**Supplementary Information**

**Critical review of catalysis-assisted nanofiltration for micropollutants removal: catalytic coupled nanofiltration system *VS* catalytic nanofiltration membrane**

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Table S1. Published reports about biocatalytic coupled NF processes for MPs removal.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalytic/NF mode | Enzymes species | Preparation method of NF membrane | Oxidant | Micropollutants | Reaction conditions | pH | Catalytic efficiency | Rejection efficiency | Removal efficiency | Membrane flux L/(h m2 ) | Enzyme activity recovery | Flux recovery | Reference |
| [P] | [C] | [O] |
| BCNS | Laccase | Commercial NF200  | - | Atrazine; carbamazepine;SulfamethOxazole; diclofenac; Oxybenzone | 1 mg L-1 | 190Mm (DMP)/min (activity) | - | 7.0 | 31%;39%;45%;83%;99% (16h) | 98%;99%;96%;98%;95% | 92%;94%;96%;97%;99% (16h) | 44.2 | 82% | 95% | [3] |
| Laccase;Horseradish peroxidase (HRP) | Polymeric NF270 | H2O2  | Bisphenol A (BPA) | 20 mg L-1 | 0.12 U mL-1;7.5% v/v | 10 mg L-1 | 6-7 | 95%;＞98% (3h) | 50% | 94%;89% (4.2h) | 61.5;71.9 (permeate) | - | 80%;90% | [4] |
| Laccase | Commercial NF270 | - | Phenolic acids (vanillic acid; P-coumaric acid; Ferulic acid) | 0.05 g L-1;0.1 g L-1;0.15 g L-1 | 1.3 U mL-1 | - | 5.15 | - | 21%;7%;22% | All: 100% | Average:12 (permeate) | - | 98% | [5] |
| BCNM | Laccase | ·PES substrates;·LBL assembly | - | BPA | 34.2 mg L-1 | 238.8 ± 3.5 μg cm-2 | - | Neutral | 79% (10h) | ＞38% | ＞90% | 21.8 | ＞85% (the 6th cycle) | ＞98.5% (the 6th cycle) | [6] |
| Horseradish peroxidase (HRP) | ·Polyamide NF270;·Surface coating/chemical grafting | H2O2 | Aflatoxin B1 (AFB1) | 200ppb | 40 μg cm-2 | 0.5mM | 5.0 | - | 85.5% | 94% | 36.4 | - | 98.7% | [7] |
| Laccase | ·NT103;NF270;NF90·Reverse filtration/dopamine coating | - | BPA | 10 mg·L-1 | 2.55 μg·cm–2;1.63μg·cm–2;1.76μg·cm–2; | - | 5.3 | 82.2% (NF270) | 36.18% (NF270) | 78.21%;84.27%;97.04 % | 15.2;48;8 | 40% (the 7th day) | ＞95% (the 7th cycle) | [8] |
| Laccase | ·Polyamide NF270;·Reverse filtration/PDA+PEI co-deposition | - | BPA | 10 mg·L-1 | 2.1μg·cm–2 | - | 5.0 | 57.54% (6h) | - | - | 46 | ~100% (the 9th day) | 92% | [1] |
| Laccase | ·Polyamide NF270;·Reverse filtration/PDA+Cu2+ co-deposition | - | BPA | 10 mg·L-1 | 1.84 μg·cm–2 | - | 5.0 | 86.79% (6h) | - | 92% | 44 | 90% (the 9th day) | - | [1] |
| Glucose oxidase (GOx);Horseradish peroxidase (HRP) | ·Polyamide NF270;·Reverse filtration/PDA+PEI co-deposition | H2O2 (produced by β-d-glucose) | BPA | 10 mg·L-1 | 29.85 μg·cm–2  | 0.25 mM (5mM β-d-glucose) | 4.8 | - | 40% (the 4th cycle)  | ~100% (the 4th cycle) | 51 | 98.64% | - | [2] |
| Laccase | ·NF270;·Dopamine coating/chemical grafting/physical adsorption | - | BPA (0.1mM ABTS and syringaldehyde as mediators) | 10 mg·L-1 | 4 μg·cm–2 | - | 5.0 | 48.3% | 90% | ＞97% (the 7th cycle)  | 10.5 | ＞90% | ＞99% (the 7th cycle)  | [9] |
| Laccase | ·NF270;·Dopamine coating/chemical grafting/reverse filtration | - | BPA | 10 mg·L-1 | 165 U m-2 (activity) | - | 5.0 | 50% | 29.3% | 80% (the 7th cycle) | 11 (bar-1) | ~100% (the 4th washing cycle) | - | [10] |
| Laccase | ·NF270;·Dopamine coating/chemical grafting/ Zn 2+ immersion precipitation/ reverse filtration | - | BPA | 10 mg·L-1 | 200 U m-2 (activity) | - | 5.0 | 52% | 28.4% | 72% (the 7th cycle) | 12 (bar-1) | ~100% (the 4th washing cycle) | - | [10] |

[P]: pollutant concentration; [C]: catalyst dosage; [O]: oxidant concentration.

Table S2. Published reports about photocatalytic oxidation coupled NF processes for MPs removal.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalytic/NF mode | Photocatalyst | Preparation method of NF membrane | Type of light (intensity) | Micropollutants | Reaction conditions | pH | Catalytic efficiency | Rejection efficiency | Combinationefficiency | Membrane flux L/(h m2 ) | Reference |
| [P] | [C] | RE | TOC |
| PCNS | TiO2 (Degussa P25, ca.70% anatase and 30% rutile) | Commercial (DK2540F1073) | UV254(465 mJ/cm2) | Atrazine;Isoproturon; Diuron; Alachlor ; Chlorfenvinphos | 500 μg L-1 | 50 mgL-1 | 7.8 | All＞90%(2.6h)(except isoproturon (76% after 6.1 h) | 83%;40%;43%;97%;99% (6h) | ＞95%;95;97.4;＞99.9%;99.9(6h) | - | 54 (permeate) | [11] |
| polycrystalline TiO2 (Degussa P25, ca. 80% anatase and 20% rutile) | Commercial (DK2540C) | Sunlight | Antibiotic (lincomycin) | 75 μM | 200 mg L-1 | 6.3 | 98% | 97.78% | ＞99% | 72% | 15 | [12] |
| polycrystalline TiO2 | Polyethersulphone NTR 7410 | UV |  Gemfibrozil; Tamoxifen | 10 mg L-1 | 0.1 g L-1 | 7-10 | 98.5%(0.5h);＞90%（1.67h） | - | 98.9% (0.67h);100% (0.25h) | 62% (2h);60%(1h) | 38.6；46(permeate) | [13] |
| PCNM | TiO2 nanoparticles | ·Al2O3 substrates;·Magnetron sputtering | UV315-400 (53 W m -2) | Diuron;Chlorfenvinphos | 1 mg L-1 | - | Neutral | - | 20%;46%  | 73%;67% (3h) | - | 149 | [14] |
| TiO2 nanoparticles | ·Al2O3 substrates;·physical-chemical deposition | UV315-400 (53 W m -2) | Diuron;Chlorfenvinphos | 1 mg L-1 | 1.4 wt% | Neutral | - | 10%;25% | 75%;80% (3h) | - | 283 | [14] |
| UiO-66\_GO nanocomposite | ·Polyamide NF membrane;·Pressure-assisted self-assembly  | UV | Carbamazepine (CBZ)；Diclofenac sodium (DCF) | 1 mg L-1 | 10 wt% | 5 | - | - | 70%;93%(2h) | - | 228 | [15] |
| CN/TiO-CNT | ·Al2O3 support;·Vacuum filtration; | Xe short arc lamp(100 mW Cm-2) | Bisphenol A (BPA);Sulfamethoxazole (SMX) | 5 mg L-1 | 500 mg L-1 | 6 | 33%;32% | 40%;18%(3h) | 82%;80%(3h) | 78%;＞70%(3h) | 48 | [16] |

[P]: pollutant concentration; [C]: catalyst dosage; RE: removal efficiency; TOC: total organic carbon.

Table S3 Published reports about Fenton oxidation coupled NF processes for MPs removal.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalytic/NF mode | Catalyst | Preparation method of NF membrane | Micropollutants | Reaction conditions | pH | Catalytic efficiency | Rejection efficiency | Combinationefficiency | Membrane flux L/(h m2) | Flux recovery | Catalyst recovery | Reference |
| [P] | [C] | [O] | RE | TOC |
| FCNS | FeSO4 | polymeric NFD； NF90；NF270 | BPA | 300 mg L-1 | 6 mg L-1 | 323 mg L-1 | 3.0 | ＞97% | 62%;63%;58% | - | 87.5%;76.5%;88.9% | 44.9;24.2;41.47 | ＜60% | 81.9%;96.2%;92.4% | [17] |
| FeSO4 | Polymeric NF270 | BPA | 20 mg L-1 | 0.4 mg L-1 | 10 mg L-1 | 3.0 | 50% (4.2h) | 50% | 96% | - | 60.6 | 70% | - | [4] |
| Fe(III)-TsPc | Polyamide NE4040-70 (200Da) | BPA; | 0.2 mg L-1 | 41 μM | 0.01M | 4.0-4.5 | ＞90% (3min) | ＞85% | 95%-99% (70h) | - | - | - | 100% | [18] |
| FCNM | Maleate ferroxane (Mf);goethite (Goe) | ·Polyacrylonitrile (PAN) powder;·Phase conversion | Amoxicillin (AMX) | 105 mg L-1 | 0.5 wt.% | 460 mg L-1 | 6.5-7 | 84.8% (2.38h);83.2% (2.63h) | 84% (2.22h);83.1% (2.58h) | 92.3% (2h);86.3% (2.42h) | 85.4%;83.5%  | 23.2;19 (permeate) | 97.3%;96.2% | - | [19] |
| FeCl3 | ·PTFE substrates;·pressure filtration/electrochemical reduction (RGO-CCNT-Fe modified EFM) | Florfenicol (FLO) | 1 mg L-1 | 20.8 at. % | - (applied potential: −0.6 V vs SHE) | 7.0 | - | 61.1% (50% CCNT) | 95.3% (50% CCNT) | 49% | 42.5 | - | - | [20] |

[P]: pollutant concentration; [C]: catalyst dosage; [O]: H2O2 concentration; RE: removal efficiency; TOC: total organic carbon.

Table S4. Published reports about catalytic ozonation coupled NF processes for MPs removal.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Catalytic/NF mode | Catalyst | Preparation method of NF membrane | Micropollutants | Reaction conditions | pH | Catalytic efficiency | Rejection efficiency | Removal efficiency | Membrane flux L/(h m2 ) | Flux recovery | Catalyst recovery | Reference |
| [P] | [C] | [O] |
| OCNS | H2O2 | Polyamide NF (150-300Da) | 1-H-benzotriazole (BZ);N,N-diethyl-m-toluamide (DEET);Nortriptyline HCl (NH) | 1 μM | 50 μM | 2.25 mg L-1 | 7.5-8.0 | 62%;63%;88% | 31.1%;100%;95.3% | 74.6%;100%;99.5% | 204 | - | - | [21] |
| OCNM | γ-Fe2O3 | ·Single channel tubular membrane support；·Sol-gel deposition | Para-chlorobenzoic acid (pCBA) | 2 μmol L-1 | 3 g L-1 | 28 g Nm-3 | 6.0 | 83% (2.5h) | 65% | 95% (2.5h) | 80 | - | - | [22] |
| MnO2-Co3O4 | ·α-Al2O3 support;·LBL assembly | Benzophenone-3 (BP-3) | 2.0 mg L-1 | 100 mg L-1 | 1.0 mg L-1 | 7.13 | 81.2% (0.5h) | 51.6% (0.5h) | 74.8% (CM coated 80 times) | - | - | ＞99% | [23] |
| CuMn2O4 | ·α-Al2O3 support;·Sol-gel deposition | Benzophenone-3 (BP-3);Benzotriazole (BZA); 2-phenylbenzimidazole-5-sulfonic acid (PBSA) | 2.0 mg L-1 | 100 mg L-1 | 1.0 mg L-1 | 7.21 | 80% (BP-3) | all~10% | 100%;100%;89.5%(2h) | - | 85.1% | ＞99% | [24] |

[P]: pollutant concentration; [C]: catalyst dosage; [O]: O3 concentratio

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