

Catalytic Wet Peroxide Oxidation of 2-Chlorophenol with Co(II)-impregnated Silica

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Abstract

Persistent catalytic wet oxidation (CWO) was explored as an acceptable technique for the industrial wastewater treatment contaminated with phenols and its derivatives. The core of this study is to evaluate the catalytic performance of Co (II)-impregnated Silica for the wet oxidation of 2-chlorophenol (2-CP) in water with or without the presence of the common chemical oxidant, H₂O₂. Use of oxidant H₂O₂ in the process is known as catalytic wet peroxide oxidation (CWPO). The catalyst was developed by refluxing silica (60-120 mesh) with conc. H₂SO₄ and then with aqueous Cobalt nitrate hexahydrate, [Co (NO₃)₂].6H₂O for 6h. The structural aspects of the catalysts were determined with powder XRD, FTIR, CEC and TGA measurement. The surface framework was studied with the help of Scanning Electron Microscope (SEM), mineralization can be acquire with COD and the amount of Co(II) entering into silica matrix was evaluate with atomic absorption spectrometry(AAS). The material was calcined at 873 K before using as a catalyst. The oxidation was carried out in a high-pressure stirred reactor at different temperatures and other process variables. The assessment results indicate that the use of this catalyst allows a convenient elimination of 2-chlorophenol (93.7% degradation) and a significant removal of chemical oxygen demand (60.1%). Results shows that with preferment of temperature, catalyst load and mole ratio of H₂O₂ in the feed, the oxidative conversion could be further improved both in presences of the chemical oxidant and in absence of it. Termination of various reaction conditions, kinetics of the process has been discussed.

Keywords: CWO, CWPO; Co (II)-impregnated Silica; 2-CP.

1. Introduction

The water on the Earth in unpreserved and thawed condition constitutes only 0.65%, where most of it is regarded as ground water. From that amount only 0.03% is considered as in surface water found in ponds, rivers, soils and climates. When that amount of water is used it will contaminated with extensive diversity of materials. Now a day's almost all variety of industries liberate wide amount of hazardous waste water unperturbed by aromatic compounds [2-4]. Among all the compounds, phenols and its derivatives were contributing approximately 23% to the waste.[15] Generally, there are found to be three types of wastewater treatment alternatives: separation, biological means and destruction[6]. Among them separations (filtration, adsorption, osmosis etc.) and biological treatment doesn't manage to attain that mark of satisfaction. The latter option achieves the excessive pollutant removal level [3]. Other treatment as chemical oxidation, electrochemical treatment, photo catalytic oxidation, wet oxidation and incineration involved high process cost and not regarded as effective observation.[1-2]

Catalytic wet peroxide oxidation (CWPO) technique, an alternative to the other processes methodically eliminate hazardous organic pollutant from the wastewater with the help of a well prepared catalysts to attain improve oxidation rates at lower pressure and temperature that allowing the process at milder condition and by accommodation of the reactions which increases product yield. Extension of degradation can be enhance to a greater extent by the appropriate selection of catalytic metal or metal oxide/nitride during CWPO observation.[9-12]

In this respect, numerous heterogeneous catalysts have been incorporate and tested in the last decades, where reportedly mixture of metal oxide/nitride of Cu, Co, Mn, Fe, Mo, Bi etc, explores to be good[4-8]. While it appears that impregnated silica improves the rule of heterogeneous containing catalysts. In this present work test and evaluation of catalyst by impregnating Co(II) on silica gel by CWPO experiment of 2-CP (2-Chlorophenol) in water with oxidizing and enhancing rate material hydrogen peroxide(H₂O₂).[21] Respective characterization of the free and used catalysts was accomplish by means of BET (surface area measurement), infrared spectroscopy (FTIR), Scanning electron microscopy(SEM),X-ray diffraction(XRD), cation exchange capacity(CEC), and atomic absorption spectroscopy(AAS).These observation were tentatively observed in terms of conditions as effect of time, catalyst load, reactant

concentration, mole ratio of the reactant, temperature and p^H respectively. Kinetics and COD of the catalytic process with probable explanation also have been discussed [15].

2. Experimental methodology:

2.1 preparation of Co (II)-impregnated SiO₂ catalyst:

Co (II)-silica was prepared by refluxing 5g of acid treated calcined silica with 50 mL of 1M cobalt(II) nitrate hexahydrate for 6hr. After refluxing, the materials were washed with distilled water for several times and were dried in an air oven at 393 K. The material was then calcined at 773 K for 6 h and was preserved in desiccators for use as catalysts.

2.2 characterizations:

The physical characterization of the catalyst was made by the following observation as- XRD observation was established for catalyst synthesis (Department of Nanotechnology, NEHU, Shillong) and comparing that with the fresh unused silica gel. The modification in surface territory of the Co (II)-impregnated silica was examined with SEM (IISER, Kolkata). The percentage in mg/g of the metal Co (II) intake by the silica was measured with AAS (Agilent 240AA, department of chemistry, B.BorooahCollege, Guwahati). The impregnation of the metal Co (II) into silica gel is confirmed by FT-IR technique (department of chemistry, B.Borooahcollege, Guwahati). By using copper bisethylenediamine complex method, CEC of the catalyst was also examined.

2.3.wet oxidation of 2-chlorophenol:

The reactants selected for this study are 2-chlorophenol(2-CP) and Hydrogen peroxide (H₂O₂) and Catalytic wet peroxide oxidation was carried out in a batch process with 50 mL conical flasks kept in a thermostatic water bath shaker under the following conditions:

Volume of reactant	: 25.0 mL
Volume of H ₂ O ₂	: 25.0 mL
2-CP concentration	: Variable [(2, 4, 6, 8, 10, 20) x 10 ⁻⁴ mol L ⁻¹]
H ₂ O ₂ concentration	: Variable [(2, 4, 6, 8, 10, 20) x 10 ⁻⁴ mol L ⁻¹]
Catalyst loading	: Variable (2, 4, 6, 8 , 10 g L ⁻¹)
Temperature	: (i) 323 K as ambient temperature (ii) 300, 313, 323, 333 and 343 K for effects of Temperature

While the reaction without H₂O₂ was carried out keeping the total volume at 50ml. Before proceeding towards the effectiveness of the catalytic activity of 2-CP with Co (II)-impregnated silica, the following four sets of blank experiments were carried out:

- I. Reactant alone without any catalyst and H₂O₂,
- II. Reactant and H₂O₂ (1:1 molar ratio) without any catalyst,
- III. Reactant with silica as the catalyst, and
- IV. Reactant and H₂O₂ (1:1 molar ratio) with silica as the catalyst.

The degradation of 2-CP was estimated spectrophotometrically at 273 nm. According to the relation the percentage conversion is calculated as-

$$\% \text{ Conversion} = [(C_0 - C_t) / C_0] \times 100$$

Where C₀ is the initial concentration (mol L⁻¹), C_t the concentration at any time after the reaction starts, at the time (min). Then establishing the optimum conditions for the oxidation of 2-CP with respect to reaction time, pH, catalyst load, reactant concentration, mole ratio with respect to the oxidant, reaction temperature and degrees of mineralization of the phenols in terms of COD.

3. Result and discussion :

3.1 physical characterization of the catalyst:

3.1.1 FTIR analysis:

The FTIR spectra of the pure, acid treated and Co(II)-impregnated silica shows a broad band of stretching vibration of hydroxyl group on its surface at 3452.9, 3459.12 and 3463.86 cm⁻¹ respectively. By carefully observing the difference in these bands, it is seen that there was a slight shift in Co (II)-impregnated sample.

The band appears at around $1622-1622.13\text{ cm}^{-1}$ corresponds to $-\text{OH}$ bending vibration. The bands near $1148-1089\text{ cm}^{-1}$ and $958.80-923.66\text{ cm}^{-1}$ are assigned to Si-O-Si stretching vibration and Si-O-Si bending vibration. A new band at about 819.39 cm^{-1} was identified, which were absent in case of pure and acid treated sample but assigned to Co(II)-Si stretching frequency of the template in agreement with the published result[10].

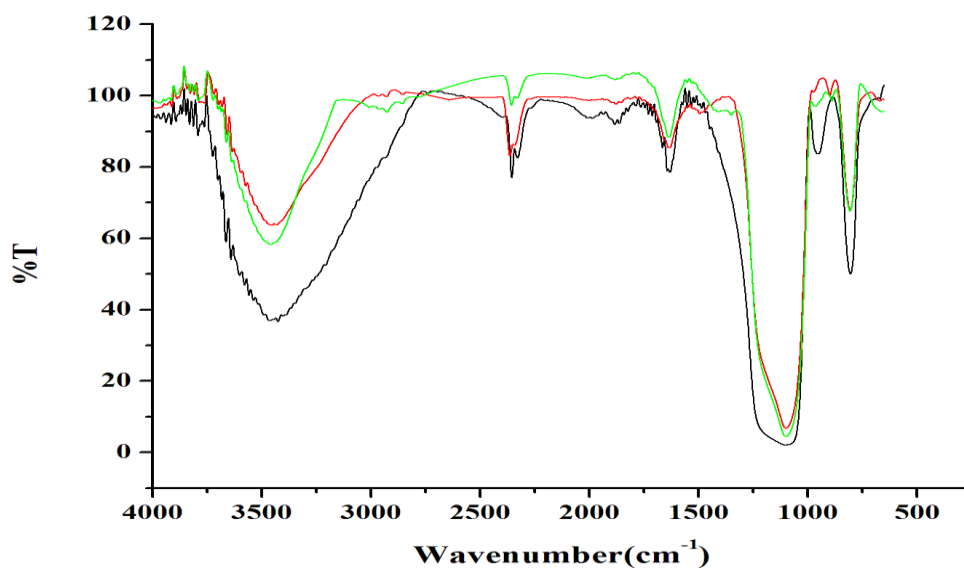


Fig 1: FTIR spectra for pure Silica (red), acid treated silica (green) and Co(II)-SiO₂ (black)

3.1.2. X-ray diffraction (XRD):

X-ray powder diffraction of silica impregnated with Co (II) shows one prominent amorphous peak located at $2\theta = 22.3$, followed by a broad band. There seems to be no new phase formation during heat treatment and alternation. Thus metal-impregnation treatment delivered structural regularity of the Silica catalyst as was assigned [10]. The experimental XRD pattern of the impregnated with theoretical silica designate that the silica construction persist after packing cobalt metals on to it.

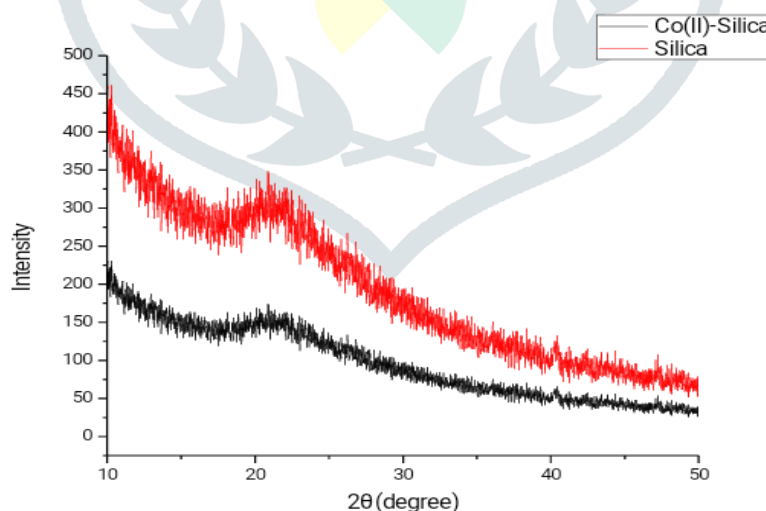


Fig 2: X-ray powder diffraction pattern silica (bottom) and silica supported Co(II) (top).

3.1.3 Atomic absorption spectroscopy (AAS):

In the present work, preparation of the sample for AAS was done by digesting 0.1 g of the catalyst with 5 mL of tri-acid mixture (HNO_3 : HCl : H_2SO_4 in 1:2:4 ratio) until a white residue was obtained, then the residue was treated with 10 mL 1:1 HCl and the volume was made up to 50 mL with double distilled water. The amount of Co (II) in Silica supported cobalt catalyst was found to be 0.00974 mg/g.

3.1.4. Scanning Electron Microscopy (SEM):

Morphological characteristics through SEM assigned comparisons between parent and impregnate silica. The surface framework has undergone significant appearance from silica to Co (II)-impregnated one. Silica particles appear as small and large flakes with a non-uniform spread creating a large number of crevices and holes in between and flaky non-uniform deposits in case of Co (II)-SiO₂

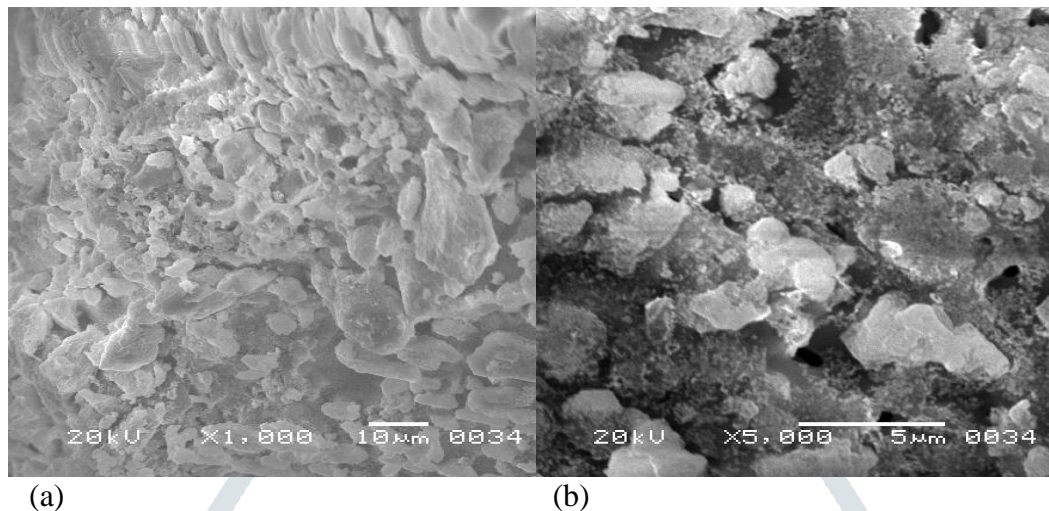


Fig 3: SEM micrographic image of (a) SiO₂(left) and (b) Co (II)-SiO₂(right)

3.1.5. Thermogravimetric analysis (TGA):

The evolution of the mass of silica is similar under inert (nitrogen) and oxidative (air) atmosphere, with the bulk of the mass loss come to pass below 250 °C and a second mass loss step between 250 and 375 °C. Above 375 °C, further mass loss occurs gradually and individual steps cannot be identified.

At 325 °C, the peak in the mass loss rate is caused by dehydroxylation of (mainly vicinal) silanol groups [23]. The removal of hydroxyl-groups continues gradually up to 1000 °C. Because of an increase in isolation of the silanol-groups, the rate keeps decreasing.

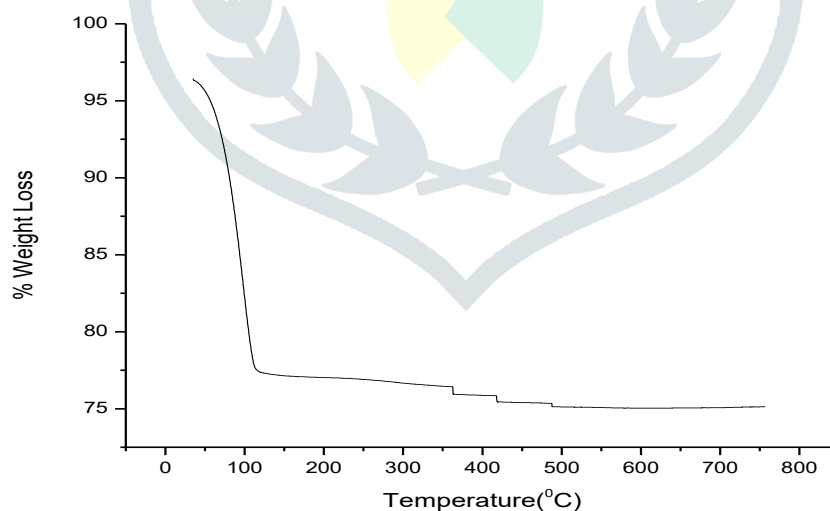


Fig 4: TGA curve for Co(II)-SiO₂

3.1.6. Cation Exchange Capacity (CEC):

Mineralization of Cation Exchange Capacity (CEC) of the material, established with copper bisethylene diamine complex method. CEC for pure silica, acid treated silica and Co (II)- impregnated silica were found to be 2.6, 3.8 and 5.2 meq/g respectively. However, the variations are minute; it is observed that CEC improved after survey.

According to literature, the CEC of a material increases due to the increase in the number of cation exchangeable sites. Thus, it may be inferred that in the present case, after acid or metal impregnation processes, the number of such exchangeable sites increases. Rodrigues *et al.* (2003) have suggested that the

increase in the exchangeable sites of a material might be due to the creation of defect sites and broken bonds present on the surface of the materials.

3.2 Wet oxidation of 2-Chlorophenol (2-CP):

3.2.1. Blank Experiment:

Blank experiments, as mention above, were carried out for the oxidation of 2-chlorophenol with water formerly exploring the effectiveness of the impregnated Co (II)-SiO₂ catalyst. From the sets of blank experiments definite deduction could be noticeable corresponding to; no measurable conversion in set (i) and (iii), however a measurable conversion remark in (ii) and (iv). Therefore the succeeding inferences may be made from the blank experiments:

- In experiment (i), hydrated 2-chlorophenol(2-CP) is immensely stable and even after 360 min signify very slight decomposition(15.15%)
- In experiment (iii), the silica gel as a catalyst itself has deficient catalytic performance (27.80%) concerning oxidation of hydrated 2-CP.
- In experiment (ii) and (iv), production of -OH radicals by partial decomposition of hydrogen peroxide (H₂O₂) effect the oxidative degradation.
- Noticeable oxidation was feasible in (iv) because on their surface of silica fragments -OH radicals were expected to adsorb for oxidation of 2-CP.

3.2.2. Effect of pH:

In the reaction mixture, the degradation value decreases from 90.8 to 31 % while changing the pH from 3 to 9 keeping the concentration of H₂O₂ constant. As phenol is itself an acidic compound therefore in pH = 3 maximum conversion was found because being negatively charged the 2-chlorophenolate ions, attach more effectively on the surface of the acidic catalyst. However, as in the reaction mixture range of the pH increases, gradually enhance the concentration of hydroxide ions which oppose with 2-chlorophenolate ions in the adsorption sites (positively charged) hence, degradation of 2-chlorophenol decreases.

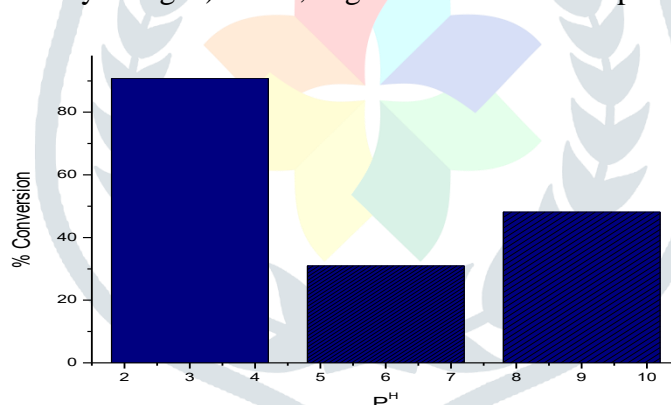


Fig 5: Effect of pH on wet oxidation of 2-CP with Co(II)-impregnated silica as a catalyst with H₂O₂ (reactant: H₂O₂ mole ratio 1:1) at 323K (catalyst load 2g/L, 2-CP 2x10⁻⁴M and reaction time 240min)

3.2.3. Effect of Time:

Degradation of 2-chlorophenol from the time interval 30-360 min was found to be 59.79 to 79.768 %, within that time interval an equilibrium time was found to be 240 min, where although the time has been varied but the conversion was likely to be similar.

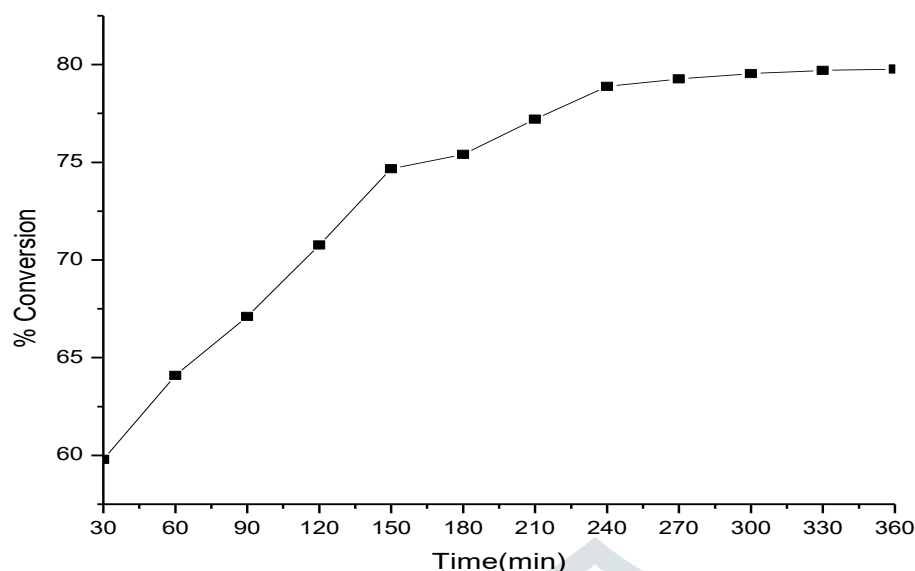


Fig 6: Effect of reaction time on oxidation of 2-CP with Co(II)-impregnated silica as a catalyst with H_2O_2 (reactant: H_2O_2 mole ratio 1:1) at 323K (catalyst load 2g/L, 2-CP $2 \times 10^{-4}\text{M}$)

3.2.4. Kinetic Study:

Both first order and second order kinetic studies were carried out and the results showed good linearity with second order kinetics.

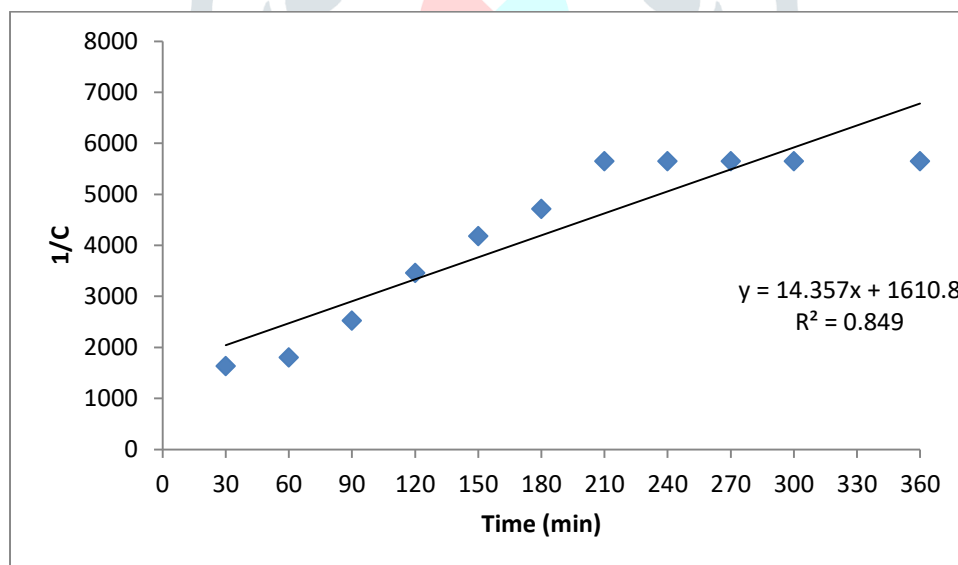


Fig 7: Catalytic Wet peroxide oxidation of 2-CP over impregnated Co(II)-Silica as a second order degradation [H_2O_2 mole ratio 1:1; Catalyst load 2g/L] at 30°C

3.2.5. Effect of Reactant concentration:

The conversion of 2-CP decreases from 88.7 to 79.7 %, when concentration of the reactants varied from 2×10^{-4} to 20×10^{-4} M, maintaining a fixed H_2O_2 concentration. The degradation is obvious because in the accessible adsorption sites where the conversion needs to be take place, struggle has been faced by 2-chlorophenol molecules. Due the competition within the adsorbed 2-CP molecules on the saturated or semi-saturated catalyst surface brings down the degradation.

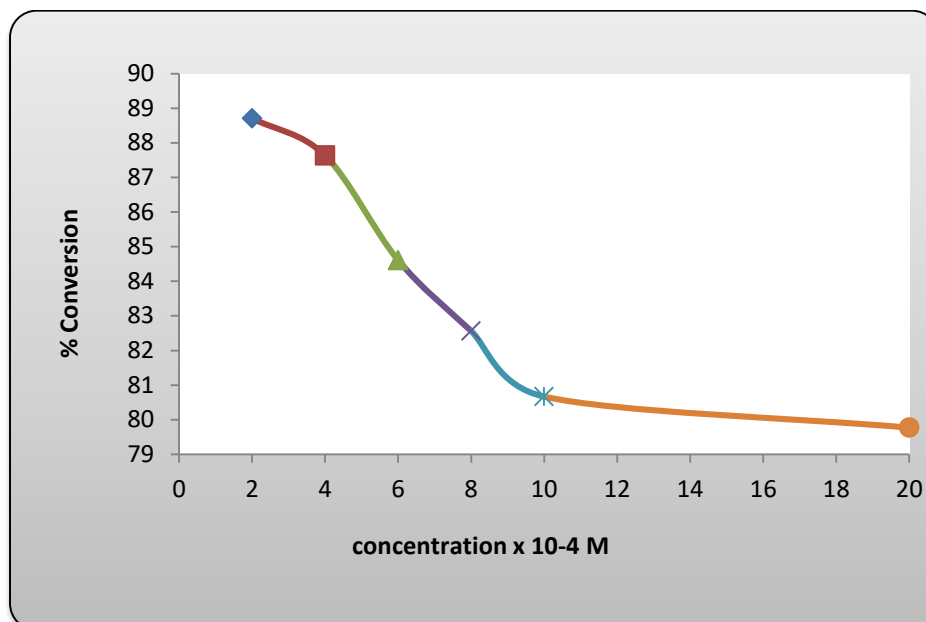


Fig 8: Effect of reactant concentration on oxidation of 2-CP over the catalyst Co(II)-Silica (catalyst load 2g/L) at 323K for reaction time at 240 min.

3.2.6. Effect of Catalyst Load:

Visualization of the results depict that different uptake of the catalyst load did not have much impact on degradation. To carry out the oxidation reactions for the determination of degradation of 2-CP five different catalyst loadings of 2, 4, 6, 8 and 10 g/L respectively were used.

Although variety of the catalyst load was introduced, persistency of the amount of the active phase per unit mass was observed. Experimentally it is account as an obvious reason for no noticeable result in the required conversion.

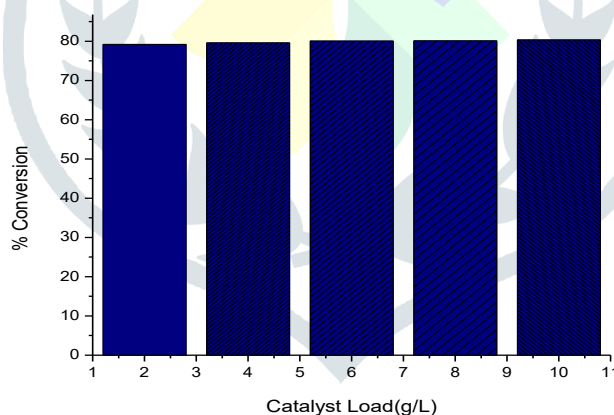
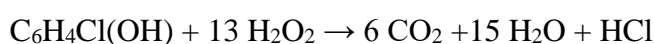


Fig. 9: Effect of catalyst load on oxidation of 2-CP (2×10^{-4} M) with Co(II)-impregnated Silica as catalyst with H_2O_2 (reactant: H_2O_2 mole ratio 1:1) for reaction time at 240 min at 323K

3.2.7. Effect of Mole Ratio:

The effects of mole ratio of increasing amount of hydrogen peroxide H_2O_2 was investigated with varying amount of H_2O_2 and the reactant from 1:1 to 20:1 with respect to H_2O_2 , 83.721 % conversion of 2-chlorophenol could be obtained. It was clearly observable that excess amount of H_2O_2 did not lead to the maximum conversion due to self-decomposition of H_2O_2 at the high temperature aided by the presence of the catalyst. Theoretically overall rate of reaction as well as the product yield might be influence by such decomposition.

Complete oxidation of 2-chlorophenol with H_2O_2 shown by the stoichiometric equation required 13 moles of H_2O_2 for 1 mole of 2-chlorophenol:



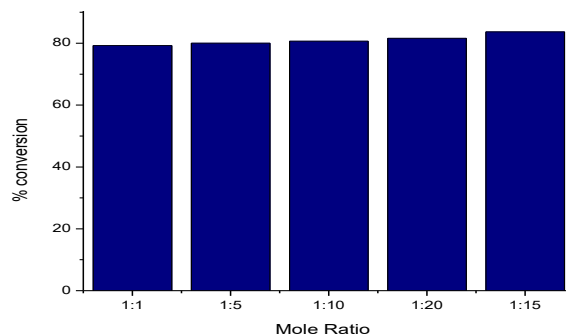


Fig. 10: Effects of mole ratio on oxidation of 2-CP and Co(II)-impregnated Silica as the catalyst with H_2O_2 (catalyst load 2 g/L ;reaction time fixed at 240 min) at 323K

3.2.8. Effect of Temperature:

The results signify that the temperature can bring a major impact on the conversion from 79.2 to 86.18 %, when five different temperature ranges 300, 313, 323, 333 and 343K were performed on the oxidation reactions. Beside these temperature ranges, after certain extent it acquires an equilibrium temperature at about 323K. That amount of temperature around 323K was assumed to be sufficient for maximum conversion.

As the temperature gradually increases, the mobility of the reactant molecules upgrade and in the absence of the transport limitation they can reach the catalyst surface, which in turn enhance the conversion.

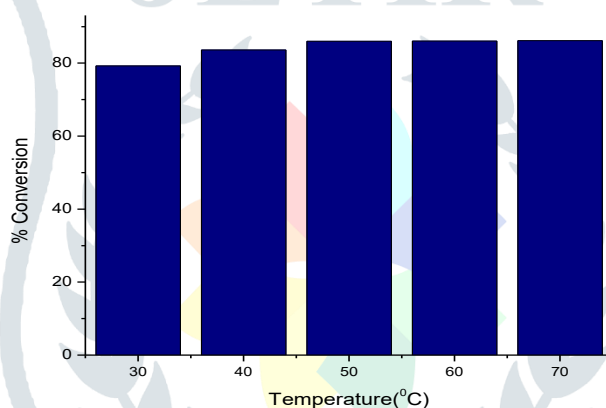


Fig.11: Effect of temperature on oxidation of 2-CP ($2 \times 10^{-4}M$), Co(II) -Silica as catalyst with H_2O_2 (reactant: H_2O_2 mole ratio 1:1 ;catalyst load 2g/L) for fixed reaction time at 240 min

3.2.9 Establishing the mineralization of 2-chlorophenol oxidation with Chemical Oxygen Demand(COD) measurement:

Degree of mineralization of phenol in terms of COD signifies another clear indication of the reaction mixture. In the starting phase COD packing of the reaction mixture reduced from 33.2 to 17.6 mg/L.

Between the two observable value i.e. COD reduction of 2-CP and 2-CP conversion, the lower value COD reduction of 2-CP in the reaction mixture clearly designate the existence of partially oxidized products formed. As long as the difference between 2-CP conversion and COD reduction goes higher, lead to the production of highly partially oxidized products.

Table. 3.1: COD, COD removal and % conversion on catalytic wet oxidation of 2-CP

Time (min)	COD (mg/L)	COD Removal (%) (X_{COD})	2CP conversion (%) (X)	Difference (X- X_{COD})
30	33.2	26.22	59.79	33.57
60	31	31.11	64.09	32.98
90	29.5	34.44	67.112	32.672
120	29	35.55	70.77	35.22
150	27.2	39.55	74.67	35.12

180	26.9	40.22	75.40	35.18
210	24.3	46	77.20	31.2
240	21.6	52	78.884	26.884
270	20.8	53.77	79.260	25.49
300	19.1	57.55	79.538	21.988
330	17.6	60.88	79.703	18.903

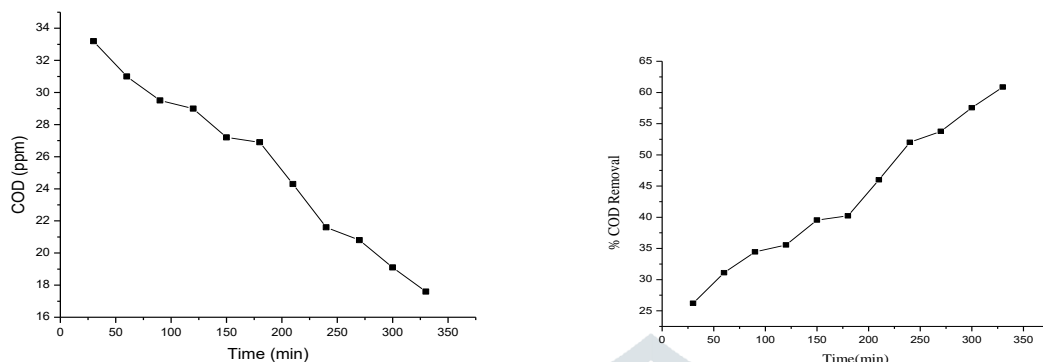


Fig.12: COD(left), Removal of COD(right) on wet oxidation of 2-CP(2×10^{-4} M) with Co(II) -Silica as catalyst (2g/L) with H_2O_2 (reactant: H_2O_2 mole ratio 1:1); COD(left), Removal of COD(right) for at 240 min reaction time.

4. Conclusion:

The result represent that impregnation of a transition metal ions through impregnation method bring out to an influential catalyst for the treatment of CWO of 2-chlorophenol because it suppress the time interval for attaining maximum conversion (240min). Among four set of process variable the composition with 2-CP, H_2O_2 and metal impregnate catalyst will signify to be more effective than the rest. The reaction mixture follow second order kinetics with the plots are linear with regression coefficient of 0.849 for 2-chlorophenol

In hydrated form maximum oxidative degradation of 2-CP might be attain with very small amount of catalyst (2g/L). Among the variable applied temperature, an equilibrium temperature around 323K delivered the satisfactory result. Similarly in the pH range due to the acidity of 2-CP, pH at about 3 lead to maximum conversion and alkaline pH doesn't favored the oxidation.

The idea and utilization of the present work is to convert the 2-CP as a safe compound and bring out harmless end products which are likely to undergo complete mineralization due the non-persistent nature of the product.

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