



Heterogeneous catalytic conversion of 4-chlorophenol via atomic hydrogen substitution induced by size-controlled polydisperse nanocobalt



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HIGHLIGHTS

- Hydroconversion of 4-chlorophenol was enforced via atomic hydrogen substitution induced by nanocobalt.
- The concentration of the polydisperse nanocobalt was in the range of 0.5–2.5 M.
- The 2 M CoNPs gave the best results for the hydroconversion reaction of the chlorophenol.
- pH, reaction time, catalyst concentration and particle size had significant influences on the reaction.
- Adsorption, surface reaction and desorption mechanisms were developed and tested to establish the ideal reaction mechanism.
- The Co-H₂ strategy adopted here, has great potential for obtaining a wide product distribution in 1 h.

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ABSTRACT

Hydroconversion of 4-Chlorophenol (4-CP) was induced via atomic hydrogen substitution and 0.5–2 M polydisperse cobalt nanoparticles (40–500 d.nm) which were synthesized via a modified-polyol route. The cobalt nanoparticles and hydrogen incursion in the 4-CP helped to enforce the hydroconversion (HDC) reaction of 4-CP. The reaction runs were conducted based on an initial 4-CP wastewater effluent concentration discharged from a pesticide company, different particle sizes, and reaction time. Also, NaOH was added as a proton scavenger to the reaction mixture in order to avoid catalyst-deactivation. Samples from the reactor were collected at different times in order to monitor the hydroconversion process. The Co-catalyst reduced the activation energy of the reaction, initiated the hydro-substitution reaction at an earlier time, as well as enhanced 4-CP hydroconversion. Of all the catalysts, the 2 M polydisperse-cobalt nanoparticles (PD-CoNPs) gave the best performance with a description that fits the desorption mechanism whose k_{eqd} value = 0.079.

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1. Introduction

Despite the wide spread industrial application of chlorinated organic compounds, they are often referred to as high priority pollutants due to their negative effects on man, the environment, aquatic life and the ozone layer (USEPA, 2011). Chlorophenols are chlorinated organic compounds, manufactured on a large scale by the chlorination and hydrolysis of phenol and chlorobenzene, respectively (Czaplicka, 2004). They are discharged into surface/

ground waters, air, sediments, and soils via effluents from industries or as biocides/by-products of water disinfection, pulp bleaching, and waste-incineration (Murialdo, 2003). Chlorophenols are toxic, weakly acidic and colourless organic compounds whose chlorine atoms are attached to a hydroxy-benzene ring. The toxicity of chlorophenol depends on the position of its chlorine atom relative to its hydroxyl group. Chlorophenols with chlorine atoms positioned at the second carbon atom (i.e., 2-chlorophenol) are considered less toxic relative to those at the 3rd, 4th and 5th carbon atoms which give compounds of 3-, 4-, and 5-, chlorophenols, respectively (Czaplicka, 2004). Dermal contact with chlorophenols can result in upper respiratory tract infections (sinuses, pharynx,

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larynx, and nasal passages), eye defects, mucous membrane-disorder, skin irritations, burns, convulsion, respiratory system-inhibition, shortness of breath, nausea/vomiting, painless whitening or reddening of the skin, hyper activeness, profuse-sweating, low blood pressure, pneumonia -preceded fluid incursion in the lungs, abdominal pain and occasional skin reactions (National Pollutant Inventory, 2020). In addition to being hazardous/ozone-depleting, chlorophenols are highly carcinogenic (Meshesha et al., 2013) hence, the reason they have to be removed from contaminated streams/effluents. Of the several known degradation and removal technologies of chlorophenols, catalytic hydrodechlorination (HDC) is one of the most promising techniques, which ensures safe transformation of the compounds into useful, but less harmful compounds (Coq et al., 1986; Karpinski et al., 1996; Ribeiro et al., 1998; Manzer and Nappa, 2001).

In this study, 4-chlorophenol is the target compound. It is a colourless, harmful, low-melting monochlorophenol solid crystal which is fairly soluble in water. It is used in the production of dye (quinizarin), hydroquinone (for skin depigmentation), drugs (e.g., clofibrate), antiseptics and other vital chemicals including chlorphenesin and dichlorophen for biocide synthesis (Theurich et al., 1996). It is a by-product of water-chlorination and an intermediate product of chlorophenolic degradation (Kathleen, 2002). Some technologies, such as, Fenton-oxidation/photo-oxidation (requires expensive reagents) (Matos et al., 2009; Shiraishi et al., 2010), sono-chemical (Hamdaoui and Naffrechoux, 2008) and electro-chemical degradation (involves complex equipment) (Anandhakumar et al., 2010), bioremediation (applicable at low concentrations) (Dilaver and Kargi, 2009; Eker and Kargi, 2008) and catalytic hydrodechlorination (Khachatryan et al., 2007; Nicolas and Jean-Pierre, 2007), have been tested over the years for chlorophenol removal from contaminated streams, however, amongst the listed technologies, catalytic hydrodechlorination remains one of the most suitable treatment-techniques for wastewaters entrained with chlorophenols (Keane, 2005). Furthermore, gas phase catalytic hydrodechlorination of 4-chlorophenol, aided by noble/transition metals, usually gives rise to a wide variety of value-added products. Wastewater treatment is the process of converting wastewater from its pollution-ridden state into a form that can be returned to the water cycle with minimal environmental and health consequences (Tanks, 2020), and according to the Nibble company, the two-fold essence of wastewater treatment include (i) to protect the ecosystem from toxins as well as, (ii) to restore water quality (The Nibble Company, 2020).

2. Previous and related works

Amongst the chlorophenols found in drinkable/wastewaters, 4- and 2,4- dichlorophenols were predominant (Czaplicka, 2004). The former is resistant to chemical/biological degradation, remains in the water cycle for a long period and is highly stable owing to its inherent halogenation (Tang, 1996). Due to the toxicity and severe health effects of 4-chlorophenol, the compound is unwanted in waters.

Meshesha et al. (2013), carried out an investigation on the use of polyol-synthesized nano-Pd-Cu alloy on alumina for the conversion of trichloroethylene to ethylene. The study by Bedia et al. (2012), focused on the hydrodechlorination of dichloromethane aided by mono- and bi-metallic Pd-Pt catalysts anchored on sulfated zirconia (SZ) and tungstated zirconia (WZ) catalysts. They observed that, despite its poor stability, the WZ catalyst gave higher dichloromethane conversions. In gas-phase catalytic hydrodechlorination, two likely issues include: (i) rapid catalyst-deactivation and (ii) short-span treatments may cause insufficient interaction of catalysts with reactants (Malinowski et al., 1998;

Bonarowska et al., 1999; Martino et al., 1999; Prati and Rossi, 1999; Mori et al., 2001; López et al., 2003; Aristizabal et al., 2004; Lopez et al., 2006; Sanchez et al., 2008; Gonzalez et al., 2009). Catalyst-stability is very crucial for successful hydrodechlorination, but it can be influenced by catalyst-poisoners (e.g., HCl), formation of inhibiting species, metal sintering, metal-loss, changes in oxidation state of catalysts, as well as metal migration (Forni et al., 1997; Ordoñez et al., 2001; Heinrichs et al., 2003; Chakraborty et al., 2004; Legawiec-Jarzyna et al., 2004; Amorim et al., 2005; Li et al., 2017; Ordoñez et al., 2010). Catalyst-supports enhance the activities and stabilities of catalysts (Kim et al., 1995). According to Cheng et al. (2013), reactive hydrogen-species also play a crucial role when reactants are adsorbed onto Pd-catalyst supports via the formation of a π - π or σ -complex. Other investigations on chlorinated phenols include those of Gómez-Quero et al. (2013), which bothered on the hydrodechlorination of 2,4-dichlorophenol at 423 K over hematite-supported Au-Fe₂O₃ catalyst, hydrodechlorination of CCl₄ on Pd and Pt supported catalysts by Ordoñez et al. (2001), hydrodechlorination of 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzenes using Pd(Phen)Cl₂ as catalyst precursor (Zhang et al., 2015), gas phase dechlorination of chloro- and 1,3-dichlorobenzene over Pd, Ni, Pd/Al₂O₃ and Ni/Al₂O₃ catalysts (Amorim and Keane, 2012), hydrodechlorination of trichloro ethylene using formic acid as hydrogen source over supported Pd catalysts (Yu et al., 2016), hydrodechlorination of 2,4 chlorophenol over Ni/Al₂O₃ and Au/Al₂O₃ catalysts (Keane et al., 2009), and hydrodechlorination of chlorobenzene over Ni/Al₂O₃ catalyst (Golubina et al., 2020).

The effect of the electrocatalytic properties of transition metals on the reductive dechlorination of polychloroethanes have been examined (Huang et al., 2012), where the reductive performances of PCEs in DMF + 0.1 M (C₃H₇)₄NBF₄ were monitored in the presence of Ag, Au, Pd, Pt, Cu, Fe, Ni, Pb, Zn and, noncatalytic glassy-carbon (GC). The reduction of the PCEs were seen to be influenced by the nature of the electrode material and the chemical structure of the compound. However, the Ag, Cu, and Au demonstrated the most powerful electrocatalytic reduction-activities. Other hydrodechlorination reactions include: dechlorination of chloromethanes using highly stable platinum-activated (Pt-AC) catalyst (Álvarez-Montero et al., 2011), Pd-catalyzed hydrodehalogenation of chlorinated olefins (Andersin et al., 2012), hydrodechlorination of 4-chlorophenol in aqueous phase using: Pd nanoparticles (Baeza et al., 2012), Pd nanocrystals (Ding et al., 2012), Pd (0.5 wt%)-AC with formic acid at 35–100 °C and 2.5 bar (Calvo et al., 2009), pillared-clays supported Pt, Pd and Rh catalysts (Molina et al., 2014), highly defective Pd catalyst via hydroquinone pathway by *Arthrobacter ureafaciens* CPR706 Bae et al., 145 (1996), continuous Flow Pd/CNT-Ni Micro Foam Reactor with formic acid as hydrogen source (Xiong and Ma, 2019), Pd-Sn bimetallic catalyst supported on AC (Fang and Fang, 2017), metal organic framework (MOF)-derived magnetic porous carbon composite attached to gold and palladium nanoparticles (Dong et al., 2014).

Based on widely published literature, it is evident that hydro-conversion (HDC) of 4-chlorophenol is a potential-green technology for the treatment of organochloride wastewaters. However, considering the fact that till date, no study has ventured into the development of catalytic models and mechanisms for 4-chlorophenol conversion via the use of polydisperse nanocobalt, hence the reason for adopting the novel approach that involves the use of a new catalyst (i.e., synthetic polydisperse nanocobalt) as well as hydrogen from sodium borohydride for the conversion of 4-chlorophenol. In addition, three mechanisms that bother on the adsorption of 4-CP onto CoNPs, the reaction of 4-CP and H₂ on CoNP-surface and the desorption of the products were developed and tested in order to establish a catalytic model and mechanism for the reaction. The strategy adopted in this study holds

great prospects for the synthesis of new products that are barely documented in related studies.

3. Materials and methods

The equipment, materials and procedure adopted in carrying out this study are discussed under the following subsections.

3.1. Wastewater collection and characterization

Wastewater sample from a pesticide company was analyzed using GCMS, for its chlorophenol contents. The chlorophenols detected include phenol, 2-chlorophenol (0.4 mg/L) and 4-chlorophenol (4 mg/L) Fig. 1.

3.2. Cobalt nanoparticle synthesis

Cobalt nanoparticles (Co-Nps) were synthesized via the polyol method as discussed by Matsumoto et al. (2015) alongside the hot-injection technique reported by Kim et al. (2006). Cobalt nanoparticles were synthesized by preparing 0.5, 1, 1.5, and 2 M solutions of cobalt (II) acetate tetrahydrate ($\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$) (AR grade: 99–100% purity, Loba Chemie, India). In order to prepare 0.5 M CoNPs, to a 100 mL cylinder, 1.9 g of the acetate was weighed using the Scout Pro, OHAUS weighing balance, made in China, and dissolved in 15 mL distilled water to give 0.5 M concentration of cobalt solution. To a heated mixture of PVP solution (0.5 M), ethylene glycol of equal concentration was added, thus giving a ratio of 1:1 (PVP: EG). The capping agent (PVP) to metal precursor (MP) solution-ratio was kept constant (i.e., PVP:MP ratio = 1:1), all through the entire process. To prepare the 0.5 M polyvinyl pyrrolidone (PVP) solution (AR grade: 94.9% purity, J.T Baker), 2.8 g of PVP and 50 mL ethylene glycol (EG) (AR grade: 99.5% purity, Fisher Chemical) were mixed in a 500 mL conical flask (JSil Borosilicate, India). The resulting mixture was stirred using a stirrer, after which it was heated on a magnetic hot plate (Hotplate Magnetic stirrer - Stuart systems) to about 70 °C for complete dissolution of the solute. 1 M solution of NaOH was then prepared in a 100 mL cylinder by dissolving 20 g of NaOH pellets (AR grade: 98.8% purity, Fisher Chemical) in 1000 mL distilled water. 25 mL of the resulting solution was then transferred to a 500 mL conical flask whose temperature was raised to 70 °C (the resulting solution appeared yellowish at this temperature). Thereafter, the prepared PVP and EG mixture were added and heated to the reaction temperature (180–190 °C, measured by a Quick-fit thermometer) while stirring on the magnetic hot plate; several colour changes were observed

until a final maroon appearance was attained. The prepared metal precursor was then injected via a syringe into the hot solution while stirring at 5 mL/min until there was complete dissolution; a colour transition of the solution to dark pink was observed which informed the time for reaction-initiation. After 30 mins, as soon as there was a colour change of the solution from dark pink to blue, heating and stirring were truncated. In order to enforce the desired reduction reaction, 1 M solution of NaBH_4 (AR grade: 97% purity, Loba Chemie, India) was prepared in a 50 mL conical flask by dissolving 0.38 g of NaBH_4 solid in 10 mL distilled water. The solution was then added in a dropwise manner into a 1000 mL conical flask while stirring. A rapid evolution of gas was observed upon adding the borohydride (reducing agent); this in turn led to the formation of a black colloidal solution within 10–30 secs, thus indicating the presence of cobalt nanoparticles. Furthermore, having allowed the solution to cool at room temperature, with the help of a centrifuge (TD5-Centrifuge, 250 W, 5000 rpm), the nanoparticles were precipitated out of solution at a speed of 3000 rpm. The resulting particulates were repeatedly washed (thrice) with ethanol and distilled water in order to precipitate the particles from the colloidal solution. The particles were filtered and left to dry at room temperature. The above procedure was then repeated for the synthesis of the 1, 1.5 and 2 M CoNPs with corresponding precursor masses of 3.8, 5.7 and 7.6 g, respectively.

3.3. Catalytic hydroconversion reactor

The chlorinated wastewater effluent from an industrial/pesticide plant, as collected in Section 3.1 was placed in a conical flask. Thereafter, catalytic-hydroconversion of the simulated concentration of 4-chlorophenol was carried out by mimicking test-concentrations of 4-chlorophenol in the wastewater sample.

The contaminated solution was prepared by adding 4 mg of 4-chlorophenol (AR grade: 98%, J.T Baker) to 1000 mL of distilled water to obtain 4 mg/L concentration of the chlorophenol. 200 mL of the resulting solution was then transferred into a 1000 mL three-neck flat bottom flask (1000 mL glass reactor-three-necked flat bottom flask, J-Sil Borosilicate, India). As discussed by Ma et al. (2015), the required stoichiometric amount of NaOH was added by dissolving NaOH-pellets in the contaminated solution in order to raise its pH. The HDC reaction was initiated at ambient pressure and temperature. Hydrogen gas was produced by heating up a mixture of methanol (AR grade: 99.9% Fisher Chemical) and sodium borohydride. The gas produced was then tapped via a rubber tubing connected to the conical flask containing the simulated 4-chlorophenol concentrated solution and



Fig. 1. Experimental set-up for the hydro-catalytic conversion of 4-chlorophenol.

the reaction was allowed to last for 1 h without the inclusion of any catalyst. The reaction was then initiated/repeated with the addition of equal portions (i.e., 0.2 g) of each catalyst synthesized in Section 3.1 to the reaction mixture. At one neck of the necks of the three-neck glass reactor, a rubber stopper was introduced, which helped to secure it tightly, while a syringe (5 mL, APEX Disposable syringe) connected to one end of the straw/hose was placed gently and tightened to the second neck of the flask. A third hose passing through a rubber stopper was also attached to the third neck and secured tightly. One end of the hose (extending from the third neck of the glass reactor) was connected to a rubber stopper fitted into the opening of a 50 mL conical flask. The reactor contents were then stirred to release hydrogen gas into the glass reactor (Fig. 1). For hydrogen generation, 0.3 g of NaBH₄ was weighed and placed in a 50 mL conical flask. 30 mL of methanol was added. Gas evolution was spontaneous, and the observation of bubbles in the glass reactor signalled the start of the HDC reaction. Vigorous stirring of the reaction mixture was ensured during the reaction. At separate times, portions of the reaction mixture were taken by means of a sample bottle for analysis in order to monitor the progress of the reaction. The samples generated from the reaction were analyzed using SEM-EDX and GC-MS while the nano-catalysts were sized using Zetasizer ZEN 1600, UK.

3.4. Gas Chromatography-Mass Spectrometry (GC-MS) and titration experiments

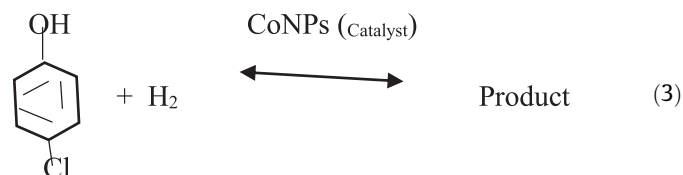
A Gas Chromatography Mass Spectrophotometer (5975C- USA) with triple axis detector and an auto injector (10 μ L syringe) which uses helium as carrier gas was used to analyze the raw water sample and the samples obtained from the hydroconversion reaction. All chromatographic separation experiments were conducted using a capillary column of dimensions: 30 m length, 0.2 μ m internal diameter and 250 μ m thickness, which was treated with phenyl methyl siloxane. The GC-MS ion source temperature was set at 250 $^{\circ}$ C, interface temperature = 300 $^{\circ}$ C, pressure = 16.2 psia, out time = 1.8 ms with 1 μ L split injector having a split ratio and injection temperature of 1:50 and 300 $^{\circ}$ C, respectively; the column temperature was initially kept at 35 $^{\circ}$ C for 5 mins, after which it was raised to 150 $^{\circ}$ C at a constant heating rate of 4 $^{\circ}$ C/min. Upon attaining 150 $^{\circ}$ C, the temperature of the column was further raised to 250 $^{\circ}$ C at a constant heating rate of 20 $^{\circ}$ C/min and maintained for 5 mins. The total elution was observed to last for about 47.5 min. Thereafter, the GCMS-solution software, supplied by the manufacturer was used for data acquisition. Identification of the compounds generated from the hydroconversion reaction was done using the NIST-library (NIST-L). Acid-base titration apparatus- burette, 25 mL pipette, conical flask, 75 mL glass funnel (J-Sil Borosilicate, India), a white tile and retort stand with metal clamps of dimension 8 \times 5 in., made of standard steel, were used to conduct experiments for the samples obtained from the HDC reaction and based on the reaction-stoichiometry, Eqs. (1) and (2) were used to estimate the residual/final concentration (g/L) of the 4-chlorophenol solution in the reaction given by eqn. (3).

$$C_A V_A / C_B V_B = N_A / N_B \quad (1)$$

$$\begin{aligned} \text{Concentration in g/dm}^3 &= \text{concentration in mol/dm}^3 \\ & * \text{molar mass} \end{aligned} \quad (2)$$

3.5. Heterogeneous catalysis

If the reaction between hydrogen and 4-CP is considered reversible and a first-order type, it then implies that the proposed reaction is as follows:



C_A = Concentration of acid, V_A = volume of acid, C_B = concentration of base, V_B = volume of base, N_A and N_B = number of moles of 4-chlorophenol and hydrogen, respectively.

3.5.1. Assumptions

Considering the steps involved in the reaction between 4-CP and hydrogen to give products, the following assumptions subsist: (i) mass transfer of the species (4-CP and hydrogen gas) from the bulk phase to the pore mouth of the catalyst (CoNPs) is very rapid. (ii) diffusion of the reactant from the pore mouth and through the pores of the CoNPs to the immediate vicinity of the catalyst's internal surface is very rapid. (iii) adsorption of 4-CP and hydrogen gas onto the internal walls of the catalyst's pores is slow. (iv) reaction of 4-CP and hydrogen gas on the internal surface of the catalyst is slow. (v) desorption of the products from the internal walls/surface of the CoNP-pores is slow. (vi) diffusion of the products from the interior of the CoNP-pellets to the pore mouth of the catalyst's outer surface is very fast. (vii) mass transport of products from the external surface of the CoNPs to the bulk mix (4-CP + H₂) is also very fast. (viii) the reactions defined by the mechanisms are elementary. Other assumptions include, the surface of the catalyst is uniform, the 2 M-CoNPs are of same size and the different products are seen to be formed together in one piece.

The above statements (i - vii) then imply that, steps i, ii, vi and vii are fast and do not have significant influence on the rate limiting step and this further suggests that one of steps (iii), (iv) and (v) is the rate controlling step. Hence, for each step, a mechanism can be developed for the catalytic hydroconversion of 4-CP to products.

3.5.2. Development of a mechanism for the 4-CP adsorption step



A, S and $A.S$ are the 4-chlorophenol, catalyst-site and the adsorbed 4-chlorophenol on the catalyst's active site

Rate law for the adsorption step:

$$-r_{AD} \propto C_S P_A \quad (2)$$

$$-r_{AD} \propto C_S P_A, \text{ then,} \quad (3)$$

$$-r_{AD} = k_A C_S P_A \quad (4)$$

$$\text{while } r_{-A} = k_{-A} C_{A.S} \quad (5)$$

hence, the net rate of 4-chlorophenol adsorption onto the CoNPs implies:

$$r_{Net} = k_A C_S P_A - k_{-A} C_{A.S} \quad (6)$$

To find a way of obtaining CAS, it is necessary to consider that equilibrium is attained, hence, at equilibrium,

$$-r_{Net} = 0, \text{ and } K_{eq} = k_A / k_{-A} \quad (7)$$

$$K_{eq} = \frac{k_A}{k_{-A}} = \frac{C_{A.S}}{C_S P_A} \quad (8)$$

Then the concentration of the adsorbed 4-CP can be estimated using the following equation:

$$C_{A.S} = K_{eq} C_S P_A \quad (9)$$

Since 4-CP is the only molecule adsorbed at the CoNP site, carrying out a site balance for the adsorption step implies:

$$C_t = C_{A,S} + C_S \quad (10)$$

Therefore,

$$C_S = C_t - C_{A,S} \quad (11)$$

Prior reaction, $C_t = 4 \text{ mg/L} + 0$; therefore, $C_t = 4 \text{ mg/L}$

Considering (11), (6) now becomes:

$$r_{Net} = k_A P_A (C_t - C_{A,S}) - k_{-A} C_{A,S} \quad (12)$$

And (9) becomes:

$$C_{A,S} = K_{eq} P_A (C_t - C_{A,S}) \quad (13)$$

Eq. (13) can be rewritten as:

$$C_{A,S} = K_{eq} P_A (C_t - C_{A,S}) \quad (14)$$

$$C_{A,S} = K_{eq} P_A C_t - K_{eq} P_A C_{A,S} \quad (15)$$

$$C_{A,S} + K_{eq} P_A C_{A,S} = K_{eq} P_A C_t \quad (16)$$

Thus, dividing through (16) by $C_{A,S} K_{eq} C_t$ gives:

$$\frac{1}{K_{eq} C_t} + \frac{P_A}{C_t} = \frac{P_A}{C_{A,S}} \quad (17)$$

Eq. (17) is the Langmuir isotherm model for the adsorption of 4-CP onto CoNP-catalyst.

A plot of $\frac{P_A}{C_{A,S}}$ vs P_A gives $\frac{1}{C_t}$ as slope and $\frac{1}{K_{eq} C_t}$ as intercept.

$C_t = 0.4 \text{ mg/L}$ (1.1 M) of 4-CP (total initial concentration of 4-CP prior adsorption)

Sample-data for the estimated adsorption parameters are discussed in a later section:

3.5.3. Development of a mechanism for the 4-CP + H₂ surface reaction step

Now, considering the surface reaction step and adopting the Eley Rideal single-site mechanism, the stoichiometric equation for the reaction is given as (18)



A.S, B and C are the adsorbed 4-chlorophenol on the catalyst's active site, hydrogen gas and the product of reaction at the catalyst's surface.

For the adsorption step,

$$-r_{A,S} = k_A C_B C_{A,S}, \text{ also, for the reaction step,} \quad (19)$$

$$r_{A,S} = k_{-A} C_{C,S} \quad (20)$$

∴ The net rate implies:

$$-r_{Net} = k_A C_B C_{A,S} - k_{-A} C_{C,S} \quad (21)$$

At equilibrium,

$$-r_{Net} = 0, \text{ then, } k_A C_B C_{A,S} = k_{-A} C_{C,S} \quad (22)$$

Which gives:

$$k_{eq} = \frac{C_{C,S}}{C_B C_{A,S}} \quad (23)$$

And

$$C_{C,S} = K_{eq} C_B C_{A,S} \quad (24)$$

Since 4-CP and H₂ are adsorbed on a site, conducting a site balance for the reaction step, gives:

$$C_t = C_S + C_{A,S} + C_B \quad (25)$$

$$C_t - C_S - C_B = C_{A,S} \quad (26)$$

At equilibrium,

$C_S = C_{A,S}$, thus,

$$C_t = C_B + 2C_{A,S} \quad (27)$$

But,

$$C_B = C_t - 2C_{A,S} \quad (28)$$

$$C_{C,S} = \frac{K_{eq} C_B C_{A,S}}{C_t - 2C_{A,S}} \quad (29)$$

Note: $C_{A,S} = C_{C,S}$, thus, dividing through (29) by $K_{eq} C_B$ gives:

$$C_t - 2C_{A,S} = K_{eq} C_B \quad (30)$$

$$C_{A,S} = \frac{1}{2} C_t - \frac{1}{2} K_{eq} C_B \quad (31)$$

So, a plot of $C_{A,S}$ vs C_B gives $\frac{1}{2} K_{eq}$ as slope and $\frac{1}{2} C_t$ as intercept.

From experience, three parameters $C_{A,S}$ and C_B can be estimated by knowing the amount of 4-CP left after adsorption from titration and experimental data

3.5.4. Development of a mechanism for the product desorption step



$$R_{D,C,S} = k_D C_{C,S} \quad (32)$$

$$R_{-D} = k_{-D} P_C C_S \quad (33)$$

$R_{D,A,S}$ = rate of desorption of A on site S, k_D = desorption rate constant, $C_{C,S}$ = concentration of product formed from 4-CP at the desorption step, S = Catalyst site on internal pore-wall, P_C = pressure of desorbed product on a site of the 2 M-CoNPs, while R_{-D} = rate of formation of C (product) at site S, k_{-D} = formation rate-constant, C_C = concentration of Product (C) transported to the pore mouth and external surface of the CoNPs.

Therefore, the net rate of desorption implies:

$$R_{D,Net} = k_D C_{C,S} - k_{-D} P_C C_S \quad (34)$$

At equilibrium, $R_{D,Net} = 0$, then,

$$k_{-D} P_C C_S = k_D C_{C,S} \text{ then,} \quad (35)$$

$$\frac{k_D}{k_{-D}} = \frac{C_{C,S}}{P_C C_S} \quad (36)$$

Since

$$\frac{k_D}{k_{-D}} = k_{eqd} \quad (37)$$

It then implies,

$$C_{C,S} = k_{eqd} P_C C_S \quad (38)$$

For the site balance,

$$C_t = C_{C,S} + C_S + C_{A,S} \quad (39)$$

$$C_S = C_t - C_{C,S} - C_{A,S} \quad (40)$$

Then (38) becomes,

$$C_{C,S} = k_{eqd} P_C (C_t - C_{C,S} - C_{A,S}) \quad (41)$$

Dividing through (41) by $k_{eqd} C_{C,S}$, and assuming the concentration of $C_{A,S}$ at the desorption site = 0 then,

$$\frac{1}{K_{eqd}} + P_C = \frac{C_t P_C}{C_{C,S}} \quad (42)$$

At equilibrium, $P_C = P_A$

Then a plot of $P_C/C_{C,S}$ vs P_C gives $1/C_t$ as slope and $1/k_{eqd}C_t$ as intercept.

To determine the conversion of 4-chlorophenol, the surface concentration was used as depicted in (43):

$$C_{A,S} = \frac{C_{AO}(1 - X_A)}{(1 + \varepsilon_A X_A)} \quad (43)$$

$$\varepsilon_A = y_{AO} \frac{\Delta n}{a} \quad (44)$$

Since the system may experience expansion as a result of hydrogen gas intrusion, and the system is heterogeneous, a variable volume process was considered which led to the estimation of the expansion factor.

$C_{A,S}$ = concentration of 4-chlorophenol remaining at the surface, C_{AO} = initial concentration of 4-chlorophenol, ε_A = expansion factor, X_A = amount of 4-chlorophenol converted (can also be in %), y_{AO} = mole fraction of 4-chlorophenol from stoichiometry, while Δn = difference in number of moles of products and reactants (i.e. $n_p - n_r$ where n_p and n_r are moles of reactants and products respectively) and a = the stoichiometric coefficient of 4-chlorophenol.

4. Results and discussion

4.1. SEM-EDX details of the polydisperse CoNPs

Figs. 2a-d are the SEM images of the nanoparticles synthesized from the 0.5–2 M concentration cobalt-precursor. It can be seen

that for higher concentrations of the precursor, the particles appear finer, hence the smoothest fines are the 2 M PD-CoNPs (Fig. 2d).

EDX results in Figs. 3a-d are all illustrative of the percentage composition by weight of cobalt in the synthesized nanoparticles. The percentage composition by weight of cobalt is highest (i.e., 92.54%) for the 2 M CoNPs whereas, it is 84.56, 92.31 and 85.14% for the 0.5, 1 and 1.5 M CoNPs, respectively. These results are also supported by the results contained in Tables 1-4. Based on the precursor and process route, the elements contained in the CoNPs are Co, Ni, Si, Ag, Fe, Ti, Cr, Ca, V, Mn, K, Nb, Y, Mo, Na, Al, P, Mg and S.

Also, in Tables 1-4, it is obvious that all the nanoparticles are made up of the same types of elements but different elemental distributions/compositions with the 2 M CoNPs having the highest weight concentration of 92.54% cobalt.

4.2. Nanosizing of the polydisperse cobalt nanoparticles

Figs. 4a-d are illustrations of the particle size distribution of the nanoparticles in d.nm; the average particle sizes are in the range of 140–600, 40–1010, 150–160 and 150–500 d.nm for the 0.5–2 M CoNPs, respectively.

4.3. GCMS-spectra of the samples withdrawn from the HDC reaction

i. GCMS for the wastewater sample

Identification of the compounds of the waste water sample and those generated during the hydroconversion reaction was done by comparing the different spectra obtained with standard mass spectra data from NIST-library (NIST-L). Fig. 5 is an illustration of the compounds present in the wastewater-sample. The compounds

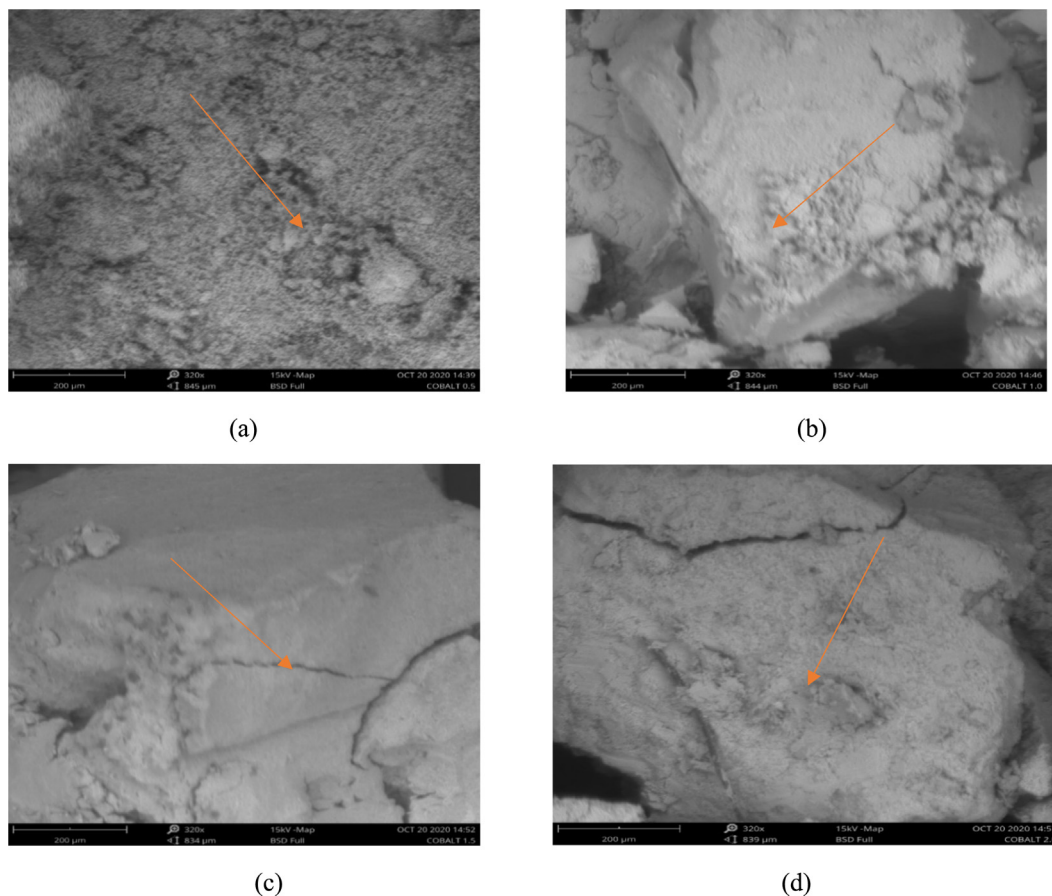


Fig. 2. SEM images of cobalt nanoparticles obtained from the: (a) 0.5 M (b) 1 M (c) 1.5 M (d) 2 M cobalt-precursors.

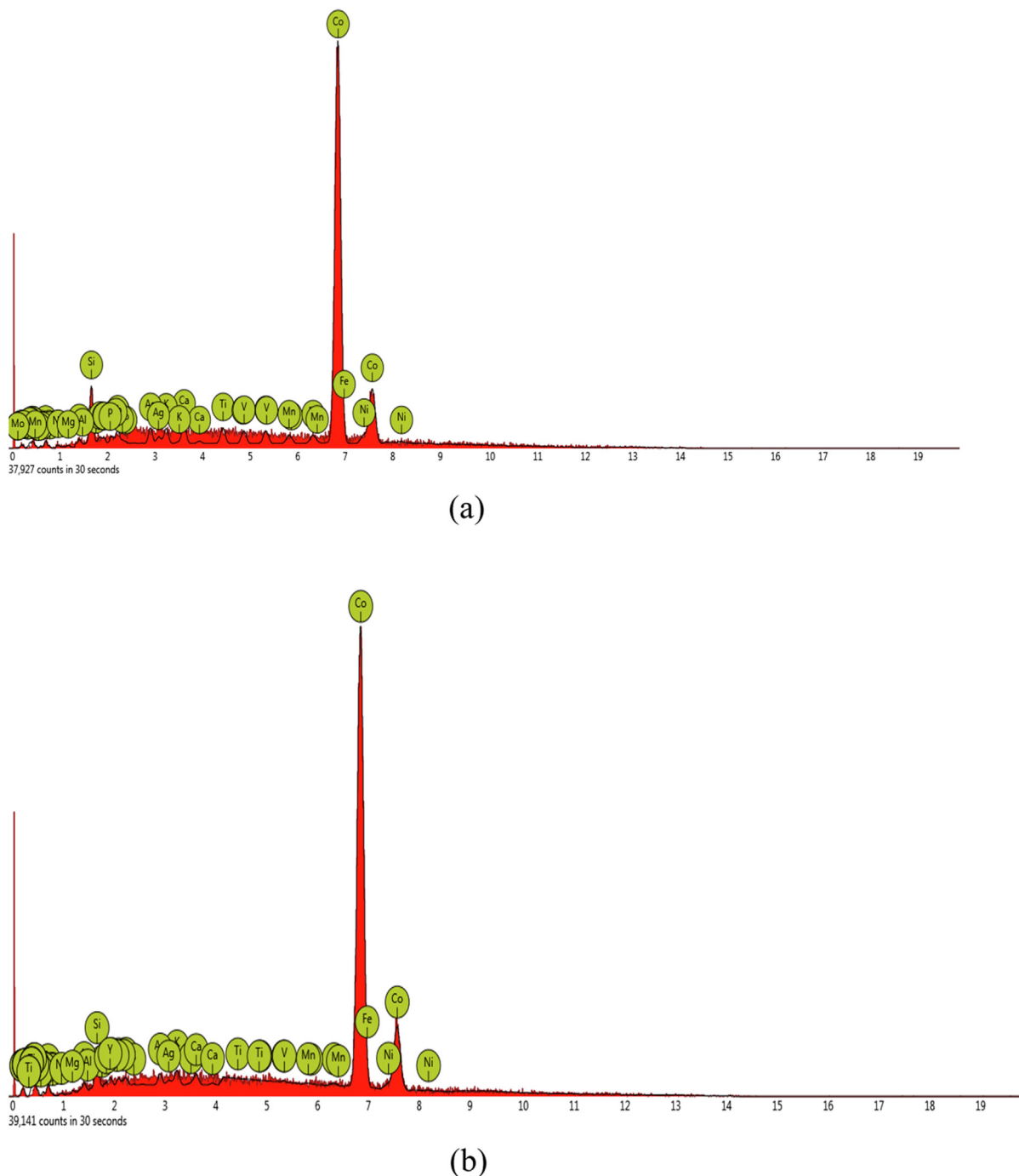


Fig. 3. EDX spectra of the: (a) 0.5 M CoNPs, (b) 1 M CoNPs, (c) 1.5 M CoNPs and (d) 2 M CoNPs.

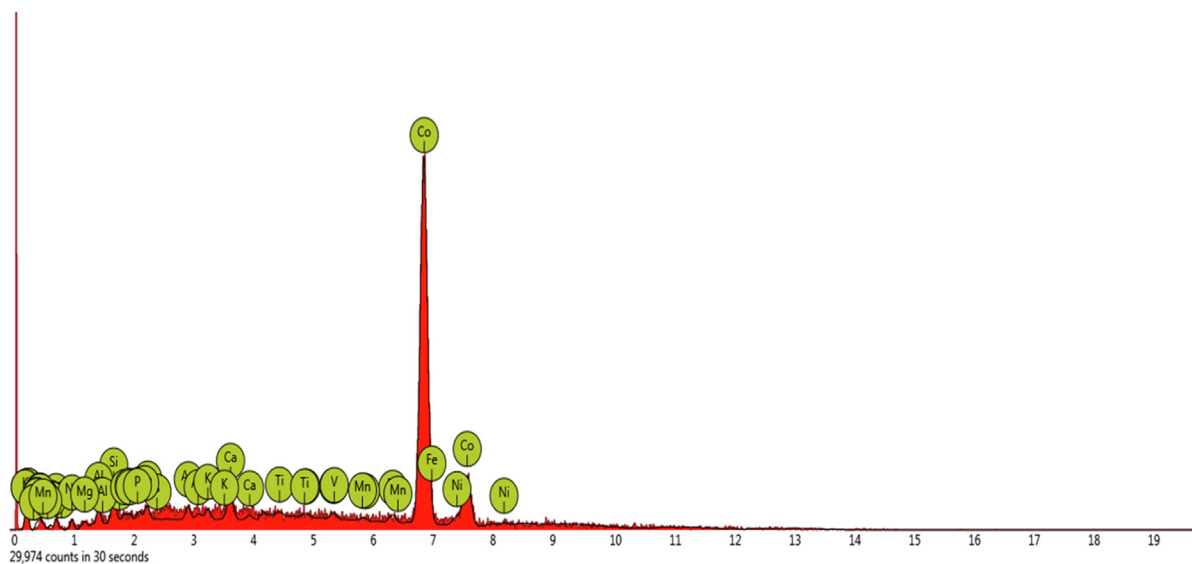
detected in the water-sample include phenol, 2-chlorophenol and 4-chlorophenol.

(ii) GCMS spectra for the products of the HDC reaction

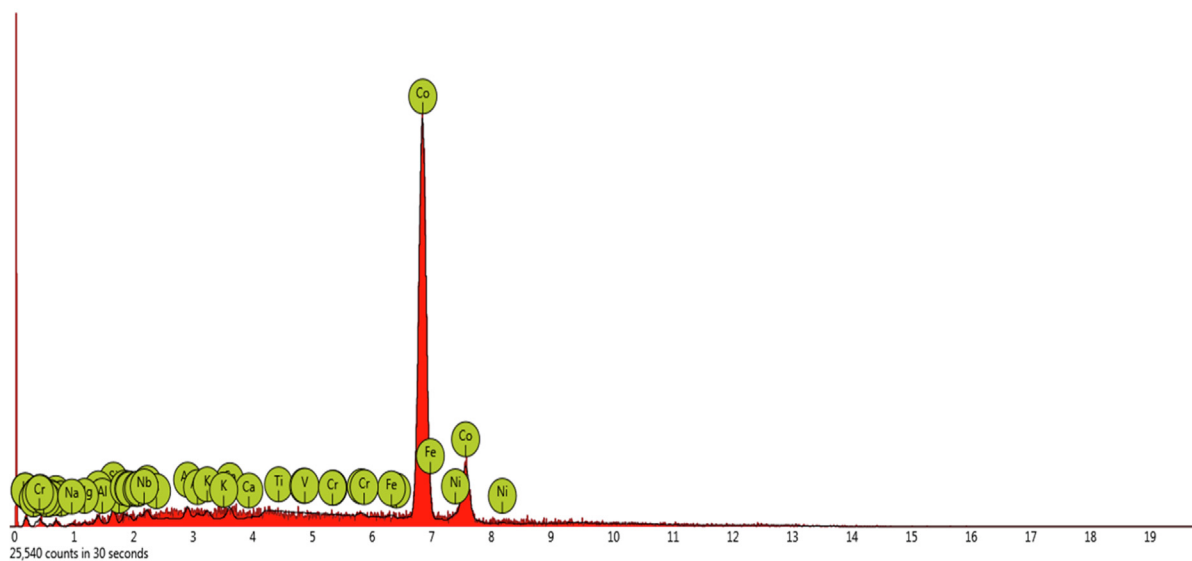
The performance of the synthesized catalysts, were determined in terms of measurable parameters such as pH, concentration, particle/catalyst-size and reaction time. Several products of phenolic and nonphenolic status were obtained and are illustrated as observed from the GC–MS results (see Figs. 6-9 and Tables 5 and 6).

For the reaction involving no catalyst (i.e., the control reaction), the resulting samples recovered from the reactor for a period of 60 mins revealed no feasible change in the sample-composition (4-chlorophenol composition) i.e., there was no inherent dechlorination within the period (1 h) for which the system was monitored,

however, for the next round of 60 mins, product formation ensued as justified by the results from GCMS Table 5, where the results of compounds formed from the HDC-reaction can be seen within 2 h of retention time as observed from GCMS. Because product formation ensued at nearly 2 h of reaction time, this then prompted the need for the inclusion of a catalyst. Based on the volcano curve, in order to ensure good catalyst activity and selectivity for prospective reactions as discussed in Sanni et al. (2020), cobalt was selected as a potential catalyst for the system owing to its high catalyst competence (as compared to Au, Ni, Fe and Cu), its existence as a transition metal and the group to which it belongs in the periodic table of elements. The cobalt nanoparticles showed great activity and selectivity for chlorine during the HDC reaction; see



(c)



(d)

Fig. 3 (continued)

Figs. 6-9 a and b for the peaks of the compounds identified at different retention times. Tables 5 and 6 and Fig. 8 a and b give the data obtained for the HDC reaction without any catalyst and those catalyzed by the 2 M CoNPs, respectively, because, from the results of the HDC- reaction, the 2 M-catalyst gave the best results. Also, the supplementary file (Tables A.1-A.5) contains the range of feasible products obtained from the hydroconversion reaction for the 0.5–1.5 M CoNPs. Generally, the products of the reaction catalyzed by less than 2 M CoNPs were less than those obtained for the 2 M CoNPs. However, a variety of products were obtained for the the 2 M CoNPs which gave the best performance owing to the range of products obtained and the final pH of the solution at the completion of the reaction.

Figs. 9 a and b are the GCMS-spectra showing the peak-absorbances of the products obtained at different retention times

i.e., 20 and 50 mins respectively. Furthermore, the synthesized cobalt catalysts (0.5–2 M catalysts) enhanced the hydroconversion process based on the evidential products of decomposition documented in Table 5 for the reaction involving no catalyst, while the 0.5–2 M CoNPs gave a wider product variation (Table 6). Based on the study carried out by Calvo et al. (2009) using Pd-Activated carbon catalyst and hydrogen from formic acid, phenol and cyclohexanone were detected as products in the effluent, whereas, based on the results obtained from this study, for the catalyst with the best performance (i.e., the 2 M CoNP-catalyst), the most predominant product is 3,5-bis-trifluoromethylphenyl] 2,3',5'-tris-trifluoro-methyl biphenyl-4-yl] methanone as indicated in Fig. 2a with an abundance of 8×10^8 and a peak value of 33.814 which was detected within 33.3 mins of retention time (Table 6), whereas, the least abundant component is 5-chloro-15-formyl-2,

Table 1
EDX mapping /elemental composition of the 0.5 M CoNPs.

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
27	Co	Cobalt	81.75	84.56
28	Ni	Nickel	2.07	2.14
14	Si	Silicon	4.14	2.04
47	Ag	Silver	0.84	1.58
26	Fe	Iron	1.43	1.40
22	Ti	Titanium	1.42	1.19
24	Cr	Chromium	1.12	1.02
20	Ca	Calcium	1.39	0.98
23	V	Vanadium	1.05	0.93
25	Mn	Manganese	0.84	0.81
19	K	Potassium	1.09	0.75
41	Nb	Niobium	0.45	0.73
39	Y	Yttrium	0.36	0.55
42	Mo	Molybdenum	0.29	0.49
11	Na	Sodium	0.61	0.24
13	Al	Aluminium	0.50	0.24
15	P	Phosphorus	0.23	0.12
12	Mg	Magnesium	0.28	0.12
16	S	Sulfur	0.17	0.10

Table 2
EDX mapping /elemental composition of the 1 M CoNPs.

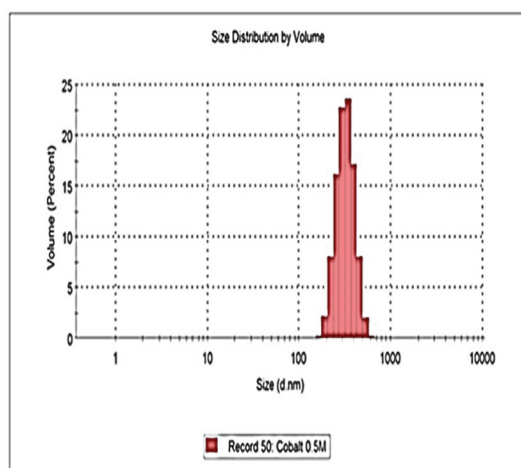
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
27	Co	Cobalt	90.10	92.31
28	Ni	Nickel	1.32	1.35
14	Si	Silicon	2.52	1.23
47	Ag	Silver	0.57	1.07
41	Nb	Niobium	0.47	0.76
19	K	Potassium	0.94	0.64
20	Ca	Calcium	0.74	0.52
26	Fe	Iron	0.45	0.43
13	Al	Aluminium	0.77	0.36
39	Y	Yttrium	0.21	0.33
16	S	Sulfur	0.44	0.25
11	Na	Sodium	0.61	0.24
15	P	Phosphorus	0.32	0.17
12	Mg	Magnesium	0.30	0.13
25	Mn	Manganese	0.12	0.11
24	Cr	Chromium	0.12	0.11
23	V	Vanadium	0.00	0.00
22	Ti	Titanium	0.00	0.00

Table 3
EDX mapping /elemental composition of the 1.5 M CoNPs.

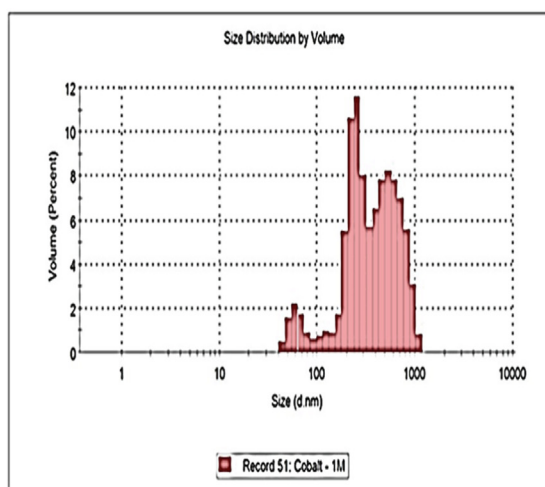
Element Number	Element Symbol	Element Name	Atomic Conc. (%)	Weight Conc.(%)
27	Co	Cobalt	80.60	85.14
28	Ni	Nickel	2.24	2.36
20	Ca	Calcium	2.46	1.77
47	Ag	Silver	0.77	1.50
11	Na	Sodium	3.17	1.31
26	Fe	Iron	1.30	1.30
14	Si	Silicon	2.19	1.10
41	Nb	Niobium	0.54	0.89
13	Al	Aluminium	1.81	0.88
24	Cr	Chromium	0.64	0.60
39	Y	Yttrium	0.35	0.56
16	S	Sulfur	0.92	0.53
19	K	Potassium	0.73	0.51
12	Mg	Magnesium	0.88	0.38
23	V	Vanadium	0.41	0.37
25	Mn	Manganese	0.35	0.34
22	Ti	Titanium	0.37	0.31
15	P	Phosphorus	0.27	0.15

Table 4
EDX mapping /elemental composition of the 2 M PD-CoNPs.

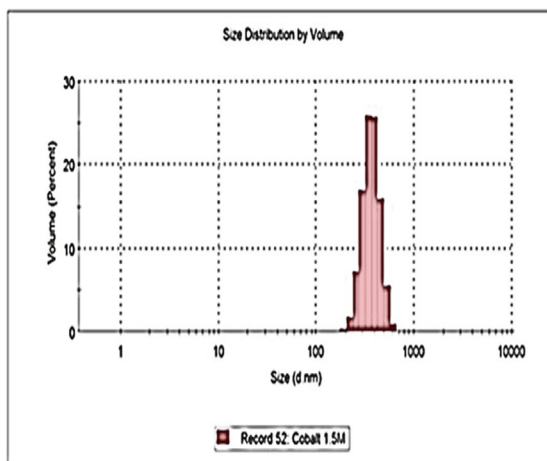
Element Number	Element Symbol	Element Name	Atomic Conc. (%)	Weight Conc.(%)
27	Co	Cobalt	90.78	92.54
28	Ni	Nickel	1.40	1.43
47	Ag	Silver	0.70	1.30
14	Si	Silicon	1.33	0.65
39	Y	Yttrium	0.42	0.65
20	Ca	Calcium	0.91	0.63
13	Al	Aluminium	0.91	0.43
41	Nb	Niobium	0.25	0.40
19	K	Potassium	0.53	0.36
16	S	Sulfur	0.64	0.35
26	Fe	Iron	0.36	0.35
25	Mn	Manganese	0.34	0.32
11	Na	Sodium	0.78	0.31
12	Mg	Magnesium	0.47	0.20
15	P	Phosphorus	0.19	0.10
22	Ti	Titanium	0.00	0.00
23	V	Vanadium	0.00	0.00
24	Cr	Chromium	0.00	0.00



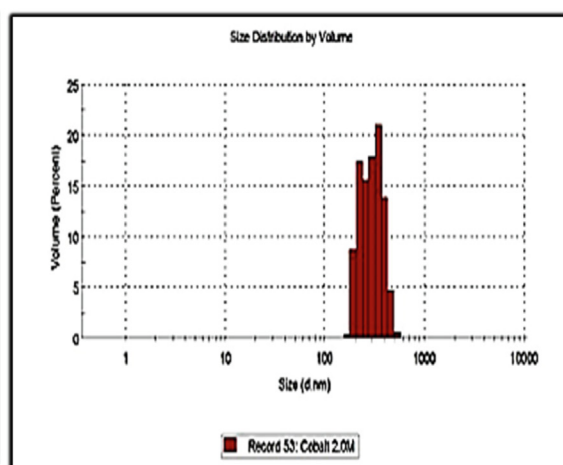
(a)



(b)



(c)



(d)

Fig. 4. Size distribution of cobalt nanoparticles (a) 0.5 M (b) 1 M (c) 1.5 M (d) 2 M.

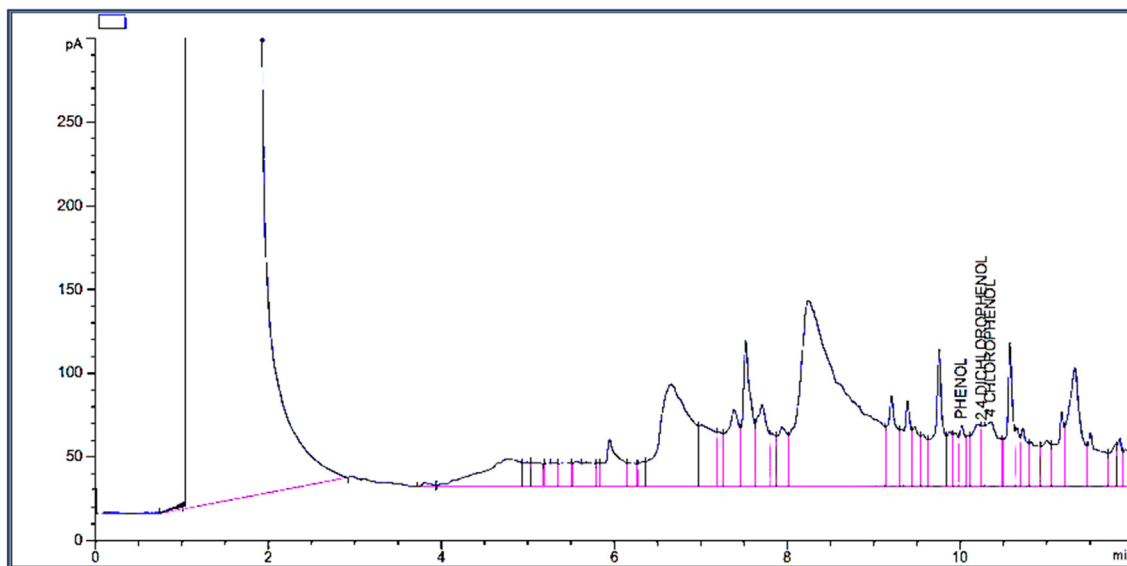


Fig. 5. Absorbance-time profile of the constituents of 4-chlorophenol in the raw wastewater sample.

3,7,8,12,13,17,18-octaethyl 21H, 23H porphine (Table 6) with an abundance of 5.25×10^8 which was identified within a retention time of 16.308 mins (Fig. 2b).

4.4. Hydrogen generation for the hydroconversion reaction

Fig. 10 gives an illustration of the time-volume variation of the hydrogen gas produced during alcoholysis of NaBH_4 . For 0.3 g of the borohydride combined with 30 mL of methanol at room temperature and pressure, the highest volume of hydrogen produced was 1110 mL. The reaction is exothermic, and hydrogen formation was rapid within the first 353 secs, which corresponds to a hydrogen volume of 1000 mL. Beyond 400 secs, hydrogen evolution dropped with only about 110 mL added to the previous value at 1260 secs. This implies that the bulk volume of hydrogen was received within 353 s of alcoholysis of the borohydride, hence, the reaction can be described as though fast, with the bulk volume of the inherent hydrogen in the borohydride recovered within the first 6 mins of the HDC-reaction.

4.5. Effect of catalyst and catalyst concentration on the reaction

(i) 4-Chlorophenol conversion with and without catalyst

The initial and subsequent concentrations of the reaction medium were determined via titration of the samples with a known concentration of acid (HCl) owing to the fact that the medium's pH was in the alkaline range for all samples. The reaction time was from 0 to 60 mins at 10 mins interval. Fig. 10 shows the variation in concentration of the 4-chlorophenol mixture with time for the reactions without any catalyst and those involving the 0.5–2 M CoNPs. For the reaction system where no catalyst was used, there was no variation in pH of the system even when hydrogen was continuously delivered to the reaction vessel. The reaction without catalyst was further allowed to last beyond 1 h in order to see the time when reaction was incipient; this was observed to be after 1 h 35 mins where the pH of the solution began to vary while the solution's concentration reduced as the HDC reaction was in progress, thus indicating the decomposition of the contaminant (4-Chlorophenol). A spike in concentration variation was noticed in the reaction after 50 mins which revealed the presence of a new compound as a result of the hydroconversion process. The concentration of the new compound also reduced as the reaction pro-

gressed; the reaction was stopped as soon as the 2 h-mark was reached. The pH values of the generated samples were measured using a pH meter, and acid-base titrations (see data in Tables A.6–A.12) were performed on the withdrawn samples so as to determine their effective concentrations. See Tables 7 and 8 for the measured pHs of the withdrawn samples from the reaction vessel. The results are in accordance with the findings of Baeza et al. (2012) and Hirai and Yakura (2001), where there was no noticeable hydroconversion of 4-chlorophenol for situations without any catalyst, however, in their work, the reaction was not left for appreciable period of time to ascertain how long it took for reaction to occur when no catalyst was used. Even at higher doses of PVP, no noticeable reaction occurred but at increased catalyst concentrations, though the HDC-reaction occurred, however, no significant variations in reaction rates were observed in terms of the Pd catalysts per unit mass used, whereas, in the present study, catalyst concentration of the cobalt catalyst had significant influence on the conversion of the 4-chlorophenol, whereas, in terms of the pH of the media, the differences/variations (i.e. 11.7–12.3) were small for other situations except for the medium with the 2 M CoNps (9.5).

(ii) Effect of Catalyst Concentration

The synthesized cobalt nanoparticles of 0.5–2 M concentrations were used in the HDC reaction and the 4-chlorophenol concentration was monitored alongside the products of the decomposition process in order to ascertain the most effective CoNPs for the hydroconversion reaction. As shown in Fig. 11, after 1 h, it is obvious that the HDC-reaction system catalyzed with the 2 M CoNps gave the lowest concentration at 10 and 60 mins of reaction time, thus indicating the most significant alteration in the mixture concentration with evidential decomposition of 4-chlorophenol. Hence, in terms of the residual concentration of the 4-chlorophenol solution, the order of performance of the catalysts is: 2 M > 1 > 0.5 M > 1.5 M > NC, thus indicating that the best catalyst for the HDC-reaction is that comprising of the 2 M CoNPs. The particle size of the 0.5 M CoNP and Co distribution are responsible for it outperforming the 1.5 M CoNPs. The CoNPs with the highest particle composition are the 2 and 1 M CoNPs, hence, the reason for their higher activity. Although, the 1.5 M CoNPs had slightly higher Co content than the 0.5 CoNPs, the lower performance of the former is due to its lesser active sites caused by the higher percentage of impurities that have the tendency of reducing the activity of

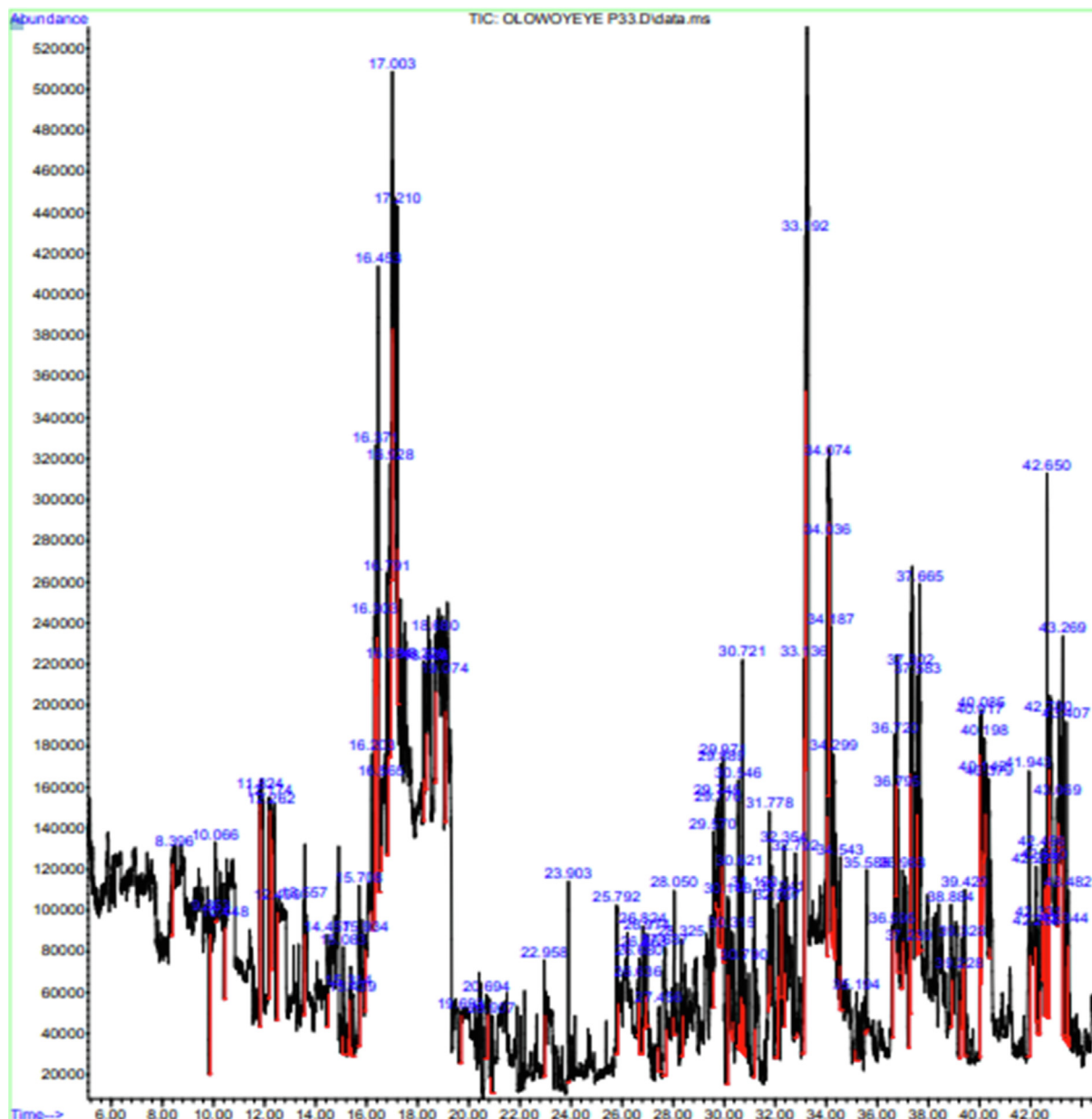


Fig. 6. Product-spectra of absorbance-time variation of 4-chlorophenol decomposition aided by 0.5 M CoNPs.

cobalt in the HDC-reaction. Furthermore, HDC has been reported to be hindered by the presence of 4-chlorophenoxyacetic acid or 4-chlorobenzoic acid, which may be formed as intermediate products during 4-chlorophenol conversion, hence, the existence of carboxylic acid groups can serve as poison to the CoNPs as was the case with the Pd particles adopted for the HDC of 4-chloroanisole which was found to significantly drop as a result of the inclusion of 4-fluorobenzoic acid and citric acid (Ding et al., 2018). Also, De Pedro et al. (De Pedro et al., 2011) reported the possibility of catalyst poisoning by the displaced chlorine from 4-chlorophenol during HDC; this may also have occurred earlier for the 0.5–1.5 M CoNPs.

4.6. The Effect of pH on the reaction system

The pH values of the withdrawn sample-solutions measured by the Hanna 211 pH meter, are given in Table 7. Comparing the results of the synthesized nanoparticles in the HDC reaction, it is

evident that the 2 M CoNPs gave the lowest pH relative to the other cobalt nanoparticles (i.e., the 0.5–1.5 M CoNPs). The observed HDC-system pHs of the reaction mixture, are in the order of $2\text{ M} > 1.5\text{ M} > 1\text{ M}/0.5\text{ M}$; these values are not in direct accordance with the trend observed in terms of the decreasing order of performance in terms of concentration. Hence, at higher concentrations of the CoNPs, the pH of the hydroconverted 4-chlorophenol solution becomes lower i.e., the pH of the residual solution is inversely proportional to the nanoparticle concentration used in the HDC reaction. The final solution concentration, pH, reaction time and the products formed within the duration of the HDC reaction, are all factors that influenced the performance of each catalyst in the HDC-reactions. The results in Table 7 show the order of reduction in pH of the initial solution; the cobalt nanoparticle-concentrations performance in terms of pH reduction is in the following order: $2\text{ M} > 1\text{ M}/0.5\text{ M} > 1.5\text{ M}$. The number of products formed from the HDC reaction, as influenced by catalyst concentration, was also seen to follow the same order and trend. However, the best results

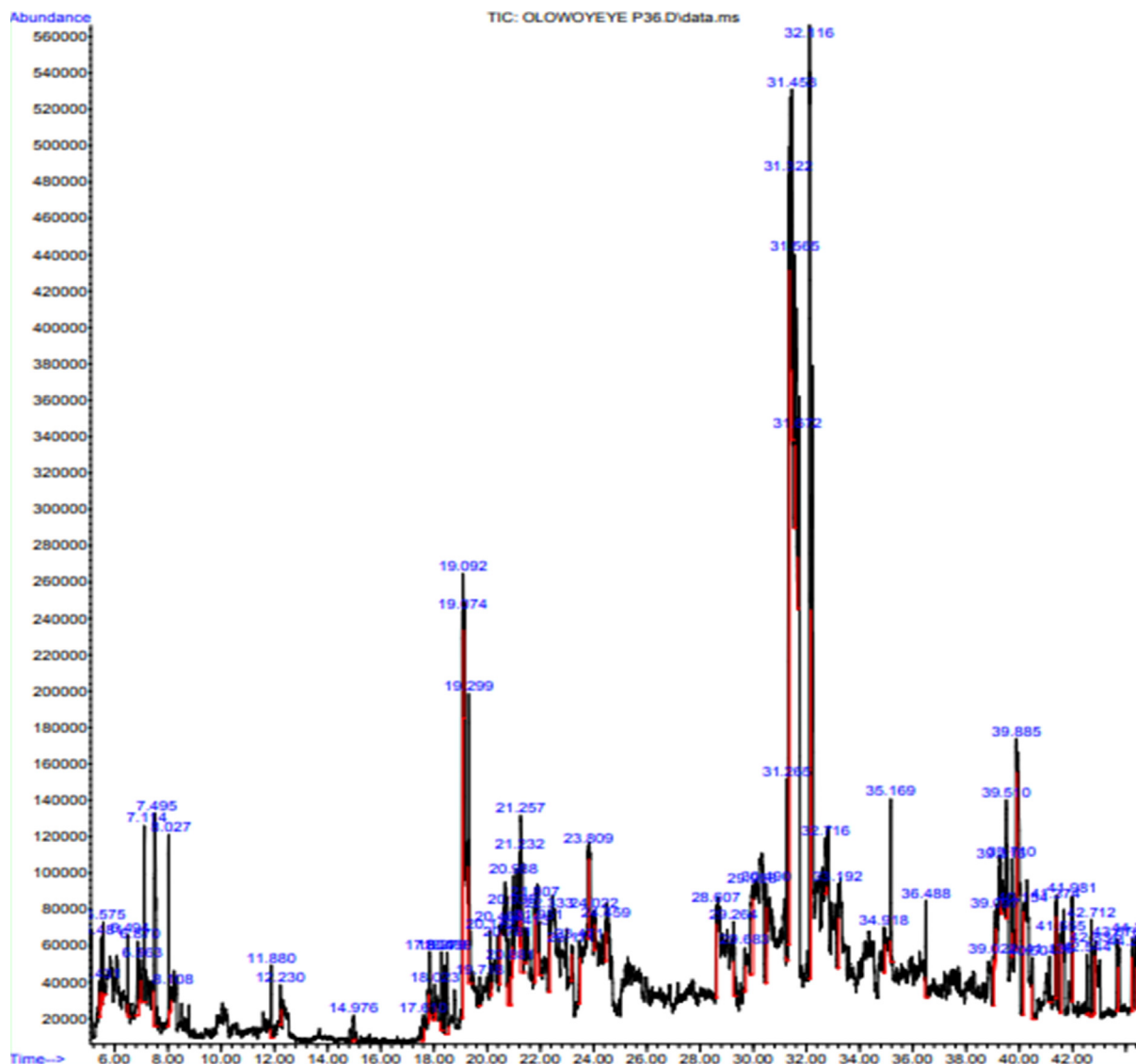


Fig. 8. Product-spectra of absorbance-time variation of 4-chlorophenol decomposition aided by 1.5 M CoNPs.

that can influence reaction rate is particle/catalyst size which is a measure of its surface area.

The sizes of nanoparticles can influence the nature/strength of interactions that exist between 4-CP and the catalyst-surface, since it determines the number of entities/particles that surround the surface of each metal atom. Also, the coordination of surface atoms has also been reported to be dependent on particle size. This then implies that smaller particles contain more surface atoms which are resident on the edges/junctions of crystallographic planes, which subsequently increase the number of active sites on the catalyst that are accessible to the 4-chlorophenol molecules (Stakheev et al., 2010). Also, literature has shown that large ensembles or single atoms may be deemed the most favourable catalyst-sites for HDC-reactions (Karpinski et al., 1996; Thompson et al., 2000; www.chemicalbook.com).

4.8. Heterogeneous catalysis

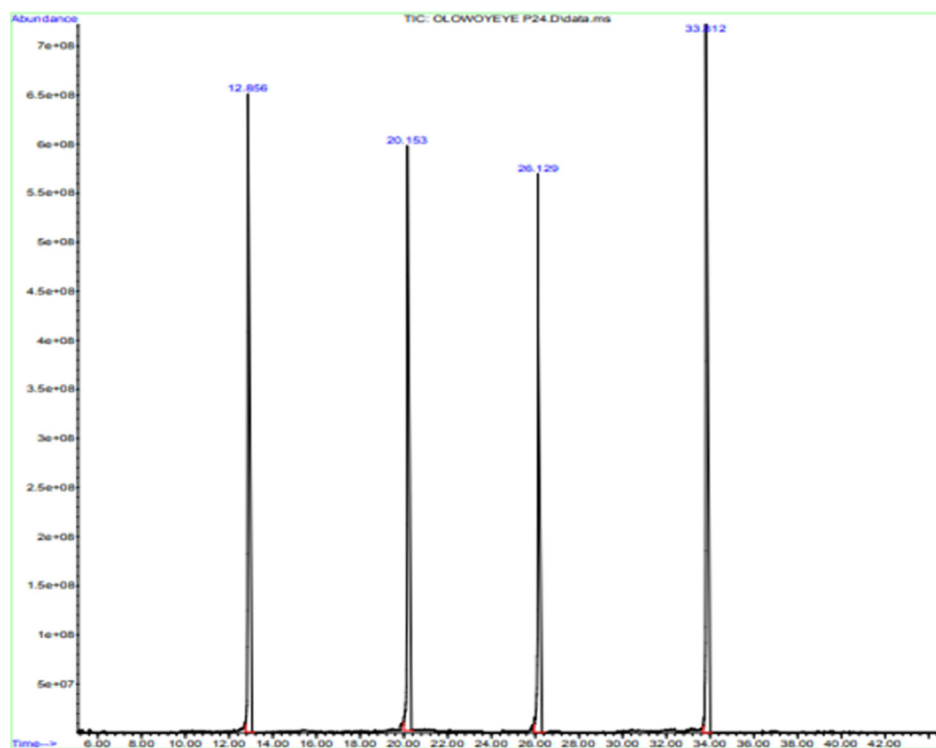
Table 10 shows the data obtained for the different kinetic parameters during the 2 M-CoNP hydrocatalytic conversion of 4-CP.

4.9. Adsorption, surface reaction and desorption kinetics

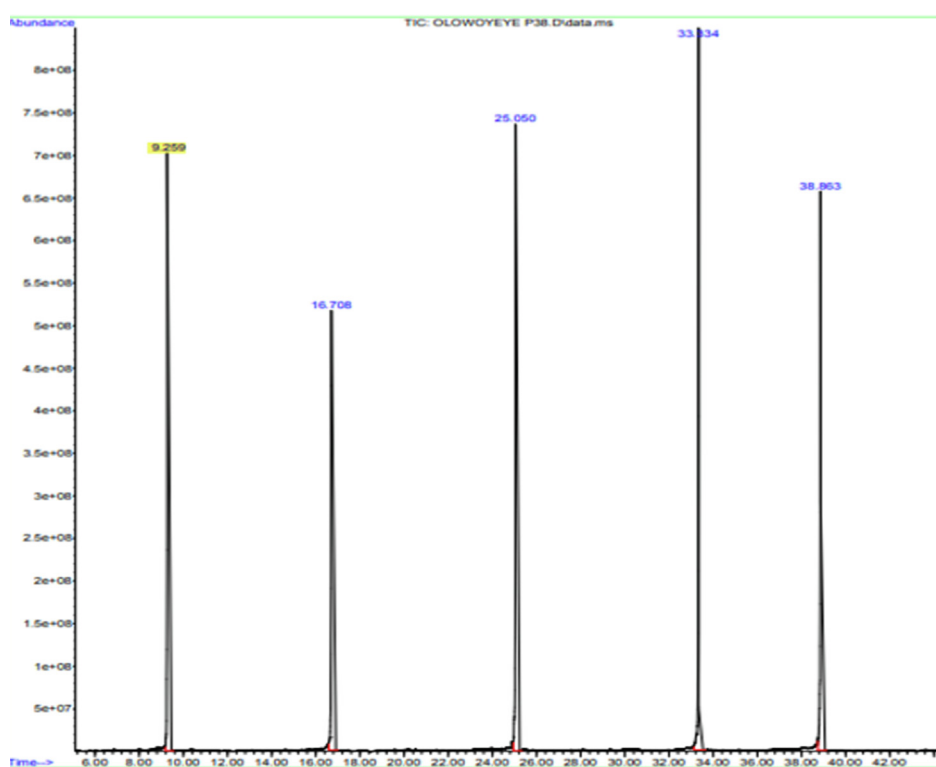
The concentration, pressure and rate-time data for the hydrocatalytic conversion of 4-CP is as illustrated in Fig. 12. The concentration of 4-CP dropped with time for the first 30 mins, after which product formation began (as indicated by the small rise in the curve to a maximum at 40 mins), thus defining an a rise in concentration of (0.12 mol/g.cat), where product formation was already in view. The concentration of the mixture dropped at the 50th min, after which it gained a consistent rise, thus indicative of the formation of more products. The rate is proportional to time, and concentration of 4-CP at the catalyst surface up to the 50th minute where the reaction rate begins to drop at increased time. This may be due to the fact that product formation is highly favoured at this time thus lowering the concentration of 4-CP at the external surface of the CoNP pore-mouth.

4.9.1. Adsorption mechanism

Considering the adsorption step, the plot- in Fig. 13a was obtained. In Fig. 13a, since the slope is $1/C_t$, then $C_t = 1/25.903 = 0.04$ mol/g.cat which was actually the total concentration of the



(a)



(b)

Fig. 9. Products of 4-chlorophenol decomposition aided by 2 M CoNPs after (a) 30 mins (b) 50 mins.

Table 5
Hydroconversion data without any catalyst at 120 mins of retention time from GCMS.

S/N	Retention Time (mins)	Area %	Compounds formed	Applications
1	8.052	21.69	(i) Pregnane-20-one, (ii) 3,11,17,21-tris [trim ethylsilyl(oxy)]- O-(phenylmethyl) oxime, 3 α , 5 β -, (iii) 11 β 5-chloro-15- formyl-2,3,7,8,12,13,17, 18 octaethyl-21H, 23H-porphine, (iv) 1H-isoinol-1-one, 3,3'-[2,5 dichloro-1,4-phenylenediamine]	(i) For the Mediation of the development/ expression of schizophrenia spectral disorders (ii) Stereospecific production of ajuquarin-IV (an insecticide (Kende et al., 1982). and microwave-assisted synthesis of 2-hydroxy-1-phenylethanone (Gennaro et al., 2010). (iii) A phosphorescent dye used for high-energy transfer efficiency (i.e., $\leq 90\%$) from singlet ariel and triplet states, in a host material doped with the phosphorescent dye (Yong et al., 2012). (iv) 2,5 dichloro-1,4-phenylenediamine is a biochemical substance that is used for carrying out proteomics-research
2	12.877	29.36	4-methoxy-2,2',3,4', 5 pentabromo diphenyl ether, (2,3,4 tribromo-6-methoxy phenyl), (2,4 dibromo phenol), ether mytiloxanthinone	Although somewhat toxic, pentabromodiphenyl ether whose other name is pentabromodiphenyl oxide belongs to the group of polybrominated diphenyl ethers; it is a brominated flame retardant.
3	17.263	23.61	1,3,4- metheno-perhydrocyclobuta [c,d] pentalene 2-pentanoic acid, 1,1a,3,3a, 4,5,5a,5b-nonachlor-2-hydroxy, gamma-, oxo- ethyl ester, Carbonic acid, monoamide N-(2,2,2) trichloroethoxycarbonyl, N-(5-chloro-2-methoxyphenyl), 2,2,2-trichloroethyl ester	A metabolite produced synthesized by C-Clostridium butyricum during the fermentation of carbohydrates (Butel et al., 1995). Also known as monohydrokelevan with no known use Carbonic acid is a dibasic acid which often refers to the aqueous solutions of carbon dioxide. It plays a pertinent role in the formation of bicarbonate buffer systems which help to regulate/control acid-base homeostasis. The 2,2,2-Trichloroethoxycarbonyl (Troc) group serves as a protective group for amines when they are organically synthesized.
4	26.752	25.34	Palladium II, diacetato [1,2-bis(dicyclohexyl phosphino) ethane], xanthene, 4,5- bis-(diphenyl phosphino) 9,9-dimethyl copper phtalocyanine	-The chlorinated form, i.e., 1,2 Bis(dicyclohexylphosphino)ethane] palladium(II) chloride aids easy, quick and efficient isolation and purification of cells, DNA, RNA, Antibodies, and proteins (Alpha Chemistry.com). -4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene is an organophosphorus derivative of heterocyclic xanthene. It is a bidentate ligand with a characteristic bite angle and is used in the hydroformylation of alkenes. It also serves as a ligand for the intermolecular coupling of alkynes with aryl iodides which is enhanced by the Cu-catalyst.

reactant remaining after 60 mins of reaction time. Then $1/K_{eq}C_t = -361.07$ and K_{eq} can be estimated to be (-0.069) . This value is very low and thus implies that the backward reaction of the adsorption step is faster than the forward reaction, hence, it has a higher velocity constant relative to the forward reaction.

4.9.2. Surface reaction mechanism

Based on the estimated R^2 (0.81) estimated from the adsorption step, the adsorption step of 4-CP onto the CoNPs, seems to be more depicting/representative of the rate controlling step relative to the surface reaction step, whose coefficient of determination (R^2 value) is 0.84 with lower slope of $-1/keqd = 0.1663$. However, based on the intercept of the graph for the surface reaction step, the extended/extrapolated intercept though the y-axis gives: $1/2/C_t = -0.1663$, which gives a K_{eq} value of -8.6 g.molcat/L and since this value is less than 1, it then implies that the forward reaction step has a lower velocity constant (proceeds at a slower pace) relative to the backward reaction step (which progressed at a faster pace as informed by the estimated k-value). Also, due to the negative K_{eq} values obtained for the adsorption and surface reaction steps, the reaction step also seems not to be the ideal mechanism for the hydroconversion reaction since negative K_{eq} values are rarely obtained/not feasible as rate constants in catalysis.

4.9.3. Desorption mechanism

For the desorption step, a plot of P_A vs $1/C_{A,S}$ as illustrated in Fig. 14. The result shows that the slope $C_t = 0.8575$ and then $1/k_{eqd}C_t = 14.821$.

From $1/k_{eqd}C_t = 14.821$, then $k_{eqd} = 0.079$ and since $1/C_t = 0.8575$, $C_t = 1.17 \text{ M}$ which is slightly above the initial concentration (1.1 M) of 4-CP (this may have been caused by the build-up of products on the catalyst surface); the estimated $R^2 = 0.79$. Furthermore, consid-

ering all three steps, it is clear that the desorption mechanism is the most descriptive mechanism of the hydrocatalytic dechlorination/conversion of 4-CP. Hence, of all the three steps, the desorption of the formed product from the internal pore wall of CoNPs is the rate controlling step.

4.9.4. Chlorophenol conversion

Fig. 15 is an illustration of the amount of 4 chlorophenol remaining at the CoNP-surface for different conversions of 4-chlorophenol to product. The conversion is highest (92%) after 30 min of reaction time and then begins to drop due to reversibility until it attains a minimum conversion of 44% after 1 h. The relationship between both parameters (time and conversion) is nonlinear.

Based on the results in Table 11, it is clear that the 2 M CoNP supported on NaOH gave higher conversion relative to some catalysts (i.e., those of Meshesha et al. (2013), Bedia et al. (2012), Ding et al. (2018) and Gryglewicz and Piechoki (2011), except for the systems involving higher thermal energies. For future studies, this then leads to the recommendation of the testing of higher temperatures as well as hybrid catalyst for the 2 M-cobalt catalyst as a way of exploring its chances of having > 92% conversion or say, 100% conversion since this is possible considering the results from Baeza et al. (2012); Calvo et al. (2009) and Alvarez-Montero et al. (2011). Based on the cost implication for the project, it cost N 117, 000 (naira)/\$260 to procure the chemicals (cobalt acetate- N 18,000/\$40, ethylene glycol- N 20,000/\$44.44, polyvinyl pyrrolidone- N 30,000/\$66.67 and sodium borohydride- N 49,000/\$108.89 = \$260) used in carrying out this research in 2021 with the dollar exchange rate to naira being 450 naira to a dollar. This then implies that the cost of producing the catalyst is not expensive compared to other existing catalysts. Also, considering the cost

Table 6
Hydroconversion products with 2 M CoNPs at 120 mins of retention time from GCMS.

S/N	Retention Time (mins)	Area %	Compounds formed	Uses/effects
1	9.256	16.35	Benzene, hexabromo-benzene, hexabromo-dibromo 6-(3,4,5-tribromo pyrrol-yl) phenol	Benzene is used in the synthesis of important chemicals such as phenols and other petrochemical products. Hexabromobenzene is a flame/fire retardant in papers, plastics and electrical systems. Hexabromo-dibromo- 6-3,4,5-tribromo pyrrol-yl phenol is a brominated phenol that can serve as a fungicide, wood preservative, and an intermediate for the manufacture of flame retardants
2	16.308	17.37	5-chloro-15-formyl-2,3,7,8,12,13,17,18-octaethyl 21H, 23H porphine Silane, [9-[[dimethyl phenylsilyl oxy-] methyl] -6a,7,8,10a- tetrahydro-6,6-dimethyl-6H-dibenzo[b,d] pyran-1-yl] oxydimethylphenyl Androsta 3,5-diene-3,17 β -diol 17-dichlorofluoroacetate 3-heptafluorobutanone	It is used in Surface Plasmon Resonance (SPR) Systems for the detection of thin film volatile organic compounds such as benzene, chloroform, methanol and toluene (Çapan et al., 2014). Use not known An alcohol with no known use Can serve as a precursor for acetic acid A compound which can serve as a precursor for 1,1,1,3,4,4,4-heptafluoro-3-(trifluoromethyl) butan-2-one which is used in chemical formulations/re-packing and at industrial sites (e.g., building materials, metal, plastic, wooden and construction). It is also used in flooring, furniture/toy-making, as construction materials, curtains, foot-wear, leather products, paper, cardboards and electronic equipment.
3	25.05	22.92	Bis(ethyltetramethyl cyclopentadienyl-nickel) Mu.-2.eta.-5 eta., 5-trimethylazulene Isonipicotic acid, N(2,5-di(trifluoromethyl) benzoyl) hexadecyl ester, 2,8-dibromo-6,12-bis-(2-chlorophenyl)-dibenzo[b,f] (Epa, 2011; Meshesha et al., 2013) diazocine	Bis(cyclopentadienyl) nickel (Cp 2 Ni) can be used as a Nickel precursor in the atomic layer deposition (ALD) of NiO-carbon nanotube-hybrids. A derivative of azulene hydride and can serve as a metabolite owing to its similar properties with <u>4,6,8-trimethylazulene</u> . Isonipicotic acid is used for the synthesis of two acids (alkyl piperidine and piperazine hydroxamic acids) as histone deacetylase (HDAC) inhibitors. It serves as an additive in nitroxoline antibiotic-derivatives for cathepsin B inhibition. Whereas, the usefulness of the whole compound has not been reported. Some screened similar derivatives of 1-[5-[4-(benzyloxy) phenyl]-3-methyl-4,5-dihydropyrazol-1-yl] oxime ester, have exhibited in vitro antibacterial against <i>bacillus subtilis</i> , <i>staphylococcus aureus</i> , <i>Escherichia coli</i> and <i>pseudomonas aeruginosa</i> (Liu et al., 2008), hence, the compound may possess some antimicrobial properties.
4	33.334	19.53	3,5-bis-trifluoromethylphenyl] 2,3',5'-tris-trifluoromethyl biphenyl-4-yl] methanone d-ribitol, 1,4-anhydro-1-C- 2,6-dichloro-3-pyridinyl)- 3,5-O-[1,1,3,3-tetrakis (1-methyl ethyl)-1,3-distiloxanediyl-, 2-(1H-imidazole-1-carbothioate)	Several <i>meso</i> -3,5-bis(trifluoromethyl)phenyl-substitutes can be sourced from 3,5-Bis(trifluoromethyl)benzaldehyde, whereas, the phenyl-based substitutes have not been discovered. Ribitol, a sugar alcohol has no known use in humans. However, in bacteria, its enzyme-synthesized RboP polymer, donated by the CDP-Rbo donor-substrate, is a component of teichoic acids found in cell walls. The compound is seen to be somewhat new (use not known)
5	38.863	23.83	Tetrakis (O-trimethylsilyl) -8,2'thioanhydroxanthosine 4-methoxy-2,2',3,4',5-pentabromodiphenyl ether Dispiro(cyclohexane-1,7'-(2) oxabicyclo(3.2.0) heptane-6'-3''-(1) oxacyclopent-4-ene) -2'',3'-dione 1'-α,5'-α,6'-β) 1',5''-bis(3-acetoxyphenyl)-4-cyclohexyldene Mytiloxanthinone	The compound is seen to be somewhat new (use not known) In a study conducted in Northern Europe by Marsh et al. (Marsh et al., 2004), methoxylated/hydroxylated polybrominated diphenyl ethers (MeO-PBDEs and OH-PBDEs) were detected in the blood of Baltic Sea salmon also known as <i>Salmo salar</i> . This is a known alkenone whose use is yet to be known. Other known triphenylethylene derivatives (tamoxifen, droloxifene, toremifene and panomifene) have found use as selective estrogen receptor-modulators that help to abate bone loss and breast cancer (Jeong et al., 2002), hence, the compound for medical application. A marine carotenoid that has been isolated from sea squirt (<i>Halocynthia roretzi</i>) (Matsuno et al., 1984).

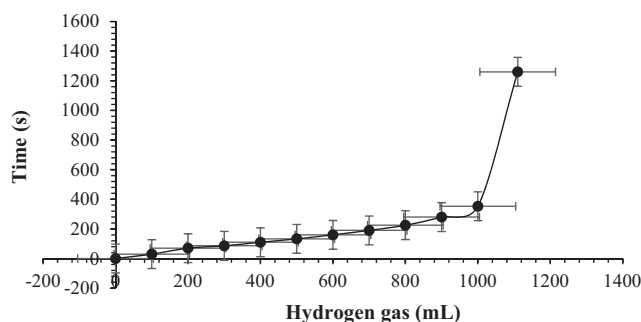


Fig. 10. Volume of hydrogen gas produced from the alcoholysis of NaBH_4 .

of all chemicals used: cobalt acetate (N 18,000), ammonium heptamolybdate (N 25,000), copper II sulphate (N 10,000), ethylene glycol (N 20,000), polyvinyl pyrrolidone (N 30,000), 4-chlorophenol (N 28,000) and sodium borohydride (N 49,000), the total cost implication of the chemicals used in carrying out this project between October 2020 and March 2021 is N 180, 000 which gives \$ 400. The advantages of this catalyst over the already mentioned catalysts is that most catalysts with > 90% hydrodechlorination of 4-chlorophenol or chloroaryl compounds are hybrid catalysts which cost a lot more to synthesize since such catalysts are alloys which are made up of more than one metal that also require catalyst-supports. Also, based on other studies, > 90% efficiencies are majorly feasible at higher than 25 °C which is not so for the catalyst described in this research.

Table 7
pH for Samples without Catalyst.

Reaction time (mins)	Solution-pH NC 0.5 M CoNPs		1 M CoNPs	1.5 M CoNPs 2 M CoNPs	
0	12.3	12.3	12.3	12.3	12.3
10	12.3	12.1	12.1	12.3	9.8
20	12.2	12.1	11.9	12.1	10.3
30	12	12	11.9	11.9	10.4
40	11.9	12.3	10.2	11.9	12
50	11.5	12.3	12.2	11.8	11.6
60	11.5	12	12	11.7	9.5

*The initial concentration of 4-chlorophenol corresponds to 1.1 M concentration; reactant concentration column refers to the pH of the reaction mixture for different concentrations of CoNPs.

NC: No Catalyst.

Note: The pH of the reaction mixture was determined in triplicates and the average value was taken as the medium pH for situations where the values obtained were not concordant.

Table 8
Titre Values for Samples Without/With Catalyst.

Reaction time (mins)	C _b (WC)	C _b 0.5 M CoNP	C _b 1 M CoNP	C _b 1.5 M CoNP	C _b 2 M CoNP
0	1.1	1.1	1.1	1.1	1.1
10	1.04	1.08	1.04	1.12	0.68
10	1.1	1.08	1.02	1.08	1.01
30	1.08	0.93	1.04	1.10	1.04
40	1.04	1.03	0.97	-	0.98
50	0.95	1.024	1.0	-	1.19
60	1.09	0.98	0.98	1.06	0.55

The concentration of the reaction mixture was indeterminable because the end point of the reaction was not reached.

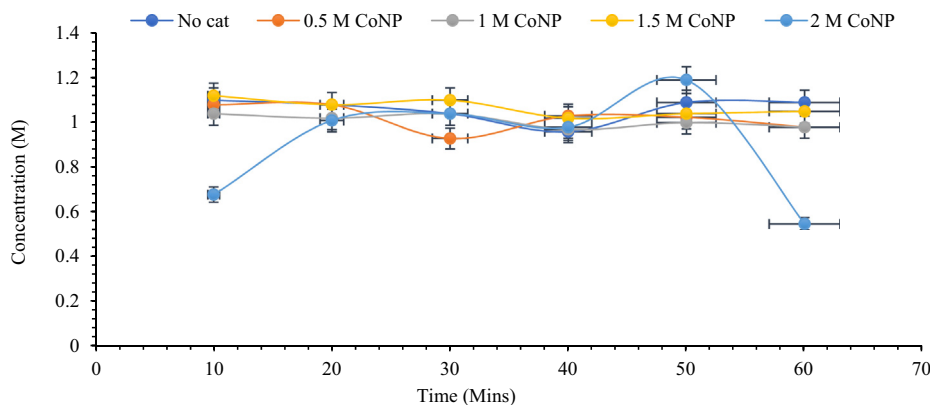


Fig. 11. Effect of CoNP-catalyst on the concentration of the 4-chlorophenol solution.

Table 9
US EPA Standard vs Final Concentration of 4-Chlorophenol in the Treated Wastewater.

Chlorophenols	Medium	Maximum Allowed Concentration	This work Concentration (mg/L)
4-Chlorophenol	Drinkable-water Wastewater	0.1 ppb < 1 mg/L	- 0.071

^a Environmental Protection Agency (USEPA, 2011).

Table 10
Kinetic data for catalysis.

t (mins)	C _{AS} = C _t - C _S	C _S (can be obtained from titration data) (mol/gcat.)	$\frac{\Delta P_A}{\Delta t} = -r_{AD}$	P _A = C _S RT (atm)	$\frac{P_A}{C_{AS}}$	P _B	Vol of H ₂ delivered @ 10 mins interval (mL)	P _B /C _{AS}	1/C _{AS}	C _B	X
10	0.42	0.68	-	16.91	40.26	62.2	360	148.10	2.38	2.53	0.52
20	0.09	1.01	9.59	25.11	279.03	31.1	720	345.56	11.11	1.26	0.88
30	0.06	1.04	19.98	25.86	430.98	20.7	1080	345.00	16.67	0.84	0.92
40	0.12	0.98	30.04	24.37	203.06	15.56	1440	129.67	8.33	0.63	0.84
50	0.09	1.09	39.95	27.10	301.13	12.44	1800	138.22	11.11	0.51	0.88
60	0.55	0.55	50.22	13.68	24.86	10.37	2160	18.86	1.82	0.42	0.44

*R = gas constant (0.08206 atm g.cat/mol.K and T = 27 °C (300 K); C_t = 1.1 mol/gcat = 4 mg/L; C_S = conc. adsorbed in cat pore at time t; C_{AS} = conc of A left or not adsorbed after time, t, X = conversion.

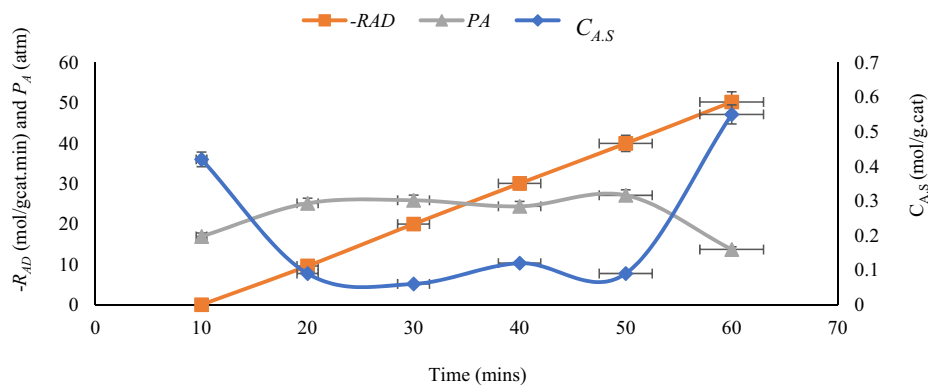


Fig. 12. Concentration, pressure and rate variation with time for the 2 M-CoNP hydrocatalytic conversion of 4-CP.

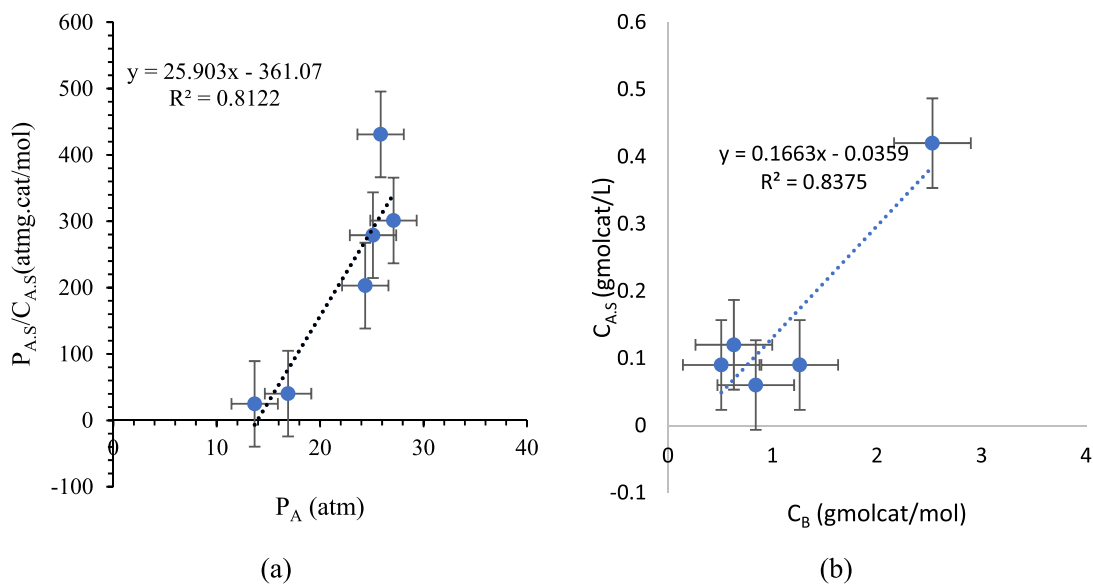


Fig. 13. a. $P_A/C_{A,S}$ vs P_A for the adsorption step, b. $P_B/C_{A,S}$ vs $1/C_{A,S}$ for the reaction step.

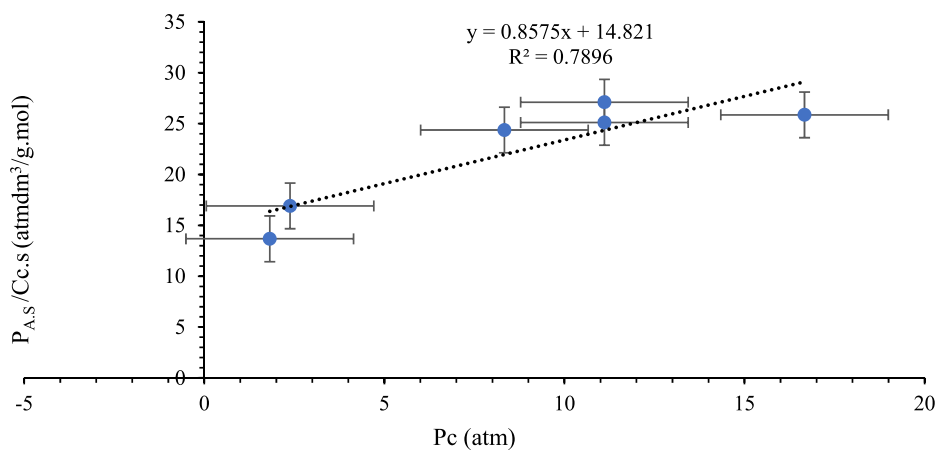


Fig. 14. $P_C/C_{C,S}$ vs P_C for the adsorption step.

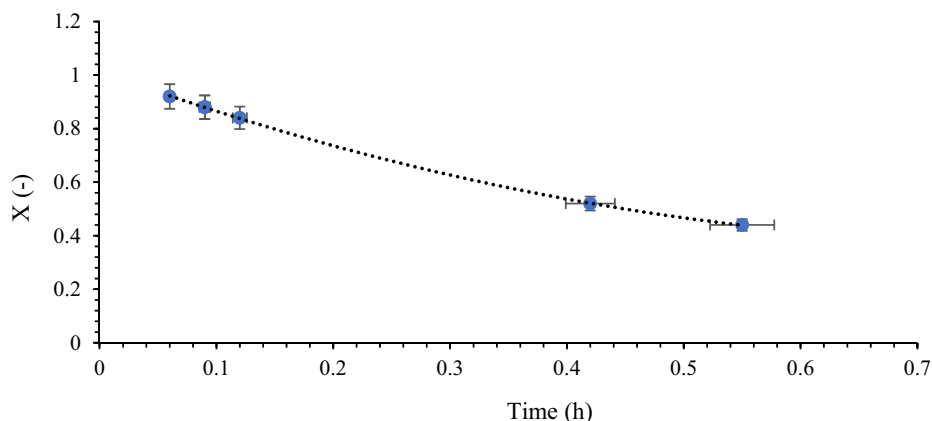
Fig. 15. C_{AS} vs conversion.

Table 11
 Compared results for the CoNP-catalyst and those of related studies.

Catalyst	Cost implication	Substrate	Reaction conditions	Catalyst size/concentration	Products	Conversion	Ref.
Pd-Cu alloy on Al_2O_3	>\$86 per kg Pd precursor	Trichloroethylene	25 °C, 92 mbar	10–15 nm	ethylene, ethane, chloroethylene and also some traces of dichloroethylenes (<0.5%).	49–75%	Meshesha et al. (2013)
Mono and Bimetallic Pd-Pt on sulphated and tungstated zirconia	>\$86 per kg Pd precursor			Dichloromethane (CCl_2)	150–250 °C	0.21–0.71 mm	
					Monochloromethane and nonchlorinated compounds such as C_2H_6 , C_3H_8 , and $i-C_4H_{10}$	90, 80 and 79% for the sulfated zirconia Pt, Pd and Pt-Pd respectively while, the values were 80, 90 and 93% for the tungstated zirconia Pt, Pd and Pt-Pd respectively.	Bedia et al. (2012)
Pt-activated carbon		Chloromethane	125–175 °C	1–12 nm	methane and monochloromethane	67–75.1% @ 125–150 Oc 97.8–100% @ 175–200 Oc (i.e., far higher temperatures than that used in this study thus it rings about high energy implications)	Alvarez-Montero et al. (2011)
Pd	>\$86 per kg Pd precursor	4-chlorophenol	29.85–49.85 °C, 1 atm	2.7–2.8 nm	Phenol, cyclohexanol and cyclohexanone	80–100%	Baeza et al. (2012)
Pd	>\$86 per kg Pd precursor	i. 4-chlorophenol ii. 4-chloroaniline iii. 4-chloroanisole iv. 4-chlorobenzaldehyde	30 °C	6.3–18.4 nm	i. phenol ii. aniline iii. anisole iv. benzaldehyde	15% 40% 69% 85%	Ding et al. (2018)
Ni-Mo/C	Nickel is cost effective, however, the inclusion of molybdenum makes the cost > \$55.56 per kg	1,2, 1,3 and 1,4 dichlorobenzene	210–230 °C, 3 MPa	–	monochloroderivatives	1500 mg/L initial concentration dropped chlorobenzene gave 300 mg/L of chlorobenzene, hence the conversion is about 80%	Gryglewicz and Piechoki (2011)
Pd	>\$86 per kg Pd precursor	4-chlorophenol	25–100 °C, 2.5 bar	–	Phenol and cyclohexane	250 mg Pd/C catalyst /L solution gave 50% conversion @25 oC, 500 mg Pd/C catalyst/L solution gave 90 and 95% conversions @ 50 and 75 °C respectively.	Calvo et al. (2009)
2 M CoNP	~\$36 per kg precursor	4-chlorophenol	25 °C, 1 atm	40–500 d.nm	Several varieties	92%	This work

5. Conclusion

Cobalt nanoparticles were successfully synthesized via the polyol, hot-injection and activated reduction technologies. Rapid generation of hydrogen was ensured by reacting methanol and

sodium borohydride for the efficient degradation of 4-Chlorophenol in aqueous phase; the resulting/residual solution concentrations were ascertained via titration. The concentration of 4-Chlorophenol which was initially 4 mg/L (very harmful and above the recommended value) was successfully brought down

to 0.07 mg/L which is far lower than the stipulated upper-limit concentration (i.e., 1 mg/L) given by US EPA (2011). The synthesized CoNPs were seen to influence the HDC reaction while the best hydroconversion performance was obtained for the 2 M CoNPs. The findings of this study, suggests the need to set-up an industrial catalytic hydroconversion plant for the efficient conversion (i.e., about 92% conversion) of 4-chlorophenol. Furthermore, the products of the hydroconversion process are indicative of the credibility of the process for the efficient conversion of 4-chlorophenol into safer and more useful products thus lowering the concentration of the poisonous chemical to a permissible limit. Although, the adsorption step of 4-CP onto CoNPs gave a moderate coefficient of determination amongst all three mechanisms, however, it gave a very low equilibrium constant (negative value) which makes the desorption step a more reliable model that is clearly descriptive of the hydroconversion process of 4-CP. Based on the results, the desorption step gave a more reliable K_{eq} , which is not only positive but also indicative of the fact that, the rate at which the backward reaction (reactant formation step) occurs, is faster than that of the forward reaction (product formation step).

CRedit authorship contribution statement

Samuel Sanni pioneered and conceptualized the idea that birthed this research, designed and planned the methodology, supervised the experimentation, developed the heterogeneous catalytic/kinetic models and reaction mechanisms, carried out formal analysis, as well as wrote, drafted and reviewed the initial and final drafts of the manuscript; Olowoyeye Philemon executed the methodology and carried out formal/data analyses; Emeka was involved in project administration, visualization and data validation; Babalola Oni and Tijani were involved with data analyses (nanoparticles, GCMS and SEM-EDX) and visualization; Oluwatosin Adegbite was involved in the methodology/setting up the equipment for the HDC reaction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- [1,2-Bis(dicyclohexylphosphino)ethane]palladium(II) chloride - Alfa Chemistry (alfa-chemistry.com).
- Alvarez-Montero, M.A., Gomez-Sainero, L.M., Mayoral, A., Diaz, I., Baker, R.T., Rodriguez, J.J., 2011. *J. Catal.* 279, 389–396.
- Álvarez-Montero, M.A., Gómez-Sainero, L.M., Mayoral, A., Diaz, I., Baker, R.T., Rodriguez, J.J., 2011. *J. Catal.* 279, 389–396. <https://doi.org/10.1016/j.jcat.2011.02.009>.

- Amorim, C., Keane, M.A., 2012. *J. Haz. Mater.* 211–212, 208–217. <https://doi.org/10.1016/j.jhazmat.2011.08.025>.
- Amorim, C., Yuan, G., Patterson, P.M., Keane, M.A., 2005. *J. Catal.* 234, 268–281. <https://doi.org/10.1016/j.jcat.2005.06.019>.
- Anandhakumar, S., Chandrasekaran, M., Noel, M., 2010. *J. Appl. Electrochem.* 40 (2), 303–310.
- Andersin, J., Parkkinen, P., Honkala, K., 2012. Pd-catalyzed hydrodehalogenation of chlorinated olefins: theoretical insights to the reaction mechanism. *J. Catal.* 290 (2012), 118–125. <https://doi.org/10.1016/j.jcat.2012.03.006>.
- Aristizabal, B., Gonzalez, C.A., Barrio, I., Montes, M., De Correa, C.M., 2004. *J. Molecular Catal. A: Chem.* 222, 189–198.
- Bae, H.S., Lee, J.M., Lee, S.-T., 1996. *FEMS Microbiol. Lett.* 145, 125–129. [PZZS0378-1097\(96\)00400-4](https://doi.org/10.1016/0924-6460(96)00400-4).
- Baeza, J.A., Calvo, L., Gilarranz, M.A., Mohedano, A.F., Casas, J.A., Rodriguez, J.J., 2012. *J. Catal.* 293, 85–93. <https://doi.org/10.1016/j.jcat.2012.06.009>.
- Bedia, J., Gómez-Sainero, L.M., Grau, J.M., Busto, M., Martín-Martínez, M., Rodríguez, J.J., 2012. *J. Catal.* 294, 207–215. <https://doi.org/10.1016/j.jcat.2012.07.023>.
- Bonarowska, M., Malinowski, A., Karpinski, Z., 1999. *Appl. Catal. A: General* 188, 145–154. [https://doi.org/10.1016/S0926-860X\(99\)00241-0](https://doi.org/10.1016/S0926-860X(99)00241-0).
- Butel, M.J., Rimbault, A., Khelifa, N., Campion, G., Szyliet, O., Rocchiccioli, F., 1995. *FEMS Microbiol. Lett.* 132, 171–176. [https://doi.org/10.1016/0378-1097\(95\)00306-P](https://doi.org/10.1016/0378-1097(95)00306-P).
- Calvo, L., Gilarranz, M.A., Casas, J.A., Mohedano, A.F., Rodriguez, J.J., 2009. *J. Haz. Mater.* 161, 842–847. <https://doi.org/10.1016/j.jhazmat.2008.04.029>.
- Çapan, I., Erdoğan, M., Güner, B., İlhan, B., Stanciu, S.G., Hristu, R., Stanciu, G.A., 2014. *Sensor Lett.* 12 (8), 1218–1227. <https://doi.org/10.1166/sl.2014.3295>.
- Chakraborty, D., Kulkarni, P.P., Kovalchuk, V.I., D'Itri, J.L., 2004. *Catal. Today* 88, 169–181. <https://doi.org/10.1016/j.cattod.2003.11.012>.
- Cheng, L., Jin, Z., Wang, X., 2013. *Catal. Commun.* 41, 60–64. <https://doi.org/10.1016/j.catcom.2013.06.014>.
- The Nibbler Company. The Importance of Wastewater Treatment. Retrieved September 28, 2020, from The Nibbler Company: <https://www.aquatestinc.com/blog/the-importance-of-wastewater-treatment#:~:text=Wastewater%20treatment%20is%20fundamental%20to%20protect%20the%20health,to%20be%20reused%20instead%20of%20going%20to%20waste>.
- Coq, B., Ferrat, G., Figueras, F., 1986. *J. Catal.* 101 (2), 434–445. [https://doi.org/10.1016/0021-9517\(86\)90271-X](https://doi.org/10.1016/0021-9517(86)90271-X).
- Czaplicka, M., 2004. *Sci. Tot. Environ.* 322 (1–3), 21–39. <https://doi.org/10.1016/j.scitotenv.2003.09.015>.
- De Pedro, Z.M., Diaz, E., Mohedano, A.F., Casas, J.A., Rodriguez, J.J., 2011. *Appl. Catal. B: Environ.* 103, 128–135. <https://doi.org/10.1016/j.apcatb.2011.01.018>.
- Dilaver, M., Kargi, F., 2009. *Bioresource Technol.* 100, 1459–1462. <https://doi.org/10.1016/j.biortech.2008.07.054>.
- X. Ding, Z. Yao, Y. Xu, B. Liu, Q. Liu, Y. She, J. Catal., 368 (2012) 336–344. <https://doi.org/10.1016/j.jcat.2018.10.008>.
- Ding, X., Yao, Z., Xu, Y., Liu, B., Liu, Q., She, Y., 2018. *J. Catal.* 368, 336–344. <https://doi.org/10.1016/j.jcat.2018.10.008>.
- Dong, Z., Le, X., Liu, Y., Dong, C., Ma, J., 2014. *J. Mater. Chem. A* 2, 18775–18785.
- Eker, S., Kargi, F., 2008. *J. Haz. Mater.* 159 (2–3), 306–312. <https://doi.org/10.1016/j.jhazmat.2008.02.019>.
- USEPA, 2011. *Toxicological Review of Pentachlorophenol. Rev. Literat. Arts Americas* 39 (110), 759–786. <http://www.epa.gov/iris/toxreviews/0070tr.pdf>.
- Fang, X., Fang, D., 2017. *Roy. Soc. Chem. Adv.* 7, 40437–40443.
- Forni, P., Prati, L., Rossi, M., 1997. *Appl. Catal. B: Environ.* 14, 49–53. [https://doi.org/10.1016/S0926-3373\(97\)00011-8](https://doi.org/10.1016/S0926-3373(97)00011-8).
- Gennaro, P.D., Bernasconi, S., Orsini, F., Corretto, E., Sello, G., 2010. *Tetrahedron Asymmetry* 21 (15), 1885–1889. <https://doi.org/10.1016/j.tetasy.2010.07.007>.
- Golubina, E.V., Lokteva, E.S., Kavalerskaya, N.E., Maslakov, K.I., 2020. *Kinet. Catal.* 61 (3), 444–459. <https://doi.org/10.1134/S002315842003012X>.
- Gómez-Quero, S., Cárdenas-Lizana, F., Keane, M.A., 2013. *J. Catal.* 303, 41–49. <https://doi.org/10.1016/j.jcat.2013.03.011>.
- Gonzalez, C.A., Bartoszek, M., Martin, A., De Correa, C.M., 2009. *Ind. Eng'g Chem. Res.* 48, 2826–2835. <https://doi.org/10.1021/ie8013742>.
- Gryglewicz, S., Piechoki, W., 2011. *Chemosphere* 83, 334–339.
- Hamdaoui, O., Naffrechoux, E., 2008. *Ultrasonics Sonochem.* 15 (6), 981–987. <https://doi.org/10.1016/j.ultsonch.2008.03.011>.
- Heinrichs, B., Noville, F., Schoebrechts, J., Pirard, J., 2003. *J. Catal.* 220, 215–225. <https://doi.org/10.1016/j.jcat.2003.07.006>.
- Hirai, H., Yakura, N., 2001. *Polym. Adv. Technol.* 12, 724–733. <https://doi.org/10.1002/pat.95>.
- https://www.chemicalbook.com/ChemicalProductProperty_EN_CB0141028.htm.
- Huang, B., Isse, A.A., Durante, C., Wei, C., Gennaro, A., 2012. *Electrochim. Acta* 70, 50–61. <https://doi.org/10.1016/j.electacta.2012.03.009>.
- National Pollutant Inventory, Chlorophenols. Retrieved September 29, 2020, from national pollutant inventory; department of agriculture, water and the environment, accessed April 12, 2020. <http://www.npi.gov.au/resource/chlorophenols-di-tri-tetra>.
- I-H. Jeong, J.D. Cha, Y.S. Park, B.T. Kim, B.T. Bullet. Korean Chem. Soc. 23, 5 (2002) 769–772. <https://doi.org/10.5012/bkcs.2002.23.5.769>.
- Karpinski, Z., Early, K., D'Itri, J.L., 1996. *J. Catal.* 164 (2), 378–386. <https://doi.org/10.1006/jcat.1996.0394>.
- Kathleen, S., 2002. *Florida Water Res. J.*, 27–32
- Keane, M., 2005. *J. Chem. Technol. Biotechnol.*, 1211–1222
- Keane, M.A., Gmez-Quero, S., Crdenas-Lizana, F., Shen, W., 2009. *ChemCatChem* 1, 270–278. <https://doi.org/10.1002/cctc.200900070>.

- Kende, A.S., Roth, B., Kubo, I., 1982. *Tetrahedron Lett.* 23 (17), 1751–1754. [https://doi.org/10.1016/S0040-4039\(00\)86731-3](https://doi.org/10.1016/S0040-4039(00)86731-3).
- Khachatryan, L., Lomnicki, S., Dellinger, B., 2007. *Chemosphere* 68 (9), 1741–1750. <https://doi.org/10.1016/j.chemosphere.2007.03.042>.
- Kim, S.Y., Choi, H.C., Yanga, O.B., Lee, K.H., Lee, J.S., Kim, Y.G., 1995. *J. Chem. Soc. Chem. Commun.* 21, 2169–2170. <https://doi.org/10.1039/C39950002169>.
- Kim, D., Jeong, S., Moon, J., 2006. *Nanotechnology* 17 (16), 4019–4024. <https://doi.org/10.1088/0957-4484/17/16/004>.
- Legawiec-Jarzyna, M., Srebowata, A., Juszczyk, W., Karpinski, Z., 2004. *J. Molecular Catal. A: Chem.* 224, 171–177. <https://doi.org/10.1016/j.molcata.2004.07.033>.
- Li, F., Liu, Y., Ma, T., Xu, D., Li, X., Gong, G., 2017. *New J. Chem.*, 1–9 <https://doi.org/10.1039/C6NJ04045D>.
- Liu, X.-H., Zhi, L.-P., Song, B., Xu, H.-L., 2008. *Chem. Res. Chinese Universities* 24 (4), 454–458. [https://doi.org/10.1016/S1005-9040\(08\)60095-1](https://doi.org/10.1016/S1005-9040(08)60095-1).
- López, E., Ordoñez, S., Sastre, H., Diez, F.V., 2003. *J. Haz. Mater.* 97 (1–3), 281–294.
- Lopez, E., Ordoñez, S., Diez, F.V., 2006. *Appl. Catal. B: Environ.* 62, 57–65.
- Ma, X., Liu, Y., Li, X., Xu, J., Gu, G., Xia, C., 2015. *Appl. Catal. B: Environ.* 165, 351–359. <https://doi.org/10.1016/j.apcatb.2014.10.035>.
- Malinowski, A., Lomot, D., Karpinski, Z., 1998. *Appl. Catal. B: Environ.* 19, L79–L86.
- Manzer, L.E., Nappa, M.J., 2001. *Appl. Catal. A: General* 221 (1–2), 267–274. [https://doi.org/10.1016/S0926-860X\(01\)00803-1](https://doi.org/10.1016/S0926-860X(01)00803-1).
- Marsh, G.O.R., Athanasiadou, M., Bergman, A., Asplund, L., 2004. *Environ. Sci. Technol.* 38 (1), 10–18. <https://doi.org/10.1021/es034671j>.
- Martino, M., Rosal, R., Sastre, H., Diez, F.V., 1999. *Appl. Catal. B: Environ.* 20, 301–307. [https://doi.org/10.1016/S0926-3373\(98\)00120-9](https://doi.org/10.1016/S0926-3373(98)00120-9).
- Matos, J., Garcia, A., Cordero, T., Chovelon, J.M., Ferronato, C., 2009. *Catal. Lett.* 130 (3–4), 568–574. <https://doi.org/10.1007/s10562-009-9989-8>.
- Matsumoto, T., Takahashi, K., Kitagishi, K., Shinoda, K., Cuya Huaman, J.L., Piquemal, J.Y., Jeyadevan, B., 2015. *New J. Chem.* 39 (6), 5008–5018. <https://doi.org/10.1039/c5nj00669d>.
- Matsuno, T., Ookubo, M., Nishizawa, T., Shimizu, I., 1984. *Chem. Pharm. Bull.* 32 (11), 4309–4315. <https://doi.org/10.1248/cpb.32.4309>.
- Meshesha, B.T., Barrabés, N., Llorca, J., Dafinov, A., Medina, F., Föttinger, K., 2013. *Appl. Catal. A: General* 453, 130–141. <https://doi.org/10.1016/j.apcata.2012.12.019>.
- Molina, C.B., Pizarro, A.H., Casas, J.A., Rodriguez, J.J., 2014. *Appl. Catal. B: Environ.* 148–149, 330–338. <https://doi.org/10.1016/j.apcatb.2013.11.010>.
- Mori, T., Kikuchi, T., Kubo, J., Morikawa, Y., 2001. *Chem. Lett.* 30 (9), 936–938. <https://doi.org/10.1246/cl.2001.936>.
- Murialdo, S.F., 2003. *Water SA* 29 (4), 457–463.
- Nicolas, V., Jean-Pierre, S., 2007. *Chemosphere* 67 (9), S144–S149. <https://doi.org/10.1016/j.chemosphere.2006.05.096>.
- Ordóñez, S., Díaz, E., Bueres, R.F., Asedegbega-Nieto, E., Sastre, H., 2010. *J. Catal.* 272 (1), 158–168. <https://doi.org/10.1016/j.jcat.2010.03.001>.
- S. Ordoñez, F.V. Diez, H. Sastre, *Appl. Catal. B: Environ.* 31 (2001) 113–122. PII: S0926-3373(00)00270-8.
- Prati, L., Rossi, M., 1999. *Appl. Catal. B: Environ.* 23 (2–3), 135–142. [https://doi.org/10.1016/S0926-3373\(99\)00071-5](https://doi.org/10.1016/S0926-3373(99)00071-5).
- Ribeiro, F.H., Gerken, C.A., Rupprechter, G., Somorjai, G.A., Kellner, C.S., Coulston, G. W., Manzer, L.E., Abrams, L., 1998. *J. Catal.* 176, 352–357. <https://doi.org/10.1006/jcat.1998.2059>.
- Sanchez, C.A.G., Patino, C.O.M., De Correa, C.M., 2008. *Catal. Today* 133–135, 520–525.
- Sanni, S.E., Alade, T., Agboola, O., Alaba, P.A., 2020. *Int. J. Hydro. Energy* 45, 4606–4624. <https://doi.org/10.1016/j.ijhydene.2019.12.121>.
- Shiraishi, Y., Suzuki, T., Hirai, T., 2010. *New J. Chem.* 34 (4), 714–717. <https://doi.org/10.1039/B9NJ00732F>.
- Stakheev, A.Y., Mashkovskii, I.S., Baeva, G.N., Telegina, N.S., 2010. *Russian J. General Chem.* 80, 618–629. <https://doi.org/10.1134/S1070363210030424>.
- Tang, W., 1996. *Chemosphere* 33 (8), 1621–1635.
- C. Tanks, Why Waste Water Treatment is So Important. Retrieved September 28, 2020, from Carlow Conceret Tanks: <https://www.carlowtanks.ie/why-waste-water-treatment-is-so-important/>.
- Theurich, J., Lindner, M., Bahnemann, D.W., 1996. *Langmuir* 12 (26), 6368–6376. <https://doi.org/10.1021/la960228t>.
- Thompson, C., Rioux, R., Chen, N., Ribeiro, F., 2000. *J. Phys. Chem. B* 104, 3067–3077. <https://doi.org/10.1021/jp992888n>.
- Xiong, J., Ma, Y., 2019. *Catalysts* 9 (1), 77. <https://doi.org/10.3390/catal9010077>.
- Yong, G., She, W., Zhang, Y., 2012. *Dyes Pigments* 95, 161–167.
- Yu, X., Wu, T., Yang, X.J., Xu, J., Auzam, J., Semiat, R., Han, Y.F., 2016. *J. Haz. Mater.* 305, 178–189.
- Zhang, G., Xu, H., Fan, Y., Wang, Y., Zhang, L., Lu, G., 2015. *J. Nanomater.* 5, 1–8. <https://doi.org/10.1155/2015/912104>.