

Fenton-like degradation of Bisphenol A catalyzed by mesoporous Cu/TUD-1

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Abstract

A family of copper oxide catalysts with loadings spanning 1 to 5 wt% were dispersed on a three dimensional, mesoporous TUD-1 silica through a hydrothermal, surfactant-free route employing tetraethylene glycol as a structure-directing agent. Their bulk and surface properties were characterized by N₂ physisorption, XRD, DRUVS, EPR, TEM and Raman spectroscopy, confirming the expected mesoporous wormhole/foam support morphology and presence of well-dispersed CuO nanoparticles (~5-20 nm). The catalytic performance of Cu/TUD-1 was evaluated as heterogeneous Fenton-like catalysts for Bisphenol A (BPA) oxidative degradation in the presence of H₂O₂ as a function of [H₂O₂], and CuO loading. Up to 90.4 % of 100 ppm BPA removal was achieved over 2.5 wt% Cu/TUD-1 within 180 min, with negligible Cu leaching into the into the treated water.

Keywords:

Copper; TUD-1; Fenton-like oxidation; mesoporous solid; Bisphenol A; excitation-emission matrix; EPR.

1 Introduction

Fenton type advanced oxidation processes (AOPs) are one of the most efficient and widely utilized wastewater treatments [1]. Heterogeneous Fenton agents have many advantages over their homogeneous counterpart for the degradation of organic pollutants in wastestreams, with many studies focused on the development of iron-derived heterogeneous Fenton catalyst systems [2–11]. Hartman et al. have reviewed the development and application of such Fe-containing porous catalysts for wastewater treatment [12]. Fe-ZSM-5 [13], Fe(II)/meso-Al₂O₃ [14], Fe(III) oxide/carbon [15], magnetic α -Fe₂O₃/MCM-41 [16], Fe/SBA-15 [17], and Fe/TUD-1 [18] are all reported to exhibit excellent degradation activity towards various organic pollutants.

Cu²⁺/Cu⁺-containing materials offer interesting alternative catalysts, since they also exhibit Fenton-like oxidation activity [19]. A range of copper catalysts including CuFe/ZSM-5 [20], stabilized CuO nanoparticles [21], CuO/CeO₂ [22], Cu-functionalized titanate nanotubes [23] and CuFeO₂ [24] have all been explored for their degradation ability towards various water pollutants. Copper promoted mesoporous materials such as MCM-41[25], mesoporous activated carbon [26], and copper-doped mesoporous silica microspheres [27] have also been reported for Fenton- or photo-Fenton-like pollutant degradation. Nevertheless, very few copper promoted mesoporous catalysts have been systematically studied for wastewater treatment to date.

We reported recently on the preparation of Cu/TUD-1 [28], based upon TUD (Technische Universiteit Delft), a mesoporous silica that can be prepared by an environmentally friendly route. The formation of Cu-atrane and silatrane complexes during TUD-1 synthesis [28,29] facilitates a high dispersion of framework Cu species in the silica network. We have also

employed tetraethylene glycol (TEG) as structure directing agent for TUD-1 (in place of triethanolamine) to prepare various metal incorporated TUD-1 materials [30–32].

Despite increasing environmental legislation and public awareness, many organic compounds are still discharged directly into water resources, especially in low and middle-income countries [33, 34]. Bisphenol A (BPA; 2,2-bis-(4-hydroxy phenyl)-propane) is one such endocrine disrupter [34–37] prevalent in different biospheres regions (e.g. water and soil sediments) of Tamil Nadu, India [34,38]. As a result of BPA's detrimental health impact on humans and animals several approaches have been developed to degrade it within wastewater [39–42].

Here we extend the application of our TEG-directed synthesis of TUD-1 to incorporate Cu, and demonstrate its application as a Fenton-like heterogeneous catalyst for BPA degradation.

2 Experimental

2.1 Synthesis of Cu/TUD-1

Cu/TUD-1 catalysts with varying Si:Cu ratios of 100, 50 and 25 (corresponding to Cu loadings of 1, 2 and 4 wt% respectively) were prepared using TEG as a template adapting our previous methodology [30–32]. In brief, 10 g of tetraethyl orthosilicate (TEOS) and the requisite amount of copper nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in water were stirred for 30 minutes. Subsequently, 7 mL of TEG was added dropwise and stirred for 1 h. Finally, tetraethylammonium hydroxide (TEAOH, 35%, 9 g) was added and stirring continued for 2 h. The resulting gel was aged at 30 °C and dried at 100 °C for 24 h, then transferred into a Teflon-lined autoclave and heated for 6 h at 160 °C. The resultant solid was calcined at 600 °C for 10 h in air to remove the template and other

organic components. The final Cu/TUD-1 catalysts contained 0.9, 2.5 and 5.4 wt% Cu from elemental analysis.

2.2 Characterization

Powder X-ray diffraction (XRD) measurements were carried out on a Bruker D8 instrument using Cu K α radiation ($\lambda = 1.5418\text{\AA}$). N₂ physisorption was performed on a Micromeritics ASAP 2020 porosimeter at -196 °C. Sample morphology was investigated via scanning electron microscopy (SEM) using FEI ESEM Quanta 200 microscope, and high-resolution transmission electron microscopy (HRTEM) using a JEOL 3010 instrument. Diffuse reflectance UV-Vis spectra (DRUVS) were recorded between 200-800 nm on a Thermoscientific Evolution 600 instrument using a BaSO₄ reference. Raman spectra were measured on a Bruker FT-Raman 1000R instrument with a 1064 nm excitation source. Electron spin resonance (ESR) spectra were recorded on a JEOL JES FA-300 spectrometer at room temperature. EPR spin trapping of Cu/TUD-1 was obtained at room temperature using a quartz liquid flat cell (Wilmad WG-812-Q) in a TE102 cavity of a Bruker ESP 300E spectrophotometer. The spectrophotometer was operated at a microwave frequency of 9.399 GHz, with microwave power of 3.188 mW, modulation frequency of 100 kHz and modulation amplitude of 3.0 G, 3200 G center field, and a sweep width of 500 G and sweep time of 20.972 s. X-ray photoelectron spectroscopy (XPS) was undertaken on an Omicron ESCA probe spectrometer with Al K α radiation (1486.7 eV). Energy referenced to adventitious carbon at 284.9 eV binding energy. Copper content was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Perkin Elmer OES Optima 5300 DV spectrometer.

2.3 Oxidative degradation of BPA

BPA degradation was performed in a 500 mL polypropylene bottle under magnetic stirring. 100 ml of a 100 ppm aqueous BPA solution was prepared with an initial pH of 6.45. The pH was adjusted to 3.5 using 1 N H_2SO_4 and 0.1 g of catalyst added to the BPA solution. Various amounts of H_2O_2 (between 20 mM to 100 mM) were then added to initiate oxidative degradation. 1 mL aliquots of the reaction solution were periodically withdrawn for spectrophotometric analysis by UV-Vis analysis [12]. Copper leaching tests were conducted on filtered Cu/TUD-1 catalysts post-reaction by atomic absorption on a Shimadzu AA spectrophotometer. Fluorescence excitation/emission spectra were recorded using a Varian/CARY fluorescence spectrophotometer under 3D mode with an excitation wavelength between 200-600 nm with a step size of 5 nm using a quartz cuvette with 1 cm path length.

3 Results and discussions

3.1 Characterizations of Cu/TUD-1

Low angle XRD patterns of the 0.9 wt% Cu/TUD-1 (Figure 1a) exhibited a single weak and broad reflection around 0.9° , also present in undoped TUD-1 prepared via the same route (Figure S1). The lack of additional reflections indicated a disordered arrangement of mesopores, commonly observed for metal incorporated TUD-1 [30–32,43,44]. The absence of this low angle reflection for 0.25 and 5 wt% Cu/TUD-1 indicates that this disorder increased with Cu loading. Wide angle XRD patterns of all Cu/TUD-1 samples exhibited a broad reflection between $15\text{--}30^\circ$ arising from the amorphous silica support, and sharp reflections characteristic of a crystalline CuO phase at 35.5° and 38.6° whose intensity increased with Cu loading associated with an

increase in mean crystallite diameter (as estimated by Scherrer peakwidth analysis) from 5 to 20 nm.

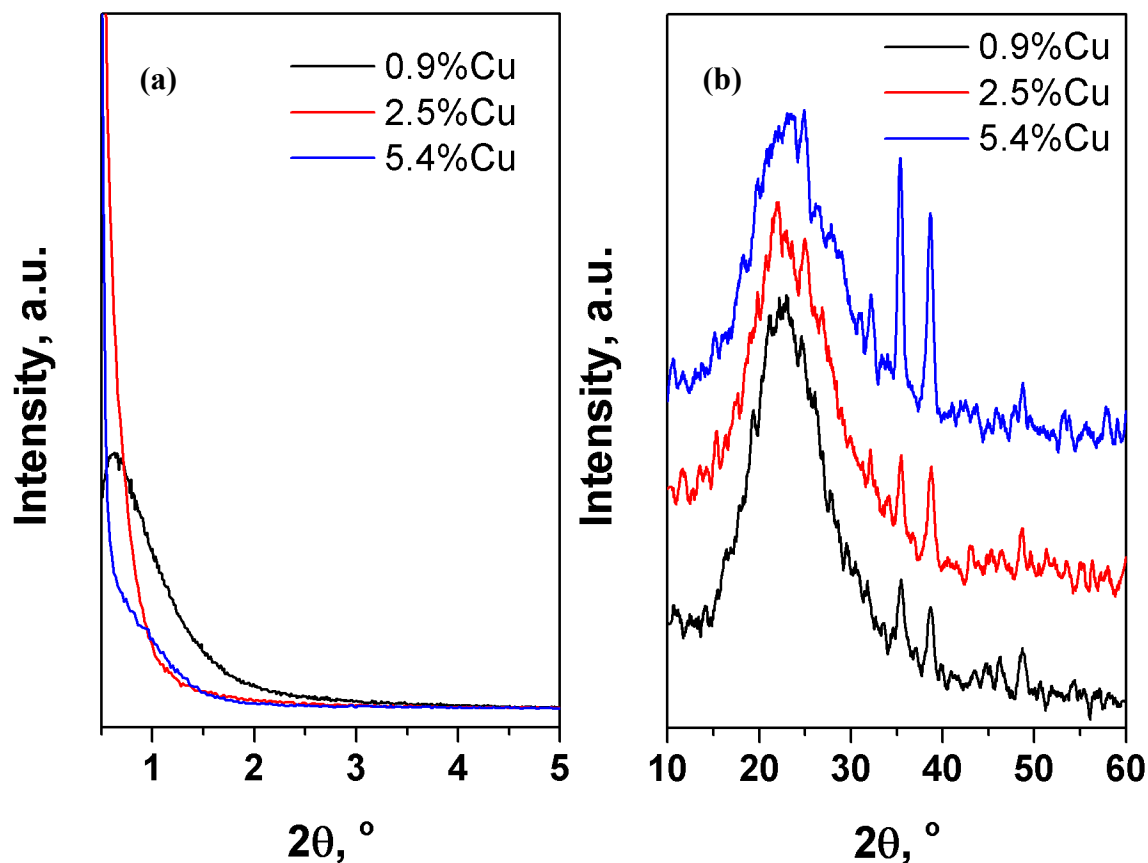


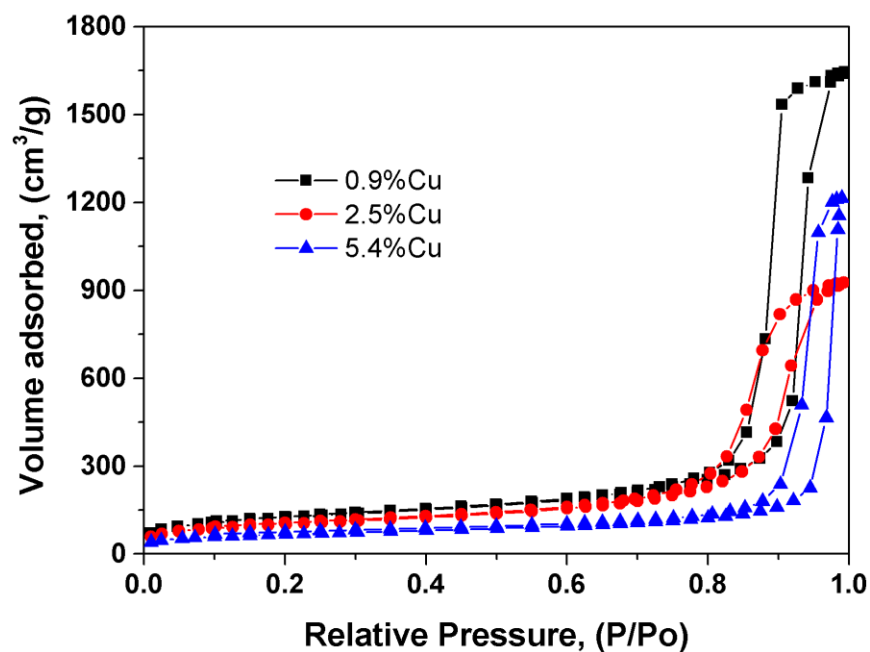
Figure 1. (a) Low and (b) wide angle powder XRD patterns of Cu/TUD-1

The mesoporous nature of Cu/TUD-1 was apparent from nitrogen porosimetry which revealed type IV isotherms with H2 type hysteresis loops for all copper loadings (Figure 2), as expected for TUD-1 type wormhole pore architectures. Corresponding BET surface areas, mean BJH pore diameters and mesopore volumes are reported in Table 1, and were similar to an undoped TUD-1 and approximately independent of Cu loading, comparable to our previous TEG-templated Mn/TUD-1, Zr/TUD-1 and Co/TUD-1 materials [30–32].

Table 1. Physical characterization of different Cu/TUD-1 catalysts

Cu loading	S_{BET}^b	$d_{\text{P, BJH}}^c$	$V_{\text{p, BJH}}^d$
/ wt% ^a	m ² /g	/ nm	/ cm ³ /g
0	490	6.0	1.72
0.9	437	7.8	1.86
2.5	425	6.7	1.39
5.4	393	8.1	1.98

^aFrom ICP-OES analysis; ^bspecific surface area; ^cmean mesopore diameter; ^dmesopore volume

**Figure 2.** N₂ adsorption-desorption isotherms of Cu/TUD-1

DRUV spectra of Cu/TUD-1 exhibited absorption bands at 235, 310 and 350-800 nm (Figure 3a), similar to those for Cu/TUD-1 prepared by a TEA template route [28]. The band at 235 nm is assigned to ligand-to-metal charge transfer (LMCT) from an O²⁻ to an isolated Cu²⁺ ion in a

tetrahedral coordination, and that at 310 nm arises from CuO oligomers. Strong absorption between 350 and 800 nm is attributed to bulk CuO (copper in a pseudo-octahedral environment), with the intensity of this band increasing with Cu concentration indicating the growth of extra-framework CuO particles in Cu/TUD-1 consistent with XRD. FT-Raman spectra of Cu/TUD-1 revealed two sharp and one broad peaks at 295, 342 and 620 cm^{-1} respectively for all Cu loadings (Figure 3b), assigned to the A_g and $2B_g$ Raman active modes of CuO [28] in agreement with XRD and DRUVS results.

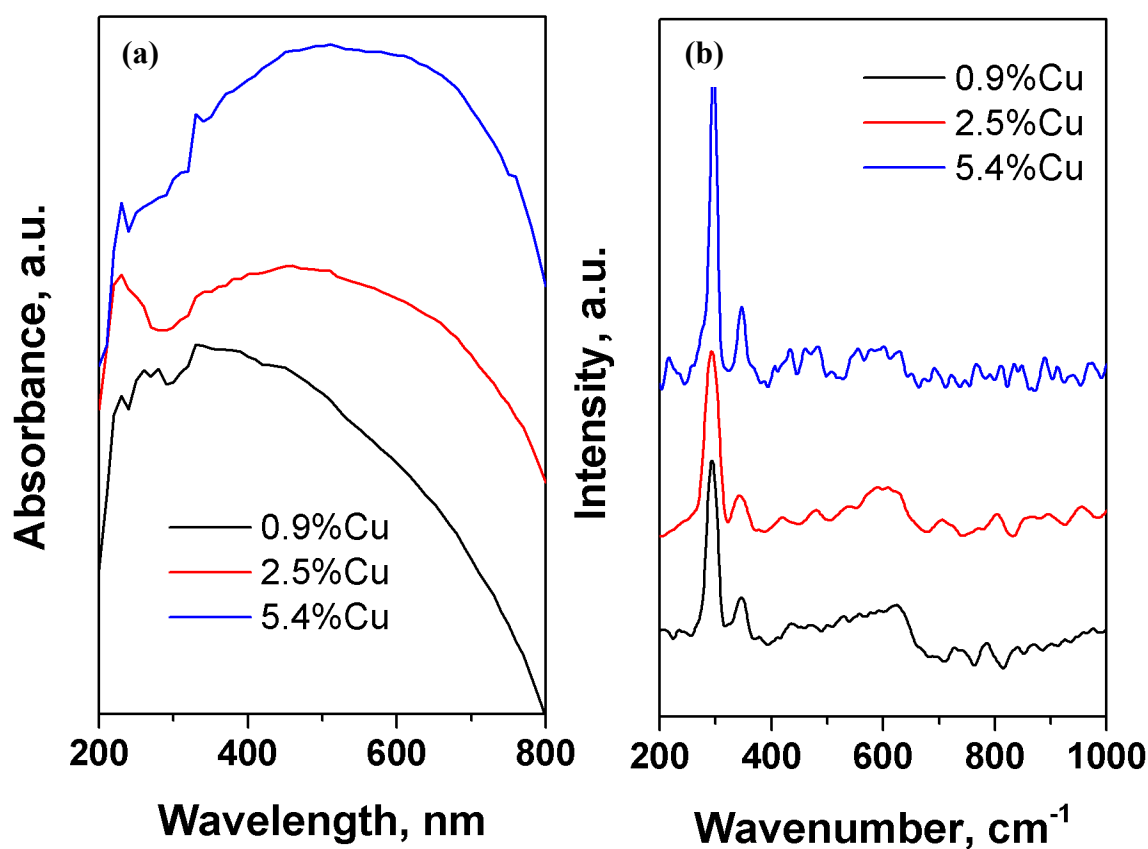


Figure 3. (a) DRUV and (b) Raman spectra of Cu/TUD-1

EPR spectra of Cu/TUD-1 at room temperature confirmed the presence of isolated Cu^{2+} ions and oligonuclear CuO species (Figure 4). Bulk CuO (the majority species for high copper loadings) in samples is however EPR silent due to strong dipole-dipole interactions of copper ions in the crystal lattice. A single, intense axially symmetric peak was observed for all Cu/TUD-1 samples, whose intensity increased from the 0.9 to 2.5 wt% samples, before decreasing for the highest copper loading. This indicates that 2.5 wt% Cu/TUD/1 contained the highest concentration of isolated Cu^{2+} and oligomeric CuO species. Calculated g_{\parallel} and g_{\perp} values were also consistent with copper in a distorted octahedral environment [28]. Such EPR signals are anticipated to correlate with strong free electron behavior in these Cu/TUD-1 materials.

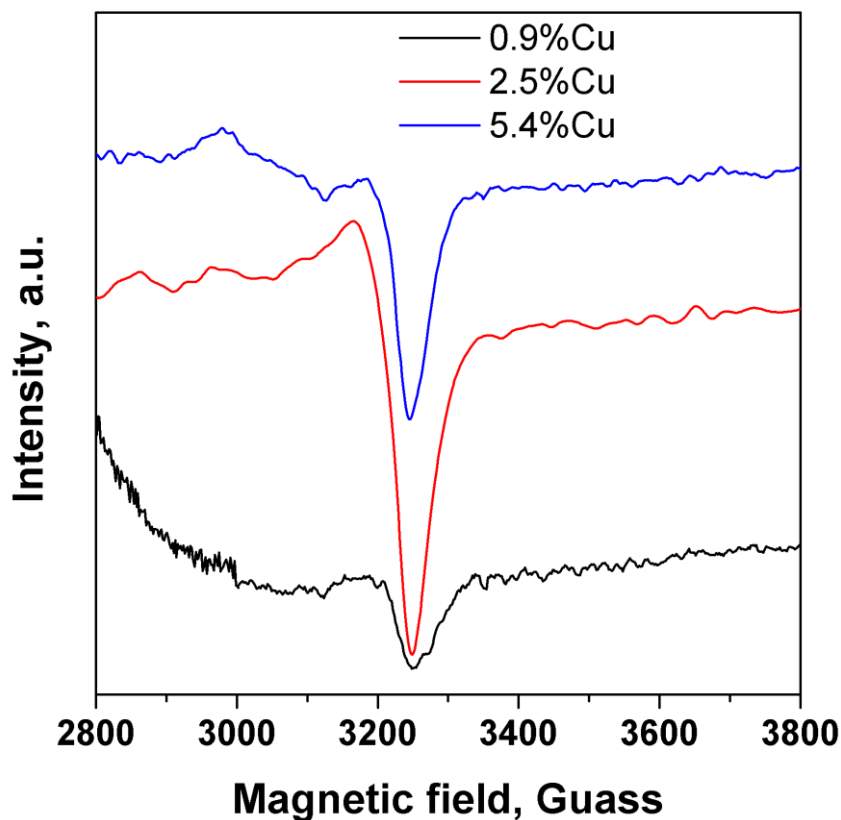


Figure 4. EPR spectra of Cu/TUD-1

The Cu 2p XP spectrum of 2.5 wt% Cu/TUD-1 (Figure S2) revealed a spin-orbit split doublet with Cu 2p_{3/2} and Cu 2p_{1/2} binding energies of 935.3 eV and 955.3 eV respectively. The Cu 2p_{3/2} asymmetric peak could be fitted with two components at 932.8 eV and 935.7 eV, assigned to bulk CuO and isolated Cu²⁺ species in octahedral sites respectively [23, 28].

SEM and TEM micrographs of 2.5 wt% Cu/TUD-1 are shown in Figure 5. SEM revealed micron-sized irregular (silica) particles (Figure 5a), while the presence of a disordered, wormhole-like pore network typical of TUD-1 type materials was observed by TEM (Figure 5b). Complementary SEM-EDX analysis (not shown) confirmed bulk Cu loadings for all Cu/TUD-1 samples in good agreement with those from ICP-OES analysis.

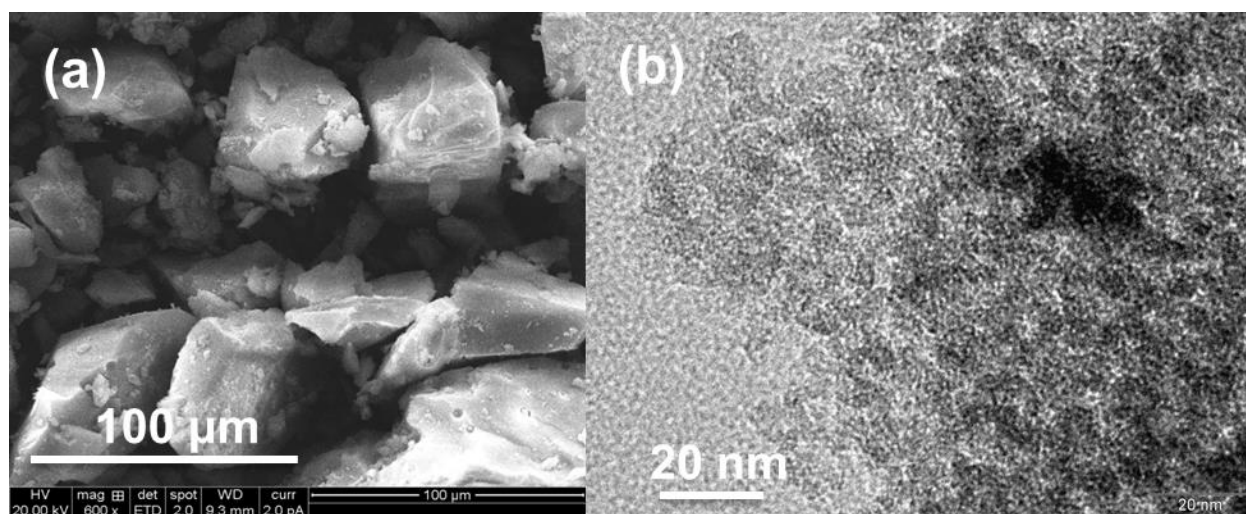


Figure 5. (a) SEM and (b) TEM micrographs of 2.5 wt% Cu/TUD-1

3.2 Cu/TUD-1 catalyzed degradation of Bisphenol A

The catalytic performance of Cu/TUD-1 materials towards Fenton-like oxidative degradation of BPA was subsequently investigated via UV-Vis spectroscopy in the presence of H₂O₂.

Illustrative time-dependent spectra are shown in Figure 6 for 2.5 wt% Cu/TUD-1, highlighting the principal UV-Vis absorptions of BPA at 220 nm and 280 nm (due to aromatic phenolics) whose intensities decreased monotonically with time due to BPA degradation. Initial BPA degradation activity (determined from the 280 absorbance) was approximately independent of Cu loading, for the first 30 min of reaction during which linearity was maintained (Figure 7). However, significant differences were observed in the limiting degree of BPA removal, with a maximum observed for the 2.5 wt% Cu/TUD-1 of 90.4 %, compared with only 68% and 78 % for 5.4 wt% Cu/TUD-1 and 0.9 wt% Cu/TUD-1 respectively (we note that all Cu/TUD-1 samples surpassed bulk CuO which only removed 40 % BPA under identical conditions). The results suggest a strong correlation between the genesis of isolated Cu^{2+} ions and oligonuclear CuO clearly during synthesis of Cu/TUD-1 and BPA degradation activity with H_2O_2 , although the possibility of pore blockage by large CuO crystallites in the 5 wt % Cu/TUD-1 sample must also be considered [28]. Control experiments in the absence of H_2O_2 showed that BPA adsorption (versus its oxidation) accounted for <10 % of the overall observed removal for all catalysts, confirmed through comparison with undoped TUD-1 for which a similar level of BPA removal was observed with or without H_2O_2 due simply to adsorption of the organic.

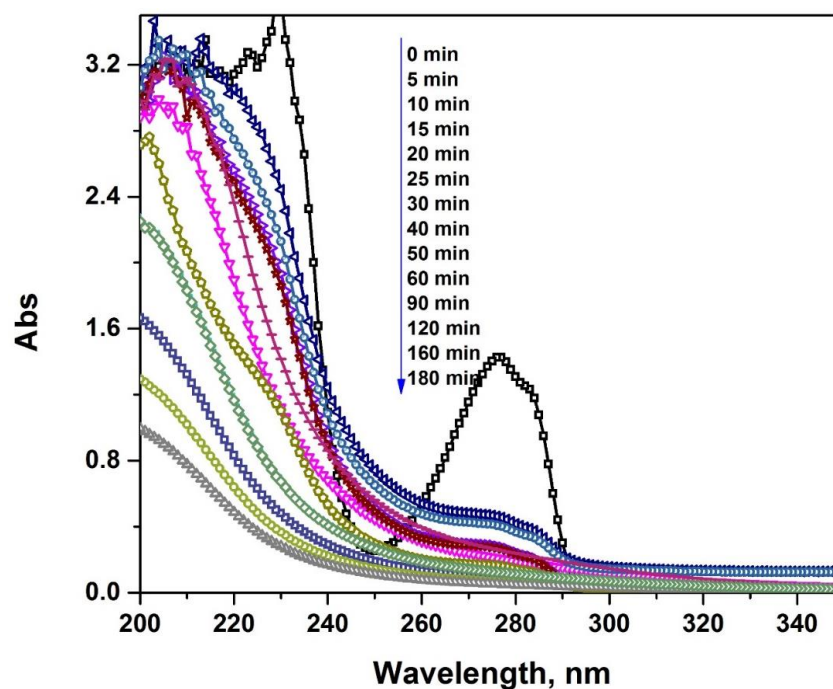


Figure 6. UV-Vis spectra showing BPA oxidative degradation over 2.5 wt% Cu/TUD-1.

Reaction conditions: 100 ppm BPA, 0.1 g catalyst, 90 mM H_2O_2 .

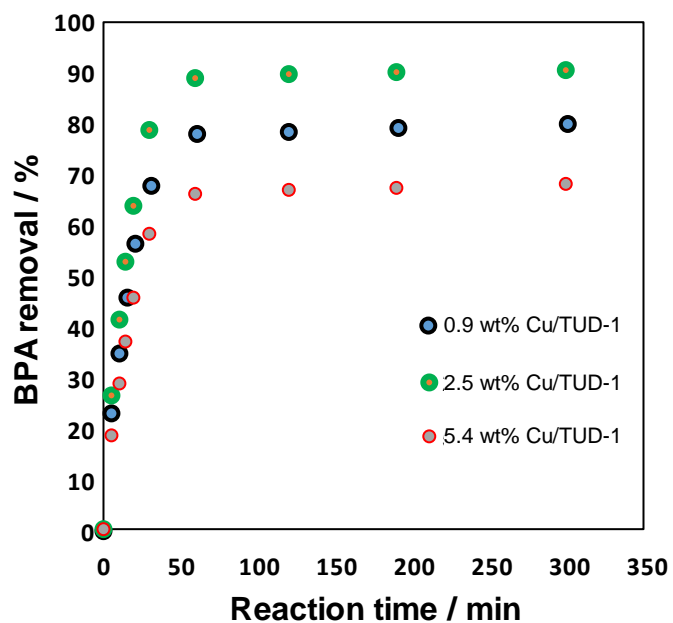


Figure 7. BPA removal over Cu/TUD-1. Reaction conditions: 100 ppm BPA, 0.1 g catalyst, 90 mM H_2O_2 .

The influence of $[H_2O_2]$ on BPA degradation over Cu/TUD-1 was also explored as a function of copper loading (Table 2). Only 8 % BPA removal was observed for 60 mM H_2O_2 in the absence of any catalyst. BPA removal increased monotonically with $[H_2O_2]$ for all loadings, spanning ~10 to 90 % removal for concentrations spanning 20-100 mM, highlighting the importance of hydroxyl radical ($\cdot OH$) chemistry (as evidenced by EPR spin trapping below). A volcano dependence on activity with copper loading was again observed, with the 2.5 wt% Cu/TUD-1 offering the highest BPA removal in all cases, and achieving 95 % degradation for 100 mM H_2O_2 . This performance surpasses heterogeneous Cu/SBA-15, Cu/MCM-41 and Cu/SiO₂ catalysts possessing a common 2 wt% loading wherein 70 %, 58 % and 40 % BPA removal are reported respectively [28], and is almost comparable to that Cu-doped titania nanotubes [23] for which 100 % BPA removal is claimed, although the presence of titania (a UV-active semiconductor) hinders comparison with the latter case wherein direct photocatalytic degradation may occur in addition to Fenton-like copper catalyzed oxidation. We note that in the case of azo dyes, homogeneous copper hydroxide nitrate catalysts exhibit comparable degradation activities [45], but undergo rapid deactivation through over-oxidation by H_2O_2 . It should be noted that the solution pH decreased slightly from around 3.5 to 3.1 during the first 1 h of reaction, presumably due to the formation of small organic acids through BPA oxidative degradation catalyzed by hydroxyl radicals produced over the Cu/TUD-1 surface.

Table 2. Influence of H₂O₂ concentrations for BPA removal % over different Cu/TUD-1 catalysts.

[H ₂ O ₂] ^a / mM	BPA removal / % ^a		
	0.9 wt% Cu	2.5 wt% Cu	5.4 wt% Cu
20	6	10	3
40	34	54	25
60	45	69	34
80	59	80	42
90	78	89	56
100	86	95	65

^aValues in table are corrected for ~10 % BPA adsorption without peroxide; ^breaction conditions: 100 ppm BPA, 0.1 g catalyst, 180 min reaction.

Additional spin trap experiments employing DMPO (5, 5-dimethyl-1-pyrroline N-oxide) as a radical quenching agent were undertaken to identify hydroxyl radical formation as shown in Figure 8. The spectrum of pure DMPO coordinated to hydroxyl radicals exhibited the expected 1:2:2:1 signals indicative of DMPO-OH formation with a split center around 3400 G [23, 46]. DMPO addition during BPA degradation over 2.5 wt% Cu/TUD-1 resulted in a qualitatively similar, albeit weaker EPR signature spectrum for hydroxylated DMPO, confirming the generation of hydroxyl radicals during oxidative degradation of the Bisphenol.

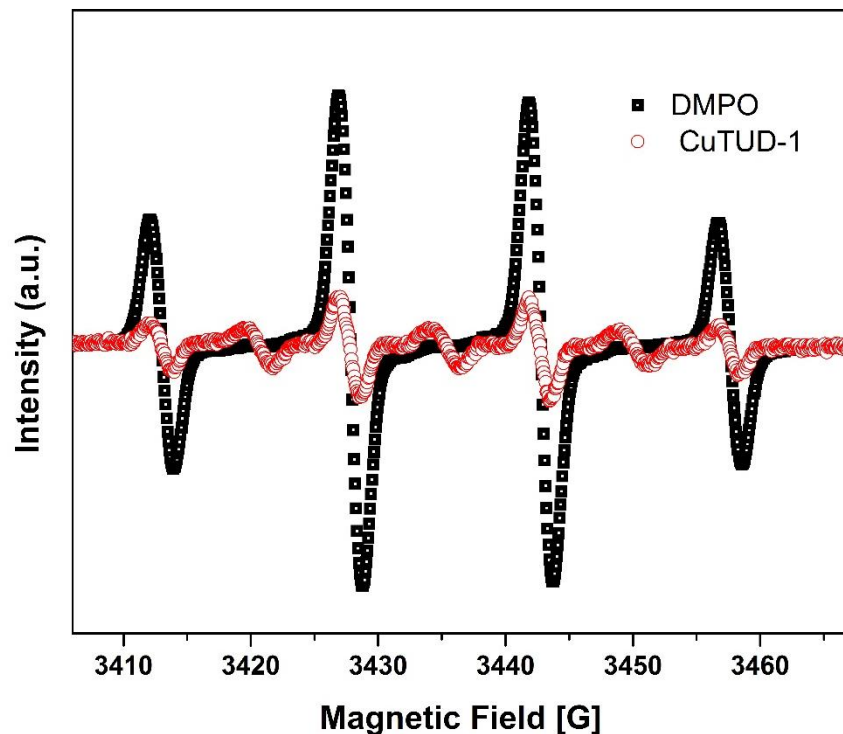


Figure 8. EPR spin trap spectra for pure DMPO and 2.5 wt% Cu/TUD-1 in the presence of DMPO highlighting the formation of hydroxyl radicals. Reaction conditions: 100 ppm BPA, 0.1 g 2.5 wt% Cu/TUD-1, 90 mM H₂O₂, 180 min reaction.

Some insight into the nature and concentration of fluorophores present during BP degradation was subsequently obtained through excitation–emission matrix (EEM) fluorescence spectroscopy [47,48]. The reaction mixture before and after Fenton-like oxidative degradation of BPA over 2.5 wt% Cu/TUD-1 was investigated by three dimensional fluorescence spectroscopy for excitation wavelengths spanning 200–400 nm, and the measurement of resulting emission profiles between 200 to 600 nm (Figure 9).

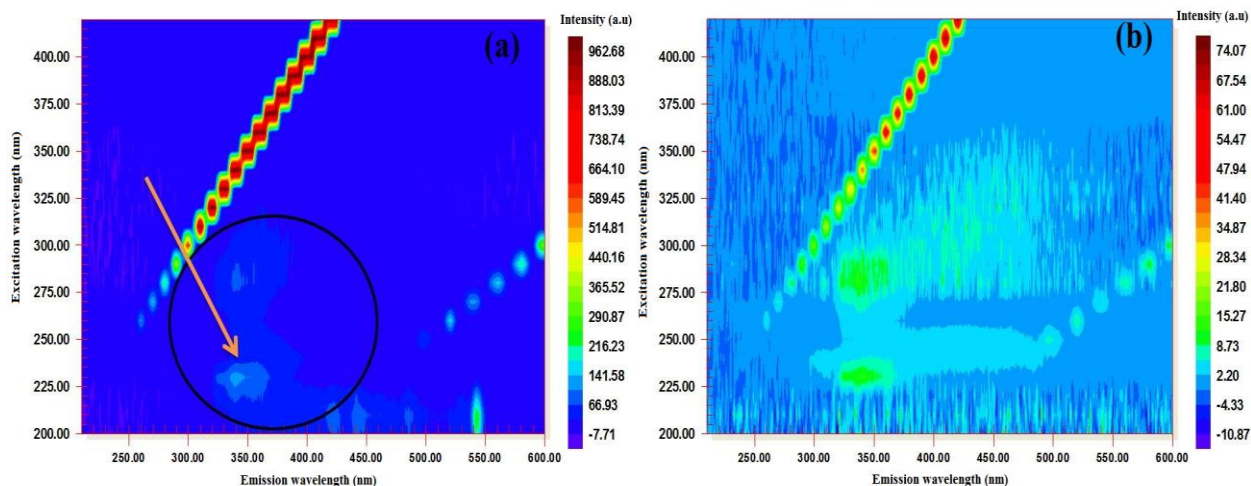


Figure 9. Excitation and emission matrix of (a) BPA and (b) 2.5 wt% Cu/TUD-1 treated BPA.

Reaction conditions: 100 ppm BPA, 0.1 g 2.5 wt% Cu/TUD-1, 90 mM H₂O₂, 180 min reaction.

EEM spectra revealed strong bands between 325-375 nm for the parent BPA, indicative of its aromatic chromophores (Figure 9a). After reaction over 2.5 wt% Cu/TUD-1, the intensity of emission peaks decreased dramatically for wavelengths between 325-520 nm, consistent with loss of aromaticity (Figure 9b). A coincident red-shift in the wavelength of the features circled in Figure 9a is attributed to the inclusion of auxochromic groups as a result of ring opening associated with the fragmentation of the parent phenol into smaller non-aromatic compounds during oxidation or the elimination of hydroxyl groups from BPA [49,50]. A possible hydroxyl radical oxidation mechanism for BPA removal based on accepted heterogeneous Fenton chemistry is provided in Scheme S1.

The stability of Cu/TUD-1 catalysts towards Cu leaching was assessed through elemental analysis of the reaction solution after 2 h of oxidation (Table 3). All three copper loadings

exhibited similar, extremely low amounts of leached copper during reaction, representing <0.1 % of the total copper present in each fresh catalyst.

Table 3. Elemental analysis of leached copper during reaction^a

Cu loading / wt%	Leached Cu^b / mg/L	BPA removal / %
0.9	0.0032	80.3
2.5	0.0027	90.4
5.4	0.0029	68.1

^bState experimental conditions; ^bValues obtained from AAS analysis

Catalyst reusability was explored for 2.5 wt% Cu/TUD-1 for BPA degradation over 5 consecutive cycles (Figure 10), through the addition of fresh BPA to the reaction mixture every 120 min. A constant BP removal efficiency of 91 ± 2 % was observed for every cycle, indicating negligible deactivation.

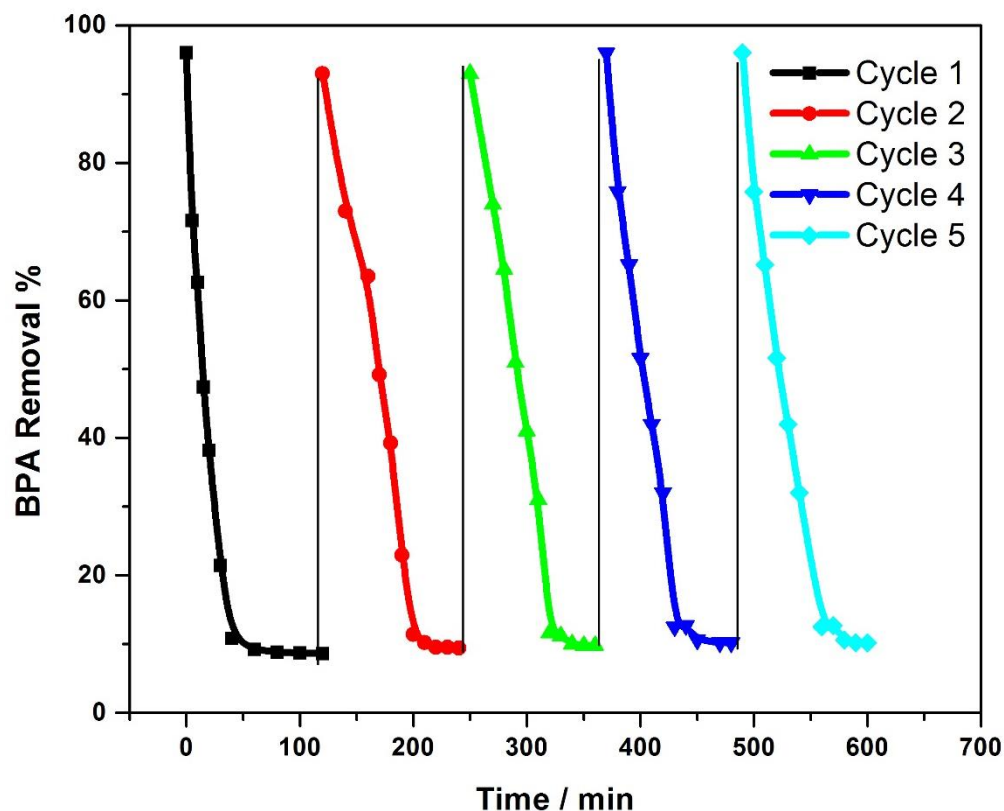


Figure 10. Stability of 2.5 wt% Cu/TUD-1 catalyst after five cycles in BPA removal efficiency during the heterogeneous Fenton-like oxidation process. Reaction conditions: 100 ppm BPA, 0.1 g catalyst, 90 mM H₂O₂, 180 min reaction.

The order of reaction with respect to [BPA] was determined from regression analysis of the first 30 min reaction as shown in Figure S3. A plot of $\ln(\text{BPA})_0/(\text{BPA})_t$ versus time revealed the expected first order dependence of degradation rate for all Cu/TUD-1 catalysts.

4. Conclusion

A family of copper modified TUD-1 catalysts were synthesized with Cu loadings between 0.9-5.4 wt% employing TEG as a soft template. The resulting materials exhibited high surface areas

and an amorphous, disordered mesopore network, containing isolated Cu^{2+} ions in a tetrahedral coordination (presumably within the silica framework) alongside CuO oligomers. High copper loadings favor the formation of CuO nanocrystallites dispersed across the TUD-1 support. Cu/TUD-1 is an excellent catalyst BPA oxidative degradation in the presence of H_2O_2 , with the optimum 2.5 wt% Cu/TUD-1 achieving 90.4 % BPA removal in 180 min. Spin trap EPR measurements confirm that oxidation occurs via the generation of $\cdot\text{OH}$ radicals from H_2O_2 , especially over isolated/oligomeric Cu^{2+} species, through a Fenton-like mechanism. Excitation–emission matrix fluorescence spectroscopy revealed that oxidation was accompanied by a loss of aromaticity and molecular fragmentation, while kinetic analysis confirmed that BPA degradation was first order in the pollutant independent of copper loading. Cu/TUD-1 exhibited negligible deactivation over five recycles, within minimal Cu leaching (0.0027 mg/L).

Acknowledgements

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