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Micro-nano bubbles assisted laccase for biocatalytic degradation of bisphenols

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ABSTRACT

Bisphenols are important industrial materials for example for the production of plastics, but are also well known for their adverse health effects, in particular bisphenol A (BPA) is an endocrine disruptor. The widespread use of plastics has raised concerns. Therefore, the removal of bisphenols from wastewater has sparked the interest of the scientific community. This work introduces a novel hybrid technique of micro-nano bubbles assisted laccase (MNB-Lac) to degrade bisphenols in water. The feasibility of MNB-Lac using BPA as a model contaminant was evaluated by comparing with MNB, Lac, ultrasound (UL), UL-Lac, and UL-MNB-Lac. Comprehensive investigations were carried out to understand the specific influences of key process parameters including the initial pollutant concentration, temperature, air intake, pH, outlet pipe length, and Lac concentration on BPA degradation. The alkaline environment and extended length of outlet pipe could improve the degradation efficiency further. MNB-Lac exhibited 2.3–6.2 folds higher BPA degradation and less time than the other above process under the optimal parameters. The mechanism of MNB-Lac revealed that the generation of hydroxyl radical, high O_2 solubility, and high mass transfer efficiency induced by MNB play important roles on enhancing the degradation catalyzed by Lac. MNB-Lac was successfully used for treating bisphenol B, bisphenol C, and the mixture of three bisphenols with high removal efficiency. Subsequently, these degradation products were analyzed by GC–MS. MNB-Lac potentially represents an innovative technology with considerable advantages in contaminant cleanup and time efficiency for treating phenolic contaminated water. Furthermore, the findings provide new insights into the enhancement of the performance of an oxidizing enzyme by introducing MNB technology.

1. Introduction

Phenolic compounds as important industrial materials have garnered substantial interest due to their poor biodegradability, long-term ecological damage, and high toxicity [1]. They frequently occur in industrial wastewater and cause serious harm to the aqueous environment and human health [2–4]. Bisphenols like bisphenol A (BPA), bisphenol B (BPB), bisphenol C (BPC), bisphenol F (BPF), and bisphenol S (BPS) are a class of compounds containing two phenol rings which are connected by a short spacer group. BPA is the most commonly known bisphenol and has been widely used for the manufacture of polycarbonate plastics and epoxy resins [5]. Numerous studies have shown that BPA is an endocrine disrupting chemical that interferes functions of the hormonal system in humans and animals and even has been shown to cause diverse diseases [6–8]. Many techniques including adsorption [9], Fenton reaction [10], activated persulfate oxidation [11], ozonation [12], catalytic oxidation [13], photocatalysis [14], electrocatalysis [15], sonocatalytic degradation [16], biodegradation [17], and enzyme degradation [18,19] have been explored to remove BPA from wastewater. However, the adoption of these remediation strategies is limited due to high cost, low efficiency, and toxic by-products.

Enzymatic treatment of contaminants in wastewater has the advantages of high catalytic efficiency, strong substrate specificity, mild operation conditions, and low toxic degradation byproducts are considerably significant [20]. Laccase (Lac), a copper-containing oxidative enzyme that has been applied in industrial applications

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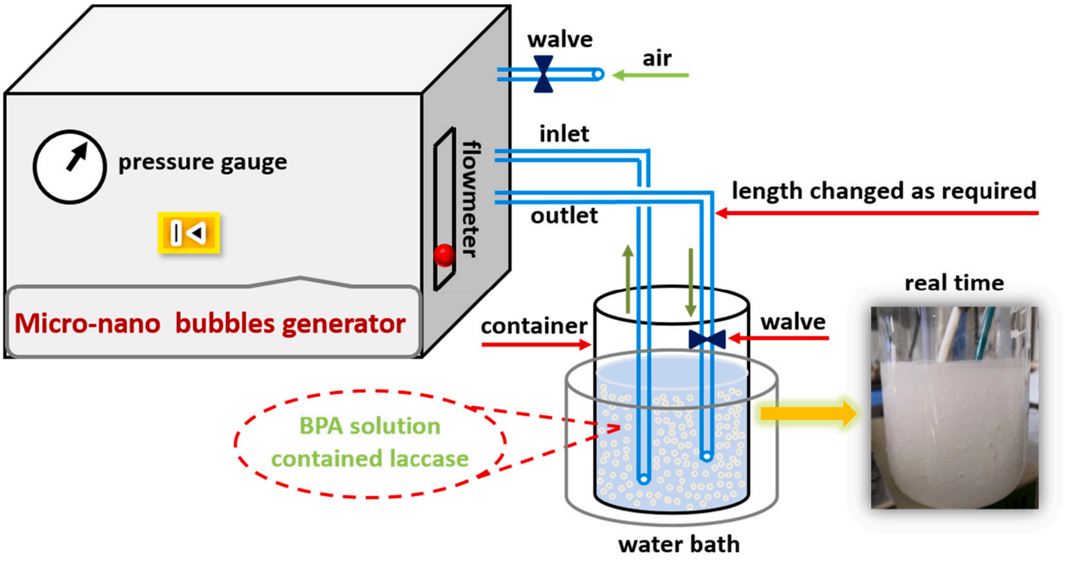

Fig. 1. The schematic diagram of MNB-Lac used for BPA degradation.

extensively, exhibits excellent catalytic activity to convert phenolic compounds [21–24]. A considerable research effort has been focused on the immobilization of Lac to improve the enzyme performance and to realize a continuous process for BPA removal [25–28]. Although the enzyme stability is generally improved, enzyme immobilization approaches can be expensive and commonly result in 10–90% decrease in enzyme activity [29]. The addition of rhamnolipids enhances BPA removal (about 23% increase) by free Lac due to improved enzyme stability in the presence of the biosurfactant [30]. Ji, Zhang, Huang and Huang [31] found that the addition of nonionic surfactant Triton X-100 to the reaction system also increased BPA degradation. Ivanec-Goranina, Kulys, Bachmatova, Marcinkeviciene and Meskys [32] reported that the use of 3-phenoxazin-10-ylpropane-1-sulfonic acid as a mediator of Lac increased the catalyzed initial oxidation rate of BPA up to 3 times compared to the rate without added mediator. Although various additives and mediators have been investigated to enhance enzyme stability, enzyme activity, and reaction kinetics during the removal of BPA, these additions may introduce more water pollution.

More recently, the hybrid process of water treatment has been shown to lead to more extensive degradation of the contaminants than achieved with the individual processes on its own, which is attributed to the synergistic effect between individual techniques [33]. Ultrasound assisted Lac (UL-Lac) not only improves ciprofloxacin hydrochloride degradation (43% increase) but also declines processing time significantly [34]. This hybrid process exhibits 5.3 folds higher chlortetracycline removal compared to individual Lac treatment [35]. UL cavitation can generate hydroxyl radical (•OH) which plays a crucial role in enhancing Lac activity and also improve the interaction between enzyme and substrate molecules.

Micro-nano bubbles (MNB), referring to bubbles with diameters ranging from tens of nanometers to tens of micrometers, have attracted recent attention owing to the advantages including large specific surface area, a negatively charged surface, long residence time in water, high mass transfer efficiency, and the generation of highly reactive free radicals [36,37]. Based on these specific characteristics, MNB has been widely used in the treatment of wastewater and even sludge. Phenol contaminated wastewater has been treated using the MNB technique resulting in 60% phenol decomposition in 2 h [38]. It has been demonstrated that hydroxyl radical (•OH), which is effective oxidant, plays an important role in the degradation of phenol. Recently, more attention has been paid to the development of hybrid processes involving MNB and other techniques for degrading pollutants in water. The environmentally benign MNB-ozone treatment has been found to be an effective way for the destruction of phenol in water [39]. The hybrid process of MNB and microelectrolysis has been successfully employed to treat phenol containing water with high efficiency [40]. The photocatalytic activity of anatase-phase TiO_2 nanoparticles in an aqueous solution was significantly enhanced by the presence of MNB, and the removal rate of methylene blue increased by 41–141% using the novelty process [41]. Tetracycline was removed effectively (92.43%) by an MNB-H_2O_2 hybrid system, which was an improvement of 3.94 folds compared to H_2O_2 alone [42]. However, to the best of our knowledge, no prior work has studied the feasibility of the combined process of MNB and Lac for wastewater treatment.

The aim of this work is to construct MNB assisted Lac (MNB-Lac) system for the degradation of bisphenols. BPA was chosen as a model compound to assess the feasibility of MNB-Lac for removing contaminants in water by direct comparison to Lac only, MNB only, UL only, UL-Lac, and UL-MNB-Lac. The influences of various operational parameters including the initial pollutant concentration, temperature, air intake, pH, outlet pipe length, and Lac concentration on BPA removal by the hybrid MNB-Lac system were systematically investigated in order to optimize the degradation conditions and to gain insight into the mechanism of the process. Furthermore, the broader applicability of the hybrid process was evaluated using other bisphenols BPB and BPC as contaminants.

2. Experimental

2.1. Materials

Trametes versicolor Lac (120 $U \cdot g^{-1}$) was obtained from Shanghai Yuanye Biological Co., Ltd. BPA was collected from Adamas Reagent Co., Ltd. BPB and BPC were purchased from Shanghai Titan Scientific Co., Ltd. Thiourea (THU) and *tert*-butanol (TBA) were supplied by Shanghai McLean Biochemical Technology Co., Ltd. Ethyl acetate, 1-octanol, sodium hydroxide, and hydrogen chloride were purchased from Chengdu Cologne Chemical Co., Ltd. Ultra-pure water was prepared by a CLW-K20 purification system (Chongqing, China). All the chemicals and reagents were of high purity grade and used without further treatment.

2.2. Determination of BPA

BPA analysis was performed by gas chromatography (GC, SCION 456C, Tianmei Scientific Instrument Co., Ltd., China) with Agilent DB-

624 column (0.53 mm × 3.0 μm × 30 m) and FID. N_2 was the carrier gas with a constant flow rate of 6 mL·min^{-1}. The temperature of injector and FID is 260 °C and 300 °C, respectively. Temperature profile: 100 °C/min from 70 °C to 100 °C hold 1 min, 100 °C/min to 260 °C hold 6 min. The injection volume was 1 μL. Retention time: BPA, 8.50 min, 1-octanol, 3.48 min.

2.3. General procedure of MNB-Lac for BPA degradation

The general procedure of MNB-Lac used for BPA degradation is depicted in Fig. 1. MNB were produced by a LF-1500 micro-nano bubbles generator (MNB generator) from Shanghai Xing Heng Technology Co., Ltd. (Shanghai, China). The averaged particle size of bubbles for LF-1500 was 199.9 ± 14.9 nm, and the concentration of bubbles was 3.44 × 10^8 ± 3.54 × 10^6 particles/mL, as shown in Fig. S1. The D10, D50, and D90 was 110.6 ± 6.5 nm, 165.0 ± 6.0 nm, and 319.0 ± 41.5 nm, respectively. A similar observation with the same MNB generator was reported by Wang, Liu, Lyu, Pan and Li [43]. The inlet pipe and outlet pipe with the same internal diameter (9 mm) from the equipment were introduced into the glass container (1 L). The length of the inlet pipe (1.5 m) was fixed, and the length of the outlet pipe was changed as required. The test pressure of the generator was a fixed value (0.5 MPa). A water bath was used to maintain the temperature of the container. BPA solution and Lac solution were put in the container before turning on the generator button. The liquid turns milky and circulates under the action of MNB in the process of operation. Aliquots were withdrawn, ethyl acetate was added (containing 1.0 mM 1-octanol as internal reference), and the samples were dried over $MgSO_4$ and analyzed by GC.

2.4. Comparison of BPA degradation by several strategies

Six different strategies including Lac, UL, UL-Lac, MNB, MNB-Lac, and UL-MNB-Lac were carried out to compare BPA degradation efficiency. The initial BPA concentration was 1.0 mM (500 mL, pH 8), and Lac concentration was 1.20 g·L^{-1}. Temperature was fixed at 30 °C. The reaction was performed in a shaker (150 rpm) when Lac was used alone. A KQ3200DE UL system from Kun Shan Ultrasonic Instruments Co., Ltd. (Kunshan, China) was employed. The power input and frequency of UL was 60 W and 40 kHz, respectively. The air intake of MNB generator was controlled at 30 mL·min^{-1}. Samples were taken for determining the BPA concentration at different time intervals.

2.5. Influences of several factors on BPA degradation with MNB-Lac

The effects of the initial BPA concentration, temperature, air intake, pH, outlet pipe length, and Lac concentration on BPA degradation with MNB-Lac were evaluated thoroughly. Initial BPA concentration (0.5, 1.0, 1.5, 3.0, and 5.0 mM), temperature of reaction system (20, 30, 40, 50, and 60 °C), air intake of MNB (6, 15, 30, 45, and 60 mL·min^{-1}), pH (3, 5, 7, 8, 9, 10, 11), outlet pipe length (1.5, 4.0, and 8.6 m), and Lac concentration (0.18, 0.30, 0.60, and 1.20 g·L^{-1}) were investigated using 500 mL BPA solution for 180 min. The residual BPA in the reactor was monitored alternately.

2.6. Active substances of BPA degradation with MNB-Lac

The active substances of BPA degradation with MNB-Lac were studied by free radical quenching experiments. TBA and THU (2 mL) was selected as quenching agents, respectively. Different THU concentrations were also tested. The other conditions for BPA degradation with MNB-Lac were performed according the results from Section 2.5. During the reaction, BPA concentration was detected by GC.

2.7. Products of BPA degradation with MNB-Lac

Degradation products of BPA by MNB-Lac under the optimum parameters were identified by gas chromatography mass spectrometry (GC–MS, QP2020NX, Shimadzu, Japan) with a sh-rxi-5sil column (0.25 mm × 0.25 μm × 30 m). He is the carrier gas with a flow rate of 1.5 mL·min^{-1}, and the column temperature is 70 °C. Temperature profile: 40 °C/min from 70 °C to 120 °C hold 4 min, 20 °C/min to 250 °C hold 4 min, 20 °C/min to 300 °C hold 5 min. The injection volume is 1 μL, ion source temperature is 220 °C, interface temperature is 250 °C, the analysis full scan range is 35–610 m/z, and solvent delay is 2 min.

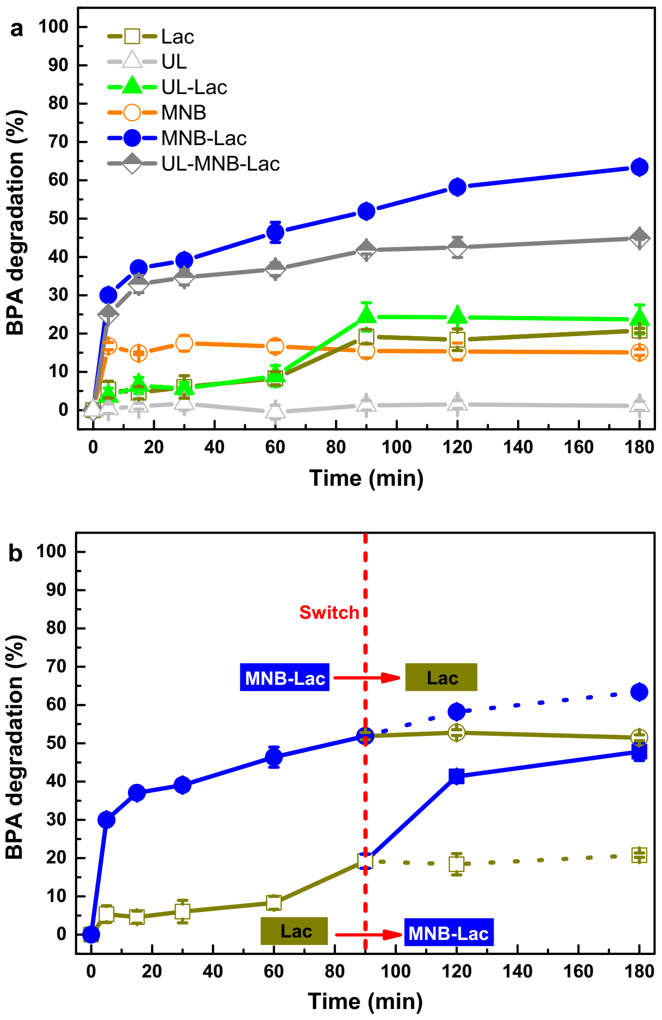

Fig. 2. a. BPA degradation by Lac, UL, UL-Lac, MNB, MNB-Lac, and UL-MNB-Lac. b. Effect of the procedural switch between Lac (90 min) and MNB-Lac (90 min) on BPA degradation. Conditions: 1.20 g·L^{-1} Lac, 1.0 mM BPA, pH 8, 30 °C. Shaker: 150 r·min^{-1}. UL: 60 W power, 40 kHz frequency. MNB: 30 mL·min^{-1} air intake, 1.5 m outlet pipe.

2.8. Applications of MNB-Lac for the degradation of bisphenols

Comparative degradations with MNB-Lac for BPA, BPB, and BPC were performed separately. The same initial concentration (1.0 mM) for all contaminants was chosen under the optimum parameters. BPB and BPC were detected using the same method as for BPA. The retention time for BPB and BPC was 9.53 min and 8.78 min, respectively. Degraded products of BPB and BPC were analyzed as described in Section 2.7. In addition, the degradation for the mixture of three substances was carried out under the same reaction conditions.

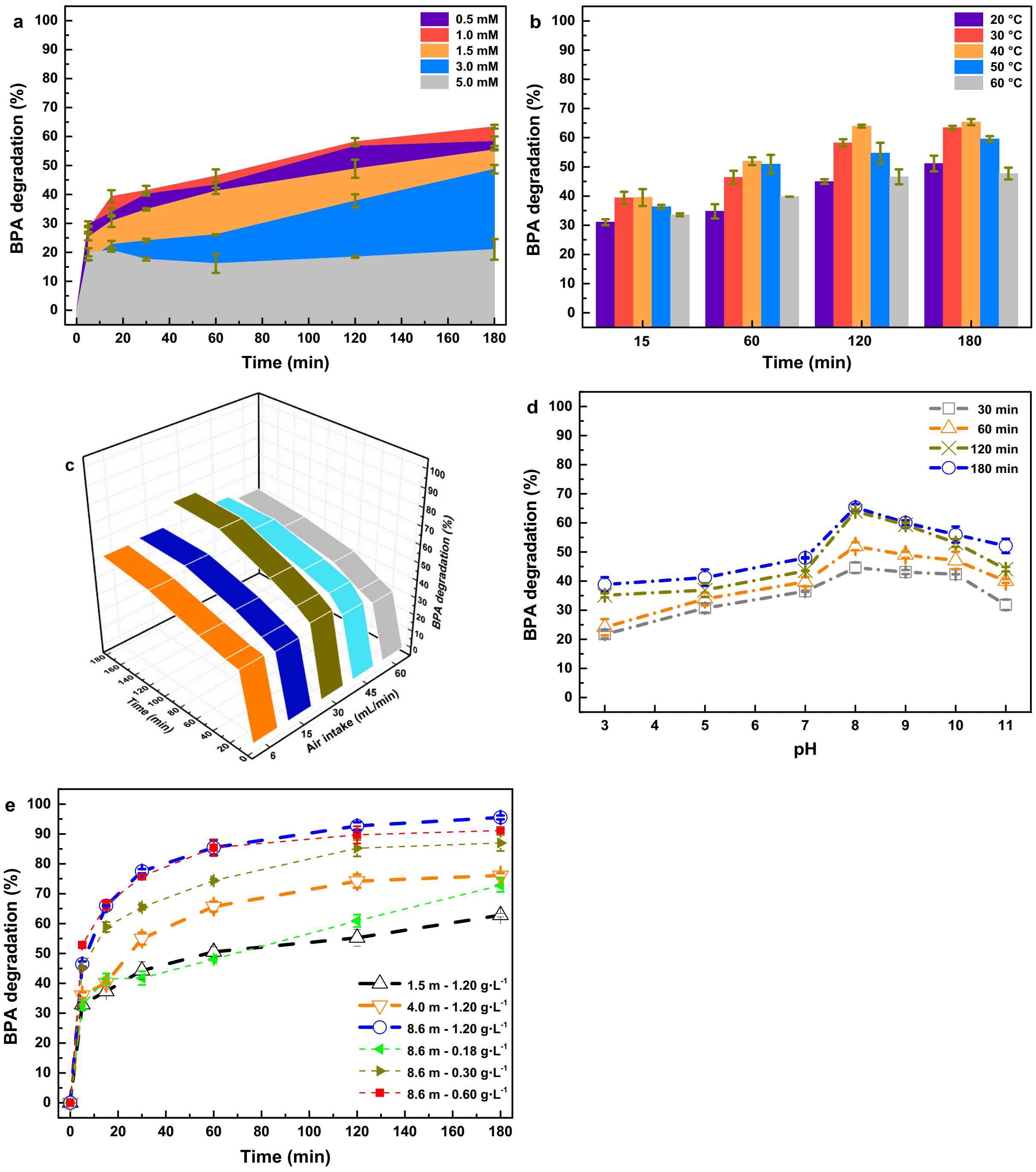

Fig. 3. Effects of the initial BPA concentration (a), temperature (b), air intake (c), pH (d), outlet pipe length, and Lac concentration (e) on BPA degradation with MNB-Lac. a. 1.20 g·L^{-1} Lac, pH 8, 30 °C, 30 mL·min^{-1} air intake, 1.5 m outlet pipe. b. 1.20 g·L^{-1} Lac, 1.0 mM BPA, pH 8, 30 mL·min^{-1} air intake, 1.5 m outlet pipe. c. 1.20 g·L^{-1} Lac, 1.0 mM BPA, pH 8, 40 °C, 1.5 m outlet pipe. d. 1.20 g·L^{-1} Lac, 1.0 mM BPA, 40 °C, 30 mL·min^{-1} air intake, 1.5 m outlet pipe. e. 1.0 mM BPA, pH 8, 40 °C, 30 mL·min^{-1} air intake. Lac concentration was 1.20 g·L^{-1} when the outlet pipe length was studied. The outlet pipe was fixed at 8.6 m when Lac concentration was investigated.

3. Results and discussion

3.1. *Validity of MNB-Lac for BPA degradation*

MNB-Lac hybrid system constructed for BPA degradation is illustrated in Fig. 1. Five different approaches of BPA removal were performed to compare with the MNB-Lac hybrid strategy, as shown in Fig. 2a. BPA degradation increased gradually over time and reached a maximum (19.2 ± 1.8%) after 90 min when Lac was used alone. The removal is significantly lower than previously reported results [44,45] due to the clear distinction of reaction conditions, in particularly the pH value. The BPA concentration using UL only treatment remained essentially unchanged all the time, so there was no significant conversion. An obvious improvement of BPA degradation with UL-Lac was observed as compared to UL only. UL assistance for Lac treatment caused a slight increase in the degradation after 60 min. We attribute the improved efficiency to an increase in Lac activity and a higher oxygen mass transfer rate between enzyme and substrate molecules due to UL [34,35]. However, the degradation with UL-Lac do not increase as much as reported by Pulicharla, Das, Brar, Drogui and Surampalli [35] which may be attributable to the difference in substrate structure. Although individual MNB achieved the highest initial BPA degradation in the first 5 min, the degradation was lower than the degradation with the Lac and UL-Lac after 90 min. MNB-Lac showed an impressive BPA degradation of over 51.9% compared to individual Lac (19.2 ± 1.8%), individual UL (0%), UL-Lac (24.3 ± 3.6%), individual MNB (15.5 ± 1.8%), and UL-MNB-Lac (41.7 ± 1.0%) under similar conditions (90 min). MNB-Lac treatment also achieved higher BPA degradation in lower time (29.9 ± 0.8%, 5 min) than the other methods. The BPA degradation reached 63.4 ± 0.6% and 71.8 ± 1.8% after 180 min and 360 min, respectively. The utilization of MNB for BPA degradation in the presence of Lac has a significant synergistic effect on the degradation efficiency. However, UL induces gradually the oscillation and collapse of bubbles during the process of UL-MNB-Lac, which may result in the decline of •OH and O_2 concentration [46]. Therefore, BPA removal using UL-MNB-Lac was slightly lower than that using MNB-Lac. The procedural switch between Lac and MNB-Lac on BPA degradation was investigated to firmly establish the effectiveness of MNB-Lac, as depicted in Fig. 2b. BPA degradation stalled when the MNB-Lac process was switched to a Lac only process after 90 min. The opposite phenomenon was clearly observed when the Lac only process was switched to MNB-Lac after 90 min. This clearly demonstrates that the combined use of MNB and Lac for BPA removal is feasible and effective.

3.2. Enhancement of BPA degradation with MNB-Lac by varying key factors

3.2.1. Effects of initial BPA concentration and temperature

A comprehensive characterization of the parameters influencing BPA degradation with MNB-Lac revealed that the innovative strategy is very well behaved as shown in Fig. 3. The relationship between BPA degradation and time at different initial BPA concentrations (Fig. 3a) showed that increasing the initial concentration from 0.5 mM to 1.0 mM resulted in a slight improvement on BPA removal. An initial concentration exceeding 1.0 mM reduced markedly the removal efficiency of BPA. The result is in accordance with previous reports of a decrease in relative BPA degradation by Lac at higher pollutant loadings [30,44]. This is related to the fact that the higher initial concentration provides a greater driving force and can overcome the mass transfer resistance. However, BPA degradation is no longer controlled by mass transfer when the initial concentration is high enough [15,47,48]. Conversely, higher BPA loading contributes to the accumulation of more free radicals, resulting in enzyme deactivation [49]. In addition, the increased BPA may also block active sites of the enzyme, weakening the Lac degradation ability.

It is well known that one of the most important factors that influences degradation processes of contaminants is temperature [50]. A temperature range of 20–60 °C was investigated as depicted in Fig. 3b. It suggested that BPA conversion using MNB-Lac was highly dependent on temperature. BPA degradation increased with the raising temperature (<40 °C) while it decreased gradually at higher temperatures (>40 °C) at any conversion time. The curves with bell shaped trends showing the effect of temperature on the MNB-Lac process are similar to that of the individual enzyme operation. Nevertheless, the optimal temperature (40 °C) of the MNB-Lac process is slightly lower than the previously found value (50 °C [30]) for treating BPA with *Trametes versicolor* Lac alone. This is due to the fact that the effect of temperature on bubble generation is actually dramatic. An increment in the temperature leads to increases in the vapor pressure and decrease in the viscosity, surface tension, and gas solubility. Furthermore, all of these changed properties with the increasing temperature have been shown to result in a significant decrease in the bubble number [51,52]. A higher bubble number at lower temperature contributed to the increased BPA degradation. Therefore, the optimum BPA conversion using MNB-Lac at 40 °C arises from the counteractive impact of temperature on bubble formation and Lac activity.

3.2.2. Effects of air intake and pH

The most efficient air intake rate was found to be 30 $mL\cdot min^{-1}$ (Fig. 3c). Quite interestingly, BPA degradation increased gradually with air intake rate up to 30 $mL\cdot min^{-1}$, and gradually decreased above 30 $mL\cdot min^{-1}$ air intake. The possible reason is that changes in air intake has effects on the concentration of dissolved oxygen and bubble formation. Oxygen is the substrate of Lac, and it is reduced directly to water by a four-electron mediator-less mechanism with concomitant one electron oxidation of an organic substrate like BPA [53]. Increases in air intake lead to higher oxygen dissolution until it reaches saturation [54]. However, the overflowing air into the system might not contribute to the dissolved oxygen concentration if the time for oxygen dissolved in the water is too short or the bubble size is too large. Additionally, the bubble concentration increases with the increased air intake firstly, and then rapidly declines as larger bubbles are formed [55]. Consequently, these findings suggested that the optimal air intake for BPA degradation with MNB-Lac is a compromise between dissolved oxygen and bubble amount.

A strong pH dependence of Lac has been reported previously, and the pH optimum of the activity of *Trametes versicolor* Lac is at pH 4.0–5.5 to maintain its structural integrity [22,35,45,53,56,57]. The pH dependence for BPA degradation with MNB-Lac was similar at all reaction times (Fig. 3d). Interestingly, high BPA degradation with MNB-Lac was obtained under alkaline conditions (pH 8–10), and unsatisfactory degradation was observed at acidic pH values. These results contradict the earlier investigations [45,56,57], which claimed that Lac showed high removal ability of BPA under acidic conditions. Hydroxyl radical could be produced by the collapse of air MNB in absence of a dynamic stimulus [36,58,59]. It has been verified that •OH can enhance Lac activity directly by serving as a much more efficient electron acceptor compared with O_2 and indirectly by oxidizing substrates [60]. Moreover, Lac activity can be improved more effectively than oxidizing substrates by •OH. The value of pH has a significant influence on the quantity of •OH produced by MNB. It is well known that alkaline solution with hydroxide ions can promote the production of •OH [36,38]. In addition, although the uncharged BPA is as readily hydrated as the ionized form, the solubility of BPA increases slightly at high pH around the pK_a value (9.56) [61–63]. The ionized BPA may be more susceptible to degradation compared with the uncharged form. As a result, the enhanced Lac activity, the increased •OH production, and ionized form of the substrate facilitate the decomposition of BPA under alkaline conditions.

3.2.3. Effects of outlet pipe length and lac concentration

Fig. 3e shows the influences of outlet pipe length and enzyme concentration on BPA degradation with MNB-Lac. Surprisingly the efficiency of BPA degradation is directly proportional to the outlet pipe length of MNB generator (Fig. 3e). BPA degradation raised from 62.8 ± 0.6% to 95.5 ± 0.7% with the increased length from 1.5 m to 8.6 m at 180 min. Many factors including the length, diameter, and type of outlet pipe have essential impacts on the bubble size [36,64]. The bubble size tends to decrease when the length of outlet pipe at the front of the valve increases. As the bubbles become smaller, the increased mass transfer efficiency leads to more effective BPA degradation [36].

The effect of the Lac concentration on BPA degradation efficiency was tested over a wide concentration range from 0.18 to 1.20 $g\cdot L^{-1}$ (Fig. 3e). Increasing Lac concentration from 0.18 $g\cdot L^{-1}$ to 0.60 $g\cdot L^{-1}$ positively influenced the removal efficiency of BPA, which may be resulted from increases in the total active sites of enzyme. Further increasing the enzyme concentration to above 0.60 $g\cdot L^{-1}$ resulted in only a slight increase in BPA degradation. This result was consistent with previous investigations on BPA degradation with Lac [30,31,65]. It was suggested that the reaction system is rate-controlling above this Lac concentration.

One-way analysis of variance was performed to check the statistical significance of these parameters on BPA degradation using MNB-Lac

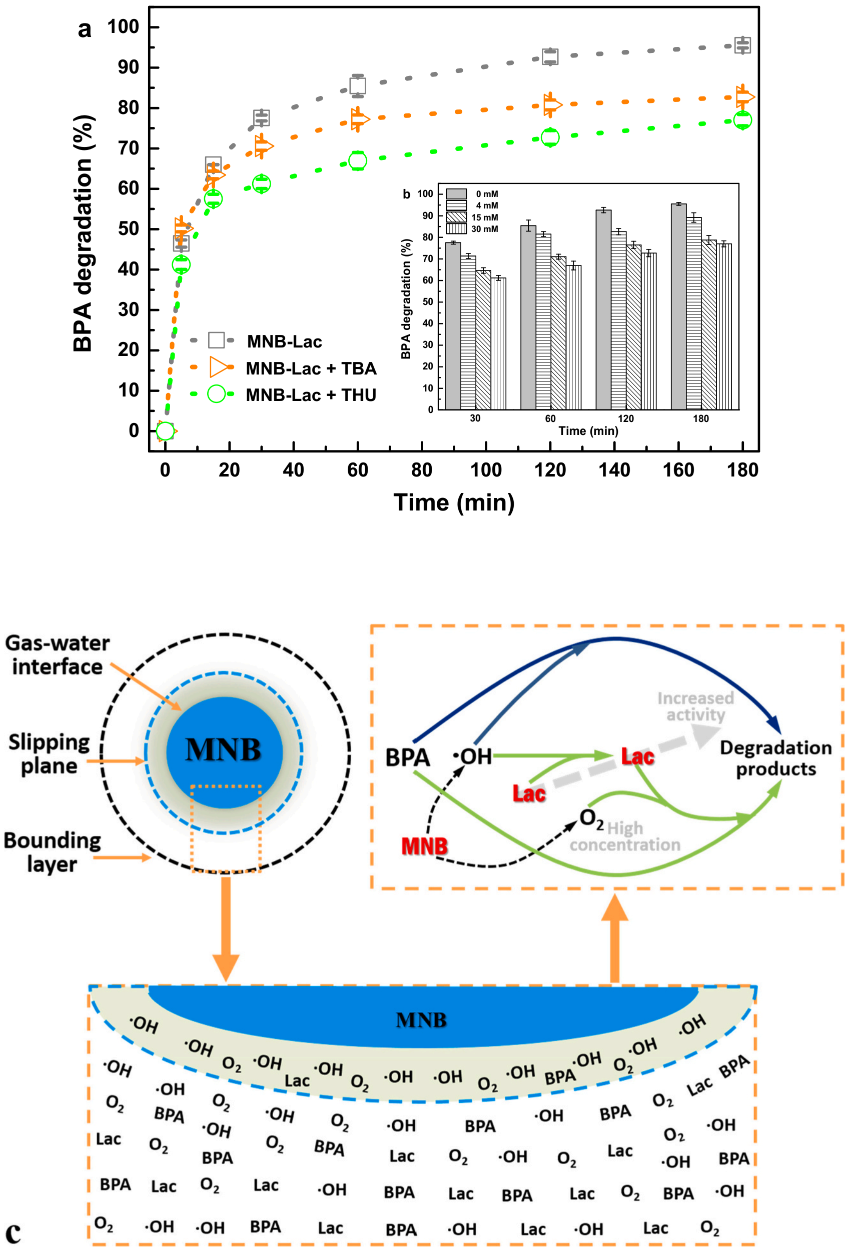

Fig. 4. a. BPA degradation with MNB-Lac contained different scavengers. Conditions: 0.60 g·L^{-1} Lac, 1.0 mM BPA, pH 8, 40 °C, 30 mL·min^{-1} air intake, 8.6 m outlet pipe, 15 mM TBA, 30 mM THU. b. BPA degradation with MNB-Lac at different THU concentrations. c. The possible mechanism of BPA degradation by MNB-Lac.

(Table S1). A small p value indicates great significance of this factor and vice versa. The factors ($p < 0.01$) including BPA concentration ($p = 0.0013$), pH ($p = 0.0004$), outlet pipe length ($p = 0.0008$), and Lac concentration ($p = 0.0046$) are highly significant and very important on BPA removal. The p value of 0.0484 for temperature is <0.05, which means the factor is significant and important. Air intake ($p = 0.0891$, $0.05 < p < 0.2$) has a weak significance and a faint influence on the experimental results. Additionally, the highest BPA degradation obtained was 95.5 ± 0.7% under the optimum operating conditions including 0.60 g·L^{-1} Lac, 1.0 mM BPA, pH 8, 40 °C, 30 mL·min^{-1} air intake, and 8.6 m outlet pipe. MNB-Lac treatment showed 5.0, 3.9, 6.2, and 2.3 folds higher extent of BPA degradation compared to Lac, UL-Lac, MNB, and UL-MNB-Lac treatment, respectively. The obtained results highlighted the enhanced BPA degradation and efficiency during MNB-Lac treatment which can be further adapted to remove other phenols.

3.3. *Mechanism of BPA degradation by MNB-Lac*

The generation of hydroxyl radical, which has a strong oxidation effect, with the continuous shrinkage and collapse of bubbles in water has been demonstrated previously [36,58,66,67]. BPA can be effectively eliminated by MNB due to the •OH production as illustrated in Fig. 2a. Zhao, Xiang, Huang, Liu and Tan [60] pointed that •OH generation causes the enhancement of Lac activity by 7.7–20.4%. Inclusion of THU [68] and TBA [42,69] as scavengers of •OH reduced the degradation efficiency of BPA with MNB-Lac (Fig. 4a). Moreover, the inhibition in BPA degradation was THU concentration dependent (Fig. 4b). We therefore propose that •OH plays a dominant role in promoting BPA degradation using MNB-Lac. Oxygen, a second substrate, can contribute to all reduction steps of the enzymatic reaction by Lac [53]. The most common application of MNB is greatly improves the solubility of gas in water, particularly O_2 [36,64,70]. The enhanced O_2 amount in aqueous solution also accounts for the increased BPA removal. Therefore, the

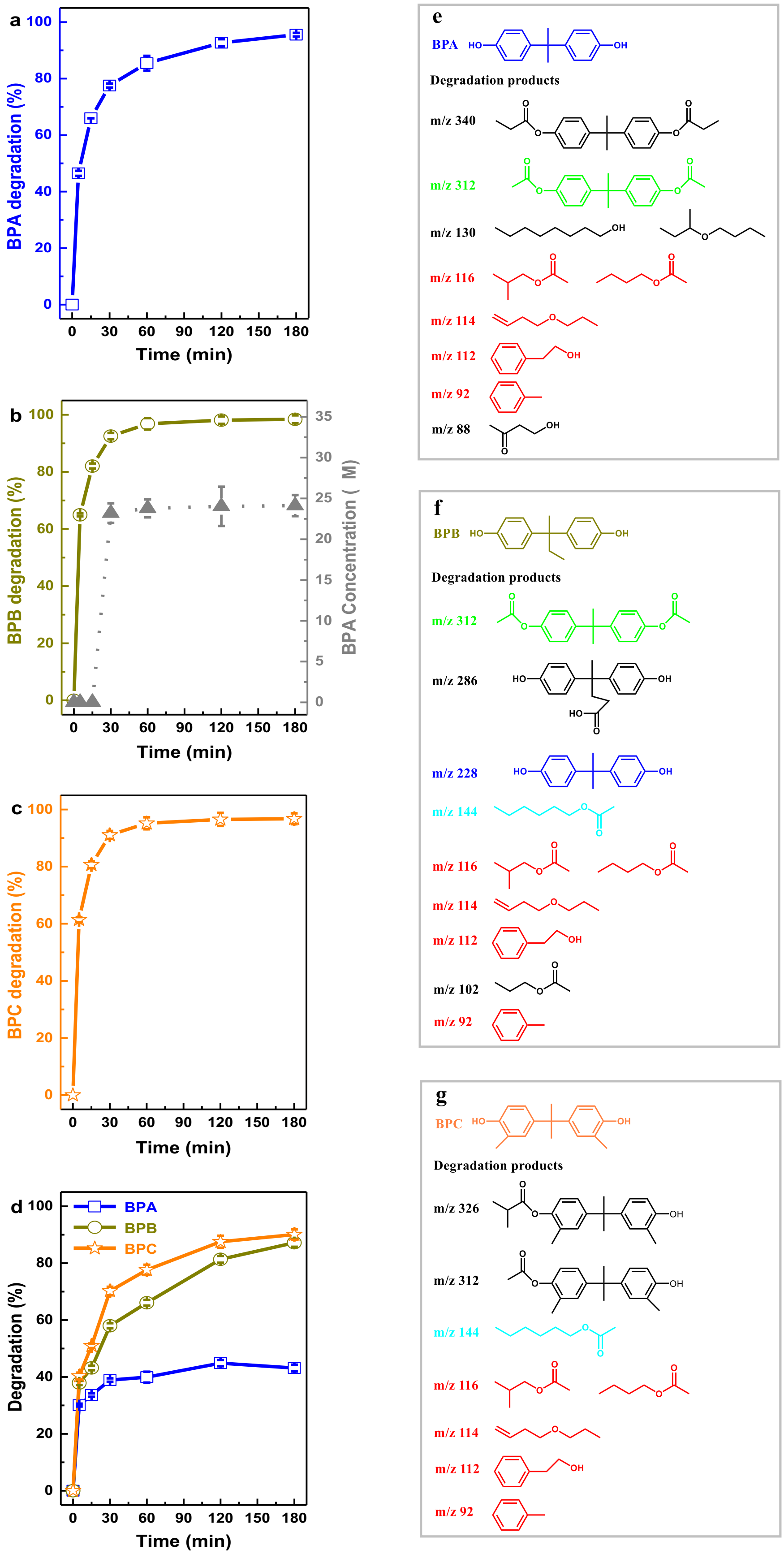

Fig. 5. Degradation of BPA (a), BPB (b), BPC (c), and bisphenol mixture (d) with MNB-Lac. Conditions: 0.60 g·L^{-1} Lac, 1.0 mM BPA, 1.0 mM BPB, 1.0 mM BPC, pH 8, 40 °C, 30 mL·min^{-1} air intake, 8.6 m outlet pipe. Degraded products of BPA (e), BPB (f), and BPC (g) with MNB-Lac.

introduction of MNB increases the Lac activity with •OH and improves the conversion of substrate with O_2, contributing to the enhanced BPA removal by Lac. In addition, as discussed earlier high mass transfer efficiency caused by MNB facilitates the degradation with MNB-Lac. Overall, the proposed mechanism of BPA degradation by MNB-Lac is illustrated in Fig. 4c. •OH generation, high O_2 solubility, and high mass transfer efficiency induced by MNB are the important drivers behind the accelerated BPA degradation using Lac. However, more specific proof is required to fully understand the precise molecular mechanism of MNB-Lac.

3.4. Applicability of MNB-Lac for bisphenols removal

Encouraged by the results described above, the applicability of MNB-Lac was further explored for other bisphenols including BPB and BPC under the optimal conditions identified for BPA. MNB-Lac exhibited a degradation efficiency in the following order BPB (98.4 ± 0.6%) > BPC (96.8 ± 1.9%) > BPA (95.5 ± 0.7%) when these bisphenols were investigated separately (Fig. 5a, b, and c). However, this isn't in agreement with the published results for Lac conversion of the different bisphenols [44,71]. Previously bisphenols with a simpler structure and lower molecular weight were found to exhibit better removal efficiency by Lac. A plausible explanation is that, three bisphenols are treated by MNB-Lac under alkaline condition instead of acidic conditions for the Lac only results reported previously. The degradation products of BPA, BPB, and BPC based on the analysis of GC–MS are shown in Fig. 5e, f, and g, respectively. Interestingly, a small amount of BPA was detected during BPB degradation in Fig. 5b, and it was confirmed by GC–MS further as shown in Fig. 5f. More different products were identified after using MNB-Lac than that using Lac only, particularly in case of BPA [72,73]. A number of similar products were observed for different bisphenols due to similarities in the bisphenolic structure. This maybe indicate that these bisphenols follow a similar degradation pathway to form these products. However, further study will clarify the degradation pathway of bisphenols using the MNB-Lac process. In addition, the conversion of an equimolar mixture of the three bisphenols by MNB-Lac was investigated (Fig. 5d). Interestingly, the removal efficiency of BPB and BPC were significantly higher than that of BPA. The removal order in the mixture is BPC > BPB > BPA, and this is different from the order in the individual conversion reactions of the different bisphenols. We attribute this to the fact that BPA is one of the degradation products of BPB, which may inhibit BPB degradation. Moreover, BPA generated by BPB degradation leads to the low apparent BPA removal.

4. Conclusions

The feasibility of the hybrid process combining MNB with Lac was verified by removing BPA from contaminated water. The process parameters including initial substrate concentration, temperature, pH, outlet pipe length, and Lac concentration were found to have significant impact on BPA degradation by MNB-Lac. Especially, the alkaline environment and extended length of outlet pipe contributed to a high degradation efficiency. The most efficient BPA removal of 95.5 ± 0.7% was achieved under the optimal conditions. This was 5.0, 3.9, 6.2, and 2.3 folds higher BPA degradation compared to Lac, UL-Lac, MNB, and UL-MNB-Lac treatment, respectively. The generation of •OH, high O_2 solubility, and high mass transfer efficiency induced by MNB contribute to a synergic effect enhancing BPA degradation by Lac. The removal efficiency of three different bisphenols individually was higher than that in an equimolar mixture of the three, and the corresponding degradation products were identified. This work represents a novel contribution towards the development of a hybrid process for treating phenolic contaminated water effectively under environment-friendly conditions. More research is needed to clarify the precise molecular mechanism of MNB-Lac and the degradation pathways of the different bisphenols.

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.

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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.2022.102880.

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