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Adsorptive removal and oxidation of organic pollutants from water using a novel membrane

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ABSTRACT

To develop an effective method to remove and mineralize trace organic pollutants, a series of composite functional membranes containing immobilized ACF (activated carbon fibre) powder (<300 mesh) and Ce^{3+}-TiO_2, a combination of adsorbent and photo-catalyst on terylene (PET) filter cloth, was prepared by using a sol–gel and dip coating method. As high as 93% BPA (bisphenol A) pollutant can be separated successfully by adsorption onto the membrane in a series of batch adsorption tests, 40% removal was achieved in dynamic filtration/adsorption test, which also removed 98% koalinite suspended solids at the same time. The measured adsorption of BPA corresponds to 37.0, 70.6 and 62.2 mg (BPA)/g(ACF) for three membranes A, B and C, where the weight ratio of ACF to ACF + TiO_2 was 29.9%, 17.6% and 11.3% respectively in batch adsorption tests (50 ml solution) and 25.48 mg (BPA)/g(ACF) for membrane A after 2 h adsorption in 200 ml solution. After dynamic filtration, the total adsorption capacity was 81.0 mg (BPA)/g(ACF) for membrane A. It is noteworthy that membrane adsorption can be regenerated by UV/Fenton treatment. Order of BPA adsorption quantity is 1st > 2nd > 3rd time use for membrane C, due to loss of ACF resulted from the supersonic treatment before oxidative regeneration. Introducing TEOS in the preparation of sol–gel solution and subsequent coating to form composite membrane, improved membrane adsorption stability in UV/Fenton regeneration treatment.

1. Introduction

The presence of trace poisonous organic substance like EDC (endocrine disruptor compounds), BPA (bisphenol A) in water, especially drinking water source is a big problem and risky to public health. Removal of these pollutants using RO is expensive, for its high investment and energy consumption, especially at a large community level, e.g. for a whole metropolis. Advanced oxidative removal of these pollutants may produce harmful by-products and require adsorption treatment, a common practice. Therefore, polymer/resin, carbon based material, or natural mineral adsorbents, and their effective regenerations have been under intensive study. Photocatalytic regeneration has been studied, it is preferred and suitable for regenerating membrane adsorbent, as regeneration of granule adsorbents has both mass transfer and light penetration limitations. Commercial membrane adsorbents are rare, but adsorption of pollutant to membranes during water treatment did take place and had been studied.

Membrane adsorbents may be made more advantageous, by a constructed adsorptive surface layer that enables fast adsorption and offers low mass transfer resistance. Adsorptive membrane, as filtration material, also removes particle or colloids in surface water. Recent progress in organic/inorganic hybrid membrane makes it possible to produce more hydrophilic, low-fouling tendency and easy to clean membranes, e.g. by combining inorganic nanoparticles and photocatalysis, and adsorptive and regenerative membranes. This research is carried out for investigating these possibilities.

A composite functional membrane containing ACF powder and TiO_2 was prepared to efficiently extract, separate and eventually oxidize BPA off-site. The preparation, characterization and use of such composite membrane in adsorptive separation of BPA from water and its regeneration are addressed in detail. Also investigated is the adsorptive removal of BPA during dynamic filtration of water containing BPA and suspended solids, using the prepared membrane. This is to demonstrate the feasibility of the membrane in cleaning up water double functionally by retention of solid pollutants and adsorption of small organic molecule pollutant in water simultaneously.

Reason for selecting BPA as model pollutant is because it is a well known endocrine disrupter [1], commonly found in environment, difficult to be biodegraded [2]. Rapid and simple removal of BPA in water is much desired. Treatment techniques such as photochemical [3], electrochemical [4] and other advanced oxidation

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[5] have been examined, TiO_2 was often used in BPA degradation [3,6,7].

Reason for selecting activated carbon fibre (ACF) as chief adsorbent in adsorptive membrane is that the highly microporous carbon material has large adsorption capacity, is ideal to support TiO_2 photocatalysts [8], and combination of ACF and TiO_2 has showed advantages in removing and mineralizing pollutants from both water and air.

2. Experiment

2.1. Materials and chemicals

Bisphenol A (BPA, (2,2-bis(4-hydroxyphenyl) propane) chemical with analytical purity was purchased from Fine Chemical Research Institute (Tianjin, China) and used without further purification. Other chemicals of analytical grade include tetrabutyl titanate (TBOT), anhydrous ethanol, 65% nitric acid, diethanolamine, polyethylene glycol (PEG, $M = 2000$), cerium(III) nitrate ($Ce(NO_3)_3{\cdot}6H_2O$), iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), 30% H_2O_2 and anhydrous methanol. Secondary distilled water was used throughout the experiment.

A shallow quartz reactor (diameter 9 cm) was used for photocatalytic experiments. 20 W germicidal ultraviolet ($\lambda = 253.7$ nm) light was used for UV irradiation. Also UV-1700 Spectrometer (SHIMADZU, Japan) and other instruments including 101-1 A oven (Rex Xinjing, China) and JB-2 magnetic stirrer (TEST, China) were used in the experiment.

2.2. Methods

The pre-treatment of PET filter cloth was carried out by immersing it in ethanol, and washing with water, followed by drying. The preparation of composite membrane was performed at room temperature as following: 5 ml TBOT was dissolved in 17.5 ml anhydrous ethanol under vigorous mixing using a magnetic stirrer, and then 1 ml of diethanolamine and 0.5 ml nitric acid (65 wt.%) were added one by one. The solution was stirred for 1 h. At the same time, 0.5 ml distilled water was dissolved in 17.5 ml anhydrous ethanol under vigorous stirring and then 0.0075 g $Ce(NO_3)_3{\cdot}6H_2O$ was added. The latter solution was added drop wise to the former one for 20 min. 0.075 g PEG was added to the mixture. Then the mixture was vigorously stirred for 2 h. A certain amount of ACF (<300 mesh, 1700 m^2/g, averaged pore size 2 nm) was introduced into the mixture and kept stirring until an ACF-containing sol was formed. PET filter clothes were immersed in the sol for 20 min, lifted out and dried at 105 °C and then followed by hydrothermal treatment in 95–100 °C water bath for 6 h. Three series of membranes A, B and C were prepared, where the weight ratio of ACF to TiO_2 and ACF was 29.9%, 17.6% and 11.3%, respectively.

2.2.1. Batch adsorption of BPA using the prepared membrane

BPA in 50 mL (10 mg L^{-1}) water was separated by adsorption onto the prepared membrane in a series of batch experiments at 20 ± 3 °C, pH 4 for 125 min. The pH of the solution is adjusted using 1 M hydrochloric acid. The time dependent concentration changes were calculated by absorption (monitored by UV-1700 UV–vis spectroscopy) at 276 nm. Later the membrane was lifted out, re-immersed in 20 ml solution, the adsorbed BPA was oxidized by 2 h UV irradiated Fenton reaction (H_2O_2 8.3 mM/L, molar ratio of H_2O_2/Fe^{2+} 50, pH 3)) in the shallow quartz reactor. Supersonic treatment was used to increase desorption of BPA and oxidation rate. Adsorption quantity of the reused membranes was measured.

Adsorption quantity of X (wt.%)–ACF/TiO_2 membrane was calculated to the weight of coated ACF.

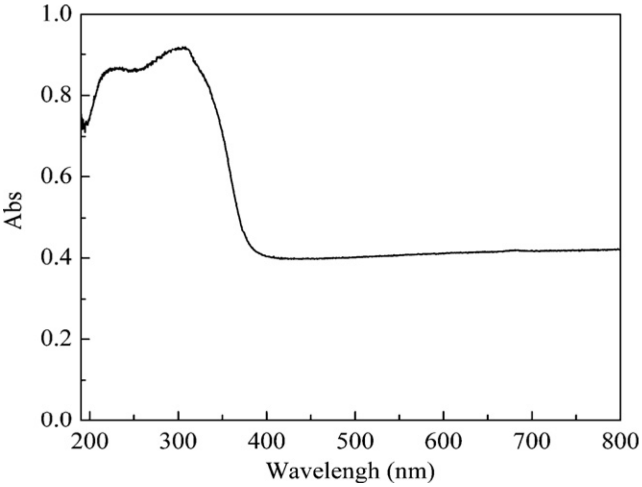

Fig. 1. UV–vis spectra of membrane C with ACFs/Ce^{3+}-TiO_2.

2.2.2. Dynamic membrane filtration and measurement of BPA removal

Immersing the prepared membrane in BPA solution, dynamic filtration/adsorption experiment was carried out, at a permeate flow rate of 0.8 ml/min from using a pump. BPA content in effluent was measured. Also tested is the turbidity removal percentage of the membrane using a mixture solution of BPA (10 mg L^{-1}) and kaolinite (50 mg L^{-1}) during the dynamic filtration test using membrane A and C.

3. Results and discussions

3.1. Characterization

UV–vis spectrum was recorded on UV-550 ultraviolet spectrophotometer (Jasco, Japan) in the range of 200–800 nm. In Fig. 1, the UV–vis spectrum of C-ACFs/Ce^{3+}-TiO_2 membrane was presented. The obvious increase of absorption in visible region is a result from Ce^{3+} doping and ACF. The spectrum clearly shows the characteristic absorption of TiO_2 in 200–400 nm region.

X-ray diffraction pattern (XRD) analysis was performed on Rigaku Dmax-2400 diffractometer in the range 5–80° (2θ) with a scan rate of 0.15°/min. The catalyst is in anatase form, all the featured peaks of anatase appeared, averaged size of crystal was calculated to be 5.3 nm (Fig. 2). Features of Ce oxide were not sig-

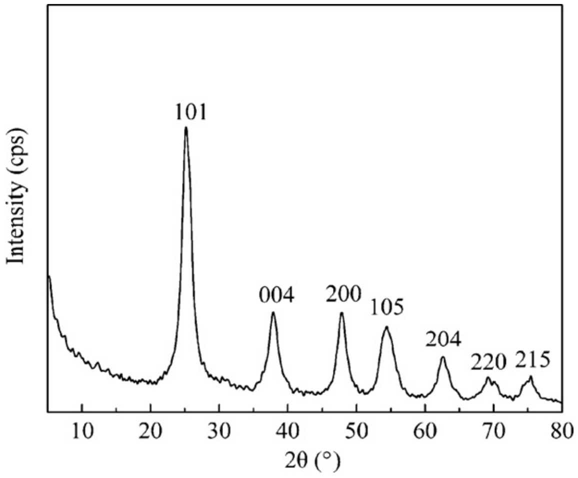

Fig. 2. XRD patterns of ACF/TiO_2 powder.

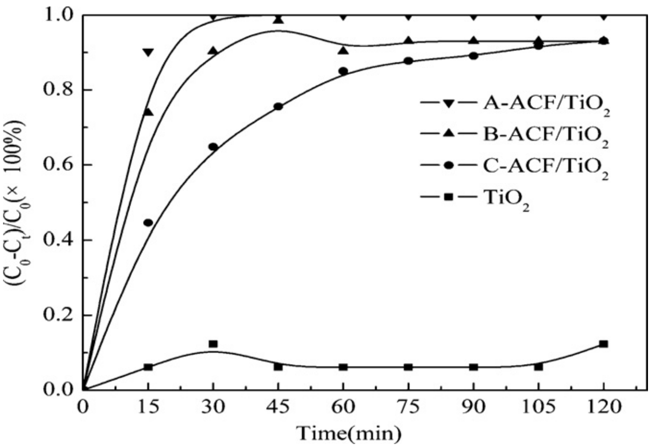

Fig. 3. Time dependent adsorptive removal of BPA on membrane A, B and C, in which ratio of ACF to TiO2 was 29.9, 17.6 and 11.3 wt.%, respectively.

nificant in the figure, as its content was possibly below detection sensitivity of the instrument.

3.2. Batch adsorption experiment

In Fig. 3, the membrane adsorption rates with different ACF loadings were shown. Measured removals of BPA were 100%, 93% and 93%, for membrane A, B and C. The adsorption quantity of the ACF/TiO$_2$ membrane A, B and C, where the weight ratio of ACF to ACF + TiO$_2$ was 29.9%, 17.6% and 11.3%, was 13.0, 37.0 and 37.0 mg (BPA)/g(ACF), respectively (Fig. 4). This means that increasing the ACF percentage in membrane increased BPA adsorptive removal. Only adsorption rate was slower for membrane C, where 11.3% ACF to the total weight of ACF + TiO$_2$ in the membrane is used to its adsorption limits. It is worth mentioning that ACF with abundant porous structure and high specific surface area provides stable adsorption site for BPA [9]. Also the excellent adsorption of membranes at the beginning can be contributed to the presence of meso-porous structures.

As shown in Fig. 5(a), the peak absorption of acidic BPA solution at different times after contact with C-ACF/TiO$_2$ membrane gradually decreased in about 90 min. The adsorption removal of BPA was 93% at the end of test. The adsorption process followed a first order kinetics as shown in Fig. 5(b).

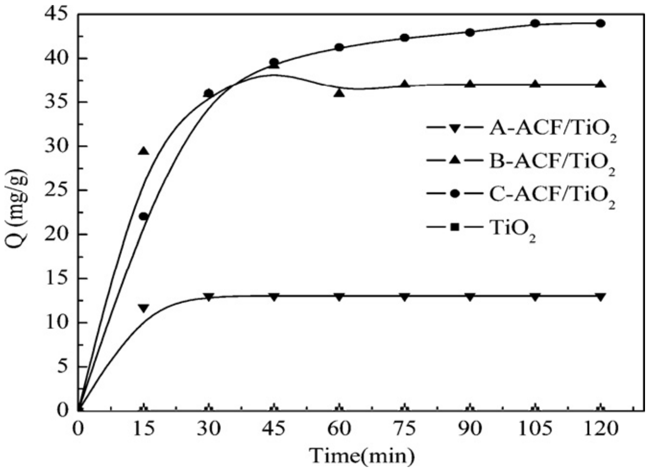

Fig. 4. Time dependence of adsorbed BPA quantity (mg) per gram ACF on membrane A, B and C, in which ratio of ACF to TiO2 was 29.9, 17.6 and 11.3 wt.% respectively.

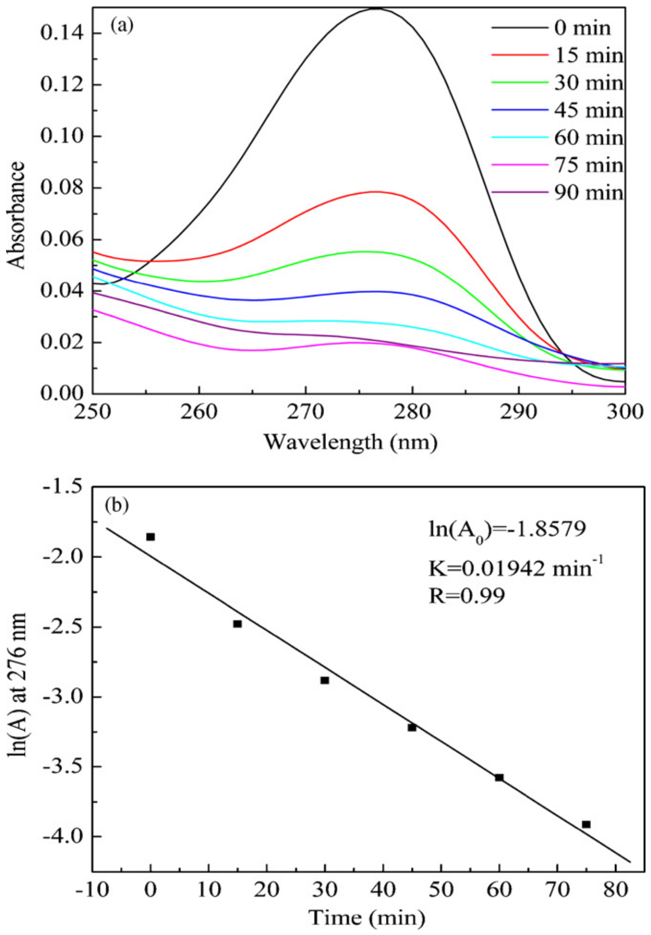

Fig. 5. (a) Variations of BPA peak absorbency at pH 4.13 during adsorption on membrane C 50 ml solution per membrane (diameter 4.5 cm). (b) [ln(*A*)–time]–BPA adsorption kinetics on membrane C 50 ml solution per membrane (diameter 4.5 cm).

3.3. Dynamic adsorption experiment

During dynamic filtration test, a mixture of BPA and kaolinite was used, after permeate filtration through ACF/TiO$_2$ membrane C, turbidity removal of over 98.7% is achieved, at the same time, overall 25–30% BPA removal is obtained, BPA level kept decreasing in the effluent as the filtration went on, which shows the retention property of composite functional membranes towards solid suspends, as well as removal ability in short contact time towards micro-pollutants. If extended the contact/adsorption time of the membrane in BPA solution to 2 h, then starts dynamically filtrating certain volume of BPA solution, the BPA level in effluent may drop to 60% of its original value using membrane A (Fig. 6). The sum of adsorbed BPA is about 0.70 mg per membrane C, while the sum of adsorbed BPA is about 1.10 mg per membrane A. The results in Fig. 6 show that the dynamic adsorption quantity of the studied ACF/TiO$_2$ membrane to BPA is close to its saturation value.

3.4. Adsorptive removal of BPA in repeated use of the membrane

The adsorption of BPA on membrane C versus time is evaluated by comparing with the blank membrane that contains only TiO$_2$ (Fig. 7). The adsorptive removal of BPA over membrane C were reduced in repeated use, 1st > 2nd > 3rd time use, but always higher than the blank TiO$_2$ membrane. Though BPA removal is reduced in repeated use, the calculated per gram ACF maximum adsorption quantity in 2 h adsorption time for membrane C was 37.0, 70.6 and 62.2 mg(BPA)/g(ACF) respectively for its 1st, 2nd and 3rd time use.

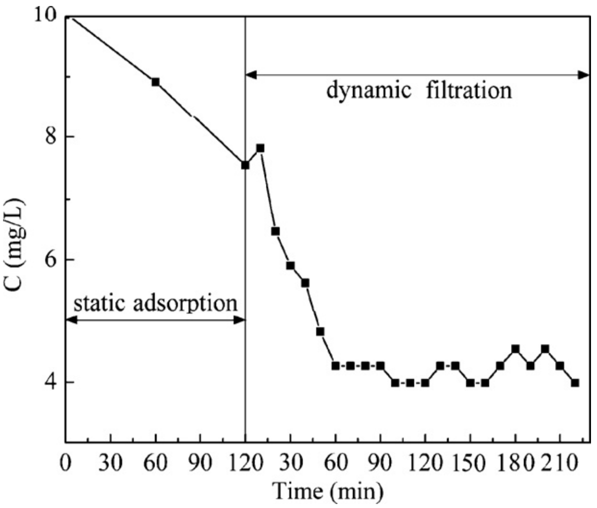

Fig. 6. . Time dependent BPA concentration during static adsorption and in effluent during dynamic filtration test, 200 ml solution/membrane A.

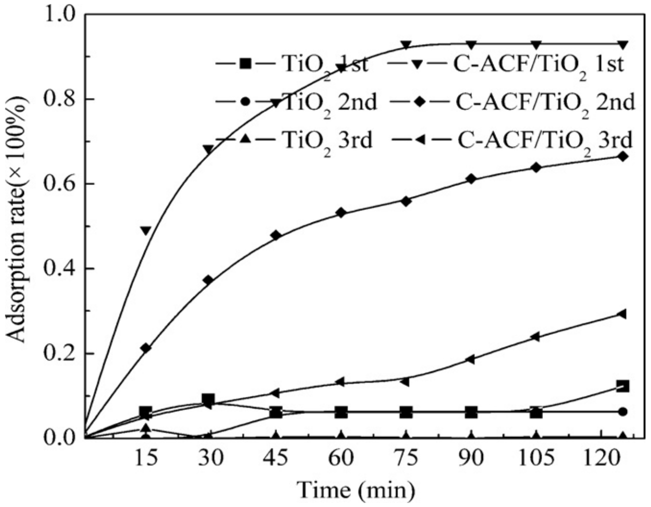

Fig. 7. Membrane regeneration and **t**ime dependent adsorptive removal of BPA by membrane C and TiO_2 coated membrane.

Repeated adsorption of BPA on membrane with only TiO_2 is stable for 2nd time use, lowered BPA removal was observed in its 3rd time use.

For membrane A, adsorption quantity was 13.0, 24.3 and 16.7 mg (BPA)/g(ACF) respectively for its 1st, 2nd and 3rd time use, though corresponding to 100%, 99% and 49% removal, the relatively small value in adsorption quantity per gram ACF in membrane A was due to the high ratio of ACF, compared to the small quantity of BPA mass in the solution. The measured increase of adsorption quantity for ACF in its 2nd and 3rd time use indicates an increase of the ACF adsorption to BPA following UV, TiO_2 and H_2O_2 treatment.

Adding TEOS in the sol–gel preparation step, followed by coating and composite membrane preparation, resulted in more stable membranes that do not have detachment problem and ACF loss, adsorption capacity after regenerative treatment by UV/Fenton actually increased, due to possible template/imprint effect.

Cross linking and binding with polymer during preparation of composite membrane is another method to lock the ACF within membrane, reduce its detachment during regeneration. This is currently under study, results will be presented later.

4. Conclusions

Novel composite tri-functional (adsorptive, regenerative, interceptive) membranes containing ACF and Ce^{3+}–TiO_2 was prepared by sol–gel and dip coating method at low temperature and drying at 105 °C. The developed membranes exhibited high adsorption capacity and photo-catalytic activity to BPA. Membranes can be cleaned by UV/Fenton regenerative oxidation of adsorbed BPA. ACF/TiO_2 membranes can be introduced as a way of extracting and oxidizing poisonous organic substance in drinking water source. The prepared membrane is effective in removing suspended particle as well as removing BPA pollutant.

In oxidizing the pollutant adsorbed on the membrane, regeneration efficiency of membrane could be improved by coupled supersonic treatment, which, however, led to loss of ACF/TiO_2. Membrane function and microstructure may be tuned by re-designing the preparation procedure, especially the functional components for better synergy. The membrane is more stable by incorporating SiO_2 into the membrane using the mixed sol from TEOS and TBOT.

This membrane based water purification process is effective and advantageous in the removal and degradation of the organic pollutants in water, a promise of good control of secondary pollution.

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