Photoconjunction of SnO$_2$/TiO$_2$-CeO$_2$ Multi-Herostructures Enhanced Molecular Imprinted Polymer for Degradation of Carbazole under Sun Light

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Abstract: The molecular imprinted SnO$_2$/TiO$_2$-CeO$_2$ photocatalyst (MIP/SnO$_2$/TiO$_2$-CeO$_2$) was successfully prepared with carbazole (carb) as the template molecule (target pollutant) and carboxymethyl-$eta$-cyclodextrine and styrene as functional monomers by the surface molecular imprinting method. The samples were characterized by FTIR, XRD and H-NMR. In addition, adsorption degradation, visible light photocatalytic performances of MIP/SnO$_2$/TiO$_2$-CeO$_2$ with different loading of CeO$_2$ were evaluated. The results showed that CeO$_2$ (25%) exhibited high degradation towards the template molecule compared to (50% and 75%). The degradation efficiency of carbazole could be obtained 75% at a CeO$_2$ content of 25% within 180 min of sunlight irradiation. The carbazole intermediate products were also elucidated using high-performance liquid chromatography (HPLC) and gas chromatography mass spectrometry analysis (GC/MS). Therefore, modifying the photocatalyst by the surface molecular imprinting is a promising method to improve the molecule recognition and photocatalytic efficiency of photocatalyst for target pollutant.

Key words: Surface molecular imprinting technique · Molecular recognition · SnO$_2$/TiO$_2$ · CeO$_2$ · Carbazole · Photocatalytic activity

INTRODUCTION

Carbazole is a heterocyclic aromatic compound they are common components of fossil fuels. They are one of the most important classes of the environmental pollutants, which have been detected in air, soil and water samples [1, 2, 3]. They are also used as chemical feedstocks for the production of dyes, medicines, pharmaceuticals, pesticides, lubricants and plastics. Due to the production of oil and coal chemicals and the use of industrial materials made from carbazole, large quantities of carbazole (nitrogenous polyaromatic hydrocarbons) dissolved in surfactant micelles have entered the surface water and soil, leading to soil, surface water and groundwater pollution [4]. When inhaled, ingested, or absorbed through the skin, carbazole may cause chronic symptoms such as low blood pressure, central nervous system demyelination, testicular damage, blindness and damage to the cerebral cortex. More acute symptoms include dizziness, weakness, blurred vision, difficulty breathing, fainting, bradycardia, occasionally leading to death [5]. They were detected in atmospheric samples, as well as soils and groundwaters contaminated with petroleum, wood-preserving wastes and coal-processing residues [6]. Carbazole and its derivatives are found to be toxic and mutagenic [7]. Moreover, they readily undergo radical chemistry to generate the more genotoxic hydroxynitrocarbazoles [6]. In an effort to remove nitrogen from crude oil, precombustion crude oil cleaning processes have been widely studied. The application of heterogeneous semiconductor photocatalysts in water cleaning and environmental remediation has recently attracted considerable attention because of their successful utilization of solar energy which is a natural abundant energy source for the excitation process.

The application of semiconductors in heterogeneous photocatalysis to remove various pollutants has attained significant attention in the last decade [8, 9]. Therefore, it...
is important to find a way to selectively eliminate the targeted pollutants. Among these methods, molecular imprinting techniques (MIT) combined with photocatalytic technology exhibit higher efficiency to enhance the selectivity of photocatalyst for degradation of targeted organic pollutants. MIT is a promising way for synthesizing three dimensional cross-linked polymers to achieve specific molecular recognition properties [10].

This work aims to prepare and characterize of molecular imprinting polymer (MIP), SnO\textsubscript{2}/TiO\textsubscript{2}, Cerium oxide (CeO\textsubscript{2}) composite coded MIP/SnO\textsubscript{2}/TiO\textsubscript{2}-CeO\textsubscript{2} by an in situ precipitation method. The as-prepared catalyst demonstrated much higher activity for degradation of carbazole as a model compound for nitrogenous polyaromatic hydrocarbons under the irradiation of solar light and also to elucidate its product.

Experimental Section

Preparation of SnO\textsubscript{2}/TiO\textsubscript{2}: 0.2 mol (0.372 g in 100 ml) stannous chloride SnCl\textsubscript{2} was dissolved in 100 ml of water and about 0.2 mol of titanium tetra chloride (TiCl\textsubscript{4}) in isopropanol was also made up to 100 ml. The two solutions were mixed together to form a homogenous solution. Then about 15 ml of hydrogen peroxide and 1 ml of ammonia solutions are mixed and about 165 ml of water was added to it. The solution containing stannous chloride and titanium tetra chloride are added to the second solution drop by drop by using a burette. The above solution was transferred in to a Teflon-lined stainless steel autoclave. Subsequently, the autoclave was laid in an oven at 120°C for 24 h under autogenous pressure and static conditions. After reaction, the suspension was cooled down to room temperature. The as-obtained powder samples were centrifuged and washed with distilled water and then dried completely in an oven at 80°C for 12 h.

Preparation of CeO\textsubscript{2}: Cerium oxide (CeO\textsubscript{2}) was prepared by following the microwave combustion synthesis pathway, In a typical procedure, 2.52 g of cerium nitrate hexahydrate (Ce(NO\textsubscript{3})\textsubscript{3}•6H\textsubscript{2}O) was used as precursor; and urea was used as fuel for combustion. Typically, the sol of metal salt was mixed with 0.697 g of urea stoichiometrically. Then the net sol was treated in a domestic microwave working at 900 W and 2.45 GHz for 3-5 min.

Synthesis of Carboxymethyl-Beta-Cyclodextrin (CMCD): Carboxymethyl-beta b-cyclodextrin (CMCD) was prepared by the following procedure [2]: A mixture of beta-cyclodextrin (\(\beta\)-CD) (10 grams, 8.818 mmol) and NaOH (9.3 grams, 232.5 mmol) was treated with a-27-ml volume of monochloroacetic acid (16.5% w/w). The mixture was reacted at 50°C for 5 hours. Then, the reaction product was cooled to room temperature and the pH was adjusted to neutral (6 to 7) using HCl. The neutral solution was filtered to separate salt containing in it. The solution was poured to a superfluous methanol solvent to produce a white precipitation. The solid precipitation was filtered and dried under vacuum. Then, it was crushed with an addition of acetone.

Preparation of MIP/SnO\textsubscript{2}/TiO\textsubscript{2}-CeO\textsubscript{2}: A typical procedure for preparing MIP is as follows: the Carbazole (0.17 gm, 1mmol), Carboxymethyl b-cyclodextrine 0.1 gm and styrene (0.11, 1mmol) were dissolved in 10mL of diethyl ether. The mixture stirred for 2hours to make intensive mixing. Then EGDMA (3.7 gm, 18 mmol) and benzoylperoxide (0.15 g, 0.62mmol) were successively added to the solution under a nitrogen atmosphere for 20 min. After mixing, the prepolymerization mixture was then polymerized by thermal initiation at 80°C for overnight. The resultant powder was coded (MIP+Carb). The freed Carb in the formed polymer were continuously extracted and washed with DMF, the obtained (MIP-carb) was dried overnight for further investigation. Nonimprinted polymers (NIP) was also prepared in the same way in absent of carbazole (Carb) template molecules. The as synthesized SnO\textsubscript{2}/TiO\textsubscript{2} powders was subsequently added to the preprepared polymer MIP (1:1) molar ratio, with various CeO\textsubscript{2} loadings such as 25%, 50% and 75% the product was denoted as MIP/SnO\textsubscript{2}/TiO\textsubscript{2}-CeO\textsubscript{2}.

Analytical Methods: High-performance liquid chromatography was performed to monitor the degradation of carbazole. An Agilent 1100 series (Hewlett-Packard) instrument equipped with a variable wavelength detector and fitted with a reversed phase C18 column (4.6×150 mm, Hewlett-Packard) was used. Carbazole was analyzed at a flow rate of 0.5 ml min\textsuperscript{-1} with methanol/\(\text{H}_2\text{O}\) (86:14, v/v) as the mobile phase. The effluents were monitored at 254 nm for the samples of carbazole. Derivatized extracts were analyzed by gas chromatography-mass spectrometry (GC–MS) as previously described (Schneider et al., 1996).

Characterization of the Prepared Materials: The structure and phase purity were determined by different techniques;
To determine the crystalline phase of the catalyst and its crystalline size, high-resolution X-ray diffractometer (XRD; PANalytical X-PERT PRO MPD, the Netherlands) coupled with a Cu Ka radiation at 40 kV and 30 mA over the 20 range of 4-80° at a scanning speed of 4°/ min with a sampling angle interval of 0.04°.

The structure of adsorbents was investigated by the FTIR spectra in the 4000-400 cm\(^{-1}\) range for the prepared samples at room temperature by Perkin Elmer (model spectrum one FT-IR spectrometer, USA). Samples were prepared using the standard KBr pellets.

The \(^1\)HNMR spectrum was measured on a Varian Gemini-200 MHz NMR spectrometer at Laser Unit, Physics Department, Faculty of Science, Cairo University, Cairo, Egypt.

**The Photocatalytic Activity:** For the batch photocatalytic degradation experiments; 1.25 g of MIP/SnO\(_2\)/TiO\(_2\)-CeO\(_2\) were dispersed in 250 mL Diethylether (pH7) contaminated with carbazole, at initial concentration of 125 mg/L. After the dispersion of the mixtures in an ultrasonic bath for 20 min, the suspension was magnetically stirred in dark at room temperature and 200 rpm, to assure adsorption/desorption equilibrium between the pollutants molecules and the surface of MIP/SnO\(_2\)/TiO\(_2\)-CeO\(_2\). After that, the photo-reactors were subjected to solar light irradiation for 240 min. Then the powder was separated from the mixture by centrifugation at 5000 rpm for 10 min. At varied irradiation time intervals, an aliquot of the mixed solution was collected and centrifuged and the residual carbazole concentration in the supernatant was analyzed by HPLC and the intermediate product analyzed by GCMS.

**RESULTS AND DISCUSSION**

**Morphology and Structure Characterization of Prepared Sample:** The crystallographic structures of the as-prepared samples were examined by X-ray powder diffraction (XRD). As shown in Fig. (1) X-ray of SnO\(_2\)/TiO\(_2\), the peak position were found at 27.05° (110), 34.5° (101) and 52.9° (211) matched to (JCPDS 01 - 070 - 4407).

Further, the crystallite size was calculated using Scherrer's formula for the high intensity peak, the estimated grain size was found to be 73.56 nm with d-spacing 0.2611 nm. The major reflections appeared at 28.67, 32.89, 47.36, 56.28 and 58.97 that correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystal planes, respectively, matched to cubic fluorite structure of CeO\(_2\) (JCPDS 00-043-1002), the crystallite size was found to be 18.14 nm with d-spacing 0.3144 nm. It is clear that the XRD patterns of the nanocomposites confirm anchoring of CeO\(_2\) and SnO\(_2\)/TiO\(_2\) on the surface of the polymer with crystallite size 18 nm with d-spacing 0.328 nm.

FTIR spectra of CeO\(_2\), SnO\(_2\)/TiO\(_2\), NIP, MIP+Carb, MIP-Carb and MIP/SnO\(_2\)/TiO\(_2\)-CeO\(_2\) are demonstrated in Fig. (2). Stretching peaks at 1140 and 1730 cm\(^{-1}\) corresponds to C–O and C=O in EGDMA, respectively. Absorption intensity of C=O peak weakened obviously in MIP/SnO\(_2\)/TiO\(_2\)-CeO\(_2\) spectrum which could be attributed to steric hindrance effect that restrain full vibration of carbonyl group. The original cross-linking agent EGDMA and styrene have abundant vinyl groups. However, the characteristic C=C peaks at 1630, 990 and 910 cm\(^{-1}\) show low intensity that verified the crosslinking polymerization reaction. The absorbance of the carbazolic band at 1597 cm\(^{-1}\). Peaks appearing at 1513 and 1339 cm\(^{-1}\) contribute from the asymmetric and symmetric stretching bands of nitro groups, respectively. After surface grafting, a new vibrational peak appears, band near 455 cm\(^{-1}\) assigned to the Sn-O stretching vibrations and the peak near 619 cm\(^{-1}\) stands for O-Ti-O bands and the value below 800 cm\(^{-1}\) were assigned to the Ti-O stretching and bending mode of bond vibration corresponding to the formation of tin titanate. The broad absorption peaks centered at 545 cm\(^{-1}\) and 1057 cm\(^{-1}\) are associated with Ce-O and Ce-O-Ce of CeO\(_2\). FTIR data strongly confirms the formation of MIP/SnO\(_2\)/TiO\(_2\)-CeO\(_2\) and the high probability for hydrogen-bonding interactions between imprinted polymer and carbazole molecules.

It can be seen from the H-NMR spectrum of compound in the DMSO solvent, The 1H NMR spectrum of peaks are seen at 4.9 ppm (H1), 3.5 ppm (H2), 3.8 ppm (H3), 3.4 ppm (H4), 3.7 ppm (H5) and 3.73 ppm (H6), these represent the b-CD. CMCD is shown in Fig. (3). The single peaks of chemical shift at 1.51 ppm and 1.25 ppm are carboxymethyl, 0.25 ppm for methylene proton and 0.5-1.0 ppm for methylic proton. The H-NMR spectrum revealed the resonances characteristic of the carbazole between 7.2 and 8.2 ppm, the hydrogens of aromatic ring are indicated in chemical shift of 7-7.8 ppm. The signals in the regions of 4.35 ppm for CH2 and 1.89 ppm for CH3 are related to EGDMA. However, from the NMR spectrum of the vinyl of styrene the sharp signal at 3.5 ppm and 4.5 ppm is ascribed to the methylene protons in the polymer. Other signals belonging to methylene protons from ester are visible at 4.4 ppm, methylene.
Fig. 1: XRD patterns of CeO$_2$, SnO$_2$/TiO$_2$ and MIP/SiO$_2$/TiO$_2$-CeO$_2$

Fig. 2: FTIR curves of the prepared materials

Fig. 3: H-NMR of the prepare materials
Fig. 4: The adsorption and solar photocatalytic degradation of carbazole over the MIP/\(\text{SnO}_2/\text{TiO}_2/\text{CeO}_2\)

Fig. 5: HPLC chromatogram of (a) carbazole and (b) after degradation

Fig. 6: Mass chromatogram of proposed intermediate for degraded carbazole (a) benzacetamide (b) 8,9 dimethyl hexadecane (c) valporic acide (d) Valine
protons linked to carbazole nitrogen (3.5 ppm). The structural formation of the copolymer can be simply determined by reducing the intensity of the vinyl peaks at 5.6 and 6.0 ppm in the copolymer spectrum, when carbazole ring entered into the hydrophobic cavity of CD, the change of the micro-environment leaded the phenyl ring proton signals split.

CONCLUSION

The surface molecular imprinting technique was used to modify the SnO₂/TiO₂-CeO₂ photocatalyst with carbazole as the template molecule. The obtained photocatalysts were characterized by FT-IR, XRD and H-NMR. SnO₂/TiO₂-CeO₂ showed higher photocatalytic activity and specific recognition ability under solar light irradiation. The degradation efficiency of carbazole could be obtained 75% at a CeO₂ content of 25% within 180 min of sunlight irradiation. This work demonstrated that the surface molecular imprinting method was an effective approach to enhance the catalytic efficiency of the photocatalyst for target pollutant.

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REFERENCES