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Optimization of photocatalytic degradation of polybrominated diphenyl ether on trimetallic oxide Cu/Ni/TiO_2/PVC catalyst using response surface methodology method

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ABSTRACT

Polybrominated diphenyl ether (PBDEs) are widely spread in the environment which posing elevated potential risks triggers world's attention due to their global distribution and accumulation in the environment and have been found to be a class of contaminants of concern. The present study involves the photocatalytic degradation of tetra (BDE-47), penta (BDE-99, BDE-100) and hexaBDEs (BDE-153, BDE-154) as the most utilized compounds in aqueous solution. The results analysed by gas chromatography-electron capture detector (GC-ECD) found that the degradation of PBDEs under UV light irradiation using the potential trimetallic oxide Cu/Ni_{10}/TiO_2 photocatalyst on the immobilized PVC underwent efficient degradation. The potential catalysts then were characterized using various physicochemical methods of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and diffuse reflectance ultraviolet visible (DR-UV Vis). Further optimization on the three critical parameters (TiO_2 loading, calcination temperature and catalyst dosage) for PBDE degradation (BDE-47) were investigated using Box–Behnken experimental design. The optimized data obtained via BBD have found that the TiO_2 loading (83 wt%, *F*-value = 33.60) is the most significant effective factor, followed by calcination temperature (800 °C, *F*-value = 10.18) and catalyst dosage (20 mg, *F*-value = 6.25) by giving 64.63% degradation of BDE-47 while the regression analysis was found to be as a satisfactory correlation between the experimental data and predicted values with R^2 value of 0.9671 and Adj R^2 of 0.9247. Interestingly, the potential photocatalyst of $CuNi_{10}Ti$/PVC (5:10:85) demonstrated good activity which is suitable for industrial application.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) is a group of brominated flame retardant (BFRs) which are added to materials such as electrical and electronic equipments, polymers, paint and textiles to prevent them from easily catching fire thus slow down the burning process and they are most frequently measured in the environment with highest concentrations. There are three technical PBDE products, commonly referred as penta-BDE, octa-BDE, and deca-BDE, with each of them varying in degrees of bromination, different physicochemical properties, and contains a limited number of congeners. Amongst PBDEs congeners reported by previous researcher, BDE-47 was found to be the most dominant congener in all waters, and BDE-154 contributed more than BDE-99 and BDE-100. Nonetheless, BDE-47 and BDE-99 were the predominant congeners in some species studied due to the extensive use of penta-BDE rather than octa-BDE. It has been revealed that tetra- and penta-substituted PBDEs are shown to be persistent, lipophilic, bioaccumulating, and ubiquitous in the environment [1], so the effect and traces of its usage is still present in the environment and may lead to contamination thus it is a need to investigate the progressive and effective removal of these pollutants, so as to protect wildlife and human health.

To cope with an uprising application, recycling and release of PBDEs into the environment, different remediation technologies should be developed. The photocatalysis process is found to be one of the most efficient and green technology process for treating organic pollutants and it has been investigated over a number of metal oxide based catalysts (for *e.g.* Al_2O_3, SiO_2 and TiO_2). Amongst them, TiO_2 is a prominent photocatalyst which was used in the photocatalytic process as based catalyst due to its several advantages. It is well established that titanium dioxide is one of the potential catalyst in the redox reaction that could enhance the catalytic activity due to unique acid–base properties, high oxygen storage capability/mobility and strong metal–support interaction. These make the TiO_2 as based materials very interesting and

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effective for photocatalysis. However, TiO_2 alone would not significantly be capable to work effectively, it need dopant or co-catalyst to assist its work. Thus in order to overcome this problem, many researchers have been explored the use of various inexpensive transition metals such as Mn [2], Ni [3–5], Cu [6–8], Zn [9] and others to be used as dopant, incorporated onto based TiO_2. Metal oxides are said to be less active than metals, but they are stable in catalytic conditions.

Presently, trimetallic oxide photocatalysts have been given more attention in catalytic reaction. In this work, $Cu/Ni/TiO_2$ semiconductor metal oxide was chosen as photocatalyst due to its low cost, stability, durability and high in catalytic activity. The potential Ni and Cu have been widely used as dopant in photocatalyst but little published paper on trimetallic oxide of $Cu/Ni/TiO_2$ in photocatalysis process [10]. The approach of combining three metal catalysts is to increase its stability, durability, lower the band gap energy and increase the catalytic activity performance. Therefore, in this present paper, the photocatalytic degradation of PBDEs in aqueous system utilizing trimetallic oxide $Cu/Ni/TiO_2$ photocatalyst immobilized on PVC is presented since it has to our knowledge not yet discovered by any researchers used as photocatalyst in photocatalysis process. The five PBDE congeners of BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 were therefore chosen as tested chemical compounds for this study.

Up to date, the optimization of catalyst preparation parameter on $Cu/Ni/TiO_2/PVC$ photocatalyst in the photocatalysis of PBDEs compound by using response surface methodology (RSM) has not been reported in literature. In this research, the optimization of PBDEs degradation utilizing trimetallic $Cu/Ni/TiO_2/PVC$ photocatalyst via Box Behnken design (BBD) was investigated. Accordingly, the main objective of this study is to investigate the influence of catalyst parameters such as based TiO_2 loading, calcination temperature and catalyst dosage in PBDEs degradation in order to find the optimum conditions for catalyst preparation and the corresponding values of the three major process parameters. Amongst five PBDEs congeners, BDE-47 was appointed as the primary degradation interest due to its importance over other PBDEs compound.

2. Experimental

2.1. Materials

All the chemicals involved in this study were used without further purification. The photocatalysts were prepared by modified sol–gel/hydrothermal method. For the preparation of sol–gel TiO_2 as based catalyst, diethanolamine (DEA) (99%) chemical was purchased from Merck, titanium(IV) isopropoxide (Sigma Aldrich) (97%), while polyethylene glycol (PEG 2000) and ethanol (96%) were obtained from QRëcTM. Two types of different metal precursor salts were used which were nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) (QRëcTM) and copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) (QRëcTM). For the preparation of supported material, polyvinyl chloride (PVC) obtained from Merck was used as support materials for the catalyst. For GC analysis purpose, the anhydrous sodium sulphate (Na_2SO_4) purchased from QRëcTM was used as water absorber. The standard PBDE (PENTABDE TECHNICAL MIX (DE-71)), 50 ppm in CH_3OH was purchased from Cambridge Isotope Laboratories Incorporation (USA). Ethyl acetate ($C_4H_8O_2$) (semipolar) used as solvent separator for GC analysis was obtained from (99%) (QRecTM).

2.2. Catalysts preparation

All the catalysts were prepared by sol–gel/hydrothermal method. Titanium dioxide used as based for photocatalysts was prepared by dissolving polyethylene glycol (PEG) (2.45 g) with absolute ethanol (50 ml) in a beaker. The solution was stirred continuously using magnetic bar to ensure all (PEG 2000) was completely dissolved and then about 12.00 g of titanium tetraisopropoxide (TTIP) was added to the previous solution. After that, diethanolamine (DEA) was added to the solution right after titanium tetraisopropoxide was completely dissolved. In the final stage, a small amount of distilled water was added. The mixture was stirred continuously until homogeneous sol was obtained. The sol was left about 3–4 days until it became off white soft gel like jelly. Then, the sol was put into the autocalve (hydrothermal purpose). The preparation of bimetallic sol Ni/TiO_2, Cu/TiO_2 and trimetallic $Cu/Ni/TiO_2$, the sol were conducted by mixing an appropriate amount of metal precursor salt into the solution of sol TiO_2 according to its desired ratio. All the sol mixture solutions were then stirred continuously in the beaker by magnetic bar for 30 min at 27 °C until the solution was homogeneously well mixed. These mixtures of sol were then dried in oven for 48 h. The obtained dry gel was put in the hydrothermal steel container (autoclave) and calcined at specific temperature for 5 h using a furnace in the air atmosphere at 400–900 °C for 5 h using a ramp rate of 5 °C/min to remove all the metal counter ions and water present in the catalyst. Polyvinyl chloride, PVC (0.25 g) powder was dissolved in tetrahydrofuran (THF) (6.25 ml) in a 50 ml beaker. The solution was continuously stirred until PVC powder was completely dissolved and clear solution was obtained. The PVC solution was then spread onto the petri dish and left for about 3 mins before the photocatalyst powder was sprinkled on top of the PVC layer. The photocatalyst on the PVC was left in the fume hood overnight. The composite was then dried in the oven at 80 °C for 2 h before it can be used for the photocatalytic activity.

2.3. Measurement of catalytic activity

The treated pentaBDEs solution was analysed by GC instrument Hewlett Packard model HP 6890 with detector of electron capture (GC-ECD, Agilent). The Electron Capture Detector (ECD) is selective to electronegative compounds, especially fluorinated, chlorinated or brominated molecules (halogenated compounds) in a gas through the attachment of electrons via electron capture ionization. A column used was HP-5MS column (25 m x 0.2 mm i.d., film thickness 0.33 μm; Agilent). Helium gas was used as mobile phase or carrier gas with flow rate 40 ml/min. The mode of separation in GC instrument used in this study was the temperature programming mode. The injector temperature was 300 °C. The initial oven temperature was set up at 150 °C withhold time for 1 min and then the temperature was increased to final temperature at 300 °C with flow rate 30 °C/min. The temperature of detector was set at 290 °C. Sample volume of 1.0 μl was injected without any solvent dilution. The concentration of PBDEs compound produced by the photocatalytic testing is calculated by referring to the chromatogram peak area. All the experiments were conducted in triplicate and results were found to show ± 5% deviation from the average value.

2.4. Catalysts characterization

The characterization of the calcined photocatalysts are importance in order to determine their chemical and physical properties, hence the data obtained could be used to relate their photocatalytic performance. In this study, the structure and phase present of the prepared catalyst was characterized by powder X-ray diffraction spectroscopy at room temperature with a Diffractometer D5000 Siemens Crystalloflex with CuKα radiation ($\lambda = 1.54060$ Å). Scans were performed in step mode of 0.20 s/step. The data obtained was analysed by a PC interfaced to the diffractometer using software called diffrac plus. The results were then compared with the accumulated Powder Diffraction File (PDF) data, which comes

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