemical coagulation and physic-chemical treatment. Now a day AOPs is playing very important role in the degradation of dye. So present work is to degrade the methylene blue dye by applying AOPs along with Pd-CoO catalyst and hydrogen peroxide. Methylene Blue dye is heterocyclic aromatic chemical compound having molecular formula $C_{16}H_{18}N_3SCl$. Its UV-visible absorption spectrum shows a characteristic, intense peak around 605nm in aqueous solution at low dye concentration.

4. Methodology

A certain volume of Methylene Blue is taken in beaker and the slab of immobilised catalyst Pd-CoO is dipped in that and certain amount H2O2 is add, and kept it for few hours. Definite volumes of resulting solution at fixed intervals of time are taken out and the samples are analysed for absorbance using UV-spectrophotometer and are compared with calibration chart prepared shown in fig. 5. Percentage Degradation is then calculated according to the following formula.

$$\% \text{ deg} = (Ai - Af) \times 100 / Ai$$

Where,
% deg = Percentage Degradation
Ai = Initial Absorbance
Af = Final Absorbance

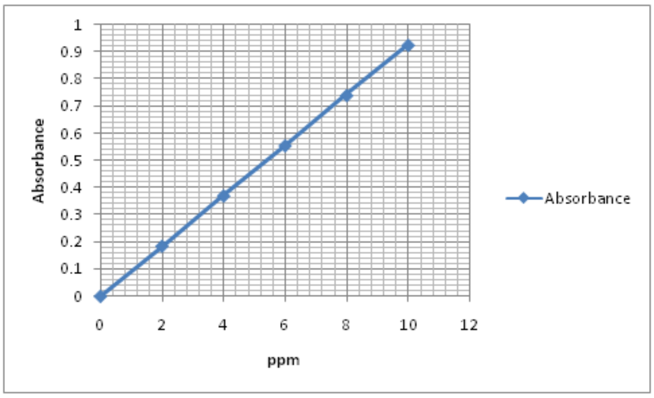


Figure 5: Calibration Chart for Methylene Blue

5. Experimental Explanation

Percentage degradation of Methylene alone by Hydrogen peroxide alone is around 5% and Percentage degradation of Methylene blue by Pd-CoO alone was around 12 %. But when both Pd-CoO and Hydrogen peroxide are combined together there were 100% degradation of dye. Since as we all know palladium is a very good hydrogenation catalyst and it can carry out oxidation reaction but at the same time palladium is one of the costly transition metal so tried to reduce the cost of palladium by reducing the amount of palladium with other transition metal cobalt. So when we add the Pd-CoO catalyst nothing start happening with the catalyst but as soon as we add the few ml of hydrogen peroxide reaction starts and some fumes start coming out which give the evidence there is some reaction happening and degradation of dye started . Then after a time period of 7-8 hrs we found that blue colour of the dye has gone and clear water is remaining as shown in Fig 6 and fig. 7 respectively.

Figure 6: before degradationFig.7 after degradation

6. Results

6.1 % Degradation of Methylene Blue dye

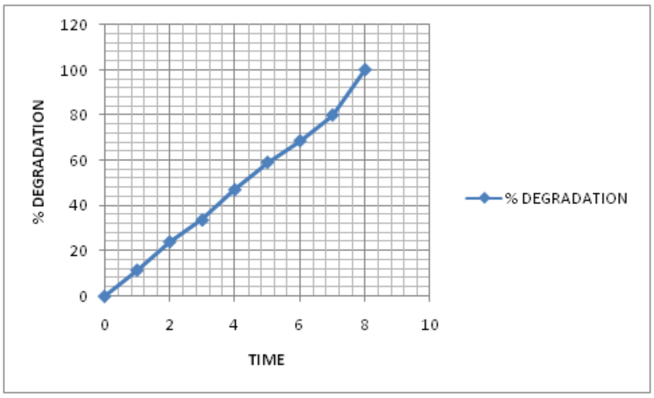
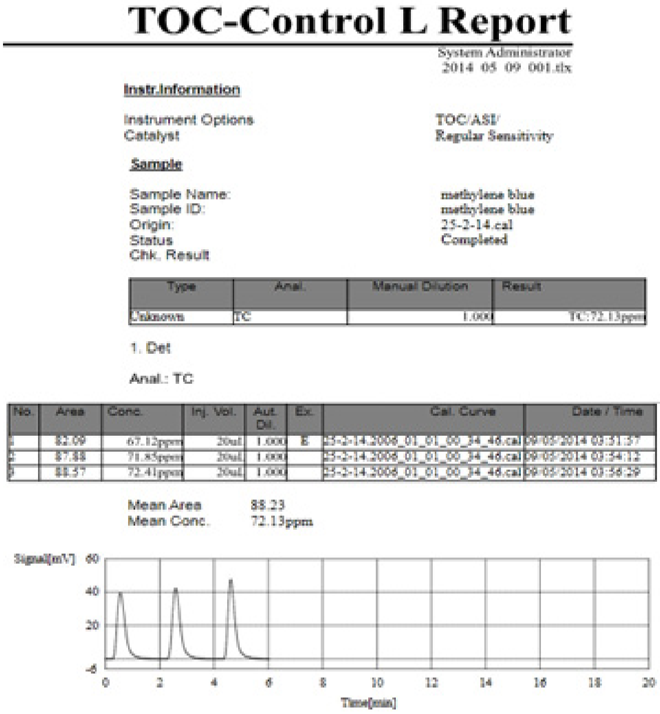


Figure 8: % degradation of methylene blue dye versus Time

6.2 TOC report Methylene blue dye degradation



TOC-Control L Report

System Administrator
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Instr.Information

Instrument Options TOC/ASI/
Catalyst Regular Sensitivity

Sample

Sample Name: methylene blue
Sample ID: methylene blue
Origin: 25-2-14.cal
Status Completed
Chk. Result

Type	Anal.	Manual Dilution	Result
Unknown	TC	1.000	TC:72.13ppm

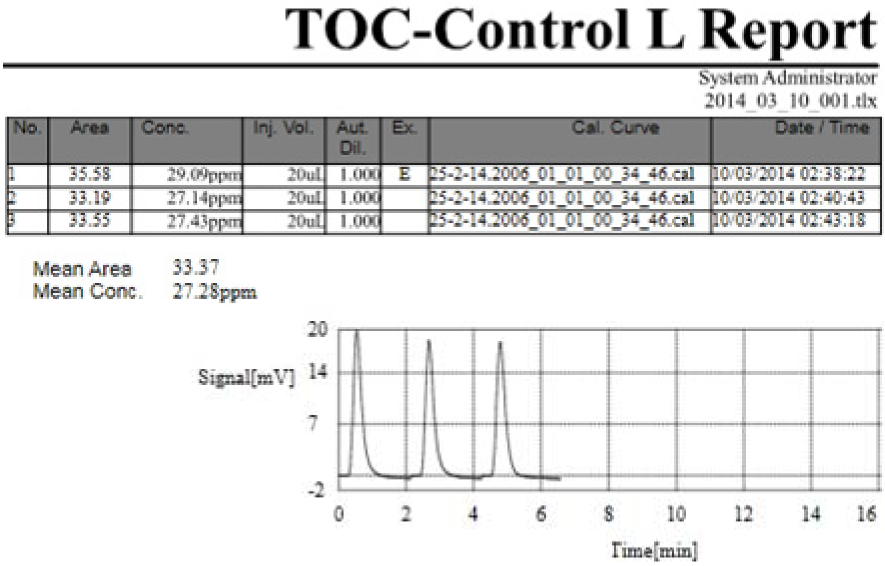
1. Det

Anal.: TC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	82.09	67.12ppm	20ul	1.000	E	25-2-14.2006_01_01_00_34_46.cal	09/05/2014 03:51:57
2	87.88	71.85ppm	20ul	1.000		25-2-14.2006_01_01_00_34_46.cal	09/05/2014 03:54:12
3	88.57	72.41ppm	20ul	1.000		25-2-14.2006_01_01_00_34_46.cal	09/05/2014 03:56:29

Mean Area 88.23
Mean Conc. 72.13ppm

Figure 9: Initial TOC of Methylene blue dye before degradation



TOC-Control L Report

System Administrator
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No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	35.58	29.09ppm	20ul	1.000	E	25-2-14.2006_01_01_00_34_46.cal	10/03/2014 02:38:22
2	33.19	27.14ppm	20ul	1.000		25-2-14.2006_01_01_00_34_46.cal	10/03/2014 02:40:43
3	33.55	27.43ppm	20ul	1.000		25-2-14.2006_01_01_00_34_46.cal	10/03/2014 02:43:18

Mean Area 33.37
Mean Conc. 27.28ppm

Figure 9: Final TOC report of Methylene blue dye after degradation.

6.3Determination of Biochemical Oxygen Demand Data Sheet

Table 1: Shows BOD Reading of the sample

Trial No.	*Day*	*Volume of Sample (mL)*	*Volume of Titrant (mL)*	*Dissolved Oxygen (mg/mL)*
Blank	0	203	1.6	1.6
1.	0	203	4.2	4.2
2.	0	203	4.2	4.2
Blank	5	203	1.5	1.5
3.	5	203	2.1	2.1
4.	5	203	2.1	2.1

7. Calculation

Initial DO of the diluted sample, Do = 4.2
DO at the end of 5 days for the diluted sample, D5 = 2.1
Blank correction = C0 – C5, BC = 1.6 - 1.5 = 0.1
Initial DO of the blank, Co = 1.6
DO at the end of 5 days for the blank, C5 = 1.5
Biochemical Oxygen Demand = (D0-D5- BC) × volume of the diluted sample
Volume of sample taken
= (4.2 – 2.1 – 0.1) × 203 ÷ 10
= 42.63 mg/mL
BOD = 42.63 mg/mL.

8. Conclusion

From the experiment we came to conclusion transition metal oxides are very good oxidation catalyst and can play an important role in the AOPs. Immobilisation of the catalyst plays a significant role in degradation because it reduces the problem of filtration. This process is very much cost effective because it does not require any external energy to carry out the process of degradation. One of the applications of this Advance oxidation process (AOPs) is to find an alternate method for the adsorption method of waste water treatment because adsorption process causes secondary pollution. So we can say that this very much effective and as proved by many researchers, removal of dyes by AOPs is economically favourable and technically easier.

References

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