

Original Article: Isolation and Characterization of Bis(2-ethylheptyl) Phthalate from Cynodon Dactylon (L.) and Studies on the Catalytic Activity of its Cu(II) Complex in the Green Preparation of 1,8-dioxo-Octahydroxanthenes

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ABSTRACT

Bis(2-ethylheptyl) phthalate is an anti-oxidant and anticancer compound that was extracted from the Cynodon dactylon plant stem extract and fully identified and characterized by FTIR, CHN, ¹HNMR, ¹³CNMR, along with various 2D NMR techniques. The phthalate compound was modified and functionalized by polyethylene glycol (PEG) chains followed by complexation to Cu(II) ions. The resultant complex was applied as an efficient and strong recyclable homogeneous catalyst for the preparation of 1,8-dioxo-octahydroxanthenes under mild conditions. The homogeneous catalyst could be recovered and reused for several times.

Introduction

Xanthene is a cyclic poly aromatic compound having an etheric structure. It forms an important group of oxygenated heterocycles [1]. Two benzene rings are attached to tetra-hydropyran, a six-

membered ether ring containing five carbons and one oxygen [2-3]. Xanthenes derivatives are among the most important biologically oxygenated heterocyclics. These compounds have various biological and therapeutic properties such as antibacterial, antiviral

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activities, anti-inflammatory pigments, and photodynamic therapy [4]. For example, 1,3-dihydroxy-benzo [b] xanthene-12-one (Scheme 1) has been reported as an inhibitor of cancer cell growth. Xanthenes are used as dyes because of their conjugate double bonds and spectral thermodynamic properties. Xanthenes luminescence dyes include fluorones, pyronines and rhodamine [5]. To date, various methods have been developed for the preparation of xanthan compounds, including: (1) condensation of phenol derivatives with oxalic acid in the presence of H_2SO_4 [1], (2) the reaction of resorcinol or 1,6-dihydroxy naphthalene with aldehydes [3], (3) three-component reaction of 2-naphthol, 2-hydroxy-1,4-naphthoquinone, and isatin [6], (4) the reaction of dimedone with aromatic aldehydes [7], and (5) the reaction of β -naphthol with aldehydes [8]. However, a most straightforward and simple way for construction of pyran ring is the condensation of 2-equivalents of a 1,3-cyclohexadione with aldehydes [9].

Among the catalytic systems, recently developed for the preparation of xanthine compounds, it can be referred to: $\text{CuFe}_2\text{O}_4@\text{SiO}_2\text{-OP}_2\text{O}_5\text{H}$ [10], cellulose- HClO_4 [5], calcined oyster shell nanoparticles (COS NPs) [2], Ce-ZSM-11 Zeolite [9], caffeine-based ionic liquid [11], nickel NPs@N-doped titania [12], FSM-16/AEPC- SO_3H [13], CoNP@SBA-15 [14], $\text{Mg}(\text{BF}_4)_2$ doped in [BMIm][BF_4] [15], cellulose sulfuric acid [16, 17], [BMIm] $\text{BF}_4\text{-LiCl}$ [18] and iron oxide [1].

However, despite numerous progress for the synthesis of the desired compounds, many of the reported protocols suffer from impediments such as long reaction times, non-cost effective formation of un-wanted by-

products, non-environmentally benign, toxic solvents, low yields, use of high amount of catalyst, tedious work-up procedure, and harsh reaction conditions. Hence, finding a more efficient, simple, cost-effective, and eco-friendly catalytic system that covers the above-mentioned drawbacks is required.

Cynodon dactylon from the family of Graminae/Poacea, is a perennial plant with 1 to 30 cm long stems in the form of ascending stems or underground stems with short divisions. Its leaves are 2.5 to 10 cm long and are greenish-blue or dark green and have stellate-like inflorescences and have hyacinths without a peduncle in two rows on one side of the hyacinth (Figure 1) [19, 20]. Proliferation of the plant is mostly done by rhizomes, seeds and its habitat is mostly in the tropics [21]. *Cynodon dactylon* has many medicinal properties for treating various diseases such as diarrhea, diabetes, hypertension, caries, wounds and fever. It also has anti-microbial, anti-coagulant, anti-inflammatory, anti-malaria, anti-pain, anti-virus, and so on [22]. Extract of this plant can produce various types of phytochemicals such as alkaloids, saponins, phenols, flavonoids, tannins, sterols, glycosides, proteins, amino acids, and carbohydrates [23, 24]. Phytochemical analyses show that *Cynodon dactylon* contains flavonoids, alkaloids, glycosides, terpenoids, triterpenoids, steroids, saponins, tannins, resins, phytosterols, reducing sugars, carbohydrates, proteins, and volatiles and non-volatile oils, and also contains nutrients such as fat, fiber, iron, calcium, phosphorus, potassium and beta-carotene. According to studies done on this plant, the highest content of glycosides is 12.2%, followed by tannins, resins and alkaloids, respectively [25].

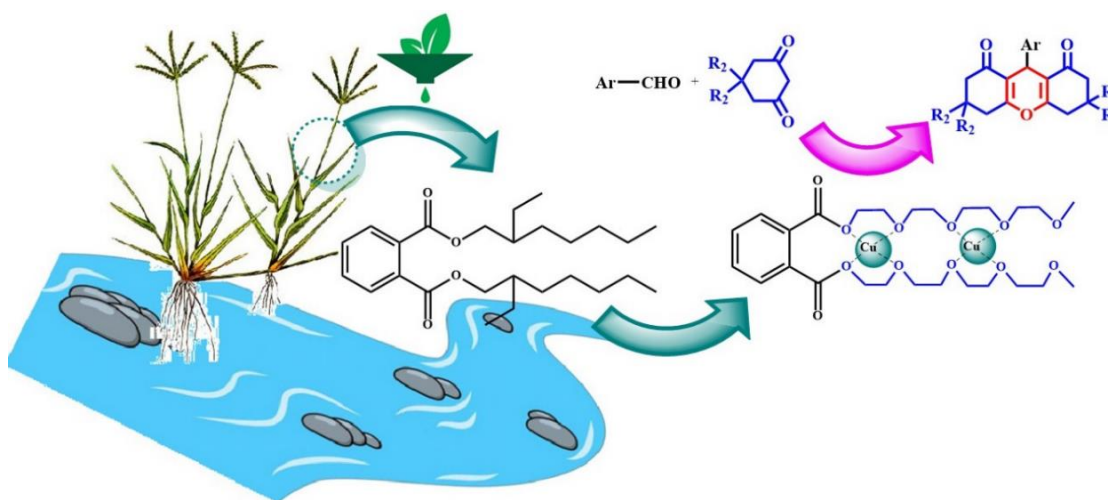


Figure 1. Images of *Cynodon dactylon*

Phthalates (also called phthalic acid diesters) are a group of chemicals commonly used in the plastics industry as lubricant. Lubricants are usually added to other materials, especially polyvinyl chloride and other polymers such as rubber and styrene, to make them flexible and elastic [26]. Phthalates can be used in some food packaging materials, adhesive used for paper, boards and plastics, cellulose resuscitated (cellophane), paper sheets, aluminum foil and sealants for bottles [27, 28].

Given the increasing importance of environmental issues and the improvement of reaction conditions for the preparation of

xanthene compounds [29, 30], bis(2-ethylheptyl) phthalate, as a biologically active compound, was successfully extracted from the plant extract, characterized, identified and used as a precursor for the preparation of an efficient catalyst. Hence, due to the importance as well as application of xanthene derivatives, herein a novel and green approach was introduced for the synthesis of xanthene derivatives by the copper (II) complex of bis(PEG) phthalate, that is extracted from *Cynodon dactylon* followed by transesterification by PEG chains, as an efficient homogeneous recyclable catalyst (Scheme 1).



Scheme 1. The extraction and chemical methodology of di(2-ethylheptyl) phthalate

Materials and Methods

Instrumentation and materials

All chemicals were purchased from Sigma and Merck or Fluka chemical companies and used as received without further purification. All the solvents were distilled under N_2 atmosphere and dried before use. Progress of the reactions and purity of the products were accomplished by thin layer chromatography (TLC). Elemental analyses (C, H, N, S) were carried out on a Perkin Elmer-2004 instrument. FTIR spectra were obtained using a JASCO FT/IR 4600 spectrophotometer using KBr pellet. The 1H NMR (300 MHz) and ^{13}C NMR (75 MHz) analyses were performed on a Bruker AVANCE3 3-300MHz instrument in $CDCl_3$ and $DMSO-d_6$ as a solvent and TMS as an internal standard. EDX spectroscopy was recorded on a field emission scanning electron microscope (FE-SEM, JEOL 7600F), equipped with a spectrometer of energy dispersion of X-ray from Oxford instruments. ICP analysis was performed using Varian Vista-PRO CCD simultaneous ICP-OES instrument.

Collection of plant materials

Healthy leaves of *C. dactylon* were collected in May 2017 from near and surrounding places of Birjand-Shokat Abad. The collected fresh leaves were washed 2–3 times with running water followed by drying up to 10 days under sterile conditions.

Preparation of plant extract

C. dactylon leaves powder (40 g) were transferred to a conical flask (800 mL), then 480 mL of chloroform was added to the flask. The conical flask containing *C. dactylon* leaves were shaken well for 24 h. Then, the extract was filtered using a Whatman filter paper No.1 and the filtrate used for further analyses.

Preparation of the catalyst (bis(PEG) phthalate-Cu(II))

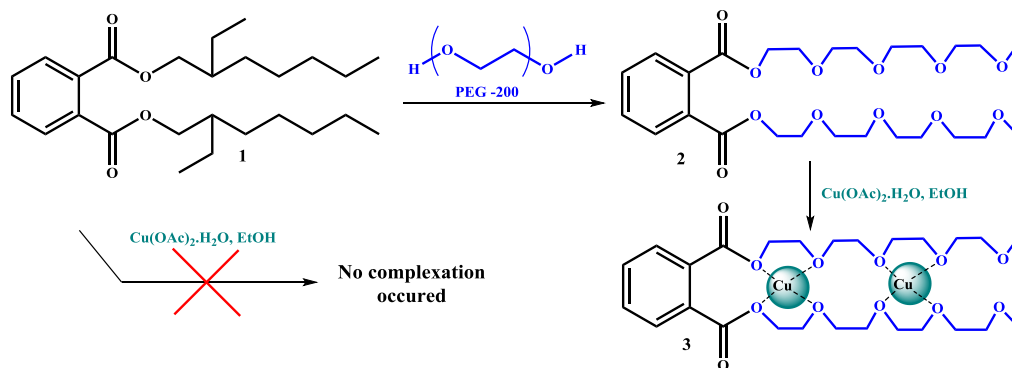
Initial attempts for the complexation of copper ions to bis(2-ethylheptyl) phthalate (**1**) was failed. It was expected that the complexation takes place through oxygen atoms. However, the heptyl groups was successfully replaced with ethylene groups by a transesterification reaction in the presence of PEG-200 (Scheme 1). Briefly, bis(2-ethylheptyl) phthalate (1.0 mmol) was added to 2 mL of PEG-200 and the reactor was sealed, vacuumed and equipped with a thermometer and N_2 flow. Then, 5.0 mmol NaOH was added to the system and the mixture was stirred at reflux conditions for 5 h. The reaction progress could be monitored by TLC. After reaction completion, the mixture was allowed to cool to ambient temperature, 10 mL water was added to the mixture, then extracted to 20 mL *n*-butanol. The solvent was removed from organic phase and compound **2** was isolated. Bis(PEG) phthalate (**2**) was dissolved in 20 mL EtOH and 1.0 mmol $Cu(OAc)_2 \cdot H_2O$ was added to the mixture. The mixture was stirred at reflux conditions for 2 h. Finally, bis(PEG) phthalate-Cu(II) (**3**) was isolated by simple filtration and isolated as stable green powder (Scheme 2).

General procedure for preparation of 1,8-dioxo-octahydroxanthenes

Aldehyde (1.0 mmol) and dimedone and/or 1,3-cyclohexadione (2.1 mmol) were added to 2.5 mL water in a 25 mL round bottom flask. The catalyst (1.0 mg, containing 0.0003 mmol Cu, 0.03 mol%) was added to the mixture and the resultant mixture was stirred at room temperature for an appropriate time. The reaction progress was monitored by TLC. Solubility of the catalyst in water facilitates the product extraction. Upon reaction completion, the product was extracted with diethyl ether (3×5 mL). The organic phases were combined

and the solvent was removed under reduced pressure. The crude product was recrystallized from EtOH to afford the pure xanthene product. The aqueous phase, that

now contains the catalyst, was poured into 30 mL cooled acetone. The catalyst immediately precipitated, then filtered and dried into oven (50 °C) for 8 h.



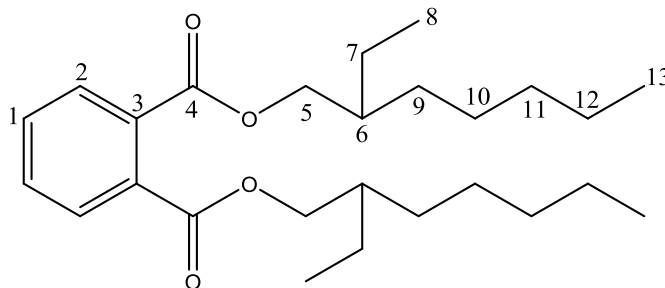
Scheme 2. Preparation of bis(PEG) phthalate-Cu(II) (3)

Results and Discussions

Characterization of bis(2-ethylheptyl) phthalate

The extracted bis(2-ethylheptyl) phthalate was fully characterized and identified by FTIR, CHN, ^1H NMR, ^{13}C NMR, DEPT and various 2D NMR techniques such as HMBC, H-H COSY, HMBC, and DEPT.

Table 1. ^1H and ^{13}C NMR data of bis(2-ethylheptyl) phthalate in CDCl_3



Position	δ_{C}	δ_{H}	#H, split (J in Hz)
1	130.88	7.53	2H, dd (8.8)
2	128.80	7.70	2H, dd (8.8)
3	132.47	-	-
4	167.74	-	-
5	68.13	4.21	4H, t (6.2)
6	38.75	1.65	2H, m
7	23.76	1.40	4H, m
8	10.96	0.90	6H, m
9	30.3	1.25	4H, m
10	28.9	1.29	4H, m
11	29.71	1.29	4H, m
12	22.99	1.31	4H, m
13	14.05	0.89	6H, m

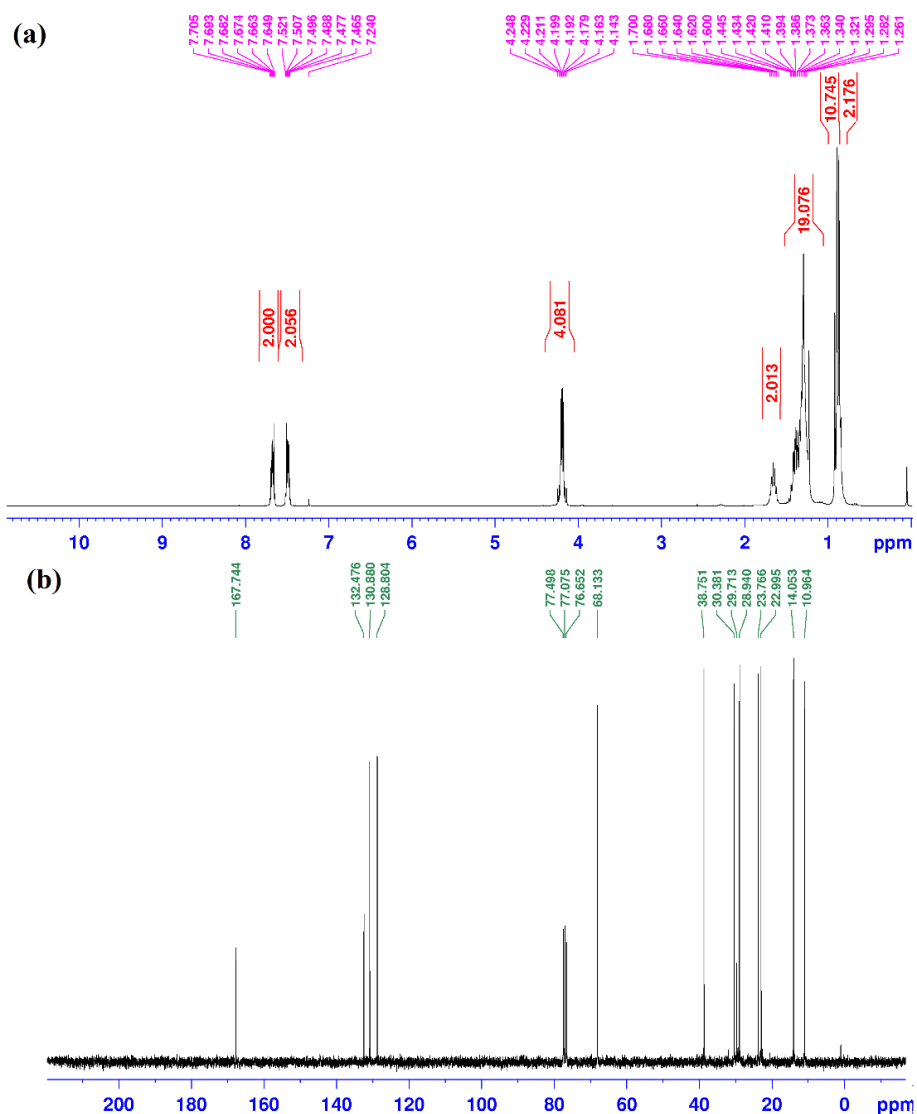


Figure 2. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) of bis(2-ethylheptyl) phthalate in CDCl_3

Elemental analysis of bis(2-ethylheptyl) phthalate (**1**) confirmed the chemical formula $\text{C}_{26}\text{H}_{42}\text{O}_4$ with 74.50%C, 10.33%H, and 15.15% O, very close to their theoretical values (74.60%C, 10.11%H, and 15.29%O). A characteristic peak at 1728 cm^{-1} represents the stretching vibration of carbonyl groups (ESI, Figure S1). Also, the stretching vibrations related to aliphatic and aromatic C-H have been appeared at 2859 cm^{-1} and 2958 cm^{-1} respectively in agreement with literature [31]. Table 1 shows the NMR data related to compound **1**. The ^1H NMR spectrum represents a typical AA'BB' system at $\delta=7.70$

and 7.53 ppm (Figure 2a). Based on the chemical shifts, coupling constants and how splitting, it was concluded that the compound is an ortho-disubstituted benzene ring involving the same substituent in both positions [32]. The ^{13}C NMR, HMQC, and DEPT, NMR signals (ESI, Figures S2-S5) confirmed the presence of two alkyl methanes, two carbonyl carbons, four aromatic methines, four methyls, and two O-bearing methyleneand groups. Based on DEPT-90 (ESI, Figure S2), there are 6 methylene groups (negative signals) at 68.1, 23.7, 30.3, 28.9, 29.7, and 22.9 ppm, respectively for C5, C7, C9,

C10, C11, and C12. The methyl groups were appeared at 14.0 and 10.9 ppm for C13 and C8 respectively. In addition, three peaks at 130.8,

128.8, and 38.7 ppm were assigned to C1, C2, and C6 respectively (Figure 2b) [31, 32]

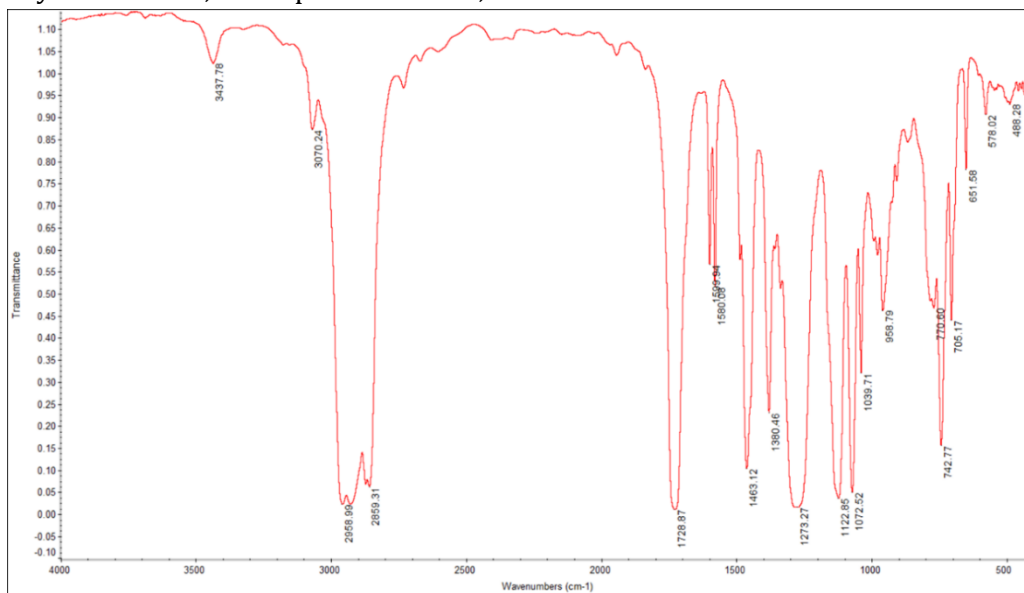


Figure S1. FTIR spectrum of bis(2-ethylheptyl) phthalate

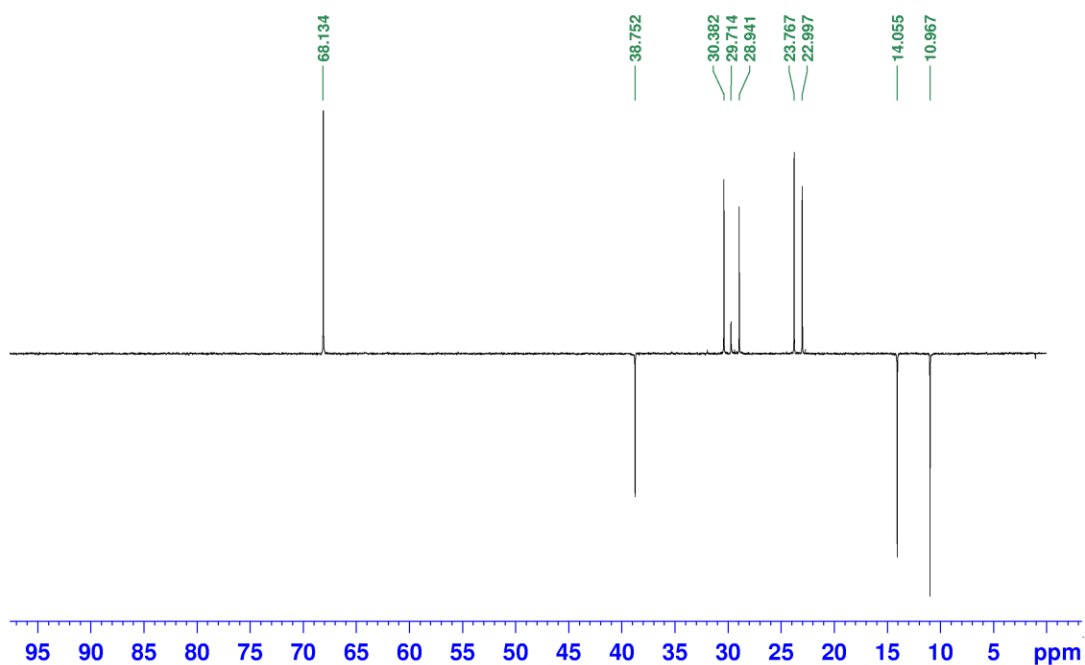


Figure S2. DEPT spectrum of bis(2-ethylheptyl) phthalate (75 MHz, CDCl_3)

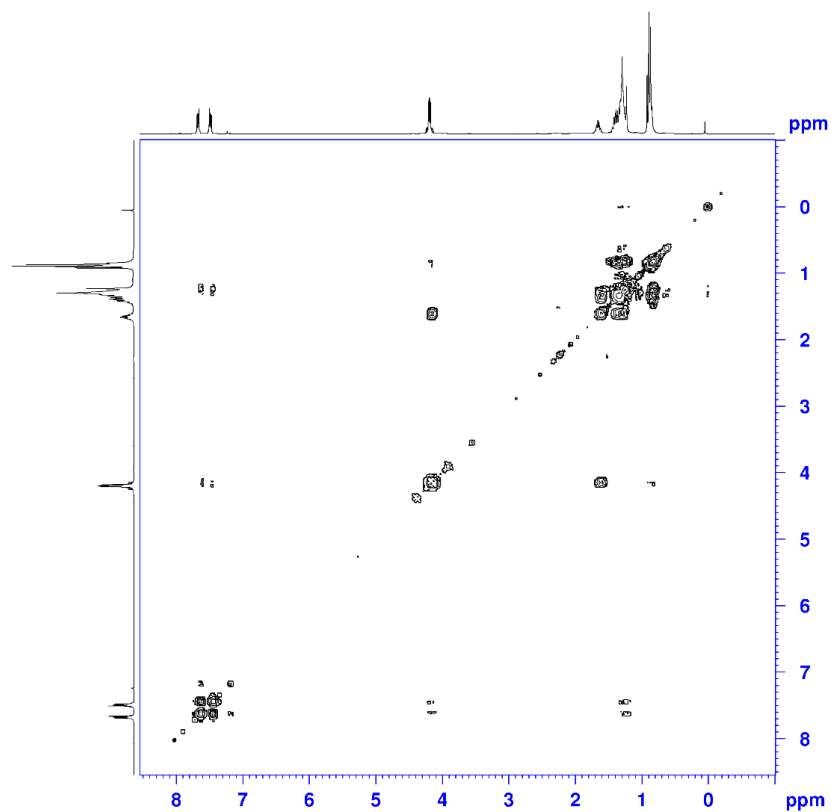


Figure S3. H-H COSY spectrum of bis(2-ethylheptyl) phthalate (300 MHz, CDCl_3)

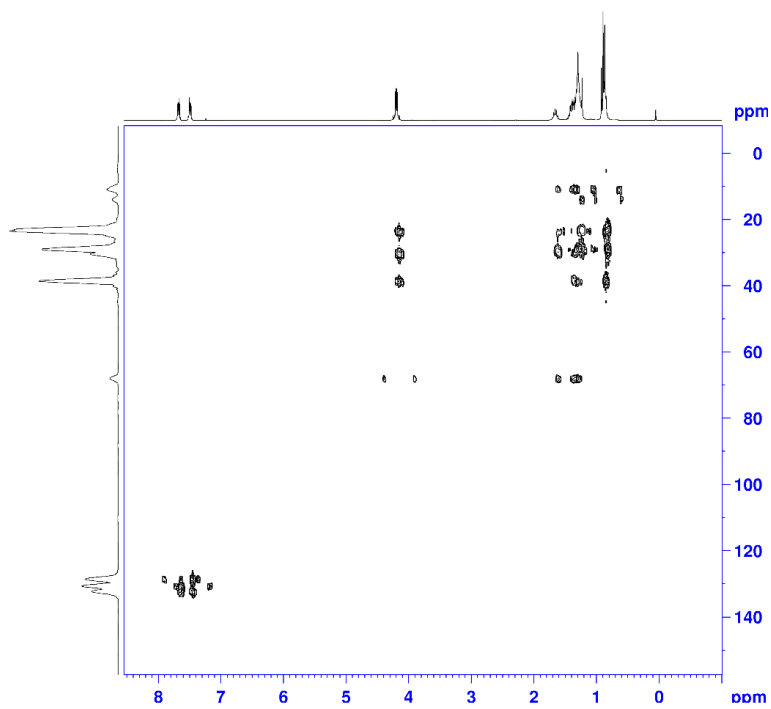


Figure S4. HMBC spectrum of bis(2-ethylheptyl) phthalate (CDCl_3)

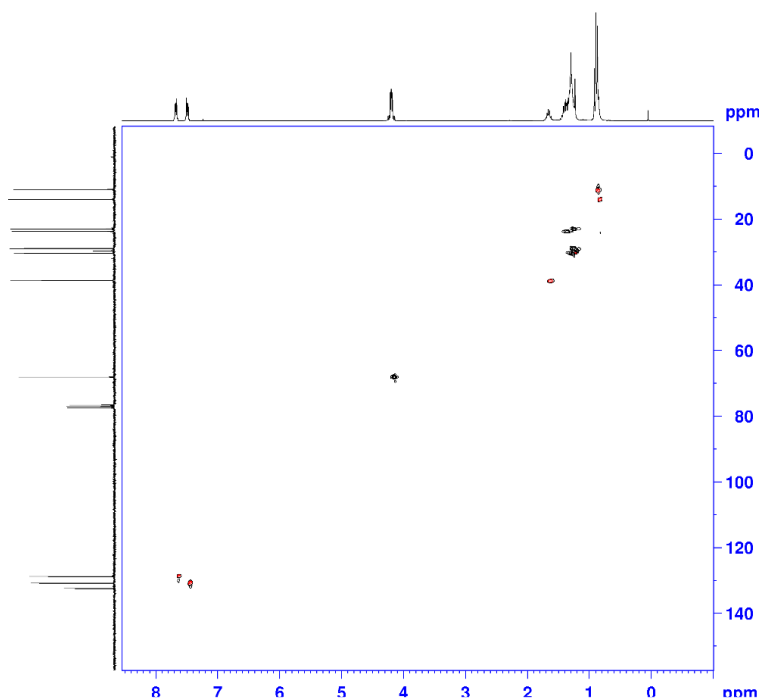


Figure S5. HSQC spectrum of bis(2-ethylheptyl) phthalate (CDCl_3)

Characterization of the catalyst

Transesterification of bis(2-ethylheptyl) phthalate with polyethylene glycol chains was performed under basic conditions ($\text{pH}=11.0$). Advent of a sharp and broad peak at 3331 cm^{-1} represents the O-H stretching vibrations in PEG terminal chains (Figure 3a). Subsequently, a series of newly formed peaks at $394\text{--}494\text{ cm}^{-1}$ were assigned to Cu-O stretching vibrations (Figure 3b), which confirmed the successful coordination of copper ions to oxygen of PEG chains (Scheme 1). Ether C-O bond stretching vibrations were appeared at 1150 and 1170 cm^{-1} for bis(PEG) phthalate (Figure 3a) and bis(PEG) phthalate-Cu(II) (Figure 3b). Electronic absorption of the

catalyst represents three strong peaks at 272 , 318 , and 386 nm that could be assigned to $\pi\rightarrow\pi^*$ and MTCT (related to coordinated-Cu) absorption [33].

The catalyst was further characterized by ^1H NMR and EDX analyses (Figure 4). The chemical shifts related to PEG chains methylenes were appeared at 3.60 , 3.70 , 3.96 , and 4.43 ppm . In addition, a peak with low intensity at 5.57 ppm demonstrated the aliphatic hydroxyl proton at terminal PEG chains. The EDX analysis indicates the presence of C, O, and Cu (1.86 wt\%).

The amount of Cu ions present in the catalyst was measured by EDX as well as ICP analyses that was 1.86 \%wt .

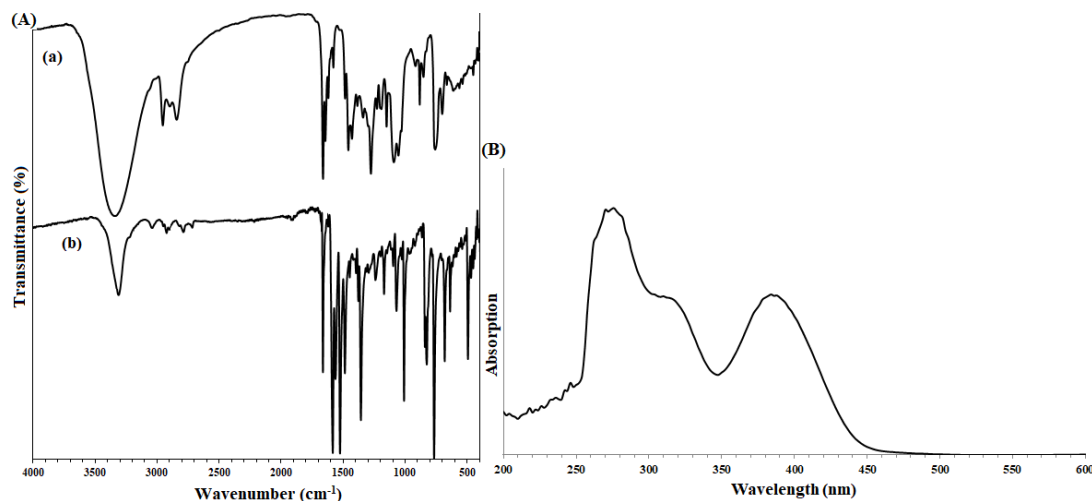


Figure 3. (A) FTIR of (a) PEG-functionalized bis(2-ethylheptyl) phthalate (2) and (b) bis(2-ethylheptyl) phthalate-PEG-Cu(II) complex (3). (B) UV-Vis spectra of bis(2-ethylheptyl) phthalate-PEG-Cu(II) complex (3)

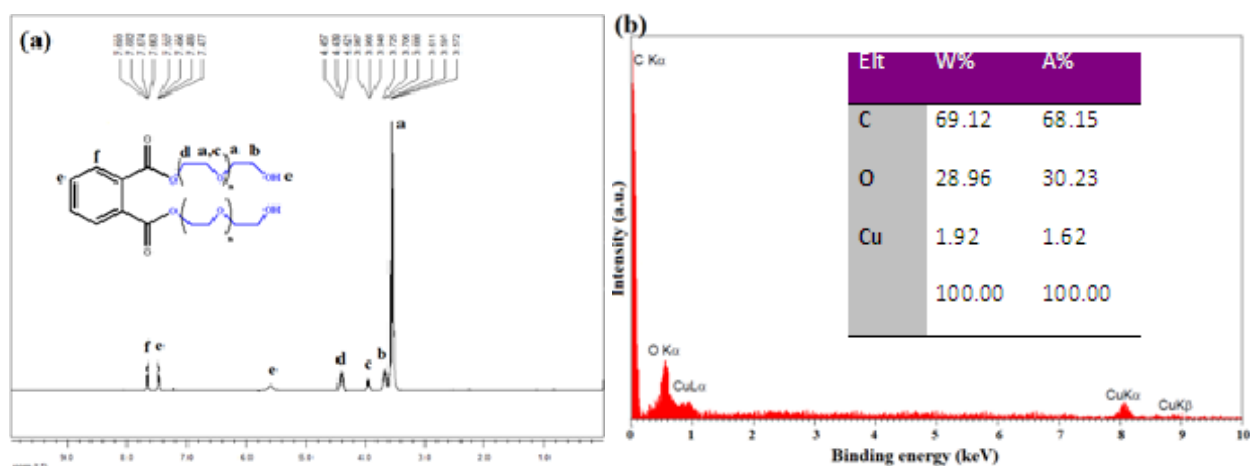


Figure 4. (a) ¹H NMR spectrum of bis(PEG) phthalate (2) and (b) EDX spectrum of bis(PEG) phthalate-Cu(II) (3)

Catalytic activity of 3

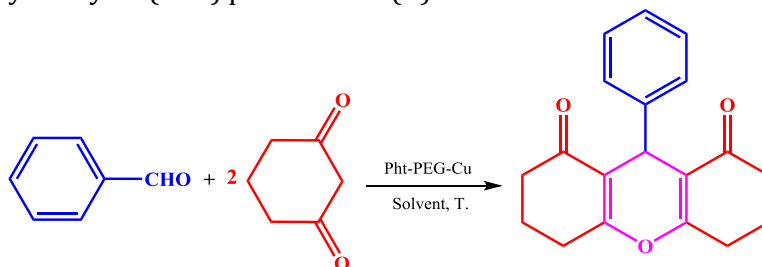
Initially, the parameters involve in the preparation of xanthenes were investigated on the condensation of benzaldehyde (1.0 mmol) with 1,3-cyclohexadione (2.0 mmol) as a model reaction. Water was found as an efficient solvent for this transformation with 95% yield at room temperature (Table 2, Entry 3). As shown in Table 2, solvents such as DMSO, PEG-200, EtOH and MeOH (Table 2, Entries 1 and 4-7), also, provide the same results, slight better in some cases. However,

note to environmental considerations, water as a safe and green solvent was chosen for the preparation of 1,8-dioxo-octahydroxanthenes. Given the presence of polar PEG groups in the catalyst, polar protic solvents exhibited more performance than others such as THF (Entry 3), CH₃CN (entry 5), and toluene (Entry 6). The reaction afforded a moderate yield under solvent-free conditions (Table 1, Entry 10, 60%). In addition, good solubility of the catalyst was another driving force and reason for this performance. The highest possible

efficiency was achieved at room temperature; and raising temperature didn't effect on efficiency (Whether for water and other protic solvents or solvents such a THF). However, a

slight increase in efficiency was observed at reflux conditions for toluene and CH₃CN. The reaction didn't give a satisfactory yield in solvent-free conditions (Table 2, Entry 10).

Table 2. Investigation of the reaction parameters on the condensation reaction of benzaldehyde with 1,3-cyclohexadione for the preparation of 9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione catalyzed by bis(PEG) phthalate-Cu(II)^a



Entry	Solvent	Cat. amount (mg)/ mol%	Yield (%) ^b
1	DMSO	1.0/ 0.03	97
2 ^c	THF	1.0/ 0.03	56
3	H ₂ O	1.0/ 0.03	95
4	EtOH	1.0/ 0.03	95
5 ^c	CH ₃ CN	1.0/ 0.03	35
6 ^c	Toluene	1.0/ 0.03	40
7	PEG-200	1.0/ 0.03	96
8	Glycerol	1.0/ 0.03	97
9	MeOH	1.0/ 0.03	97
10 ^d	-	1.0/ 0.03	60
11	H ₂ O	2.0/ 0.06	95
12	H ₂ O	3.0/ 0.09	95
13	H ₂ O	0.05/ 0.0015	80
14	H ₂ O	-	Trace
15	H ₂ O	1.0/- ^e	N.R.

^aReaction conditions: Benzaldehyde (1.0 mmol), 1,3-cyclohexadione (2.0 mmol), bis(PEG) phthalate-Cu(II) (as a catalyst), temperature, solvent (2.5 mL), 30 min.

^bIsolated yield.

^cIn these solvents, the catalyst does not have good solubility and it remains heterogeneous partially in some cases.

^dSolvent-free, 110 °C. ^eBis(2-ethylheptyl) phthalate was used as a catalyst

Note to homogeneous nature of the catalyst, a very small amount of catalyst (0.1 mg) was sufficient for the preparation of 9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione in water at room temperature (Table 2, Entry 3). As the catalyst content increases, the efficiency remains constant (Table 2, Entries 11-13). The catalytic activity of bis(PEG) phthalate-Cu(II) was understood when the reaction took place in the absence of

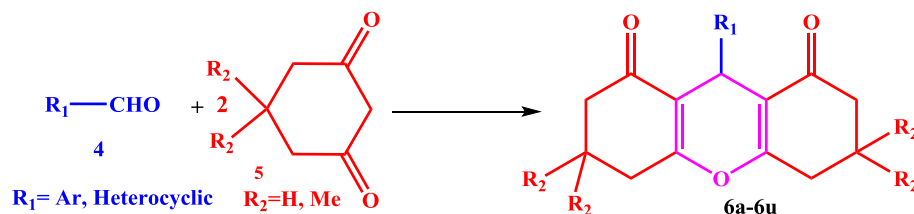
the catalyst, which a negligible product was found in absence of **3**.

With optimum conditions in hand, various aldehyde derivatives were condensed with dimedone or 1,3-cyclohexadione. The results were tabulated in Table 3. High to excellent yields were achieved for all entries. Electronic effects were demonstrated that activated aldehydes with electron donating substituent accelerates the reaction and increases the

reaction yield (Table 3, see and compare **6f** with **6g**; **6h** with **6i**; etc.). Another result from Table 3 was the higher efficiency of xanthenes

with dimedone than 1,3-cyclohexadione (Table 3, compare **6e** with **6r**; **6b** with **6p**; etc.).

Table 3. Synthesis of 1,8-dioxo-octahydroxanthenes (**6a-6w**) catalyzed by bis(PEG) phthalate-Cu(II) in water at room temperature^a



Entry	R ₁	R ₂	Product	Time (min)	Yield (%)
1	4-Me-phenyl	H	6a	25	95
2	4-Cl- phenyl	H	6b	20	90
3	3-Me- phenyl	H	6c	40	93
4	4-OH- phenyl	H	6d	20	96
5	Phenyl	H	6e	30	95
6	2-OH- phenyl	H	6f	25	98
7	4-NO ₂ - phenyl	H	6g	50	90
8	4-MeO- phenyl	H	6h	25	98
9	4-CN- phenyl	H	6i	40	92
10	2-Furyl	Me	6j	45	90
11	2-Picolin	Me	6k	40	88
12	3-1 <i>H</i> -indole	Me	6l	55	89
13	2-Thiophene	Me	6m	60	85
14	2-Naphthyl	Me	6n	80	80
15	4-Me- phenyl	Me	6o	20	88
16	4-Cl- phenyl	Me	6p	20	98
17	4-OH- phenyl	Me	6q	15	98
18	Phenyl	Me	6r	30	97
19	2-MeO- phenyl	Me	6s	30	98
20	4-NO ₂ - phenyl	Me	6t	25	94
21	4-MeO- phenyl	Me	6u	20	98

^aReaction conditions: 1,3-dione (2.2 mmol), aldehyde (1.0 mmol), catalyst (7.0 mg), water (3.0 mL), room temperature

Mechanism studies

The homogeneous catalyst provides a suitable interaction between reactants in water because of PEG hydrophilic chains in the catalyst that drives the organic compounds towards the catalyst in aqueous medium.

Figure 5 shows this phenomenon that may be responsible for the high efficiency observed for xanthan compounds. As shown in Figure 5, the PEG hydrophilic groups help the solubility of the catalyst in the medium and help to other organic reactants to interact more with the catalyst.

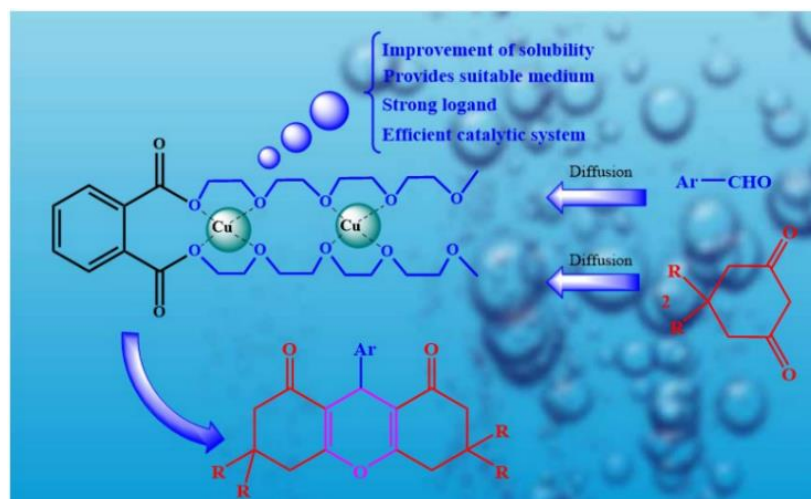
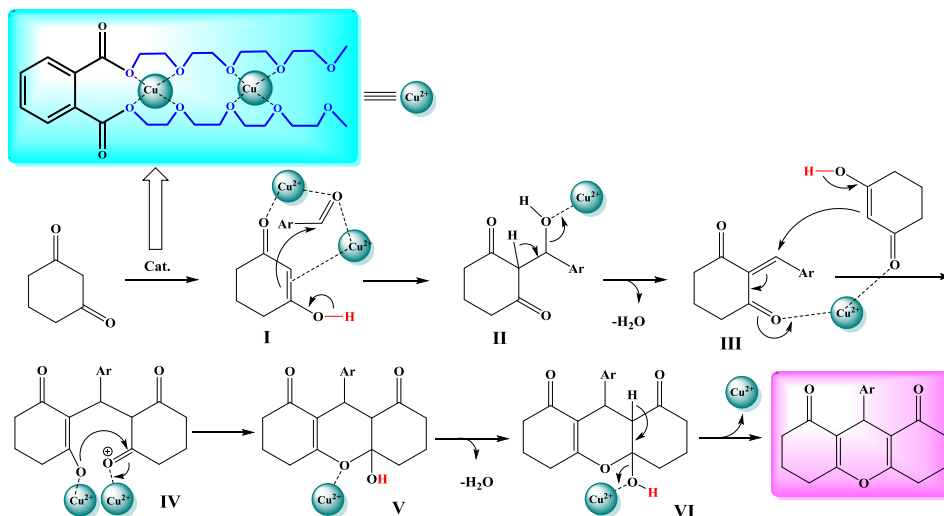


Figure 5. A plausible interaction of bis(PEG) phthalate-Cu(II) with the reactants in water to efficient preparation of 1,8-dioxo-octahydroxanthenes

According to the literature reports regarding to the transition metal-catalyzed preparation of 1,8-dioxo-octahydroxanthenes [32, 33], a plausible mechanism for bis(PEG) phthalate-Cu(II) was suggested. As shown in Scheme 2, the reaction begins with the nucleophilic attack of 1,3-dione compound to the activated aldehyde by Cu(II) sites in the catalyst (Scheme 3, I). By removing a H_2O molecule, the Knoevenagel intermediate III is formed. The reaction proceeds with the one

more nucleophilic attack of 1,3-dione compounds that has been pre-activated by Cu(II) sites in the catalyst and forms intermediate IV. Further cyclization (intermediate V) and dehydration (intermediate VI) give the desired xanthene product. It is also important to note that the homogeneous catalyst could be recovered from the mixture by the precipitation from the aqueous solution into cooled acetone. In this way, the catalyst was used for several times.



Scheme 3. A plausible reaction mechanism for bis(PEG) phthalate-Cu(II)-catalyzed preparation of 1,8-dioxo-octahydroxanthene derivatives

Although the catalyst is homogeneous in aqueous medium, it is insoluble in acetone. So, after completion of the reaction and during product extraction, the catalyst was precipitated by 30 mL cooled acetone, dried into oven (50 °C) and reused for the next run. Although the efficiency loss for the homogeneous catalyst **3** is much higher than for a heterogeneous catalyst, this capability is extremely valuable for a homogeneous catalyst [34]. The recyclability was evaluated

for four consecutive runs, wherein the average efficiency loss was about 6% per cycle. In addition, this feature also made it possible to measure metal leaching in each cycle. As shown in Figure 6, the rate of leaching was similarly high. However, this recoverability facilitates the catalyst extraction from the reaction mixture and product purification, the advantage that most homogeneous catalysts lack.

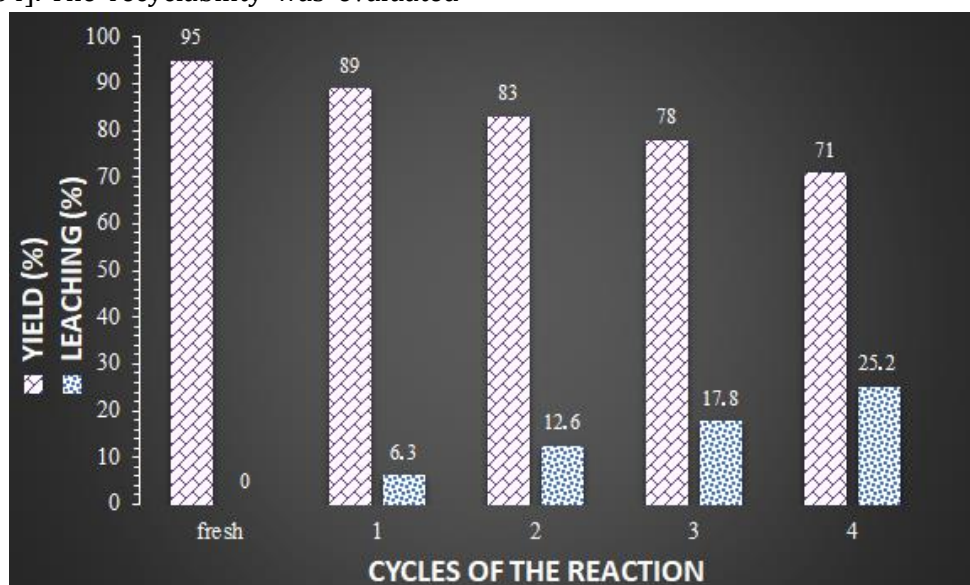


Figure 6. Recyclability and leaching studied of the bis(PEG) phthalate-Cu(II) over the reaction of bezaldehyde (1.0 mmol) with 1,3-cyclohexadione in water at room temperature

Conclusion

In this study, the biologically active bis(2-ethylheptyl) phthalate was extracted from the *Cynodon dactylon* plant stem extract. Its structure was identified and proved by FTIR, CHN, 1D (^1H NMR, ^{13}C NMR, DEPT), and 2D (H-H COSY, HSQC, HMBC) NMR methods. The characterized phthalate compound was functionalized by PEG chain *via* a transesterification reaction in one step and subsequently complexed to Cu(II) ions. Bis(PEG) phthalate-Cu(II) was found as a simple, efficient homogeneous catalyst for the synthesis of 1,8-dioxo-octahydroxanthene

derivatives in water at room temperature. High to excellent yields were obtained for all derivatives. Mild reaction conditions, high efficiency, ecofriendly, cost-effective preparation of the catalyst with cheap, green and accessible material are some of the advantages of the present methodology that makes it as an efficient and reliable alternative for the preparation of xanthene derivatives. More importantly, the homogeneous catalyst could be readily recovered from the reaction mixture and reused for at least 4 consecutive runs, however with a significant reactivity loss.

Conflicts of interest

There are no conflicts to declare.

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