A Hybrid Ultrasound Assisted Advance Oxidation Process Using Ruthenium based Catalyst and its Application to Waste Water Treatment

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Abstract: *An experimental study has been conducted on the Degradation of Congo Red dye using a Hybrid Ultrasound Assisted Advance Oxidation process. The effects of initial dye concentration, Sonication time, amount of Catalyst and Hydrogen Peroxide Dosage were investigated The Degradation capabilities of the bimetallic catalyst was tested by a fixed concentration of Congo Red Dye at the same operating conditions. Degradation of the dye was found to increase as the given conditions like Sonication time, Catalyst amount and hydrogen peroxide dosage increases but decreases as initial concentration of the Congo Red dye increases, this due to the fact that the active site of the Catalyst can degrade a certain concentration of the dye. Characterization of the Bimetallic catalyst (Ru + NiO) was confirmed by XRD & SEM.*

Keywords: Sonication, Congo Red, Bimetallic Catalyst Ru- NiO, AOP, Waste Water Treatment, SEM, XRD

1. Introduction

Advance oxidation process involves various chemical treatment procedures through reactions with includes highly reactive hydroxyl radicals which can be obtained through Hydrogen Peroxide or Ultrasound/Ultraviolet light or ozone. This technique doesn't cause secondary pollution as compared to the techniques involving adsorption, here the organic /inorganic content in the waste water is degraded into simpler compounds which are very less toxic to the environment and make the water potable without conducting any secondary treatment. Using a Bimetallic catalyst Ru-NiO impregnated on Activated carbon using ultrasound waves passed in the solution (Sonication) along with a drop wise addition of hydrogen peroxide leads to a very effective degradation of Congo Red dye in a very short span of time (2-3 hours).

2. Material and Methods

2.1) Catalyst Synthesis

0.5 gram of $RuCl_3$ (Ruthenium Chloride) was mixed with 20 ml of Ethanol in a single beaker and 0.5 gram of $NiCl_2$ (Nickel Chloride) was mixed with 70 ml of distilled water in a separate beaker. Both the solutions were mixed together along with the addition of 1 gram PVP and 9 gram of Activated Carbon. This mixture was then sonication for 1 hour (Direct Sonication) with the following conditions:

- Pulse = 05 On/ 02 Off
- Probe temperature = 46 °C
- Set point temperature = 70 °C
- Amplitude = 30%
- Timer = 1 hour

Thus obtained solution was dried at 110 °C using Hot Air Oven to achieve the catalyst in a dry powder form. This powder is then characterized using XRD (Figure 3) & SEM (Figure 1,2) for determining the size and morphology.

3. Characterization Result
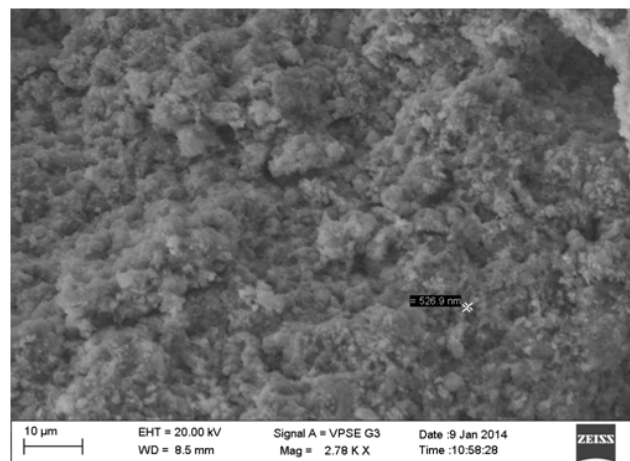
3.1) SEM Result

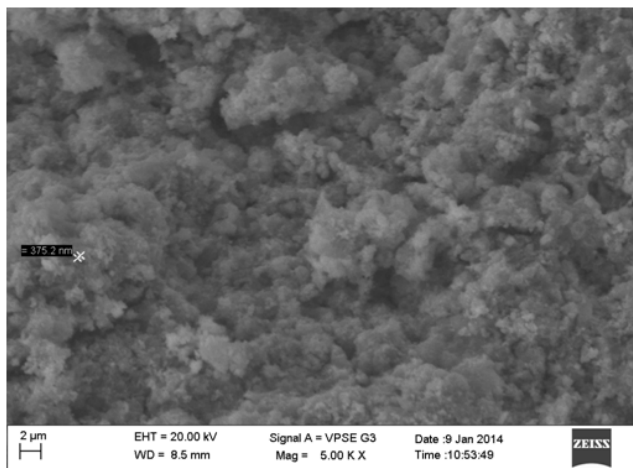**Figure 1:** Particle size of 526.9 nm on SEM (Scanning Electron Microscope)

Figure 2: Particle size of 375.2 nm on SEM (Scanning Electron Microscope)
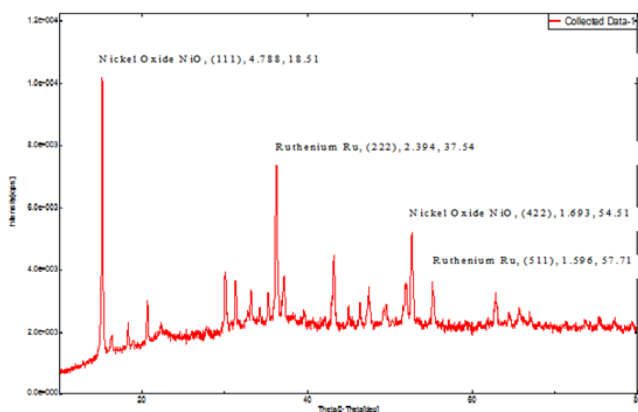
3.2) XRD Result

Figure 3: XRD result of the Bimetallic Catalyst Formed

Waste Water Treatment

Waste water is a major issue which consists of commercial, residential and industrial processes. Various methods have been employed to convert this unfit water into potable water including biological treatment or chemical treatment, chlorination & physio-chemical treatments but the efficient technology now-a-days is Advance oxidation process. Using a hybrid method of combining Sonication along with AOP's with dropwise addition of hydrogen peroxide leads to an efficient degradation of Congo Red Dye. We get the intense peak at 498 nm on UV-Vis Spectrophotometer in aqueous solution at low dye concentration.

4. Methodology

A fixed concentration of Congo red dye is taken in a beaker and along with a fixed quantity of the catalyst synthesized is mixed in the beaker with drop-wise addition of hydrogen peroxide. During the direct sonication process, Definite volumes of resulting solutions at fixed intervals of time are taken out and was analyzed using UV-Vis Spectrophotometer. The resulting absorbance values were compared with the calibration chart of Congo-Red

dye. Degradation of the dye can be calculated by using this formula:

$$\% \, deg = (A_i - A_f) \times 100 \, / A_i$$

Where,
% deg = Percentage Degradation
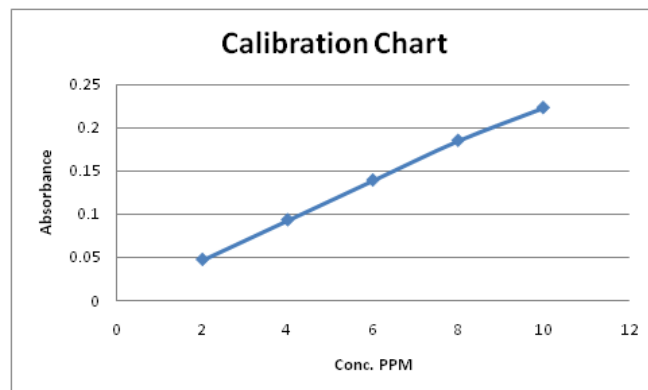A_i = Initial Absorbance
A_f = Final Absorbance

Figure 4: Calibration chart for Congo Red Dye

5. Experimental Explanation

The percentage degradation of Congo Red dye alone with addition of hydrogen peroxide & no sonication for a 50 ppm of dye takes 6 hours time for 100 percent degradation while using the bimetallic catalyst along with sonication, 50 ppm of dye takes 2 hours to completely degrade the dye. Being Ruthenium as a good Hydrogenation Catalyst, it can carry out oxidation reaction but being a costly transition metal, i have incorporated Nickel Oxide and the combined catalyst impregnated over Activated Carbon to reduce the cost of the operation in an effective manner. Figure 5 shows before and after effect of the bimetallic catalyst.

Figure 5: Before and After Degradation with Bimetallic Catalyst (Congo Red)

6. Results

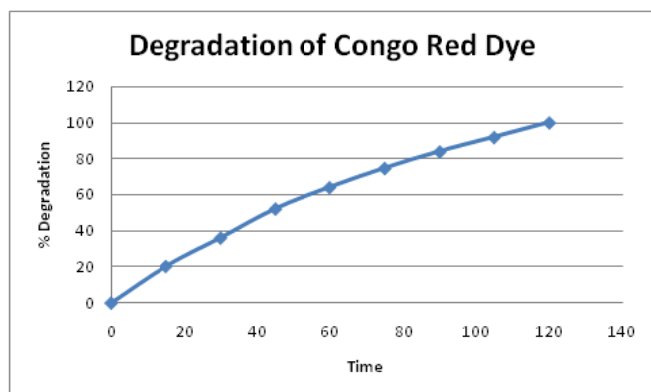**7.1)** Plot for Congo Red Degradation

Figure 6: Degradation Result of Congo Red Dye

7.2) TOC report Methylene blue dye degradation

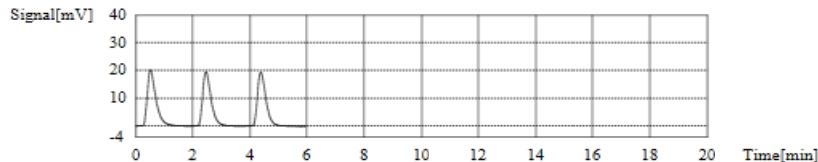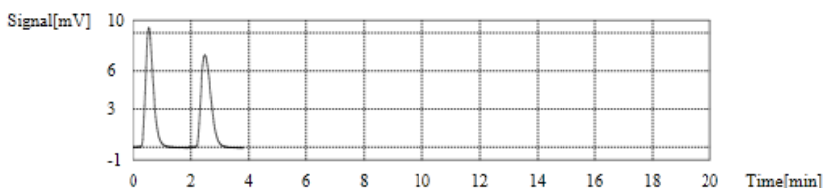Initial TOC of Methylene blue dye before degradation

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Final TOC report of Methylene blue dye after degradation

Anal.: TC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	17.27	14.12ppm	20uL	1.000		25-2-14.2006_01_01_00_34_46.cal	09/05/2014 04:11:07
2	17.17	14.04ppm	20uL	1.000		25-2-14.2006_01_01_00_34_46.cal	09/05/2014 04:13:16

Mean Area 17.22
Mean Conc. 14.08ppm

7. Conclusion

The bimetallic catalyst Ruthenium & Nickel oxide impregnated over Activated carbon gives the best results for the degradation of Congo Red dye. Though Ruthenium and Nickel being the transition metals and highly oxidative catalyst, the combination of Nickel oxide with Ruthenium resulted in reducing the cost to half while the impregnating both with AC minimized the cost further, so this combination helps in the AOP's for the proper degradation and neglecting secondary pollution which is caused by adsorption in the conventional methods.

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