

Surface functionalization of bauxite hollow fibre membrane using copper oxide (CuO) and its reusability for photodegradation of bisphenol A from aqueous solution

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ABSTRACT

This work developed and applied a CuO-impregnated bauxite hollow fibre membrane (BHF) using hydrothermal method for bisphenol A (BPA) photodegradation. BHF was synthesized through a phase inversion method at optimum sintering at 1300 °C. Subsequently, the physico-chemical properties of CuO-coated BHF were characterized, while its performance for the BPA degradation was investigated at varying time of hydrothermal exposure and compared to ceramic hollow fibre membrane from alumina (AHF) as control and commercial membranes. Oxidation by-products, resulting from BPA photodegradation, were identified and after treatment, the saturated membrane was regenerated to sustain its cost-effectiveness. As compared to the pristine BHF membrane, we found that functionalizing BHF surface with CuO significantly improved its mechanical strength by 130 % from 18.5 to 42.5 MPa. The removal of BPA was enhanced with the increasing hydrothermal time to 5 h due to the even distribution of CuO-impregnated BHF on its membrane surface. 97 % of BPA removal with 10 mg/L concentration was substantially attained by the same CuO-impregnated BHF under visible light (VIS) irradiation. Treated effluents, resulting from the BPA photocatalysis, could meet the required effluent limit of 20 mg/L set by national legislation. The possible oxidation by-products cover 4-(2-hydroxy-2-propanol)phenol, 4-isopropylphenol and dihydroxybenzene. With 25 % of efficiency, the saturated CuO-impregnated BHF was subsequently regenerated for consecutive five cycles. This implies that functionalizing BHF surface with CuO enabled it to possess outstanding stability and removal performance for treatment of BPA-laden wastewater.

1. Introduction

Over the past years, water pollution due to xenobiotic such as bisphenol A (BPA) has become one of the most serious environmental problems worldwide. Its trace concentration ranges from 0.01 to 13 µg/

L. As the xenobiotic possesses serious hazards to aquatic environment, BPA-laden contaminated water needs to be treated using state-of-the-art of environmental technologies.

Recently, scientists have tested environmental technologies such as coagulation and flocculation (CF) [1] and adsorption [2] to treat BPA-

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contaminated water. Each has its own limitations. Despite CF is cost-effective to treat the contaminated wastewater, its application has drawbacks due to the additional operational cost caused by sludge generation [3]. In spite of its applicability, adsorption treatment could not generate treated effluents that meet the requirement of discharge standard limit [4]. Therefore, there is a growing need to deal with the remediation of BPA-contaminated wastewater, while contributing to the 2030 UN Sustainable Development Goals No. 6 "Clean water and sanitation" [5].

To mitigate undesirable impacts on the aquatic environment, recent advances in materials sciences have further promoted interests among water scientists in functional materials for water treatment [6]. Their applications for advanced oxidation process (AOP)-based water treatment facilitate the degradation of target pollutant in aqueous solutions through the formation of $\cdot\text{OH}$ [7]. The radicals indiscriminately mineralize the pollutant rapidly into smaller and more biodegradable oxidation by-products [8].

To optimize wastewater treatment using ceramic membranes, the search for various raw materials from non-conventional sources has intensified recently. To promote circular economy (CE) in wastewater treatment, industrial waste such as bauxite, fly ash, or mud from cyclone laundries has been explored. To valorize the unused waste into value-added composites, functional hollow fibre membrane, derived from bauxite, represent integrated parts of sustainability solutions to protect the environment. The BHFM pristine exhibits outstanding stability under highly acidic and basic environment. Its unique characteristics could give an anti-fouling resistance toward micro-organisms. The presence of CuO in the bauxite strengthens its ability for self-cleaning.

Morphologically, the macrostructure of BHFM consists of two void structures that are sponge-like, as they undergo through a phase inversion process [9]. According to Ismail et al. [10], fabricated BHFM possessed crystalline phase of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, 00-005-0143) with minor traces of Fe_2O_3 [11]. The existence of Fe_2O_3 in the bauxite was beneficial to photocatalysis (Esham et al., 2019).

A study undertaken by Li et al. [12] reported that the calcination of bauxite at high temperature altered its composition (Al_2O_3 : 81 %; Fe_2O_3 : 3 %), respectively. The FTIR spectra indicated that the Fe-O peak was present in the sintered BHFM, as Fe_2O_3 was a major component in bauxite [13–15].

To reflect the technological value of the work, hybridization strategies that incorporate ceramic membrane and catalytic oxidation have been explored to decrease treatment cost and to enhance treatment efficiency, the two key issues in the industrial application of ceramic membranes. To make them ceramic highly efficient and economically attractive for treatment of contaminated water laden with trace pollutants, their surface needs to be impregnated with metal oxide such as CuO.

Due to its outstanding oxidation ability [16] and high surface area [17], CuO was selected as an ideal metal doping to modify the physico-chemical properties of the BHFM for photocatalytic degradation under UV-Vis irradiation (Shao et al., 2018). Because of the difference between their conduction band (C_b) and valence band (V_b), this transferred photo-generated electron and hole on the CuO of C_b . An increasing content of CuO in the BHFM may decrease the electron-hole recombination rate [18] and shift absorption to a longer wavelength [19].

Convenience in changing its oxidation state makes the CuO play roles in redox through catalytic mechanisms. Under visible light, the metal oxide may act as electron-hole trappers by creating energy levels in the band gap and increasing the charge carrier lifetimes, while avoiding recombination, enhancing the treatment performance of the adsorbent [20]. Because of the presence of unpaired electrons, the Cu^{2+} reacts with $\text{HO}_2\cdot$ and $\text{O}_2^{\cdot-}$. While keeping its surface functionality remains, we uncover the novelty of CuO-impregnated BHFM by adding technological values to it for photocatalytic degradation of BPA in aqueous solutions.

In spite of its promising performance for wastewater treatment, to the best of our knowledge, no study has studied the effects of

impregnating BHFM with CuO on its membrane surface. In this study, we developed and applied CuO-impregnated bauxite hollow fibre membrane (BHFM) using hydrothermal method for bisphenol A (BPA) photodegradation. By choosing this material, we intent to develop photocatalytic ceramic membrane which able to undergo photocatalysis under visible light. To fulfill the goal, the characterization of CuO-BHFM synthesized at different hydrothermal exposure time and the performance of BPA using the fabricated membrane were carried out. This fabricated membrane possessed hybrid function where the removal of BPA can be achieved through photocatalysis and microfiltration simultaneously by using a unit of membrane. In addition, a comparative study with respect to the degradation rate of BPA between this study and previous studies was conducted. The mechanism of BPA photodegradation by CuO-BHFM and its oxidation by-product were presented and identified.

It is expected that treated effluents, resulting from the photocatalytic degradation of BPA, would meet the requirement of effluent limit set by national legislation. Eventually, this work promotes CE applications in water treatment by minimizing the disposal of unused non-organic waste such as bauxite into local landfills and contributes to global climate change mitigation through resource recovery that reduces greenhouse gas (GHG) emission into the atmosphere.

2. Material and methods

2.1. Materials

Sieved bauxite powder of 50 μm , *N*-methyl-2-pyrrolidone (NMP), polyethersulfone (PES), and Aralcel P135 were supplied by Aras Kuasa, Merck, Solvay Advanced Polymers, and Uniqema, respectively. They were used as ceramic particle, solvent, binder, and dispersant, respectively. Distilled water was used as coagulant during ceramic extrusion. For hydrothermal reactions, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and NaOH were obtained from Sigma-Aldrich. BPA was selected as a model of endocrine disruptor compound (EDC) for photocatalytic degradation.

2.2. Methods

2.2.1. Fabrication of hollow fibre membrane (BHFM)

BHFM and AHFM (50 % (w/w)) were produced by homogeneously mixing bauxite powder for BHFM, alumina powder for AHFM, NMP (42.75 % (w/w)), PES (6.25 % (w/w)), and Aralcel P135 (1 % (w/w)) to form a bauxite suspension. The degassed suspension was then extruded through a phase inversion technique at 9 mL/min of flow rate, while it was also extruded at 10 mL/min for internal coagulant via tube-in-orifice spinneret with internal diameter (ID) of 1.2 mm and outer diameter (OD) of 2.8 mm directly into an external coagulant bath with 5 cm of air gap. The BHFM precursor was subsequently immersed in the external coagulation bath overnight to complete the phase inversion process before drying at ambient temperature. Before further modification, both the BHFM and AHFM precursors were subjected to a sintering process at 1300 °C in a tubular furnace (Magna value, XL-1700) using the same sintering profile from the previous work [21].

2.2.2. CuO synthesis and its impregnation on the surface of BHFM

CuO nanoparticles (NPs) were synthesized based on a hydrothermal route in presence of NaOH. Initially, 0.2 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and copper precursor solution were mixed in a reactor. After adding 0.2 M NaOH into the mixture under continuous stirring, the solution was transferred into a 60 mL Teflon-lined stainless steel autoclave. About 15 cm of BHFM was transferred into the solution and underwent a hydrothermal process at varying time (2.5, 5.0, and 7.5 h). The autoclave was maintained at 150 °C for 2.5 h to 7.5 h and then cooled to ambient temperature. The obtained precipitate on the surface of BHFM was repeatedly washed with double distilled water before being washed ethanol to remove any impurities without affecting the CuO loading. All the

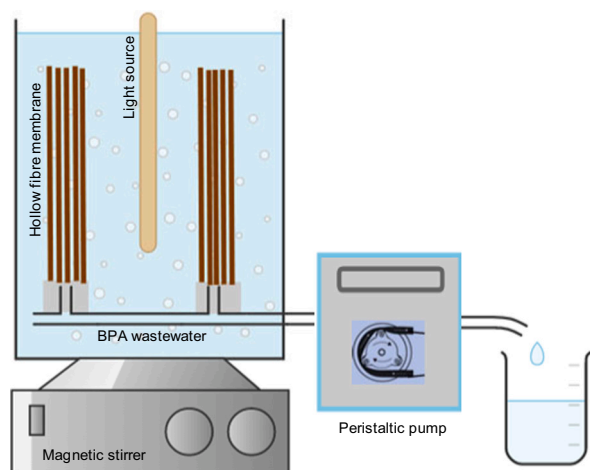


Fig. 1. Illustration of submerged photocatalytic membrane reactor (SPMR).

samples of CuO-BHFM were preserved in a desiccator for further use.

2.2.3. Characterization of CuO-BHFM composite

The morphology of CuO nanoparticles on the outer membrane surface of the BHFM support were analyzed using a scanning electron microscope (SEM) model Hitachi TM 3000 (Japan) at varying magnifications. CuO-BHFM was cut neatly to obtain its cross-section and placed on metal holder before being sputter-coated with gold under vacuum for 3 min. The distribution of the same sample was analyzed using energy dispersive X-ray (EDX), whereas the atomic force microscope (AFM) model SE 100 Park System (US) was applied to observe the roughness of the CuO-BHFM's surface. The presence of the crystalline phase of CuO on the outer surface of CuO-BHFM was detected by X-ray diffractometer (XRD) model Rigaku Smartlan X-Ray (Japan).

The wettability of CuO-BHFM was also characterized by a contact angle measurement based on sessile drop method (Dataphysics, OCA 15EC) and deionized water was used as its contact droplet. The average contact angle was calculated based on ten measurements obtained from different spots of the membrane. Ultrafiltration (UF) system in the cross-flow filtration mode was used to determine water permeability of CuO-BHFM with a length ranging from 3 to 4 cm at 3 bar of pressure under ambient temperature. Before undertaking any measurement, it is vital to ensure that the reading was stable before compacting the CuO-BHFM with water as the feed at 1.5 bar for about 30 min. The water permeation of the CuO-BHFM was calculated based on the Eq. (1):

$$L_p = \frac{\Delta V}{A_m \Delta t \Delta P} \quad (1)$$

where: L_p and ΔV are the water permeation ($L/m^2 \cdot h \cdot bar$) and the volume of water permeated through the membrane (L), respectively, while A_m and Δt represent the effective membrane area (m^2) and the permeation time (h), and ΔP is the transmembrane pressure (bar). The average water permeation was measured from three measurements for each membrane sample.

2.2.4. BPA photodegradation using CuO-BHFM

A batch submerged ceramic photocatalytic membrane reactor was used to evaluate the efficiency of BPA photodegradation under ambient temperature (Fig. 1). The submerged system consisted of membrane modules fitted in a photoreactor system and a beaker. A 10-L perspex tank, which served as the body of the submerged system, was covered with aluminium foil to prevent the UV irradiation from interfering. The visible light bulb (LED flood light: model IP65, 100 W) was turned on to initiate photocatalysis. Aeration was provided using an air compressor with 2 L/min of air bubble flow rate. BPA was used as a model

compound for evaluating the technical applicability of photocatalysis by CuO-BHFM under visible irradiation. Varying BPA concentrations ranging from 10 to 30 mg/L were studied. Ten units of the CuO-BHFM with 10–15 cm of length were pot in the membrane reservoir prior to BPA photocatalysis using a submerged system. Periodically, the samples were collected from a feed tank. Permeation rate was evaluated every 30 min.

For permeation of the feed, a peristaltic pump model Masterflex L/S (Cole Palmer Instruments) was used to create 15 cm/Hg vacuum pressure at the permeate end of membrane module with 0.1 L/min.

Before undergoing tests, BPA was oxygenated in the dark situation for 2 h to attain adsorption/desorption equilibrium. About 10 mL of aliquot was collected as a blank sample prior to visible light irradiation. Subsequently, the remaining solution was irradiated under visible light for 30 min. The lamp was placed in the middle of the reactor.

About 10 mL of treated aliquot was collected periodically throughout the experiment for chemical analysis of the remaining BPA concentration using HPLC model Agilent Technologies 1260 (USA), coupled with a UV detector. The mobile phase used was acetonitrile (A)–HPLC-grade water (B) in gradient mode. The column was maintained at room temperature. The sample injection volume was injected in triplicate and peak measurement was done at ambient temperature using identifying intermediate compounds at 278 nm.

2.2.5. Regeneration of CuO-BHFM

The antifouling performance and reusability test of BHFM were investigated using SPMR. To sustain its cost-effectiveness, the CuO-BHFM was regenerated for BPA photodegradation. Freshly prepared BPA solution was used in every cycle to maintain the concentration of feed tank. Each cycles lasted up to 300 min, where samples were collected periodically. The length of membrane module was set at 10 cm. The fabricated membranes were fitted into PVC modules and potted using epoxy resin. Epoxy resin was used to prevent water leakage at the permeate end. The feed was allowed to be adsorbed on membrane for 30 min. After the adsorption time has lapsed, during regeneration, the membranes were repeatedly washed for 30 min without applying pressure after the membranes were used for BPA photodegradation. The rejection rate was determined based on the Eq. (2):

$$F_R = \frac{F_i}{F_w} \times 100\% \quad (2)$$

where: FR is the flux recovery rate (%), while F_i and F_w are the initial and final BPA flux (mL).

2.2.6. Toxicity analysis

Microtox tests were conducted using the Basic Text method, which is intended for use with materials of low to medium toxicity. The response of toxicity is assessed as a change in luminescence of the bacterium *Vibrio fischeri*. The vials containing BPA synthetic wastewater had Microtox Acute Reagent with bacteria added to them. To obtain toxicity blank values, initial measurements were made using just bacteria. The toxicity of the samples was connected with the measured light, and information was generated to calculate the EC50 values both after 5 min and after 15 min. All samples were subjected to a screening test in the initial phase. Undiluted samples were tested for toxicity. According to the presumption, the sample is considered non-toxic when the toxic effect (PE) is <20 % when compared to the control.

2.2.7. Leaching compound detection

Copper leaching analysis of the degraded BPA water sample using CuO BHFM was analyzed using inductively coupled plasma—optical emission (ICP-OES) spectrometry, model: 710, (Agilent Technologies, Santa Clara, CA, USA). BPA permeate was used as test ample to ensure that there was no copper leaching was occurred during the photocatalysis of BPA using CuO BHFM. All selected spectral lines for ICP-OES

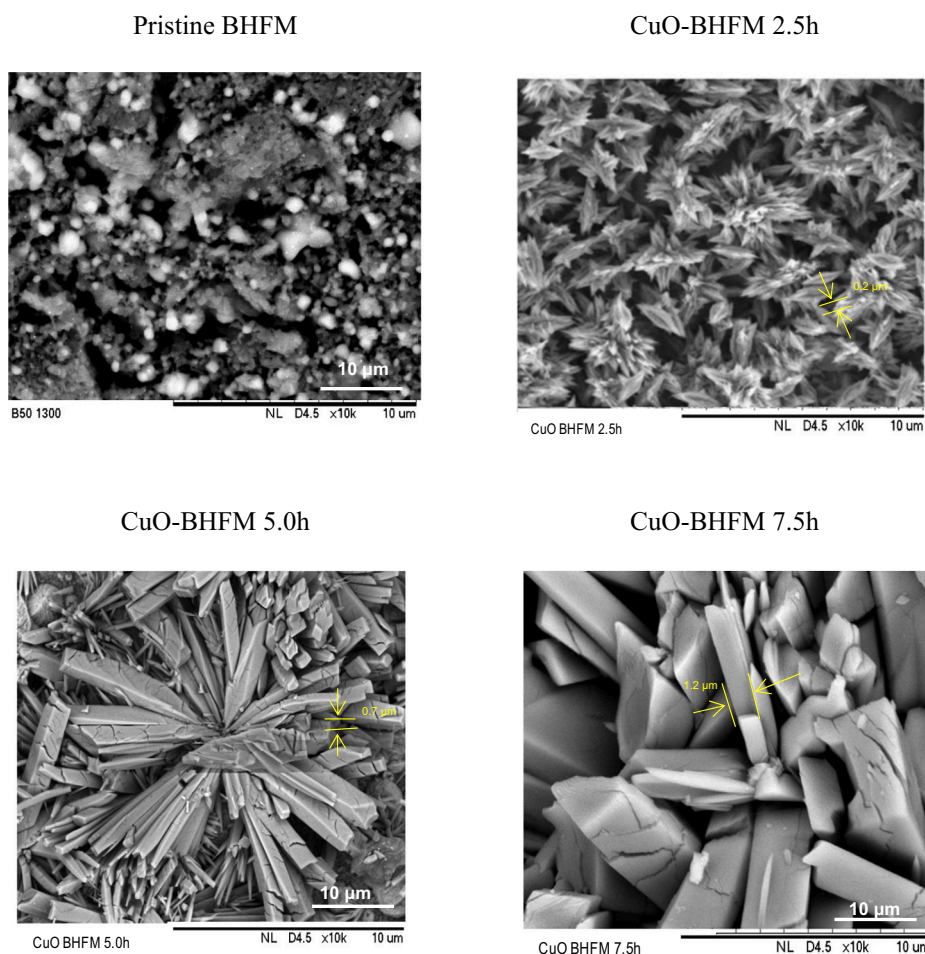


Fig. 2. SEM analysis of CuO-BHFM.

were free of interference. The sample and calibration solutions were prepared in the same media, which reduced background emission.

3. Results and discussion

3.1. Characteristics of CuO-BHFM

The morphology of CuO nanoparticles on the surface BHFM was analyzed using SEM (Fig. 2). As compared to the pristine membrane, the surface of the BHFM was covered with a layer of CuO particles. Homogeneous defect was observed with average thickness of coating layer for 2.5, 5.0, and 7.5 h of hydrothermal exposure was 0.2, 0.7, and 1.2 µm respectively. A strong affinity of CuO particle toward ceramic support after hydrothermal treatment was observed [22]. Since the substrate is highly porous in nature and fall in the microfiltration range, thus, there is possibility of CuO nanoparticles penetrate into the pores of the substrate.

The elemental composition on the outer surface of CuO-BHFM was analyzed using EDX (Fig. 3). The chemical composition of the CuO-BHFM is presented in Table 1. The elements on the outer membrane surface of CuO-BHFM were Al and Fe for membrane, while Cu and O were for the nanoparticles. At 2.5 h of hydrothermal exposure, only a small amount of CuO nanorods grow on the BHFM surface. However, the thickness of the nanorods increased with the increasing hydrothermal time. As the reaction time increased to 5.0 h, the fraction of CuO nanorods indicating an increasing nanorods loading resulted in the proper distribution of CuO on the membrane. A good distribution of CuO on the top layer of membrane was crucial, as they were consistently

exposed to the Vis during the photo degradation of BPA.

The XRD patterns of the CuO-BHFM (5.0 h) and the pristine BHFM presented in Fig. 4 confirmed the crystallinity of the membrane after hydrothermal exposure. The decorated CuO-BHFM exhibited sharp and firm peaks with a higher peak intensity than the bauxite support. This finding was in agreement to that of Yoo et al. [23], who found that different peaks existed because of the *d*-spacing values of CuO originated from alumina support tube. Diffraction pattern also confirmed the crystallinity of the CuO-BHFM that encompassed a monoclinic crystalline phase. The diffractions were in agreement with the formation of the CuO-BHFM and matched with the JCPDS file no 45-0937 [24]. The pattern revealed the mixed phase of CuO at a peak of $2\theta = 58.2^\circ$. However, a low CuO intensity was observed. This might be due to the disruption of crystal symmetry by CuO contents, which minimized the differences between the diffraction pattern of CuO and other elements (Shen et al., 2005).

The contact angle, mechanical strength and water flux of pristine membrane and CuO-BHFM were measured (Table 2). The contact angle of CuO-BHFM increased slightly. Increasing trends of 52.3° , 62.9° and 72.0° were observed with increasing hydrothermal exposure from 2.5, 5.0, and 7.5 h, respectively. A similar trend was reported by Hubadillah et al. [25], who found that the increasing angle of water droplet was attributed to the agglomerate nanoparticles on the membrane's surface. This resulted from the combination of nano/micro, hierarchical and re-entrant structures on the CuO-BHFM surfaces with the increasing time of hydrothermal exposure [26]. The mechanical strength of the CuO-BHFM increased from 18.5, 34.6, 38.8 and 42.5 MPa for CuO-BHFM synthesized at hydrothermal exposure of 2.5, 5.0, and 7.5 h, respectively, with

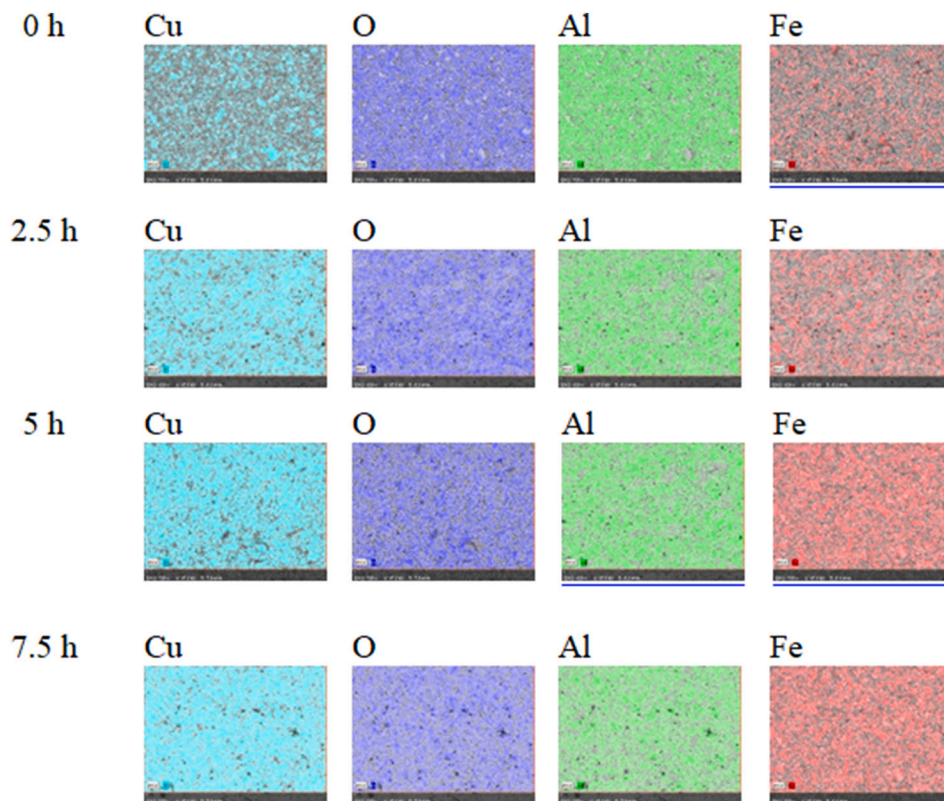


Fig. 3. EDX of pristine BHF and CuO-BHF at varying hydrothermal time.

Table 1
Elemental composition of CuO-BHF.

Element (%)	Duration of hydrothermal exposure (h)			
	0	2.5	5.0	7.5
Oxygen	38.46	44.82	50.72	55.64
Aluminium	25.31	16.43	4.54	9.21
Copper	30.33	37.15	42.49	45.17
Iron	3.45	0.98	0.31	0.28
Titanium	2.19	1.15	0.82	0.65

Table 2
Contact angle, mechanical strength, and water flux of pristine membrane and CuO-BHF at varying hydrothermal time.

Hydrothermal time (h)	Contact angle (°)	Mechanical strength (MPa)	Water flux (LMH/bar)
0	49.0	18.5	352.1
2.5	52.3	34.6	301.4
5.0	62.9	38.8	281.4
7.5	72.0	42.5	253.7

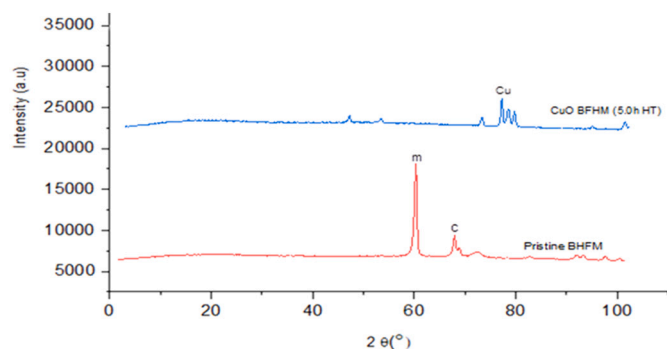


Fig. 4. XRD spectra of modified CuO-BHF 5.0 h and pristine membrane.
*(m = mullite; c = corundum; Cu = copper).

the 7.5 h having the highest mechanical strength.

In addition, the water flux of the CuO-BHF decreased with the increasing hydrothermal exposure on the membrane surface. This was attributed to the fact that the CuO layer significantly reduced the pore size of the ceramic membrane. Although a membrane with the highest mechanical strength value was desirable, a thicker membrane gave a

low flux. Gitis and Rothenberg [27] reported that a thicker membrane not only was strong and stable, but also resistant to transmembrane flow. About 5.0 h of hydrothermal exposure was the optimum reaction time for BHF modification, as the particles were evenly distributed on the membrane surface. For this reason, the performance of CuO-BHF at 5.0 h of hydrothermal exposure was selected for photocatalytic degradation of BPA at varying concentrations.

3.2. Photodegradation of BPA using CuO-BHF

Among the semiconductor materials, CuO nanostructure has unique magnetic and superhydrophobic properties. Furthermore, these nanostructures showed promising applications in heterogeneous catalysis in the complete conversion of hydrocarbons to carbon dioxide. CuO crystal has a monoclinic structure and belongs to the C_{2h}^6 symmetry. CuO has four formula units per cell unit. The coordination number of the copper atom is 4, which it is connected to four neighboring oxygen atoms in a plane configuration approximately rectangular on the plane (110). In all crystallized solids, the divalent copper environment is always highly distorted by the strong Jahn-Teller effect which often leads to more stable rectangular groups. The O atoms coordinate into four Cu atoms in the form of a distorted tetrahedron. It is generally accepted that CuO has a mixture of ionic and covalent bonds, although the oxidation state of Cu

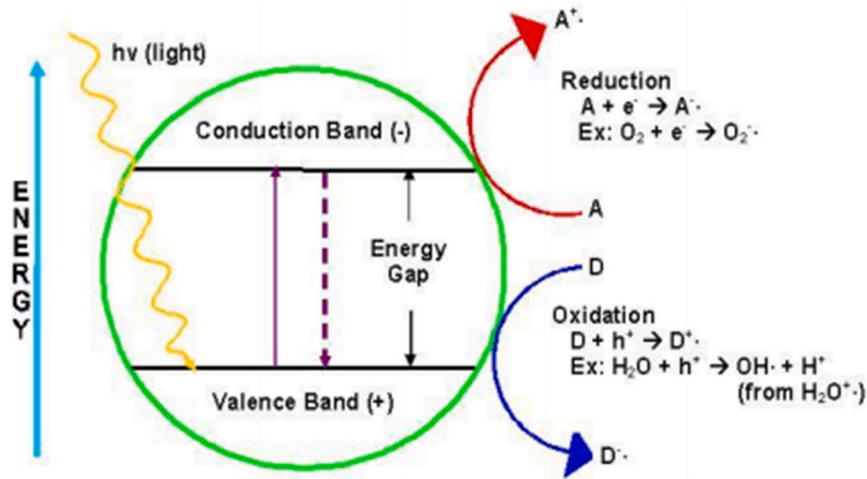


Fig. 5. Photocatalysis of CuO particles under irradiated light.

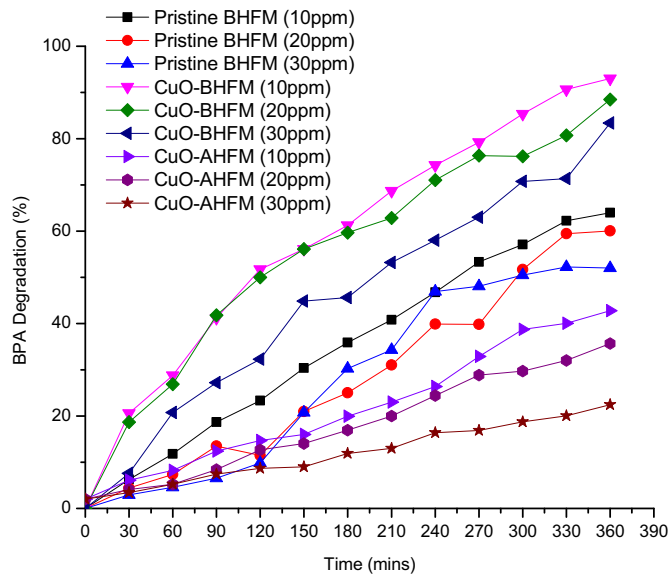
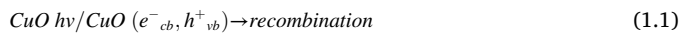


Fig. 6. Degradation of BPA under Vis irradiation for 6 h.

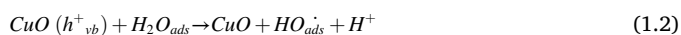
in CuO is undoubtedly Cu^{2+} .

The schematic diagram on the how photocatalysis reaction of CuO took place is per Fig. 5. The illustration of interfacing between desorbed species on the surface of semiconductor and charge carrier above can be explained as a series of complex reactions (Reactions (1.1)–(1.12)). This reaction is called heterogeneous photocatalytic reaction as it involves the application of semiconductor photocatalyst in the reaction.

Reaction (1.1) represents the formation of the charge carriers upon the illumination of CuO. If these generated charge carriers are not involved in any further reactions, they can quickly recombine.



The holes react with physisorbed water or chemisorbed OH to produce hydroxyl radicals (Reactions (1.2) and (1.3)).



The hydroxyl radicals are thought to be the main oxidants responsible for the degradation of the organics (D: electron donors) (Reaction (1.4)).

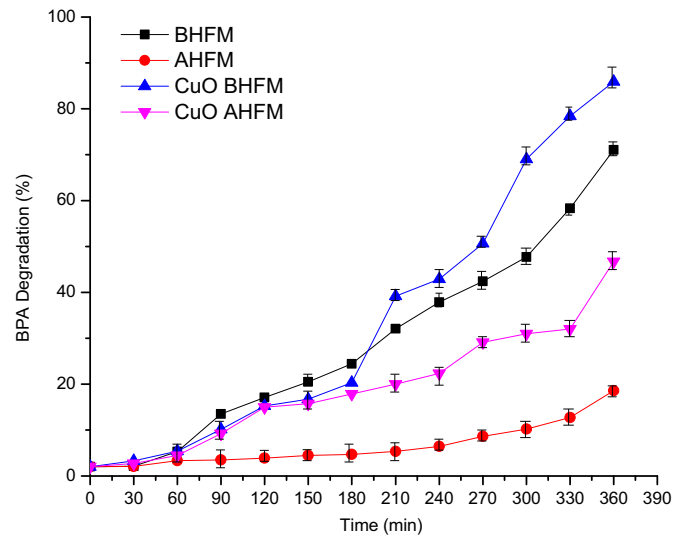
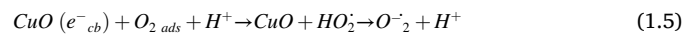


Fig. 7. Photocatalytic degradation of BPA using several types of membrane under Vis irradiation (BPA concentration: 10 mg/L).



The electrons react with the dissolved oxygen to lead superoxide ions (Reaction (1.5)).



These can also form hydroxyl ions after further reactions (Reactions (1.6)–(1.10)).



The direct reaction between the organic molecules and the holes can also lead to the destruction of the organics (Reaction (1.11)) and between the electrons and the electron acceptors (A) (Reaction (1.12)).

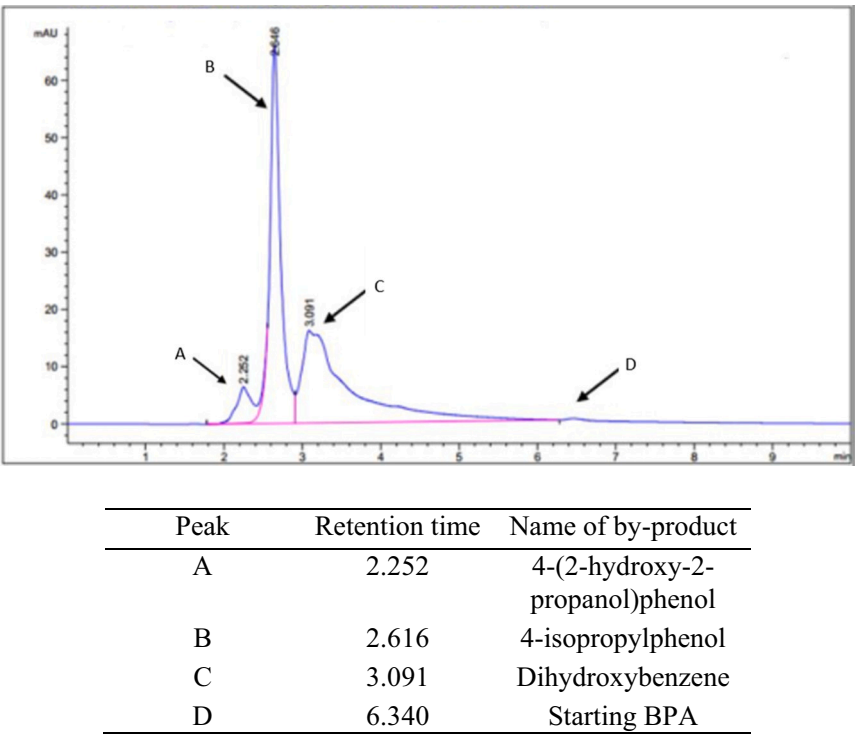


Fig. 8. HPLC chromatogram for BPA degradation.

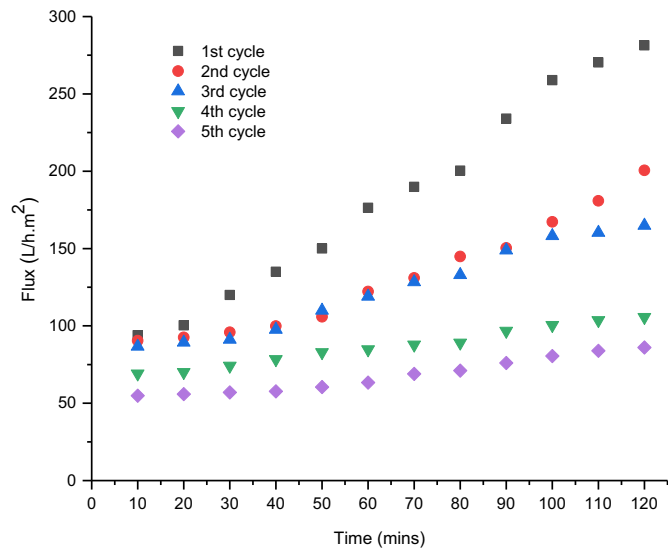


Fig. 9. Flux of CuO BHF membrane for BPA photocatalytic degradation.

$CuO(h^{+}_{vb}) + D_{ads} \rightarrow CuO + D^{+}_{ads}$ (1.11)

$CuO(e^{-}_{cb}) + A_{ads} \rightarrow CuO + A^{-}_{ads}$ (1.12)

BPA has been the subject of considerable aquatic toxicity testing in recent years and its concentration ranged from 10 to 30 mg/L and correlated with the Predicted No Effect Concentrations (PNECs) of BPA in Asia [28] was used in this study. Since the aquatic environment could receive discharges of BPA from production, processing, and sewage treatment plant effluents, most research on toxicity to wildlife has focused on aquatic organisms. In comparison to the allowable standard, the finding based species sensitivity distribution (SSD)-based no-effect concentration for aquatic communities was used to evaluate the risk

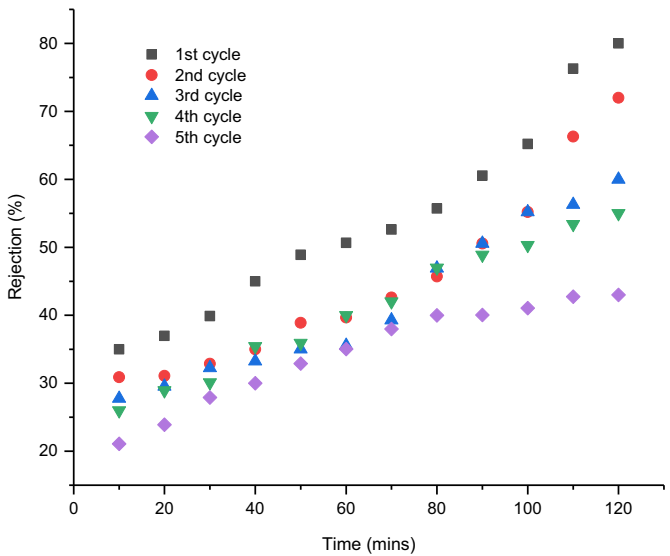


Fig. 10. Percentage of BPA rejection of CuO BHF membrane after 5 different cycles.

assessments [29]. The toxicity study of BPA was tabulated as in supplementary Table T1. Thus, comprehensive understanding the CuO particle's adverse effects and the mechanisms of their action are of great importance to assess the environmental risk of this material.

The degradation of BPA was conducted using 5.0 h CuO-BHF membrane for 6 h under Vis irradiation. The finding was compared to the pristine BHF membrane as a control set and alumina hollow fibre membrane (AHFM), a representative for commercial ceramic hollow fibre membrane.

Under visible light irradiation, CuO-BHF membrane controlled the degradation rate as CuO particles had a narrow band gap. This allowed the CuO-BHF membrane to perform under Vis irradiation. Fig. 6 shows that 93 % of BPA degradation was achieved by CuO-BHF membrane with initial BPA concentration of 10 mg/L. The degradation efficiency of BPA decreased with the

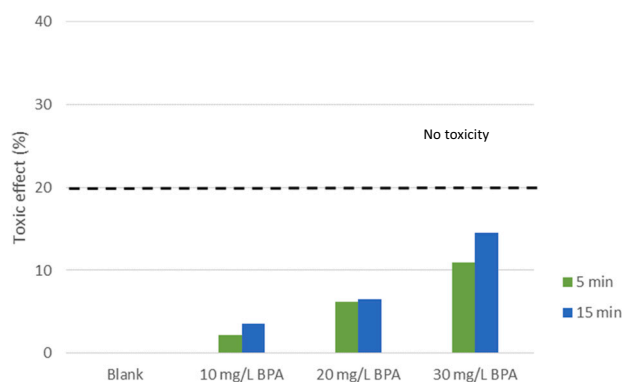


Fig. 11. Toxic effect of various BPA concentration.

Table 3

Toxicity class.

Toxicity class	Toxicity	Range
I	No	PE ≤ 20 %
II	Low risk	20 % < PE ≤ 50 %
III	Acute risk	50 % < PE < 100 %
IV	High acute risk	PE = 100 %
V	Very high acute risk	All used tests showed the effect PE = 100 %

increasing BPA concentration. A comparison of BPA removal was made between these pristine BHFM, CuO-BHFM and CuO-AHFM. This reveals that CuO-BHFM controlled the BPA degradation after 6 h under Vis irradiation, of which CuO-AHFM attained the lowest BPA degradation. The addition of CuO on the surface of BHFM facilitated the formation of reactive oxygenated species (ROS), enhancing the BPA degradation by the CuO-BHFM.

Fig. 7 shows that the CuO-impregnated BHFM exhibited excellent BPA degradation, as this modified membrane could remove 93 % of BPA, while the pristine AHFM had the lowest degradation rate of 16 % under the same optimized conditions. The lowest BPA removal using AHFM corresponded to the existing membrane, which main component was alumina that did not possess photocatalytic features. On the other hand, the presence of Cu in the bauxite facilitated the fabricated CuO-BHFM to have outstanding photocatalytic property. The addition of decorated CuO on the surface enhanced the capability of the CuO-BHFM for photocatalysis purposes. Previous study done by Ismail et al. [10] showed that low degradation of 10 mg/L BPA (approximately 62 %) was observed when the photocatalysis was conducted under visible light. As the BPA concentration increase gradually up to 30 mg/L, the degradation percentage becomes lower than 62 %. Similar pattern on BPA concentration versus rate of degradation was displayed when the activity was conducted under UV light irradiation. However, the findings clearly indicated that fabricated BHFM was preferable to UV light irradiation as high removal of BPA was attributed to the presence of the mixed anatase/rutile crystalline phase [30]. The degradation of BPA using BHFM can be improved through membrane's surface modification to enhance the capability of BHFM as novel photocatalytic ceramic hollow fibre membrane.

To ensure that the BPA degradation was occurred due to photocatalysis, the degradation test was done using both CuO AHFM and CuO BHFM in the dark condition was carried out as in supplementary figure

(Fig. S1). All batch experiments were performed triplicate and the means of three data sets were reported in order to ensure the accuracy, dependability and repeatability of the obtained data. Since the relative standard deviation was <1.0 % almost always, the data's accuracy was quite good. The data were ignored when the relative error went beyond this threshold, and a third experiment was run until the relative error was within acceptable bounds. Thus, it can be concluded that the degradation of BPA in this study was most contributed through photocatalysis and less significant on other reaction such as catalysis or adsorption.

3.3. Identification of intermediate compounds

The generation of reactive oxygen species (ROS) through electron's photoexcitation during photocatalysis has contributed to the BPA removal and formation of intermediate compound such as phenolic and carboxylic intermediates, which might be more toxic than the starting compound. Their presence was analyzed by HPLC according to their retention times and UV spectra. The HPLC chromatogram for BPA degradation in aqueous solution under degradation conditions of 10 mg/L of BPA for 360 min under visible light has been carried out in this study and the data is illustrated in Fig. 8. Based on the finding, it can be seen that there are several common peaks at the retention times of 2.25 min, 2.61 min, 3.09 min, and 6.34 min. There were four possible by-product detected namely 4-(2-hydroxy-2-propanol)phenol, 4-isopropylphenol, dihydroxybenzene and parent BPA. As reported by Neamtu and Frimmel [31], these peaks represent the formation of by-products of BPA. These products also decreased with time due to the decomposition to CO₂ and H₂O and this was attributed to the fast adsorption and further degradation of the intermediates on the catalyst surface [32].

3.4. Reusability of saturated CuO-BHFM

CuO-BHFM was subjected to dynamic photocatalytic filtration for 5 different cycles, with visible light exposure between the intervals. This was conducted to study the recyclability of membrane and its anti-fouling capabilities. The membranes were exposed under visible light irradiation for 30 min between every cycle interval. Fig. 9 shows the flux of CuO BHFM for photocatalytic filtration after 5 different cycles, under visible light irradiation.

When membrane technology is applied in treatment of effluent laden with organic pollutant, a persistent problem that hinders membrane usability is fouling. Fouling occurs when foreign molecules attach on membrane surface and pores which compromise membrane rejection and permeability over time. It is showed that there was a significant drop in membrane flux during each cycle. Each cycle exhibited a flux drop of 28.7 %, 17.7 %, 35.9 % and 18.6 %, respectively. However, when membrane was exposed under visible light, it was able to recover its flux for the subsequent four cycles. Since CuO BHFM exhibited good hydrophilic properties based on contact angle results, the attachment of foulants can be mitigated by visible light treatment for some periods.

Furthermore, by preventing the buildup of a cake layer on the membrane surface, the photocatalytic activity that occurs on the membrane surface as a result of the presence of the photocatalyst may also reduce fouling. The non-selective oxidation and reduction of BPA bound to membrane surfaces is made possible by the highly reactive electron hole pair on the photocatalyst surface, which also causes surface redox reaction. The flux recovery is consistent with previous studies that found

Table 4

Leaching test data of Cu.

Sample	mg/L					Test method
	Element	Replicate 1	Replicate 2	Replicate 3	Replicate 4	
Degraded BPA	Cu	0.05	0.00	0.00	0.00	Agilent 710 ICPOES method

that incorporating photocatalysis to membranes at the surface of BHFM can provide them self-cleaning capabilities, as was also observed in this work [33]. This surface redox also affects the entire rejection characteristics of the membrane.

Fig. 10 displays the CuO BHFM's 5-cycle rejection performance when exposed to visible light. The membrane showed a slight improvement in membrane rejection over time during dynamic photocatalytic filtration. For cycles 1, 2, 3, and 4, the increase in rejection between 0 and 360 s is 10.0 %, 16.7 %, 8.37 %, and 21.8 %, respectively. Continuous contact between the photocatalyst in the membrane and the feed solution occurs when dynamic photocatalytic filtration is used, and this can cause photocatalytic degradation. Additionally, in the continuous degradation experiment, this rise could be explained by the feed solution's ability to permeate through the membrane, which increased the interaction between the photocatalyst and pollutant. The results indicate that the membrane can exhibit consistent rejection performance under four different dynamic filtration cycles, which parallel to the fact that the membrane flux did not exhibit a significant drop.

3.5. Ecotoxicological by-products

It is well recognized that the principal disadvantage of oxidation technologies is the potential for the production of unintended chemicals that may be even more harmful than the parent molecules. Although certain organic by-products have also been identified, earlier research on the removal of BPA using CuO BHFM indicates that the main danger is the production of inorganic by-products. The development of by-products following this EDC elimination, however, has not been widely described.

In the first stage of the sorption materials and their mixtures analysis was used screening test. The pH of all samples was adjusted to neutral value. Samples of BPA wastewater characterized PE value below 20 % (Fig. 11), which they were considered as non-toxic (Table 3). Since only samples showing the effect of toxic $PE \geq 20$ were subjected to further analysis of Basic test 2 %, thus no further analysis on this test was conducted.

3.6. Leaching test

The leaching of copper element from the membrane into the treated BPA water sample was investigated during the treatment process. There was almost none significant trace of copper in the water sample as per Table 4, indicating that there is no copper leaching from the membrane. It is important to mitigate copper leaching in order to avoid disrupting ecosystem balance and to ensure that the membrane could work ideally without losing any photocatalyst particles that could impact its photocatalytic activity. Copper leaching is common for CuO/ZnO matrices [34], however in this study, there was no zinc compound was used, thus the leaching of copper was not detected. Hence, the CuO BHFM is an safe and ideal membrane to be used for further application in the environment.

4. Conclusion

This study has demonstrated the technical feasibility of CuO-BHFM for BPA photodegradation. As compared to the pristine BHFM membrane, we found that functionalizing BHFM surface with CuO significantly improved its mechanical strength by 130 % from 18.5 to 42.5 MPa. The removal of BPA was enhanced with the increasing hydrothermal time to 5 h due to the even distribution of CuO-impregnated BHMF on its membrane surface. At optimized conditions (pH: 7.0, dose: 5.0 g/L), about 97 % of BPA removal with 10 mg/L of its initial concentration was substantially attained by the same CuO-impregnated BHFM under visible light (VIS) irradiation. Treated effluents, resulting from the BPA photocatalysis, could meet the required effluent limit of 20 mg/L set by national legislation. Possible oxidation by-products

cover 4-(2-hydroxy-2-propanol)phenol, 4-isopropylphenol and dihydroxybenzene. With 25 % of efficiency, the saturated CuO-impregnated BHMF was subsequently regenerated for consecutive five cycles. This implies that functionalizing BHMF surface with CuO enabled it to possess outstanding stability and removal performance for treatment of BPA-laden wastewater.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Mohd Hafiz Dzarfan Othman reports financial support was provided by University of Technology Malaysia.

Data availability

Data will be made available on request.

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Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent

Informed consent was obtained from all individual participants included in the study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2022.103205>.

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