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Synthesis of *N*-benzylated cobalt phthalocyaninetetrasulfonamide and its application in oxidative desulfurization catalysis

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ABSTRACT

The FeCl₂/K₂CO₃ catalyst system was used successfully for the synthesis of oil soluble N-benzylated cobalt phthalocyaninetetrasulfonamide by the reaction of benzyl alcohol on water-soluble cobalt phthalocyaninetetrasulfonamide via heating at 135 °C for 20 h under N2. The new oil-soluble peripherally N-benzylated phthalocyanine was characterized by elemental analysis, FT-IR, UV-vis, TG and mass spectrometry. The catalytic activity of this new cobalt complex for oxidation of dibenzothiophene (DBT) was evaluated in n-dodecane (a middle distillate model compound) using H_2O_2 as an oxidant. The acetonitrile was taken as an extracting solvent for further extracting DBT sulfoxide and sulfone. The novel peripherally substituted cobalt(II) complex showed better oxidative desulfurization catalytic activity than cobalt phthalocyanine and cobalt phthalocyaninetetrasulfonamide. DBT oxidation kinetics were evaluated by lumped n^{th} - and first-order kinetic models. The maximum removal of the DBT was found to be 85% at the optimized dose and experimental conditions.

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1. Introduction

Due to environmental and health concerns, regulatory agencies and federal bodies have introduced stringent fuel specifications. This has increased the demand for desulfurization technologies that can limit the sulfur content to less than 10 ppm in the finished liquid fuels. Sulfur has negative effect on the air quality and human health. From the initial crude pretreatment to crude distillations and finally in every secondary petroleum refining process, sulfur is treated as egregious substance. Apart from foul odor, its high corrosiveness to the reactor internals (column surface, plates, distributors, packing supports, etc.) increases the maintenance cost of refinery operations. In addition, catalytic poisoning behavior increases the operation cost and damages the exhaust devices [1].

In order to achieve deep desulfurization of fuels, many efforts have been made for enhancing the desulfurization potential of conventional processes. Hydrodesulfurization (HDS) has limited prospects in achieving deep desulfurization due to its incapability in efficiently removing sterically hindered sulfur of the organic sulfur-containing species like dibenzothiophene (DBT) and its derivatives. Apart from this, the high H_2 cost and requirement of high temperature and pressure conditions have made research in other desulfurization technologies like adsorption, oxidation, extraction and bio-desulfurization highly interesting [2, 3]. Oxidative desulfurization (ODS) has gained the attention of many researchers to achieve the deep desulfurization due to less energy requirements, ease of operation and efficiency to work on the refractory sulfur species like DBT [4]. In the ODS, the organo-sulfur compounds are oxidized to corresponding polar sulfoxides and sulfones which can then be extracted in a polar immiscible organic solvent or removed by adsorption. Although ODS can be done by employing an oxidant only, e.g. hydrogen peroxide, ozone, organic hydroperoxides and molecular oxygen, many other methods are in use to increase the efficiency of oxidation using catalysts [5, 6], photocatalyst [7] and electrochemical oxidation [8]. For catalytic ODS, simple metal salts [9-11], metal complexes [12–17], polymer encored metal complexes [18, 19], and polyoxometalates [20, 21] have been examined. Some macrocyclic metal complexes were also found to possess good catalytic activity in ODS, e.g. iron porphyrin and metal phthalocyanines [22, 23].

Phthalocyanine (Pc) is a symmetrical 18π -electron aromatic macrocycle, closely related to naturally occurring porphyrins. Like porphyrins, the Pc macrocycle can make complexes with metal ions, and metal phthalocyanines have attracted interest due to their similarity in structure with the active site of the metalloenzymes [24, 25]. Apart from their well-explored catalytic applications, several other uses have been explored as dyes, pigments, solar cells, light emitting diodes, laser cancer therapy, etc. [26]. Several peripherally and non-peripherally substituted phthalocyanines have been prepared recently because these substituents modulate their chemical, physical and catalytic properties and their solubility [27]. Metal phthalocyanines with peripherally substituted sulphonamides [28–30] are important merox catalysts for sweetening of various petroleum products and have improved catalytic and solubility characteristics as compared to phthalocyanines.

Efforts were also made to utilize these peripherally substituted phthalocyanine sulphonamides as oxidation catalysts [31]. To utilize this water-soluble tetra sulphonamide phthalocyanine complex as an ODS catalyst and also to enhance its catalytic 2984 😉 D. TRIPATHI ET AL.

activity by modulating the solubility characteristics, this manuscript presents a process for synthesizing an oil-soluble peripherally substituted phthalocyanine sulphonamide, i.e. *N*-alkylated cobalt phthalocyaninetetrasulfonamide by direct reaction of benzyl alcohol with water-soluble cobalt phthalocyanine tetrasulfonamide.

N-alkylation of sulfonamide using alcohol as alkylating reagent has some advantages. First, alcohol is readily available and second there is no generation of harmful byproducts as with conventional methods using alky halide or aldehyde [8, 32]. Along with alcohol as alkylating reagent, homogeneous or heterogeneous transition metal complexes catalyze this reaction via hydrogen transfer methods [33, 34]. The cupric acetate/K₂CO₃ system has been reported to provide an excellent yield of secondary amines [35]. FeCl₂/K₂CO₃ efficiently catalyzed coupling between *p*-toluene sulphonamide and benzylic alcohol also [36]. However, the reaction has not reported on the Pc macrocycle. In this work, *N*-benzylated cobalt phthalocyanine tetrasulfonamide was synthesized by benzyl alcohol reaction on cobalt tetrasulfonamide using FeCl₂/K₂CO₃ as catalyst. The complex was further evaluated as an ODS catalyst for DBT in model fuel by H₂O₂. Comparison of catalytic activity has been made with the cobalt phthalocyanine tetrasulfonamide.

2. Materials and methods

2.1. Chemicals and materials

4-Sulfophthalic acid, $CoCl_2 \cdot 6H_2O$, nitrobenzene, benzyl alcohol and cobalt(II) phthalocyanine were purchased from Sigma-Aldrich, Bangalore, India. Ammonium molybdate, cobalt(II) acetate tetrahydrate, FeCl₂, DBT, *n*-dodecane, ethanol and acetonitrile were purchased from Merck Millipore (formerly E-Merck, Darmstadt, Germany). Thionyl chloride was obtained from Acros Organics, Mumbai, India. Other chemicals like ammonium chloride, urea, methanol, pyridine, sodium hydroxide, K₂CO₃ and acetone were of the highest available grade and used without purification.

2.2. Synthesis of cobalt tetrasulfophthalocyanine 1

Cobalt tetrasulfophthalocyanine **1** was prepared by the previously described procedure [37].

2.3. Synthesis of cobalt tetrachlorosulfophthalocyanine 2

Cobalt tetrachlorosulfophthalocyanine **2** was prepared as previously described procedure [37].

2.4. Synthesis of cobalt phthalocyaninetetrasulphonamide 3

In preparation of cobalt phthalocyaninetetrasulphonamide [37], total wet cake of 5.0 g cobalt tetrachlorosulfophthalocyanine **2** was homogeneously dispersed in 100mL methanol/ice water (10%). The reaction mixture was stirred at 5–8 °C and ammonia gas was passed until the mixture was alkaline (pH 8–9). Pyridine (5 mL) was then added and the mixture stirred at room temperature for 20 min. This was followed by

addition of 6 mL of 10% sodium hydroxide solution followed by stirring the reaction mixture for 40 min at room temperature. The contents were then heated to 80 °C and held for 1 h. Thereafter sample was cooled to room temperature and poured over a mixture of ice and concentrated hydrochloric acid keeping the pH acidic (2–3). The precipitated cobalt phthalocyaninetetrasulphonamide was filtered, washed thoroughly with cold water and dried in a vacuum oven to yield 4.4 g of the product. The blue cobalt phthalocyaninetetrasulphonamide **3** was obtained in 95.8% yield (4.4 g). IR (KBr cm⁻¹): 3400, 3188, 1770, 1719, 1608, 1518, 1466, 1397, 1324, 1158, 921, 747. Anal. Calcd for $C_{32}H_{20}N_{12}O_8S_4Co$, calcd: C, 43.29%; H, 2.27%; N, 18.93%. Found: C, 43.85; H, 2.05; N, 19.10. UV–vis: λ_{max} 663.0, 331.0.

2.5. Synthesis of N-benzylated cobalt phthalocyaninetetrasulfonamide 4

Cobalt phthalocyaninetetrasulphonamide (171 mg, 0.25 mmol), benzyl alcohol (540 mg, 5.0 mmol), 5 mol. % FeCl₂ (10 mg) catalyst and 20 mol. % K₂CO₃ (69 mg) were added to the reaction tube, respectively. Thereafter, the reaction was carried out by using a round bottom flask (RB) under nitrogen at 135 °C for 20 h, and then cooled to room temperature. Acetone (20 mL) was added to dissolve the reaction mixture and filtered through celite. Acetone and benzyl alcohol were removed under vacuum and blue solid was obtained. The blue *N*-benzylated cobalt phthalocyaninetetrasulphonamide **4** was obtained in 98% yield (3.7 g). IR (KBr cm⁻¹): 3403, 1659, 1583, 1519, 1466, 1395, 1325, 1194, 920, 747. Anal. Calcd for C₆₀H₄₄N₁₂O₈S₄Co, Calcd: C, 57.73%; H, 3.55%; N, 13.47%. Found: C, 58.21; H, 3.83; N 13.54. UV–vis: λ_{max} 664.0, 332.0.

2.6. Characterization

Elemental analysis was performed on a Perkin Elmer Series II CHNS/O 2400 analyzer. Fourier transform infrared spectra (FT-IR) were recorded on a Thermo-Nicolet 8700 Research spectrophotometer with a 4 cm⁻¹ resolution using potassium bromide. Spectra in the UV–vis region were recorded with a Varian Cary 50 UV–Vis spectrophotometer using 1 cm path length cuvettes at room temperature. Thermogravimetric analyses (TGA) of samples were carried out using a Perkin Elmer EXSTAR TG/DTA 6300 in aluminum pans. Analysis was carried out from 30 to 900 °C under nitrogen (200 mL min⁻¹) with heating rate 10 °C/min. Mass spectra were measured on a MALDI TOF MS (AB Sciex, MALDI TOF/TOF 5800) using DHB (2,5-dihydroxybenzoic acid) as MALDI matrix and analysis was performed in + ve ion mode.

2.7. Catalytic desulfurization

N-benzylated cobalt phthalocyaninetetrasulfonamide **4** was evaluated as ODS catalyst on a heterocyclic model sulphur compound, i.e. DBT taken in *n*-dodecane (a model compound for fuel). H_2O_2 was taken as an oxidant in different concentrations while different amounts of acetonitrile were taken as an extractant for the formed sulfoxide and sulfone. The batch oxidation experiments were performed at 1 atm pressure in a glass reactor equipped with a stirrer. The cobalt complex amount was optimized by taking 0.05 mmol DBT in 100 mL *n*-dodecane, 0.5 mmol H_2O_2 and 100 mL of acetonitrile. After the catalyst optimization, sulfur mass proportion to oxidant was optimized taking 0.05 mmol DBT and varying the H_2O_2 ratio as 1:5, 1:10, 1:15 and 1:20. Thereafter, the extractant amount was optimized by varying its ratio to *n*-dodecane as 1:1, 1:2, 2:1 and 2.5:1. Effects of temperature (30, 40, 50 and 60 °C) and reaction time (15, 30, 60, 90 and 120 min) were studied at the optimized catalyst amount, oxidant proportion and extractant amount. Comparative catalytic activity was evaluated at the optimized conditions taking the cobalt phthalocyanine and cobalt phthalocyaninetetrasulfonamide **3** in the same amount. DBT oxidation efficiency was estimated by analyzing *n*-dodecane layer using XRF (X-ray fluorescence) analysis with a Lab-X3500, Oxford Instruments, UK, and also by estimating the DBT oxides in the extractant layer by measuring the amount of evaporated content and analyzing the oxide ratio with a Perkin-Elmer gas chromatograph-sulfur chemiluminescence detector (GC-SCD).

3. Results and discussion

3.1. Synthesis and characterization

The synthetic procedure is shown as Scheme 1. *N*-benzylated cobalt phthalocyaninetetrasulfonamide was prepared from cobalt phthalocyaninetetrasulfonic acid by a multistep reaction sequence. First, cobalt phthalocyaninetetrasulfonic acid **1** was obtained from 4-sulfophthalic acid, ammonium chloride, urea and $CoCl_2$ reaction. Refluxing of the mixture containing **1** with thionyl chloride readily gave cobalttetrachlorosulfophthalocyanine **2** in almost quantitative yield. Amination using NH₃ of **2** gave the cobalt phthalocyaninetetrasulfonamide **3**.

Elemental analyses, FT-IR, color, yield and other physical properties of **1**, **2** and **3** were very similar to previous work [37]. The FeCl₂/K₂CO₃ catalyst system was used for *N*-alkylation of cobalt phthalocyaninetetrasulfonamide **4** with benzyl alcohol [36]. Literature reports that 1.0 mmol *p*-toluene sulphonamide needs 5 mmol benzyl alcohol and 5 mol. % of catalyst FeCl₂ with 20 mol. % base, i.e. K₂CO₃ for reaction under inert atmosphere for 20 h to achieve 100% conversion. Therefore, the same ratio of the reactant was taken for conversion of the cobalt phthalocyaninetetrasulfonamide to *N*-benzylated derivative. Finally, dark blue crystalline powder of *N*-benzylated cobalt phthalocyaninetetrasulphonamide **4** was obtained in 98% yield (3.7 g) and was characterized by elemental analysis, FT-IR, TG, UV-vis spectroscopy and mass spectrometry.

Elemental analysis gives evidence in support of synthesis of **4**. For $C_{60}H_{44}N_{12}O_8S_4Co$, calculated values of various elements are: C, 57.73%; H, 3.55%; N, 13.47%, in good agreement with the found values as: C, 58.21; H, 3.83; N 13.54. The synthesis of **4** was also confirmed by the FT-IR spectra (Figure 1). In the FT-IR spectrum of **3** (Figure 1(a)), the absorption bands at 3188 and 3400 cm⁻¹ were characteristic of the primary NH stretch while the band at 1608 cm⁻¹ was due to primary NH bending vibration. Peaks at 1770 and 1719 cm⁻¹ were also present due to the C=O stretch from anhydride impurities. C=C stretches due to the aromatic nuclei from the phthalocyanine ring were present at 1608, 1518 and 1466 cm⁻¹. Sulphonamide S = O stretches are present at 1397, 1324 and 1158 cm⁻¹. The S-N group is present at 921 cm⁻¹ and C-H def (aromatic) out of plane stretch at 747 cm⁻¹. The FT-IR spectrum of



Scheme 1. Synthesis of 4.

4 (Figure 1(b)) was in accord with the structure shown in Scheme 1. Comparison of the FT-IR spectra of **3** and **4** prove successful *N*-benzylation in the products, e.g. the presence of the secondary NH group was indicated by an intense stretch at 3403 cm⁻¹ and the observed characteristic vibrations of the secondary NH def at 1659 and 1583 cm⁻¹ confirmed the *N*-benzylation. The aromatic C=C stretching peaks were observed at 1583, 1519 and 1466 cm⁻¹ while the S = O stretch from sulphonamide is at 1395, 1325 and 1194 cm⁻¹ along with the S-N band at 920 and aromatic C-H def



Figure 1. FT-IR spectra of (a) 3 and (b) 4.

(out of plane) at 747 cm⁻¹. No impurities due to anhydride are observed in **4**, revealing the high purity of the sample after *N*-benzylation.

Compound **4** was also confirmed by observing difference in the thermal stability curves. Figure 2 presents the recorded TG curves of weight loss of **3** and **4** with their thermal stabilities **3** > **4** in nitrogen. The initial weight loss of **4** was due to water loss. Major weight loss occurs due to decomposition of side chains of cobalt phthalocyanine at 300 °C; the second major weight loss is due to decomposition of the phthalocyanine rings (starting at 650 °C). Final residual weight at 800 °C was lower for **4** (25%) than **3** (43%) which was due to the higher content of decomposed benzylic side chains in **4**, and this phenomenon indirectly confirmed the successful *N*-benzylation.

Because of insolubility of **4** in aqueous solution, both cobalt phthalocyanines were dissolved in DMSO and their electronic spectra were evaluated as shown in Figure 3. Both showed electronic spectra with two strong absorption regions. In the B band region, **3** and **4** showed peaks at 331 and 332 nm, respectively, with two shoulders at 255 and 300 nm. Both **3** and **4** showed intense Q band absorptions at 663 and 664 nm, respectively, together with a shoulder at 600 nm. Although the position of the absorption bands did not change because of no significant reduction in electronic density of the phthalocyanine, the intensity of both the B and Q band was enhanced for the *N*-benzylated cobaltphthalocyaninetetrasulfonamide due to the increased solubility of **4** in DMSO.

Mass spectrometry is a powerful method for confirming the structure of the proposed *N*-benzylated phthalocyanines structure. The MALDI-TOF-MS spectrum of *N*benzylated cobaltphthalocyaninetetrasulfonamide **4** (Figure 4) shows different peaks



Figure 2. Thermogravimetric curves of 3 and 4.

and the m/z peak assignments are given in Table 1. Although using DHB (2,5-dihydroxybenzoic acid) as MALDI matrix, the molecular ion peak was not observed, interpretation of the fragmentation pattern shows that benzyl alcohol reacted with the FeCl₂/K₂CO₃ catalyst system with *N*-benzylation of the cobaltphthalocyaninetetrasulfonamide leading to formation of *N*-benzylated cobaltphthalocyaninetetrasulfonamide **4**.

3.2. Oxidative desulfurization studies

Catalytic potential of **4** was evaluated for ODS of refractory ograno-sulfur compounds. DBT can be considered as representative for such refractory compounds, and the oxidation reaction shown in Scheme 2 was used to examine the comparative catalytic activity of **4** in comparison to cobalt phthalocyanine and cobalt phthalocyaninetetrasulphonamide **3**. Many metal salts and complexes have already been reported as catalysts for this reaction since the oxidized DBT sulfoxides and sulfone species can be easily extracted in acetonitrile [12–14, 18–20, 22, 23]. H₂O₂ was oxidant while *n*-dodecane was used as the DBT oxidation reaction medium since it is a model fuel compound. Reaction optimization was done with respect to the catalyst amount, oxidant (H₂O₂) to sulfur mass proportion, ratio of extractant (acetonitrile) relative to the *n*-dodecane, temperature and time of reaction (Table 2).

Experiments were performed in 100 mL *n*-dodecane solutions containing 0.5 mmol DBT, 5.0 mmol H_2O_2 and varying molar ratios of **4** to DBT (Figure 5(a)). Acetonitrile (100 mL) was added as an extractant and reaction was performed by stirring at 40 °C for 2 h under atmospheric pressure. Best activity of DBT removal of 81% was obtained for catalyst:DBT molar ratio of 1:10. For catalyst:DBT molar ratio of 1:15 and 1:20, amount of catalyst and thus active sites were not high enough to cause oxidation of DBT to DBT sulfoxide and DBT sulfone. Similarly, at higher catalyst dosage, the clogging/agglomeration of catalysts may have not allowed DBT to reach the active sites [38].

2990 🕒 D. TRIPATHI ET AL.



Figure 3. UV-vis spectra of (a) 3 and (b) 4 in DMSO.



Figure 4. MALDI-TOF-MS spectra of 4.

m/z	Species	m/z	Species				
806.95	N N N N N N N N N N N N N N N N N N N	820.99					
847.97	0 = S = 0 N	885.93	$\begin{array}{c} HN \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $				
901.78	$(\mathbf{A}) = (\mathbf{A}) = ($	925.87	$\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$				
938.94	H_2C NH O N N N N N N N N	1005.84	$(\mathbf{x}_{1}, \mathbf{x}_{2}, x$				

 Table 1. The major peak assignment in MALDI-TOF-MS spectra of N-benzylated cobaltphthalocyaninetetrasulfonamide 4.

The H_2O_2 to sulfur molar proportion was optimized by doing oxidation experiments with varying H_2O_2 ratio as 1:5; 1:10; 1:15 and 1:20 keeping the catalyst:DBT molar ratio = 1:10; temperature = 40 °C; time = 2 h and acetonitrile:*n*-dodecane



Scheme 2. Oxidation of DBT by H2O2 in the presence of 4.

Table 2. Percentage DBT oxidation and kinetics by different catalysts for DBT present in *n*-dodecane along with H_2O_2 at optimized conditions.

		n th Order kinetics					1 st Order kinetics			
Catalyst	DBT removal efficiency (%)	Reaction order	k _n ((mmol/L) ⁽¹⁻ⁿ⁾ /min)	R ²	ARE (%)	k ₁ (min ⁻¹)	R ²	ARE (%)		
Without catalyst	38	6.8	1.760	0.930	3.91	0.0053	0.686	12.92		
Cobalt acetate	51	7.1	13.441	0.968	4.73	0.0118	0.653	25.29		
Complex 3	58	5.1	1.497	0.941	7.30	0.0143	0.853	19.79		
Cobalt phthalocyanine	73	3.7	0.959	0.979	7.88	0.0215	0.807	36.64		
Complex 4	85	3.3	1.904	0.926	15.01	0.0314	0.896	42.82		

Note. ARE: average relative error.

Experimental conditions: catalyst: DBT molar ratio = 1:10, DBT: H_2O_2 molar ratio = 1:15, acetonitrile:*n*-dodecane volume ratio = 2:1, temperature = 40 °C, time = 2.00 h.

volume ratio = 1:1 (Figure 5(b)). At lower DBT:H₂O₂ molar ratio (=1:10), hydroxyl radicals generated were not enough to oxidize the DBT. DBT:H₂O₂ molar ratio of 1:15 gave maximum 83% DBT and no further increase was observed by increasing H_2O_2 .

Different volume ratios of acetonitrile to the *n*-dodecane were tried while fixing the catalyst:DBT molar ratio at 1:10, DBT:H₂O₂ molar ratio at 1:15, temperature = 40 °C and reaction time = 2 h; acetonitrile:*n*-dodecane volume ratio of 2:1 gave the best extraction efficiency of 85% and no measurable increase was observed at higher extractant volume ratios, e.g. 2.5:1. As per the results shown in Figure 5(c), the lower volume of extractant (1:2) resulted in low oxidation of 56% only.

Optimization with respect to temperature and time were done as these are important parameters which affect the DBT oxidation. However, when the experiments were performed at different reaction temperatures, it was observed that there is no effect on increasing the temperature beyond 40 °C (Figure 5(d)). H₂O₂ is decomposed to form oxygen instead of hydroxyl radicals at temperatures \geq 50 °C [38]. This reduces the DBT removal efficiency at higher temperatures.

ODS catalytic activity of **4** in comparison to cobalt phthalocyanine and **3** was examined. The higher activity of **4** in comparison to **3** may be explained on the basis of increased solubility of **4** in *n*-dodecane due to N benzyl peripheral substituents. Higher activity than cobalt phthalocyanine can be explained on the basis of slightly reduced electron density around the active metal center due to the presence of electron withdrawing peripheral *N*-benzylated sulphonamide moieties. The active metal



Figure 5. Effect of various parameters on DBT oxidation efficiency in presence of **4** as catalyst. (a) catalyst:DBT molar ratio; DBT:H₂O₂ molar ratio = 1:15, acetonitrile:*n*-dodecane volume ratio = 2:1, temperature = 40 °C, time = 2.00 h. (b) DBT:H₂O₂ molar ratio; catalyst:DBT molar ratio = 1:10; acetonitrile:*n*-dodecane volume ratio = 2:1, temperature = 40 °C, time = 2.00 h. (c) Acetonitrile: *n*-dodecane volume ratio; catalyst:DBT molar ratio = 1:10; DBT:H₂O₂ molar ratio = 1:15, acetonitrile:*n*-dodecane volume ratio = 2:1, time = 2:00 h.

center is more electron deficient in **4** compared to unsubstituted cobalt phthalocyanine, leading to higher catalytic efficiency.

3.3. Comparative assessment and kinetics

In order to evaluate the ODS catalytic potential of **4** in comparison to **3**, cobaltphthalocyanine and simple cobalt acetate experiments were performed at optimized reaction conditions of catalyst:DBT ratio of 1:10 (mmol), DBT:H₂O₂ ratio (mmol) of 1:15, acetonitrile:*n*-dodecane ratio of 2:1, 40 °C temperature and time varying from 15 min to 2 h (Figure 6). Under these conditions, **4** is the best catalyst followed by the cobaltphthalocyanine and **3** showing a maximum of 85, 73 and 58% DBT oxidation, respectively. Cobalt acetate shows very low activity of 38% DBT oxidation (Table 2). The higher activity of **4** in comparison to **3** may be explained on the basis of increased solubility of **4** in *n*-dodecane due to N benzyl peripheral substituents.



Figure 6. DBT oxidation kinetics by different catalysts for DBT present in *n*-dodecane along with H_2O_2 at optimized conditions. Experimental conditions: catalyst:DBT molar ratio = 1:10; DBT: H_2O_2 molar ratio = 1:15, acetonitrile:*n*-dodecane volume ratio = 2:1, temperature = 40 °C; time = 2.00 h.

For performing kinetic study, residual DBT content in the extract layer was noted after various reaction times as shown in Figure 6. Maximum oxidation could be achieved in 1 h (Figure 6) which does not increase in 2 h; 1 h gives maximum oxidation of 85%. The n^{th} order and 1^{st} -order reaction models represented by Equations (1) and (2) were chosen to determine the oxidation kinetics [38, 39]. n^{th} -order kinetic expression can be written as [40]:

$$C_t^{1-n} - C_0^{1-n} = (1-n)k_n t \tag{1}$$

where, C_t is the residual concentration of DBT at time t (mmol/L), C_o is the initial concentration of DBT (mmol/L), n is the order of reaction and k_n is reaction constant for the n^{th} order reaction. First-order kinetic expression can be written as:

$$C_t = C_o \exp\left(-k_1 t\right) \tag{2}$$

where, k_1 is the first-order rate constant. A non-linear regression method was used to solve Equations (1) and (2) by minimizing the average relative error as given by:

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{(C_{t, \exp, i} - C_{t, cal, i})}{C_{t, \exp, i}} \right|$$
(3)

where, C_{exp} and C_{cat} are the experimental and calculated value of DBT concentrations in mmol/L. Table 2 shows the values of n, k_1 , k_n and ARE for different catalysts. Comparison of three kinetic models was carried out by plotting a graph between experimental values and calculated values of C_t as shown in Figure 4. Data represented in comparison of R^2 and ARE values in Table 2 for two models show that the n^{th} -order kinetic model better represented the kinetic data. Order of reaction and the first-order rate constant were least with **4** as catalyst indicating its efficacy over other tested catalysts.

4. Conclusion

Oil-soluble *N*-benzylated cobalt phthalocyaninetetrasulfonamide (**4**) was synthesized by reaction of benzyl alcohol on water-soluble cobalt phthalocyaninetetrasulfonamide using the FeCl₂/K₂CO₃ catalyst system. This *N*-benzylated phthalocyanine was characterized by elemental analysis, FT-IR, UV–vis, TG and mass spectrometry. It was further used to remove a refractory sulfur compound, DBT, via oxidative-extractive desulfurization using H₂O₂ as an oxidant and acetonitrile as an extracting solvent. Effects of various parameters were studied and the optimized parameters were: **4**:DBT molar ratio = 1:10; DBT:H₂O₂ molar ratio = 1:15, acetonitrile:*n*-dodecane volume ratio = 2:1, temperature = 40 °C; time = 2 h. Oxidation kinetics were best represented by the *n*thorder kinetic model with *n* = 3.3 using **4** as catalyst. At the optimized conditions, maximum removal of the DBT was 85% by **4**.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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