

Removal of bisphenol A from synthetic and treated sewage wastewater using magnetron sputtered Cu_xO /PVDF thin film photocatalytic hollow fiber membrane

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ABSTRACT

Flexible hollow fiber polymeric membrane based thin film substrate sputtered with thin layer photocatalyst is a novel configuration for photocatalytic applications. This article focuses on the fabrication of copper oxide/polyvinylidene fluoride thin film hollow fiber membrane (Cu_xO /PVDF TF HFM) by using radio frequency (RF) magnetron sputtering of Cu_xO over PVDF hollow fiber membrane (HFM). Different phase of copper oxide (Cu_xO) detected on the layer of PVDF HFM by X-ray diffraction (XRD) and attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) and confirmed by X-ray photoelectron spectroscopy (XPS), depending on oxygen flow rate. 10–20 mL/min O_2 flow rate produces Cu_2O phase while 25 and 30 mL/min produces CuO phase. Sputtered Cu_2O /PVDF TF HFM at 20 mL/min O_2 shows bigger grain size of 2.1 nm with 0.35 nm of dislocation density and 0.019 nm of lattice strain. The higher the O_2 flow rate, the thicker and the more uniform the sputtered Cu_xO /PVDF TF HFM was produced as indicated by field emission scanning electron microscopy (FESEM). The atomic force microscopy (AFM) analysis showed the increasing surface roughness of the sputtered 10 mL/min Cu_xO /PVDF TF HFM at 8.26 nm, as compared to the neat PVDF HFM at 6.15 nm. About 74 % of 2 mg/L bisphenol A (BPA) in synthetic wastewater was successfully photodegraded and filtered while outstanding 91 % removal of BPA in real treated sewage wastewater achieved using 20 mL/min Cu_2O /PVDF TF HFM after 360 min light irradiation. About 71.33 % of regeneration efficiency was achieved after 3 consecutive cycles that this technique promises the good reusability with strong adhesion capability.

1. Introduction

Wastewater with refractory pollutants such as bisphenol A (BPA), one of the endocrine disrupting compound (EDC), not only affects public health, but also gives adverse effects to the ecosystem [1]. The pollutant, known as synthetic oestrogen, been discharge into the water bodies [2] contributes to human chronic diseases [3]. The endocrine disruptor,

which has unique structure, has the capability to block the natural hormones [4]. BPA is frequently traced in water, wastewater, sewage sludge and sediments where the higher amount of BPA causes risks of diabetes and heart disease to humans [5]. Small percentage of BPA can be detected in industrial and municipal sewage treatment plant outlet around 1.3 to 215 ng/L, in tap water around 3.5 to 59.8 ng/L, and 3.3 ± 2.6 ng/L in mineral bottled water, at room temperature [6]. In Malaysia,

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BPA is not listed in the national water quality standard (NWQS) and Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations. Hence, the issue of BPA toxicity is a global concern and sustainable approaches of its advanced treatments need to be highlighted.

For this reason, wastewater managers have the responsibility to ensure that the effluent that is eventually released into the environment does not degrade the quality of the recipient water bodies [7]. As attaining the sustainability in wastewater management is the top priority of Sustainable Development Goals (SDGs) Agenda, so, the realization of a more sustainable wastewater management requires a holistic and balanced approach in evaluating a specific management strategy. Promoting the use of safe, affordable and approachable wastewater treatment techniques is a step towards wastewater treatment for sustainability. Wastewater treatment is the overall process that involves the improvement of the quality of wastewater between points of production and points of discharge. Several technologies have been developed for BPA removal including adsorption [4], ozonation [5], ion exchange [7], biosorption [8] and photocatalysis [9]. Adsorption is considered as a promising method due to simple operation, low-cost treatment, as well as reasonable treatment efficiency [10]. However, the recovery and filtration of adsorbent is a key bottleneck.

Other methods also encounter drawbacks such as the formation of harmful oxidation by-products and high operational cost [11]. Among the present treatment technologies, advanced oxidation processes (AOP) especially photocatalytic degradation is considered as a seminal method to treat BPA-contaminated wastewater. Photocatalysis is actually a chemical photoreaction between a catalyst with UV, visible or near infrared light and the photoexcitation occurred depends on the energy band gaps and a wide range of inactivate waterborne microbes through simple photocatalytic redox mechanism [12,13]. In photocatalysis basically, a light penetration towards catalyst is required to produce electrons (e^-) in valence band (VB). After that, e^- excite towards conduction band (CB) by producing holes (h^+) in VB. The redox reaction between e^- and h^+ produces hydroxyl radicals ($\cdot\text{OH}$) and superoxide anion radicals ($\text{O}_2^{\cdot-}$) that break target pollutant into carbon dioxide (CO_2) and water (H_2O) [12]. Photocatalysis using membrane has been popular in water treatment due to the environment-friendly approach in maintaining a sustainable ecosystem.

Although TiO_2 is the promising material for photocatalytic application in previous literature, however it only functions to ultraviolet light illumination where the light causes drawbacks such as bacterial growth after the process and high energy consumption [12]. Cu_2O is an inexpensive, non-toxic and abundantly available compound. It has a narrow band gap (1.2–2.5 eV) suitable for photocatalytic degradation under visible light [14,15]. As a promising photocatalyst, Cu_2O nanocrystal removed 99 % of congo red dye [16], while CuO nanowire successfully degraded methylene blue up to 79.47 % after 4 h of reaction [17].

Although the powdered catalysts have benefits such as numerous active spaces for light illumination, but there are some limitations of separation and recovery process after treatment. Therefore, the immobilization of catalyst on a suitable support is needed to overcome the powder catalyst issues [18]. The physical deposition of catalyst on substrate-produced thin film can provide different photocatalytic properties.

Sputtering technique can produce higher deposition rate, simple operation, safe method as well providing a large area deposition which is recommended for industrial applications [18,19]. This technique also delivers a uniform deposition, which is highly adhesive and free from contamination [21]. In spite of its above mentioned benefits, so far no one has reported the deposition of copper oxide catalyst on polymer substrate, especially hollow polymeric membrane configuration for photocatalysis application.

To bridge the existing gap, this study investigated the deposition of copper oxide thin film on PVDF HFM using radio frequency (RF) magnetron sputtering technique with varying oxygen flow rates. Oxygen

flow rates play as an important key in producing different phases of copper oxide that influence the photocatalysis efficiency. PVDF HFM was chosen due to its versatility including outstanding thermal and chemical stability [21,22]. The technical feasibility of $\text{Cu}_x\text{O}/\text{PVDF}$ TF HFM for BPA photocatalytic degradation in synthetic and real treated sewage wastewater was evaluated. Photocatalysis analysis towards real treated sewage wastewater was carried out to evaluate the capability of $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM as good photocatalytic membrane to be used in real wastewater treatment. Flexible hollow fiber PVDF membrane-based thin film substrate sputtered with copper oxide acts as a novel configuration for photocatalytic applications and filtration performance in providing a good membrane reusability with strong adhesion of photocatalyst for excellent photocatalytic performance.

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride (PVDF, Kynar 760 pellets) as polymer material was obtained from Solvay Specialty Polymers (France). Both *N,N*-dimethylacetamide (DMAc) and triethyl phosphate (TEP) were provided by Sigma-Aldrich and Merck, respectively. Lower molecular weight additive, polyethylene glycol 400 (PEG 400) was obtained from Evergreen Engineering & Resources. Bisphenol A (BPA) as a model of pollutant was purchased from Merck.

2.2. Fabrication of PVDF hollow fiber membrane (PVDF HFM)

PVDF pellets were placed inside the vacuum oven at 60 °C to remove excess moisture for 24 h. A mixture of TEP (50%w/w) and DMAc (33 % w/w) were homogenously stirred at 240 rpm inside a Scott bottle at 80 °C [23]. Subsequently, PVDF (15 % w/w) was added into the solution and stirred until completely dissolved under same condition [24]. The reaction was continued by adding PEG 400 (2 % w/w) into the mixture and stirred homogenously for another 24 h.

Afterward, doping solution was further used in dry-wet spinning system for fabricating polymeric hollow fiber membrane via phase inversion method [24]. Single orifice spinneret and normal tube were implemented to produce a single layer of polymeric hollow fiber membrane. Initially, dope solution was degassed inside the sonicator bath (Ultrasonic cleaner, delta, DC-150H) for 30 min to remove bubbles. Then, it was poured into the reservoir (Table 1).

When dope solution reached into a coagulation bath (water), phase inversion process took place for solidification. Subsequently, as-spun hollow fiber was collected from the collector and soaked into a water tank for 24 h to extract residual diluent. Afterwards, post treatment occurred by immersing the as-spun hollow fiber membrane into ethanol (50 % v/v) for 60 min and another 60 min into concentrated ethanol to prevent membrane from being shrinkage. Finally, the PVDF hollow fiber membrane was dried at ambient temperature for 24 h.

Table 1

Parameters for fabrication of PVDF hollow fiber membrane using dry-wet spinning technique.

Sample name	Dope flow rate (rpm)	Bore fluid type	Bore fluid flow rate (mL/min)	Coagulation bath	Spinneret dimension (mm)	Air gap (cm)
Neat PVDF HFM	26	Water	8	Water	0.8/1.2	20

2.3. Preparation of Cu_xO/PVDF thin film hollow fiber membrane

Deposition of Cu_xO onto the surface of PVDF hollow fiber membrane was executed by radio frequency (RF) magnetron sputtering (Model: MSS LAB350 (2018)). Round copper disk (99.999 % purity) with 2.54 cm of diameter and 0.32 cm of thickness was used as target [25]. PVDF hollow fiber membrane with 12 cm of length was used as substrate. Argon gas of 20 mL/min was introduced into the sputtering chamber to ionize the copper ion. Afterwards, 10 mL/min of oxygen gas flow rate was introduced into the chamber for formation of Cu_xO. Substrate was rotated at 15 rpm to ensure that the Cu_xO thin film has been deposited uniformly on the surface of PVDF hollow fiber membrane. The sputtering process was carried out at 9.8×10^{-6} Torr of base pressure and 5×10^{-3} Torr of operating pressure. The power consumption was 200 W, while sputtering time was 10 min with 14 cm of target-substrate distance [26]. The experiment was repeated by varying oxygen flow rates at 15, 20, 25 and 30 mL/min. The sputtering parameters were presented (Table 2), while the schematic preparation of Cu_xO/PVDF TF HFM is illustrated in Fig. 1.

2.4. Characterization

Sputtered thin film of Cu_xO/PVDF TF HFM was characterized using X-ray diffraction (XRD) (Model: D5000, SIEMENS) to detect the crystallinity of Cu_xO/PVDF TF HFM and different phases of Cu_xO formed on the surface of membrane at varying O₂ flow rate. The analysis was carried out with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) at ambient condition. Diffraction patterns of 2θ was measured in the range between 5° and 80° with a scanning speed of $10.1245^\circ/\text{min}$, while its width was 0.05° , at a voltage of 40 kV. The phase changes of Cu_xO were confirmed with attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) (IR Tracer-100 Shimadzu) by scanning at a range from 4000 to 400 cm^{-1} was used to detect the functional groups of thin film formed. The morphology of Cu_xO/PVDF TF HFM was revealed by using field emission scanning electron microscopy (FESEM) (Model: TM3000, Hitachi), while energy dispersive X-ray (EDX) was used to detect the presence of elements on the sputtered surface of PVDF HFM. Atomic force microscopy (AFM) (Model: Hitachi) was used to detect the surface roughness of the sputtered thin film.

Optical band gap of sputtered thin film was analyzed by using UV-Vis NIR spectrophotometer (UV-310PC Shimadzu, Japan). The samples were clamped and scanned at the range between 200 and 800 nm. The energy value was calculated using Tauc Plot based on Eq. (1) [20]:

$$\alpha h\nu = A(h\nu - E_g)^m \quad (1)$$

where α is absorbance, $h\nu$ is photon energy, A is band tailing and m is $\frac{1}{2}$.

Contact angle was measured using a contact angle goniometer (Model: OCA15EC, Dataphysics). Deionized water was used as a contact liquid. Multiple points of the sample were measured to obtain the result. Porosity of sputtered film was calculated based on Eq. (2) below:

$$\varepsilon = \frac{(w_1 - w_2)}{\left(\frac{w_1 - w_2}{\rho_w}\right) + \left(\frac{w_2}{\rho_p}\right)} \quad (2)$$

Table 2
Sputtering process parameters.

Sample	Target	Sputtering power (W)	Ar:O ₂ Flow rate (mL/min)	Target distance (cm)	Sputtering time (min)
10	Cu	200	20:10	14	10
15			20:15		
20			20:20		
25			20:25		
30			20:30		

where: W_1 and W_2 represented as weight of sample after and before soaked with water respectively, ρ_w is water density (0.997 g/cm^3) and ρ_p is polymer density (1.78 g/cm^3).

2.5. Photocatalytic degradation of synthetic BPA and water flux performance

The submerged membrane photoreactor setup (Fig. 2) was employed for photodegradation of BPA using Cu_xO/PVDF TF HFM. A bundle of 20 strands of Cu_xO/PVDF TF HFM with 10 cm of length were potted into PVC tube using epoxy resin (E-30CL Loctite® Corporation, USA). Synthetic (2, 5 and 10 mg/L) of BPA solution was transferred into a photoreactor. Air pump was used for providing aeration. The treatment was started without light irradiation for 1 h to obtain adsorption-desorption equilibrium. After achieving an equilibrium, the solution was irradiated by visible light (LED lamp, 100 W, Philips (Japan)) in the dark for 6 h. Periodically, 10 mL of aliquot was collected and analyzed using a UV-visible spectroscopy (Model: HACH DR5000, Perkin Elmer) at a wavelength (λ) of 280 nm [27,28]. The removal efficiency of BPA was calculated based on Eq. (3).

$$\% \text{Removal} = \frac{C_1 - C_2}{C_1} \times 100 \quad (3)$$

where: C_1 is initial concentration, while C_2 is final concentration of BPA solution.

First-order kinetic model was used to measure the rate of BPA photodegradation by Cu_xO/PVDF TF HFM thin film by using Eq. (4):

$$k = -\ln(C/C_0)/t \quad (4)$$

where C_0 and C indicate as initial and final concentrations of BPA with degradation rate constant ($1/\text{min}$), k as well its values calculated from plot $\ln(C/C_0)$ against time (t). Air pump was used for water movement inside the container and peristaltic pump for water flux analysis. Photocatalytic study and water flux analysis were carried out simultaneously. The water flux analysis was operated at 20 rpm and the result was determined using Eq. (5),

$$F = \frac{V}{A \times t} \quad (5)$$

where: V is a permeate volume (L) collected, while A is an exposed membrane filtration area (m^2) and t (h) is time. The aliquot was analyzed using UV-visible spectroscopy (Model: HACH DR5000, Perkin Elmer) at a wavelength 280 nm after 360 min of visible light irradiation.

Leaching of Cu_xO into the BPA solution was tested by taken out 10 mL aliquot of sample after degradation process. Then, the sample was analyzed using inductive coupled plasma mass spectrometry ICP-OES (Agilent 710) to detect the presence of copper inside the sample. The reusability test of copper oxide thin films was conducted for BPA solution. Three cycles were carried out for Cu_xO/PVDF TF HFM used for the photocatalysis. Cu_xO/PVDF TF HFM that been used from previous analysis was reused again in the same condition. Between each cycle of experiments, the films were taken out, washed with distilled water and dried in air. The unknown concentration of BPA was analyzed using UV-visible spectrophotometer to discover the percentage degradation efficiency.

2.6. Treated sewage wastewater sampling methods

Sampling of treated sewage wastewater was carried out using the grab technique [29] at four sewage wastewater treatment plants around Klang Valley, Malaysia. On-site measurements, in-situ parameters were performed using a portable YSI Pro Plus multiparameter meter (YSI Incorporated, Yellow Springs, Ohio, USA). In the grab technique, samples were taken directly from the sampling access point (final discharge

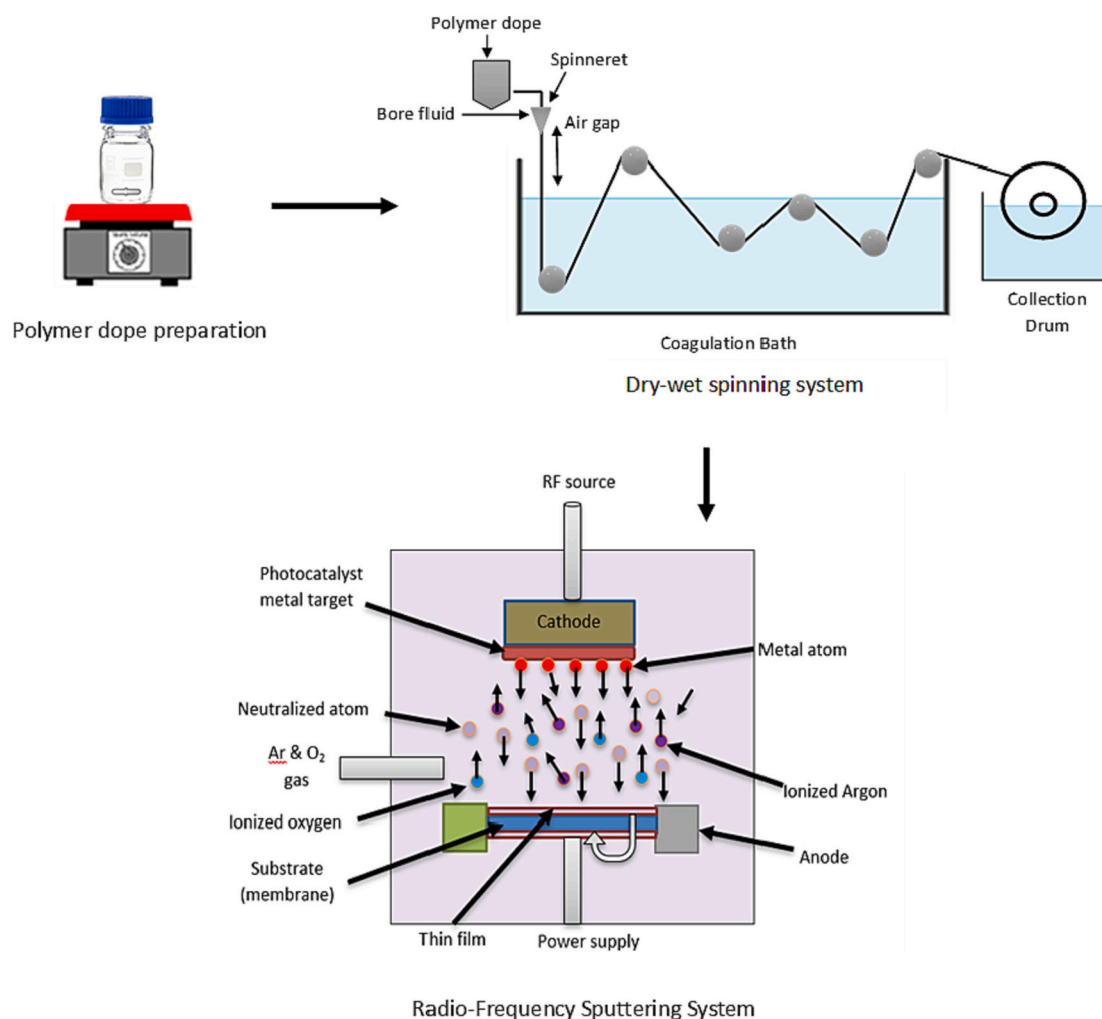


Fig. 1. Schematic preparation of $\text{Cu}_x\text{O}/\text{PVDF}$ TF HFM.

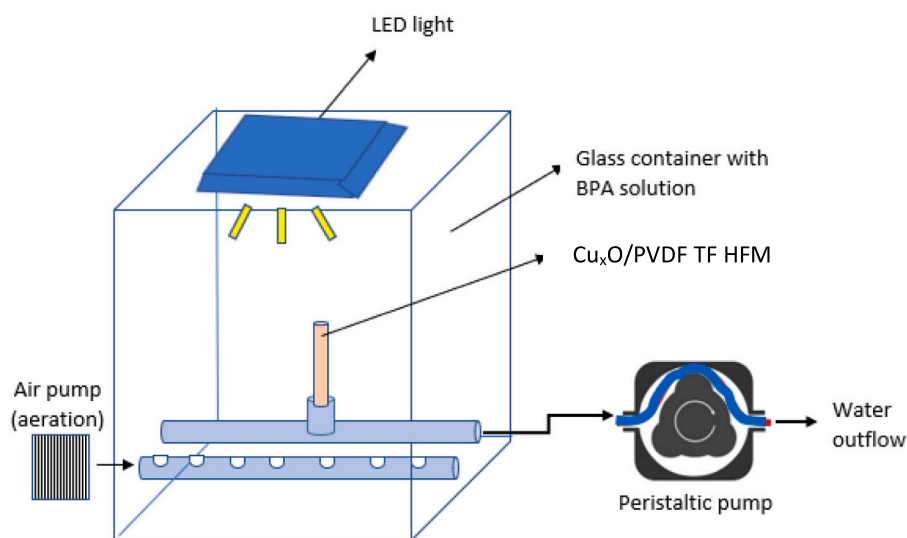


Fig. 2. Schematic diagram of photocatalytic reactor and water flux performance.

treated wastewater before to river bodies) and performed on a dry day. Gloves were worn during sampling to avoid contamination of the sample. Sampling stainless steel pail and amber bottles were cleaned and

rinsed with wastewater at the sampling point before being filled with the wastewater sample. A total of 10 L of sample was collected in amber glass bottles. The amber glass bottles were fully filled to prevent air

bubbles, reduce air pollution and evaporation of the sample. Samples were cooled in ice at a temperature of less than 4 °C for preservation purposes so that analysis could be carried out. All sample bottles were labelled with the station number, date and time of sampling.

2.7. Chemical analysis of treated sewage wastewater

About 9 L of unknown concentration of treated sewage wastewater was transferred into an acrylic reactor and the photocatalytic setup was same as mentioned in Section 2.5 with 20 mL/min sample of Cu₂O/PVDF TF HFM. Air pump was used for providing aeration. The treatment was started without light irradiation for 1 h to obtain adsorption-desorption equilibrium. After achieving an equilibrium, the solution was irradiated by visible light in the dark for 6 h. About 250 mL of aliquot was collected and analyzed using the Gas Chromatography-Mass Spectrometry (GCMS) techniques. In GCMS technique, BPA were extracted into dichloromethane. After evaporation on rotary vacuum evaporator, BPA were derivatized with *n*-methyl-*n*-(trimethylsilyl) trifluoroacetamide (MSTFA) by silanization and cleaned up by solid-phase extraction (SPE) method on W-AEOGMS01-Zebron ZB-5 sample column. The parameters were determined by the gas chromatography with mass detection. The method is based on document CSN EN ISO 18857-2.

3. Results and discussion

3.1. Characterization

3.1.1. Morphology and element mapping in sample

The surface morphology of the sputtered Cu_xO was successfully attached onto the surface of PVDF HFM by bombardment of Cu_xO using process pressure inside the magnetron sputtering chamber by varying the oxygen flow rate. Fig. S1 shows that produced thin films of sputtered Cu_xO with different thickness were detected and observed via FESEM analysis. The obtained images of deposited Cu_xO exhibited densely packed grains that uniformly distributed along the surface of PVDF HFM. The thickness of Cu_xO sputtered on the polymer substrate was 194, 189, 184, 174 and 164 nm for 10, 15, 20, 25 and 30 mL/min of the samples, respectively.

By applying lower oxygen flow rate (10 mL/min) during sputtering, micro-cracks appeared on the surface of the sample that can be attributed to the dense and thicker deposition of Cu_xO, although the other samples showed uniformity when O₂ flow rate was increased up to 30 mL/min. The thickness of the sputtered material decreased when oxygen flow rate increased from 10 to 30 mL/min by maintaining the target substrate distance at 14 cm. By increasing the O₂ flow rate, the sputtered Cu atoms reduced and lowered the film deposition rate [30,31]. It was attributed to the higher oxygen flow rate with higher energy that reached the film surface, which bombarded the Cu atoms by allowing them to migrate on the surface of substrate. This suggests the connection between Cu_xO particles and promotes the layer-by-layer growth [32]. Compared to neat PVDF, no deposition of Cu_xO appeared and pores shown at outer surface view.

The uniform distribution of Cu_xO at the outer surface of the PVDF HFM was verified by EDX analysis (Fig. S2). The red dots referred to the presence of Cu, while blue dots were assigned to O. The presence of high loading of Cu_xO as a photocatalyst on the outer surface membrane enhanced the photodegradation of target pollutants. However, there was also diffusion of the Cu_xO particles into the intermediate space of the PVDF HFM due to the single layer of porous PVDF HFM as substrate and it might easily enter through the pores as compared to dual layer PVDF HFM (Fig. S3). Compared to neat PVDF, no red dots on the membrane surface and cross-section shown while only little blue dots appeared due to the triethyl phosphate solvent for neat PVDF HFM fabrication.

The elemental composition of Cu_xO thin film on the PVDF HFM surface and cross section layer was shown in Table 3. From the surface, it indicates that the higher the oxygen flow rate, the lower the Cu element.

Table 3

Elemental composition of Cu_xO thin film on membrane's surface and cross section layer.

Sample (mL/min)	Surface elements (wt%)			Cross section elements (wt%)		
	Copper	Oxygen	Carbon	Copper	Oxygen	Carbon
10	7.6	29.7	62.7	2.6	26.6	70.9
15	6.3	28.8	64.9	5.6	36.2	58.2
20	5.0	28.0	67.0	3.2	33.3	63.5
25	4.5	27.3	68.2	5.9	33.2	60.9
30	3.9	26.5	69.6	5.3	22.5	72.2

The same finding was also reported by Jilani et al. [33], who found that the Cu element reduced with the rising oxygen flow rate. Carbon element was also analyzed to detect its atom on the PVDF HFM. Carbon was considered as a contaminant on the surface during the transfer of films from sputtering [34]. As the PVDF HFM was a single layer, the Cu_xO was easily diffused inside the porous PVDF HFM layer. Cu and O were also detected on the surface thickness of the coating layer. The change in their contents is related to phase change [35]. The higher the oxygen flow rate, the greater the tendency for Cu_xO diffused inside the pores and attached inside the finger-like projections. It could be due to the pressure during the sputtering which pushed the Cu_xO into the porous PVDF HFM layer. The oxygen content inside the PVDF HFM layer originated from the oxygen of the polyethylene glycol (PEG 400) and triethyl phosphate (TEP) during the fabrication of PVDF HFM.

3.1.2. X-ray diffraction

The structural analysis of the sputtered Cu_xO thin films on the membrane's surface was investigated using an XRD. Fig. 3 depicts the XRD pattern of different phases of Cu_xO formation after being deposited on the PVDF HFM surface at varying oxygen flowrates. According to the ICDD 00-045-0937 crystallographic information, the main diffraction of Cu₂O was observed at (110) plane, which referred to ~26° peak at all sample details [36]. According to Kumar et al. [37], Cu₂O phase was detected at same peak in the XRD spectra, while other Cu₂O peak, which appeared at ~36° indicated (111) diffraction plane in 10, 15, and 20 mL/min of the samples. This reveals the formation of pure cubic crystalline phase of Cu₂O [38]. The diffractions of single CuO were also observed at 40.4° for 25 mL/min sample, which implied as (111) diffraction plane, while sample 30 mL/min revealed CuO peaks at 36.5°, 40.75°, 56.6° and 68.15°, which referred to (111) and (002) diffraction planes based on the ICDD 01-071-4310 crystallographic information.

The same pattern was also shown by Radjehi et al. [31], where CuO phase emerged when the sample with 30 mL/min of oxygen flow rate was applied. According to Jilani et al. [33], CuO was also observed at (111) and (002) planes using direct current (DC) sputtering techniques. This can be explained due to the fact that different CuO phase was successfully implemented on the surface of membrane by sputtering due to the effects of oxygen flow rate. This suggested that higher O₂ flow rate produced O⁻ [39]. Cu₂O formation at lower O₂ flow rate was due to insufficient O₂ and less energy of O⁻. At a higher O₂ flow rate, the higher energy of O⁻ enhanced the reaction between Cu⁺ and O⁻, of which of the Cu⁺ was oxidized to Cu⁺² to produce pure CuO with the increasing O₂ flow rate [40].

The higher the oxygen flowrate, the higher the intensity of the peaks, which in turns, increases the crystallinity of CuO thin film. As a result, the intense semi-crystalline peak at 18.31° and 19.62° were also observed at the sputtered PVDF HFM, which corresponded to the existence of PVDF [41]. The Scherrer Eq. (6) was used to calculate grain size [33],

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (6)$$

where: *D* is the crystalline size of diffraction planes and *K* is the constant, while *λ* is the wavelength and *β* refers to a corresponding diffraction

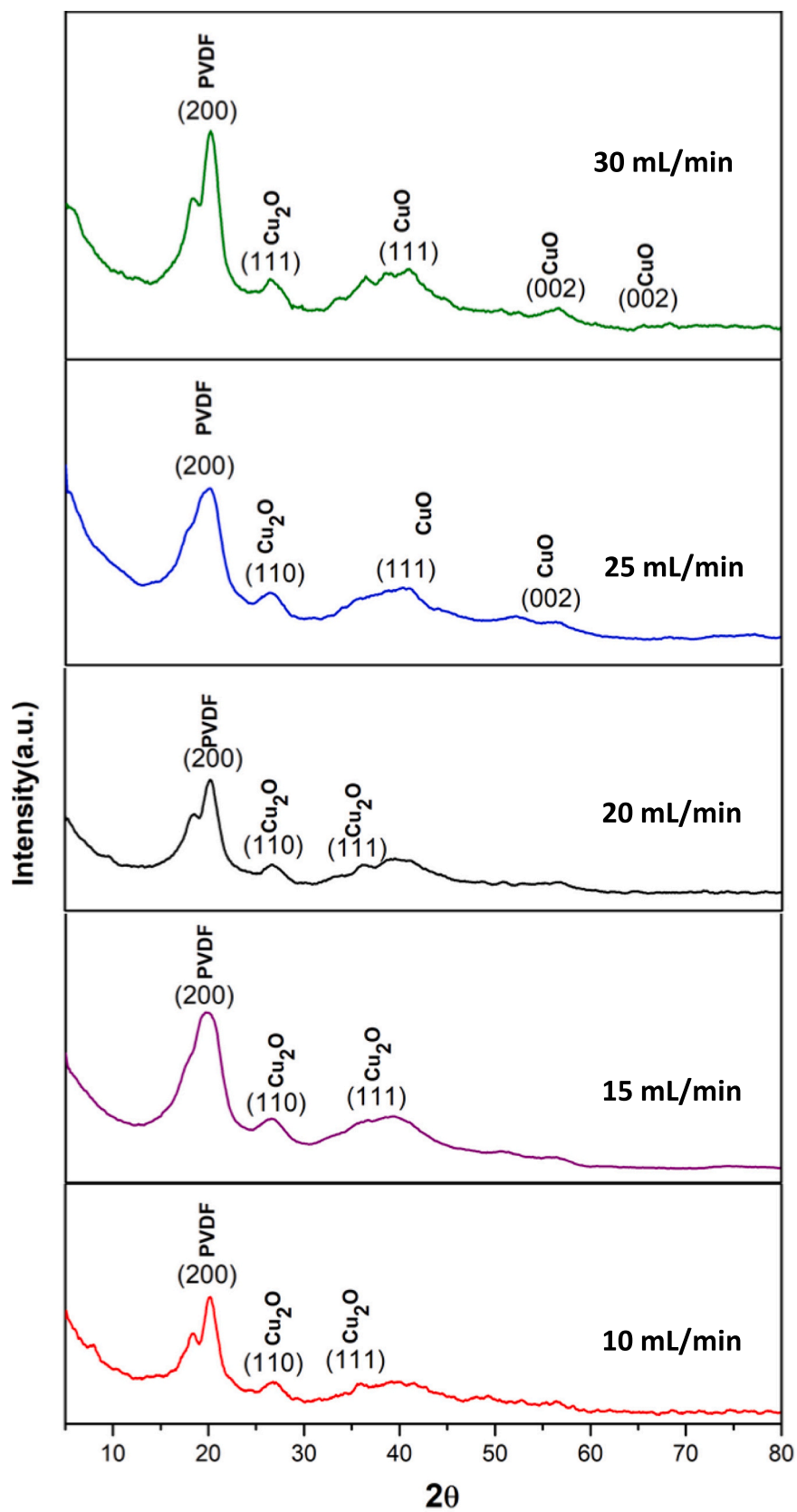


Fig. 3. XRD spectra of Cu_xO thin film at varying oxygen flowrate.

plane.

Table 4 shows that the grain size of Cu₂O was calculated to be 2.11 nm in 10 mL/min sample. When the oxygen flow rate was increased to 15 mL/min, the grain size was reduced to 1.32 nm. However, when the oxygen flow rate was increased to 20 mL/min, the grain size of Cu₂O was again increased to 2.15 nm. Subsequently, the grain size of sputtered CuO reduced when it started developing at 25 and 30 mL/min of O₂ flowrate (Table 3). The decreasing grain size could be due to the migration effects of constrain grain boundary, which restricts the grains growth [42].

The effect of oxygen flow rate in sputtering can further alter the dislocation density of sputtered CuO and Cu₂O. Number of defects in the material was calculated using Eq. (7) [43],

$$\delta = \frac{1}{D^2} \quad (7)$$

where D is the grain size based on the Scherrer equation. The higher the oxygen flow rate in the sputtering, the higher the dislocation density and vice versa (Table 3). As a result, the variation of dislocation density influenced the lattice strain of the material. The lattice strain of sputtered Cu_xO can be calculated using Eq. (8):

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (8)$$

where: β represents a full-width half maximum of diffraction peaks, while θ is a diffraction angle.

The lattice strain of 10 mL/min of the sample was 0.020 nm and increased to 0.027 nm when 15 mL/min of oxygen flow rate was employed. However, the lattice strain dropped to 0.019 nm at 20 mL/min sample. After further increment of the oxygen flow rate to 25 and 30 mL/min, the lattice strain rose again. The lattice strain of the sputtered CuO showed the same trend for dislocation density. This data suggests that the higher the oxygen flow rate, the lower the grain size of the sputtered CuO, which improved the grain boundaries, leading to the increment in strain and dislocation density. Furthermore, this can also be explained due to the higher interstitial oxygen defects introduced into CuO film with the increasing oxygen flow rate.

By rising the oxygen flow rate during the sputtering, the growth of the grains impeded and reduced the crystallinity of film formation, resulting in a large number of grain boundaries [44]. The same trend was also reported by Dolai et al. [45], who found that the grain size became smaller as a higher oxygen flow rate was applied using D.C sputtering technique. Different phase of the Cu_xO was further analyzed by the FTIR analysis.

3.1.3. Attenuated total reflectance Fourier-transform infrared spectroscopy

To measure vibrational bond frequency in a molecule, FTIR analysis of neat PVDF HFM and Cu_xO/PVDF TF HFM at various oxygen flow rates, scanned in the range of 4000–400 cm⁻¹ at ambient temperature was conducted as given (Fig. 4). When the PVDF HFM was sputtered with copper oxide by varying oxygen flow rate, different phase of the Cu_xO was formed. Fig. 4 reveals that the Cu₂O bond appeared at ~610 and ~680 cm⁻¹, in agreement with Dulma et al. [46] and Renuga et al. [47]. By increasing the oxygen flow rate to 25 and 30 mL/min, the band

Table 4

Calculated crystallinity through diffraction pattern for Cu_xO thin film at varying oxygen flow rate.

Sample details (mL/min)	Grain size (nm)	Dislocation density (nm)	Lattice strain (nm)
10	2.11	0.39	0.020
15	1.32	0.61	0.027
20	2.15	0.35	0.019
25	1.60	0.67	0.025
30	1.69	0.75	0.026

at 478.35 cm⁻¹, 466.77 cm⁻¹ and 435.91 cm⁻¹ revealed Cu—O bond [48] and the intensity of their peaks also increased, as compared to neat PVDF HFM. Moreover, the peak at ~534 cm⁻¹ found in 30 mL/min sample was also identified as CuO. Fig. 3 also displays the intense band at 1178.51 cm⁻¹ that corresponded to CF₂ bond from the PVDF, while the band at 975.98 cm⁻¹ and 759.95 cm⁻¹ were assigned to alpha-phase PVDF crystal according to Kamaludin et al. [24] and Shi et al. [47]. The phase of Cu₂O in 20 mL/min sample was further confirmed by XPS analysis.

3.1.4. X-ray photoelectron spectroscopy

The a) XPS survey spectra and b) XPS spectra of Cu 2p of 20 mL/min sample Cu₂O/PVDF TF HFM was shown in Fig. 5. Three peaks at 281 eV, 528 eV and 931 eV attributable to C 1s, O 1s and Cu 2p were observed in the XPS survey scan spectrum of 20 mL/min sample Cu₂O/PVDF TF HFM (Fig. 5 (a)). The existence of C 1s attributable to the PVDF HFM while O 1s and Cu 2p correspond to the existence of Cu₂O. The similar report of C 1s from PVDF can be seen from Akashi and Kuroda [49]. Fig. 5 (b) show the Cu 2p XPS spectrum. Two peaks at 930.55 eV and 950.95 eV corresponding to the Cu 2p_{3/2} and Cu 2p_{1/2} peaks of Cu⁺, respectively, confirm the existence of Cu₂O in the sample. Moreover, the existence of Cu⁺ in the sample can be further confirmed by the two extra peaks at 940.55 eV and 959.05 eV which similar with previous literature [50,51].

3.1.5. Surface roughness

The surface topography of the neat PVDF HFM and Cu_xO/PVDF TF HFM at different oxygen flow rate were scanned at an area of 10 × 10 μm using AFM. The changes in oxygen flow rate affected the surface morphology and the roughness of the sputtered Cu_xO (Fig. 6). The sputtering of Cu_xO onto the surface of PVDF HFM increased the roughness of the membrane. At 10 mL/min of oxygen flow rate, it was observed that the surface roughness was 8.26 nm, higher than the neat PVDF HFM (6.15 nm). The average surface roughness (Ra) was found to be 8.05, 7.92, 5.95 and 5.17 nm for each film deposited at 15, 20, 25 and 30 mL/min of samples, respectively. The surface roughness increased after Cu₂O deposition at 10 mL/min of oxygen. However, the roughness reduced once the oxygen flow rate increased. Jilani et al. [33] found that the surface roughness of CuO film decreased on applying higher oxygen pressure. This implied that a smaller grain size was produced by sputtered CuO as oxygen flow rate increased which reduced the surface roughness of the sputtered material. This was also reported by Dustgeer et al. [52], who found the surface roughness depends on the particle size of the deposited material.

3.1.6. Optical band gap

The direct optical bandgap of the sputtered thin films was determined by the Tauc's model (Fig. 7). The intercept of the straight line to $h\nu$ axis at zero indicated the optical band gap (E_g). The Cu₂O thin film deposited at 10 mL/min of O₂ flow rate had a band gap of 2.41 eV. The thin film deposited at 15, 20 and 25 mL/min of O₂ flow rate had a band gap of 2.34 eV, 2.29 eV and 2.24 eV, respectively, while the band gap at 30 mL/min exhibited at 2.15 eV. The higher the O₂ flow rate, the lower the band gap. This can be explained that the band gap of CuO exhibited at 25 and 30 mL/min was lower than Cu₂O in 10, 15 and 20 mL/min of the samples. The band gap of Cu₂O film was 2.3–2.5 eV, while for CuO it ranged from 1.9 to 2.3 eV [20,52]. Therefore, samples with lower band gap were suitable for visible light irradiation of the photocatalysis.

3.2. Water flux performance

Water flux study was conducted during photodegradation to observe the filtration performance of the Cu_xO/PVDF TF HFM. The water flux performance showed an improvement when higher O₂ flow rate was applied during the sputtering (Fig. 8). Samples with 10, 15, 20 and 25 mL/min achieved 16.39, 20.18, 26.53 and 33.99 L/m²·h, while sample

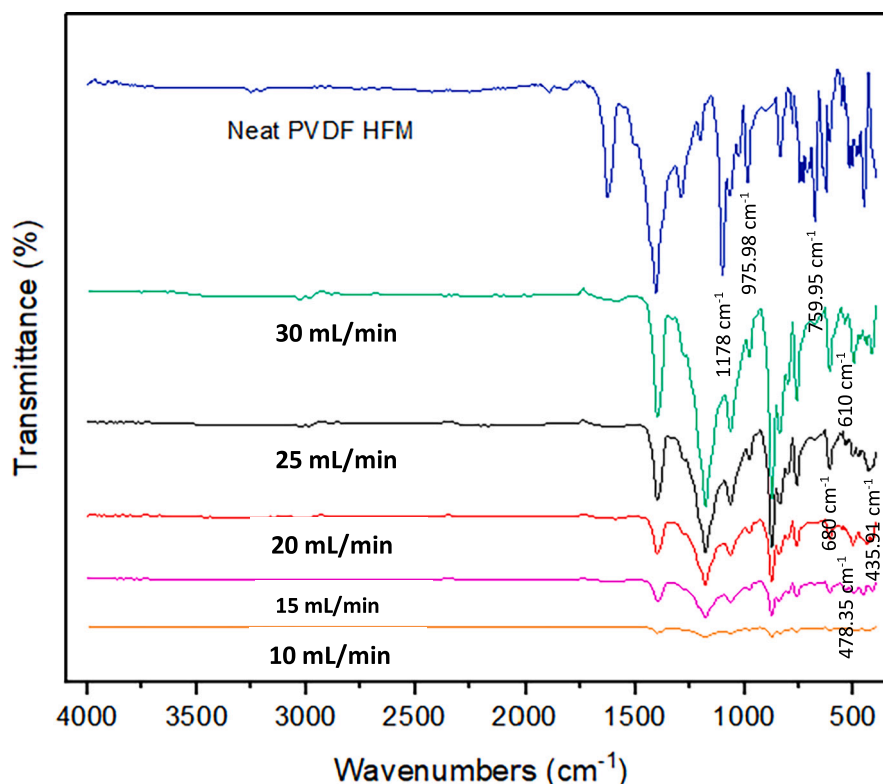


Fig. 4. FTIR spectra of neat PVDF HFM and sputtered Cu_xO /PVDF TF HFM at different O_2 flow rate.

of 30 mL/min achieved the highest water flux at $37.96 \text{ L/m}^2\cdot\text{h}$ after 6 h, comparable to the contact angle and porosity of the sputtered membrane.

Table 5 shows that samples with 10 and 15 mL/min exhibited a higher contact angle at 100.85° and 109.1° respectively, as compared to the neat PVDF HFM. It could be due to the agglomerated sputtered thin film developed as a thicker layer covered on the membrane's surface, leading to hydrophobicity.

When increasing the O_2 flow rate to 20 mL/min, the contact angle reduced to 67.88° . This could be due to the fact that the uniform sputtered CuO thin film was successfully deposited and had a strong bonding with the PVDF HFM, resulting the hydrophilic nature of membrane. A lower contact angle produced good wettability, hence increasing the water flux. As the O_2 flow rate was increased to 25 and 30 mL/min, the contact angle increased dramatically up to 98.82° and 104.05° due to the thinner film deposition. Although 25 and 30 mL/min exhibited a greater contact angle, the water flux showed the porosity achieved by the samples (Table 5).

The porosity of the sputtered membrane showed that the porosity increased when higher oxygen flow rates were applied. This resulted in the thickness of the sputtered CuO onto the membrane's surface. The lower the thickness of CuO deposition, the higher the porosity of the sputtered membrane, thereby enhancing the water flux performance. A higher porosity of the sputtered membrane at 30 mL/min of O_2 flow rate could be due to the porous CuO distribution on the surface of the PVDF HFM, increasing the water flux performance. Pedram et al. [53] reported that a flat sheet polytetrafluoroethylene (PTFE) sputtered PES membrane at 20 mtorr of argon pressure, 50 W power of RF magnetron sputtering and 10 min of deposition achieved a lower water flux at $3 \text{ kg/m}^2\cdot\text{h}$.

3.3. Photocatalytic activity of BPA in synthetic wastewater

The photocatalytic degradation of BPA was carried out to evaluate the photocatalytic performance of Cu_xO /PVDF TF HFM by using 10, 15,

20, 25 and 30 mL/min (Fig. 9). After potting Cu_xO /PVDF TF HFM inside PVC pipe and in photocatalytic reactor, 10 mg/L of BPA solution was introduced into the photoreactor. The experiment started without any light irradiation for 1 h to achieve adsorption-desorption equilibrium. Subsequently, it was irradiated using visible light for 6 h. About 10 mL suspension was collected periodically every 30 min and analyzed using UV-vis spectrophotometer at 280 nm of wavelength. Fig. 9 (a) revealed a plot for the first-order kinetic model for BPA photodegradation. A low removal of BPA was shown during adsorption-desorption process when no visible light irradiated at the first hour. While, sample of 20 and 25 mL/min shows no BPA reduction during the adsorption-desorption process. After adsorption in the dark for 60 min, the reactor was exposed to visible light and the photocatalytic decomposition of BPA by Cu_xO /PVDF TF HFM increased with the increasing reaction time.

Fig. 9 (b) demonstrates the apparent rate constant that the photocatalytic activity was enhanced by the hybridization of Cu_xO with PVDF HFM at 10, 15, 20, 25 and 30 mL/min of O_2 flow rates. This was attributed to the oxygen vacancy and the greater grain size that led to a higher surface to the volume ratio of the sputtered Cu_2O with lower thickness. The lower the thickness of thin film, the higher the oxygen vacancy in the Cu_2O /PVDF TF HFM [30] to enhance the photocatalytic activity. The average of kinetic rate of 25 and 30 mL/min of the samples was reduced to 0.00028 min^{-1} and $0.000312 \text{ min}^{-1}$ respectively. This was due to the low adhesion of CuO attached on the PVDF HFM substrate, due to which the photocatalyst leached out into the BPA solution.

Fig. 9 (c) indicates that after 6 h of UV irradiation, BPA removal increased as a higher O_2 flow rate (20 mL/min) was applied. The Cu_2O /PVDF TF HFM sputtered at 10 and 15 mL/min of O_2 flow rate degraded 30 % and 31 % of BPA, respectively, while thin film sputtered at 20 mL/min sample degraded 60 % of BPA at an initial BPA concentration of 10 mg/L and at neutral pH scale. The efficient photocatalytic activity of the Cu_2O /PVDF TF HFM under visible light irradiation was due to the presence of Cu_2O , which enhanced the absorption capability that possessed a lower band gap that was suitable in visible light region. The band gap energy of 20 mL/min of sample was 2.29 eV, which is lower

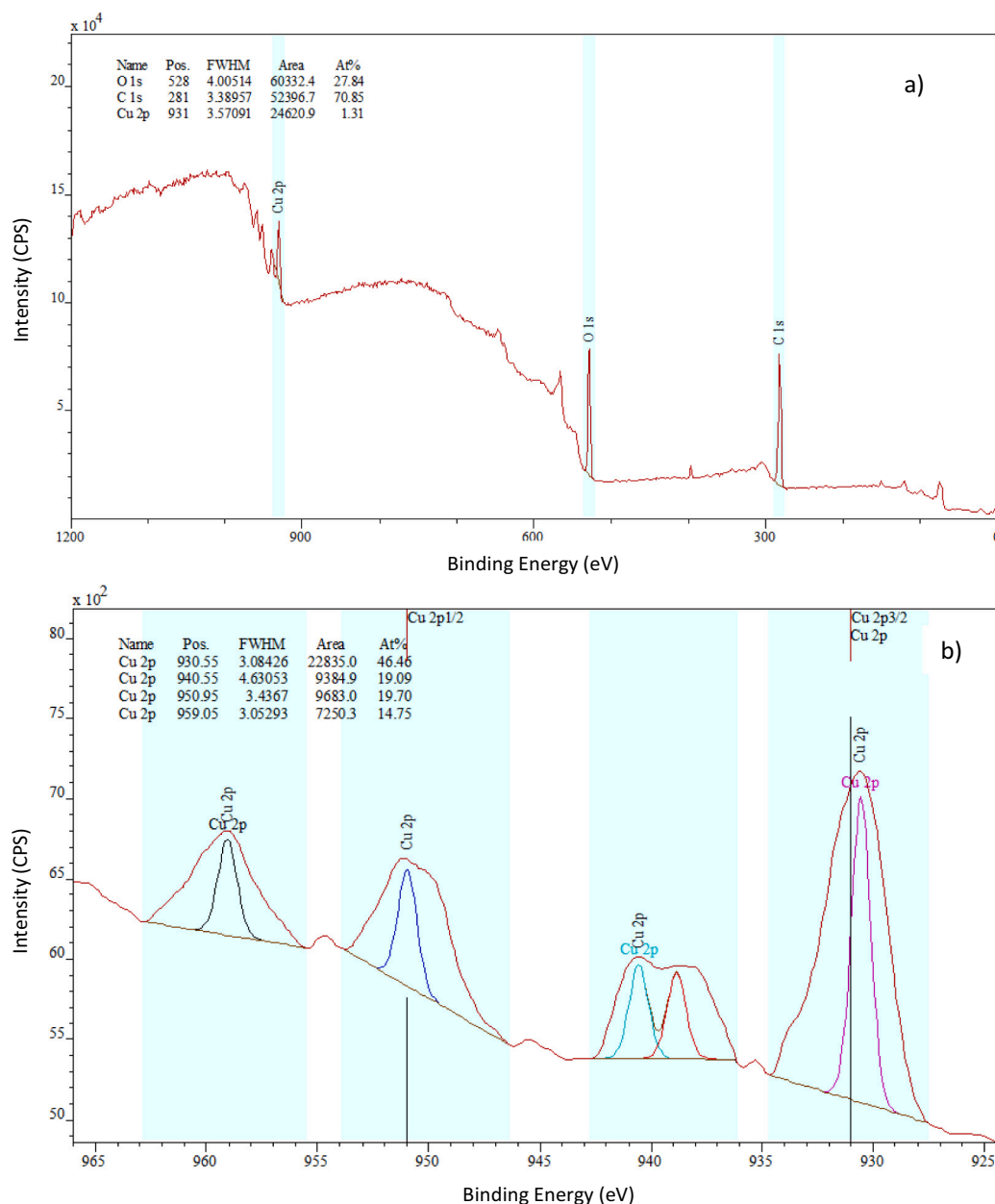


Fig. 5. a) XPS survey scan and b) XPS spectra of Cu 2p of 20 mL/min sample Cu₂O/PVDF TF HFM.

than 2.34 eV and 2.41 eV for 15 and 10 mL/min of samples, respectively. Moreover, 20 mL/min sample shows outstanding result with 60 % removal of BPA by using shorter 20 strands of 10 cm of Cu_xO/PVDF TF HFM compared to 20 strands of 23 cm of Cu₂O/PVDF dual layer hollow fiber membrane that achieved 75 % photodegradation of BPA stated by Mohamed Noor et al. [54].

However, a low BPA removal with only 9 % and 11 % was attained by sample deposited with 25 and 30 mL/min of O₂ flow rate, respectively. Cu₂O shifted its phase to CuO at higher O₂ flow rate and formed CuO/PVDF TF HFM. During the photocatalysis, color of CuO thin film was faded and it was detached from the fiber membrane and leached out into BPA solution. This finding was in agreement with Akbari et al. [55], who found that CuO possessed a low adhesion towards substrate and that it was easy for CuO to be separated from the fiber membrane substrate and leached into the BPA solution, reducing the photodegradation efficiency. The Cu_xO detached from the fiber membrane was detected by leaching test. Leaching test was confirmed by the presence of Cu in BPA solution using ICP-OES (Agilent 710) after 6 h of photodegradation. It

was found that 20 mL/min of sample had no leaching of Cu inside the BPA solution, while 3.33 and 22.22 µg/L of Cu were found inside the solution after irradiation by 25 and 30 mL/min of the samples.

Rejection by filtration occurred simultaneously and the results show that the BPA reduced more than photodegradation process only. The photodegradation with rejection achieve the highest 65 % removal of 10 mg/L BPA using Cu₂O/PVDF TF HFM at 10 min deposition time sample after 360 min illumination with visible light. Small difference on the results shown by the photodegradation and photodegradation with rejection. It shows that the degradation is the main key of BPA removal. The photodegradation process helps to break down the BPA molecules with radicals while the rejection process by PVDF HFM helps again in the rejection of the degraded BPA. Table 6 shows the summary of the photocatalytic performance of photodegradation and rejection of BPA by Cu_xO/PVDF TF HFM at different O₂ flowrate.

An excellent degradation of BPA by the Cu₂O/PVDF TF HFM sputtered at 20 mL/min was due to the agglomeration-free and a larger grain size of the Cu₂O sputtered on the PVDF HFM, which increased the

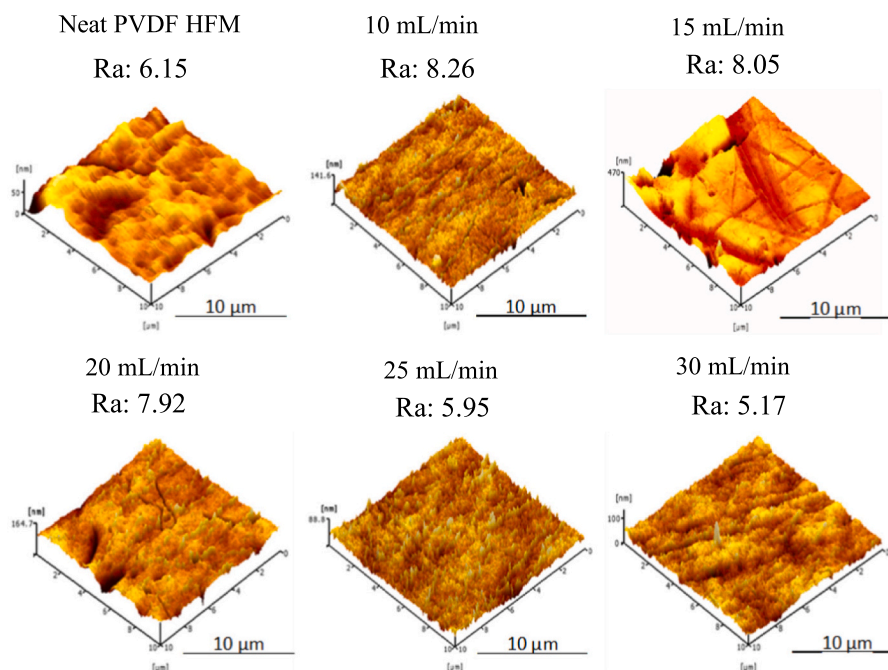


Fig. 6. Surface roughness comparison between neat PVDF HFM and sputtered Cu_xO/PVDF TF HFM at different O₂ flow rate.

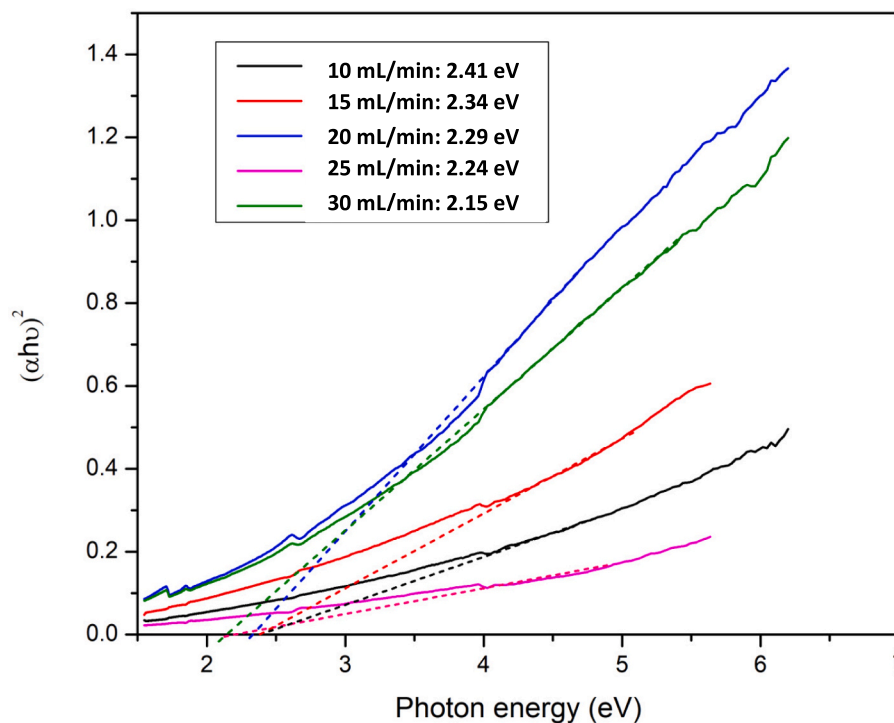


Fig. 7. Optical band gap analysis of sputtered Cu_xO/PVDF TF HFM at different O₂ flow rate from Tauc plot.

exposed surface area for light penetration and enhanced the production of e^- and h^+ for photodegradation process. The enhanced photocatalytic efficacy of 20 mL/min of sample could be explained due to the catalytic oxidation of BPA by the Cu₂O.

With respect to the photodegradation mechanism, BPA photodegradation by Cu₂O/CuO under visible light irradiation activated the adsorbed BPA molecules to become excited molecules. When the light penetrates the active site of Cu₂O/CuO, the electrons (e^-) in valence band (VB) excited to the conduction band (CB), resulting holes (h^+) in

VB. The e^- and h^+ were involved in the redox reaction [12], while the reduction of oxygen and oxidation of water produce $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$. The radicals entrapped inside the organic pollutant decomposed BPA into harmless CO₂ and H₂O.

Fig. 10 depicts that the BPA molecules were degraded by $\cdot\text{OH}$ attack and oxidative ring-opening reaction at C=C bond produced aliphatic compounds followed by a mineralization into CO₂ and H₂O. This degradation pathway has also been reported by Zhu et al. [56]. The BPA removal increased with the increasing functionality of Cu₂O

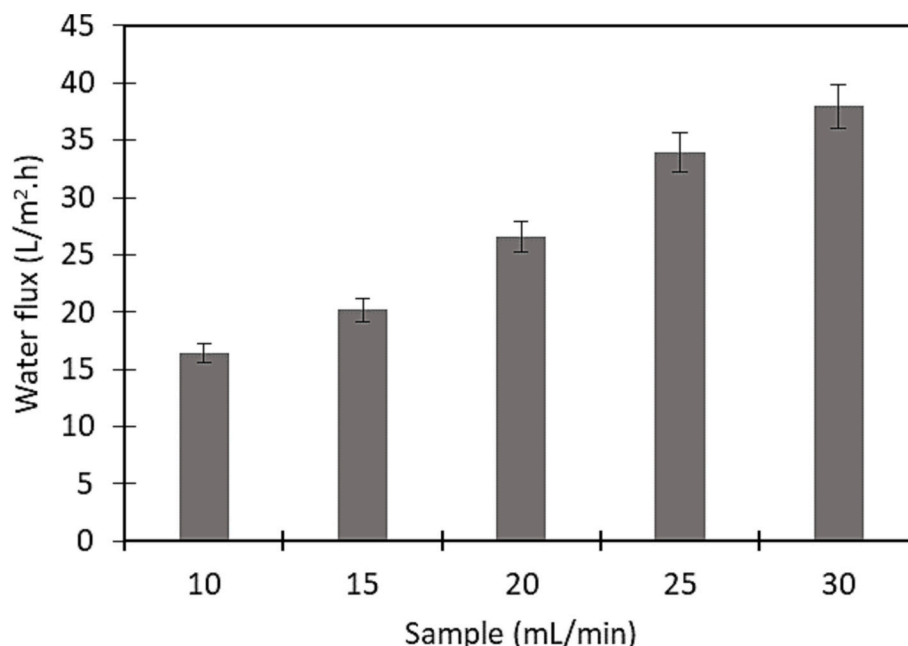


Fig. 8. Water flux performance for $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM at different sputtering O_2 flow rate operated at 30 rpm flow rate.

Table 5

Contact angle and porosity values of $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM.

Sample	Contact angle (°)	Porosity (%)
Neat PVDF HFM	82.95	40.67
10 mL/min	100.85	50.90
15 mL/min	109.10	52.56
20 mL/min	67.88	53.13
25 mL/min	98.82	53.98
30 mL/min	104.05	57.75

hybridization with PVDF due to additional binding sites for adsorbing the BPA. In addition, the mechanism of BPA degradation can also be seen from previous literature [57], where BPA molecules adsorbed on photocatalyst, $\text{GO@BiOI}/\text{Bi}_2\text{WO}_6$ surface and oxidized due to photo-generated holes (h^+). The BPA molecules oxidized by $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ as well degraded into non-harmful by-products consist of CO_2 and H_2O .

3.3.1. Regeneration of $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM

The reusability test of $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM was conducted for the photocatalytic study of the BPA. Three cycles were carried out using 20 mL/min of the $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM. Between each cycle of the experiments, the films were taken out by washing with distilled water. Fig. 11 depicts the BPA degradation and rejection performance of the thin films over consecutive cycles. After 3 cycles, the degradation reached 42.8 %, lower than 60 % for the first cycle of regeneration where it is about 71.33 % of regeneration efficiency was achieved after 3 consecutive cycles.

Less photodegradation activity was due to the adsorbed intermediate by-products that blocked the active sites on the surface of $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM. Srinivasan et al. [30] found that the photocatalytic activity was reduced after 5 cycles of irradiation with Cu_2O thin film, while Ansari et al. [58] indicated a small decrease in the photocatalytic activity by the $\text{CuO}/\text{GN@Pani}$ thin film after 3 cycles. Although the degradation efficiency is reduced but the reusability of spent $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM was still promising. The sputtered $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM still exhibited reasonable reusability in the BPA photodegradation after 3 consecutive cycles.

3.3.2. Photocatalytic efficiency at lower concentration of BPA

Due to the highest degradation of BPA shown by 20 mL/min sample of $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM in synthetic wastewater, therefore, it is chosen to be used for photocatalysis at different BPA concentration. After chemical analysis of photocatalytic activity of BPA at higher BPA concentration completed, photocatalytic activity of BPA was further analyzed at lower concentration of BPA consist of 5 and 2 mg/L. Lower BPA concentrations were chosen because lower BPA levels have been detected in Malaysian rivers [59]. Photocatalytic degradation of 2 mg/L BPA results in 70 % BPA removal in synthetic wastewater as can be seen in Fig. 12. Final rejection of the BPA sample shows that BPA reduced more than photodegradation process only and photodegradation with rejection achieve the highest 74 % removal of 2 mg/L BPA. It indicates that the lower the BPA concentration, the higher the photocatalytic performance. According to the previous literature by Garg et al. [60], increasing the BPA concentration from 10 mg/L to 50 mg/L tend to reduces the photodegradation of BPA from 98 % to 40 %. More BPA molecules were adsorbed on the catalyst's surface as the initial concentration of BPA increased, occupying the active sites and thus lowering the production of hydroxyl radicals [57,58].

3.4. Photocatalytic efficiency in real treated sewage wastewater

Compared to synthetic wastewater, photocatalytic degradation of BPA was further analyzed in treated sewage wastewater to evaluate the efficiency of $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM in real situation. It exhibits excellent performance under same condition. The initial concentration of BPA in treated sewage wastewater was detected in very low concentration around 0.54 $\mu\text{g/L}$. It reveals that the presence of EDC especially BPA in treated sewage wastewater is very small after the conventional treatment before discharging it into the river bodies. It can be proven by the literature reported by Wee et al. [63], 100 % detection of BPA was observed in all river water and tap water samples around Malaysia. Small concentration of 8.24 ng/L and 0.06–66.40 ng/L of BPA was detected in river water and tap water respectively. From this study, it is found that BPA concentration in treated wastewater is higher compared to river water stated by Wee et al. [63]. The sustainability and treatment efficiency indicate as the key matters of concern when higher EDC levels detected in treated water than raw water. It may be attributed to the parent compounds formation from metabolites, desorption of EDC

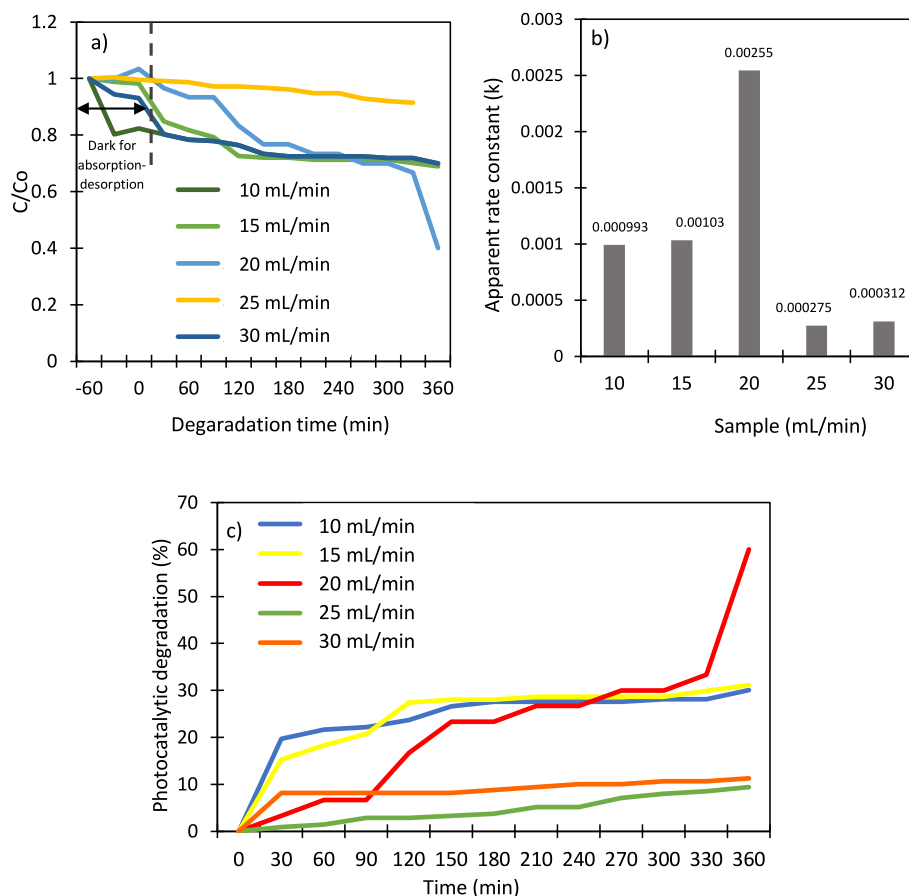


Fig. 9. a) Plot for the first-order kinetic model, b) apparent rate constant and c) photocatalytic degradation of 10 mg/L BPA by $\text{Cu}_x\text{O}/\text{PVDF}$ TF HFM in neutral pH condition after 360 min under 100 W light irradiation.

Table 6

The summary of the photocatalytic performance of photodegradation and rejection of BPA by $\text{Cu}_x\text{O}/\text{PVDF}$ TF HFM at different O_2 flowrate.

Sample	Photodegradation (%)	Photodegradation and rejection (%)
10 mL/min	30	33
15 mL/min	31	36
20 mL/min	60	65
25 mL/min	9	13
30 mL/min	11	13

during the operation, lower adsorption rates of saturated absorbents, dissolution of EDC aggregates, insufficient wastewater treatment for EDC and leaching of plasticizers as well contamination occurred in the treatment pipeline [53–55]. After treated with photocatalytic membrane, the concentration of BPA reduced to 0.06 $\mu\text{g/L}$, up to 88.89 % degradation of BPA while achieved after 360 min of visible light irradiation as depicted in Fig. 13. Photodegradation and rejection result of the final sample after 360 min irradiation shows excellent result which achieves 91.0 % of BPA removal. The efficient performance of photocatalytic activity shown could be due to the lower amount of BPA presented inside the treated sewage wastewater compared to synthetic wastewater. Thus, easier for BPA to be degraded in small concentration. The degradation of BPA using light shows the main role in higher removal of BPA.

3.5. Comparison of membrane performance between this study and previous work

Table 7 summarizes a comparison between $\text{Cu}_x\text{O}/\text{PVDF}$ TF HFM and

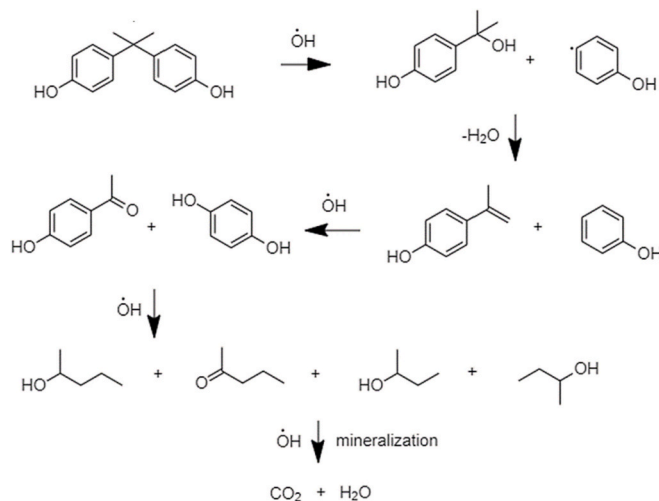


Fig. 10. Proposed visible light photocatalytic degradation pathway of BPA by $\text{Cu}_2\text{O}/\text{PVDF}$ TF HFM.

other sputtered photocatalyst. Compared to the previous work of Kacprzynska-golacka et al. [67], which corresponds to the flat sheet $\text{TiO}_2\text{-AgO}/\text{Polyamide}$ membrane prepared by magnetron sputtering technique with 10 mL/min O_2 flow rate, eliminated only 20 % and 8 % of methylene blue using UV light and visible light irradiation respectively after 8 h. Meanwhile, the 20 mL/min of $\text{Cu}_x\text{O}/\text{PVDF}$ TF HFM from this work can remove 60 % and 88.89 % of complex BPA demonstrating

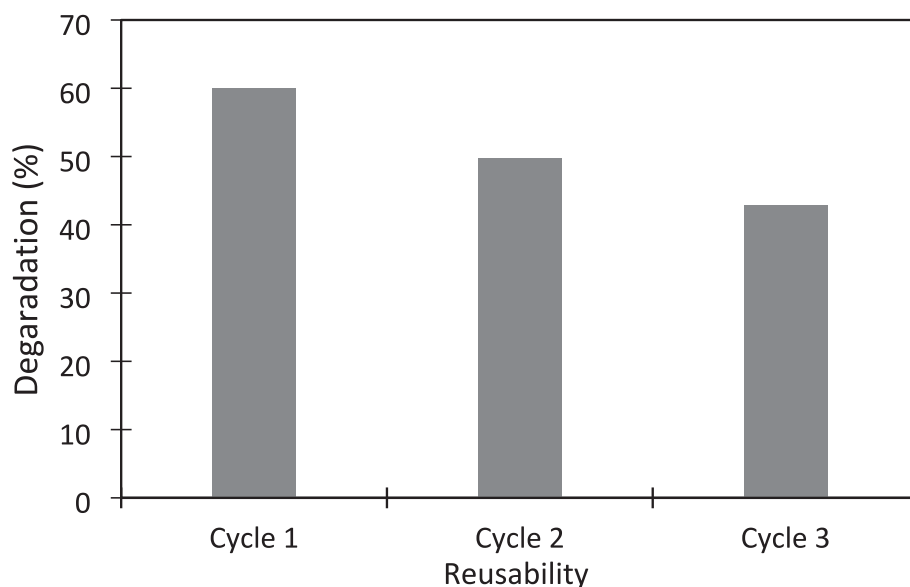


Fig. 11. Reusability of Cu_2O /PVDF TF HFM in photodegradation and rejection of 10 mg/L BPA solution in neutral pH condition after 360 min under 100 W light irradiation.

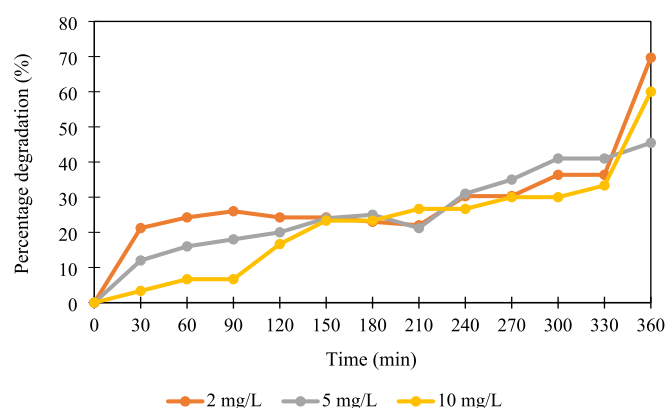


Fig. 12. Photocatalytic degradation of BPA by Cu_2O /PVDF TF HFM at different BPA concentration.

that the Cu_xO /PVDF TF HFM has higher removal efficiency. Similarly, the sputtering of TiO_2 /CuO on glass substrate using 35 mL/min O_2 flow rate successfully eliminated 5 mg/L of 94.1 % rhodamine B dye after 2 h irradiation with 150 W visible light [68]. Although the percentage degradation of dye exhibits high efficiency, however, filtration cannot be done simultaneously during the photocatalytic study due to glass substrates.

In addition, poor photocatalytic degradation of 10 % of 10 mg/L BPA was detected with 150 W visible light irradiation using sputtered Cu/ TiO_2 film on soda lime glass substrate without any O_2 flow rate application during the sputtering process [69]. The poor removal of BPA was due to the lower porosity of sputtered Cu/ TiO_2 hence difficult for BPA molecules to access the catalytic sites. Moreover, the film showed more oxygen vacancies that enhance charge carrier recombination that reduce the photocatalytic process.

Besides, other study also reported on sputtering of Ni/ZnO on fluorine-doped tin oxide glass without any O_2 flow rate implementation during the procedure. From the study [70], higher removal of 95.55 % of

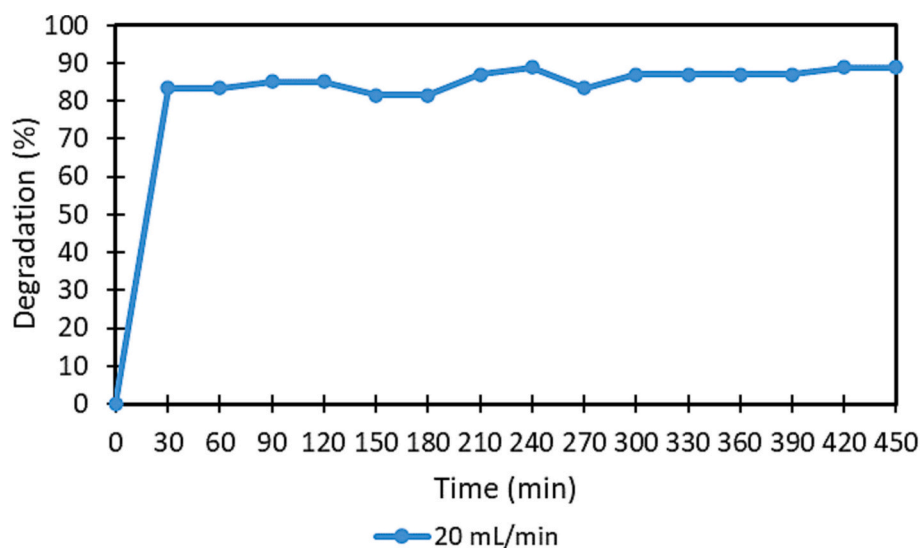


Fig. 13. Photocatalytic degradation of BPA in treated sewage wastewater by 20 mL/min Cu_2O /PVDF TF HFM in neutral pH condition after 360 min under 100 W light irradiation.

Table 7Comparison between Cu_xO/PVDF TF HFM and other sputtered photocatalyst for photocatalytic activity.

Material	Substrate	Sputtering power (W)	Ar:O ₂ flowrate (mL/min)	Deposition time (s)	Water flux (Lm ⁻² h ⁻¹)	Irradiation light	Irradiation time (min)	Photocatalytic degradation	References
TiO ₂ /AgO	Polyamide flat sheet	Ti: 1000 Ag: 80	90:10	30	850	UV light	480	20 % methylene blue	[67]
TiO ₂ /CuO	Glass substrate	TiO ₂ : 125 CuO: 100	3:35	TiO ₂ : 120 CuO: 20	–	Visible light	120	8 % methylene blue	[68]
Cu/TiO ₂	Soda lime glass substrate	250	30:0	–	–	150 W visible light	450	94.1 % of 10 mg/L rhodamine B	[69]
Ni/ZnO	Fluorine-doped tin oxide glass	100	25:0	60	–	150 W visible light	450	10 % of 10 mg/L BPA	[70]
Cu ₂ O	PVDF HFM	200	20:20	10	25	6 W UV-A light	90	95.55 % of 10 mg/L ciprofloxacin	[70]
						100 W visible light	360	70 % (photodegradation), 74 % (photodegradation & rejection) of synthetic 2 mg/L BPA 88.89 % (photodegradation), 91 % (photodegradation & rejection) of 0.54 µg/L BPA in treated sewage wastewater	This study

10 mg/L of ciprofloxacin detected after 90 min irradiation with visible light. The outstanding photodegradation efficiency was due to the oxygen created from electrocatalytic oxidation that can accept the electron for photocatalytic process and large electro-active surface area provide large number of active sites to generate oxidants for degradation of ciprofloxacin. Although the removal of EDC was high, however, the filtration process cannot be done by sputtered photocatalyst compared to this study that can simultaneously run for photocatalysis and filtration on the same time. Another photocatalytic study reveals 80.3 % decolorization of reactive black 5 dye by photocatalytic kaolin/TiO₂ nanorod hollow fiber ceramic membrane. The higher efficiency shown by photocatalytic ceramic membrane for dye degradation however may not suitable for EDC removal since larger band gap of TiO₂ incompatible for visible light BPA photocatalysis reaction and brittleness of ceramic material give drawback during the photocatalytic process [71].

Based on these findings, it can be stated that the Cu₂O/PVDF TF HFM shows promising result compared to other photocatalyst since the Cu₂O/PVDF TF HFM can undergo 2 processes namely photocatalysis and filtration simultaneously for better water treatment applications. The outstanding 20 mL/min Cu₂O/PVDF TF HFM in this study has successfully photodegrade and rejects 74 % and 91 % of BPA from synthetic wastewater and real treated sewage wastewater respectively. Moreover, the PVDF hollow fiber membrane configuration gives flexible and easy operation with good reusability which can be used repetitively for the next cycle of photocatalysis process. Expectantly, Cu₂O/PVDF TF HFM may be a good photocatalytic membrane for degradation of small percentage of BPA detected and might be also beneficial to be applied in wastewater treatment plant in Malaysia for EDC removal. In addition, this research may be preferential to tackle The Malaysian National Water Resources Policy and National Key Results Area that aims “to provide clear directions and strategies for water resources management, with collaborative governance to ensure water security and continued sustainability and ensuring public access to clean and treated water” [63].

4. Conclusion

Fabrication of Cu_xO/polyvinylidene fluoride thin film (Cu_xO/PVDF TF) hollow fiber membrane was successfully achieved by radio frequency (RF) magnetron sputtering technique. A different phase of Cu_xO was produced where Cu₂O formed when 10, 15 and 20 mL/min oxygen flow rate was applied during sputtering procedure, while CuO formed when 25 and 30 mL/min oxygen flow rate was implemented. Cu₂O shows more active in the Bisphenol A photocatalysis degradation which can be seen from the 20 mL/min sample. Oxygen flow rate of 20 mL/min

is the best sputtering conditions due to the uniform Cu₂O deposition on PVDF HFM surfaces and producing the highest photocatalytic performance up to 74 % degradation and rejection of 2 mg/L BPA in synthetic wastewater while 91 % in treated sewage wastewater in neutral pH condition after 360 min irradiation with visible light. About 71.33 % of regeneration efficiency was achieved after 3 consecutive cycles which confirms that this technique promises the good reusability with strong adhesion of Cu₂O photocatalyst. This can be concluded that the Cu₂O/PVDF TF HFM is capable in 2 in 1 function, efficient in photocatalytic activity, BPA filtration and achieve excellent water flux as well. Moreover, it might be an effective and potentially reusable membrane for BPA photodegradation to be applied in real sewage wastewater treatment plant in Malaysia for EDC removal.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2022.103425>.

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