

Photo-removal of 3,4,4',5-Tetrabromodiphenyl ether ($C_{12}H_6Br_4O$) and 2,2',3,3',4-Pentabromodiphenyl ether ($C_{12}H_5Br_5O$) with Graphene oxide-Ag@Ag₃PO₄/g-C₃N₄ Nanocomposite

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Abstract: - Polybrominated diphenyl ethers (PBDEs) are a class of organo-bromine compounds that are used as flame retardants. Like other brominated flame retardants, PBDEs have been used in a wide array of products, including building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, and textiles. They are structurally to polychlorinated diphenyl ethers (PCDEs), polychlorinated biphenyls (PCBs) and other polyhalogenated compounds, consisting of two halogenated aromatic rings. In this study, 3,4,4',5-Tetrabromodiphenyl ether ($C_{12}H_6Br_4O$) (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether ($C_{12}H_5Br_5O$) (PBDE-82) photo-removal process was investigated with graphene oxide-silver loaded silver phosphate doped graphitic carbon nitride (GO-Ag@Ag₃PO₄/g-C₃N₄) nanocomposites under different experimental conditions. The effect of increasing pH values (3.0, 4.0, 6.0, 7.0, 8.0 and 11.0), increasing photodegradation times (30, 60, 90, 120 and 150 min), increasing GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites concentrations on photodegradation yields of PBDE-81 and PBDE-82 were investigated with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites. The characteristics of the synthesized NCs were assessed using XRD, SEM, TEM, DRS, XPS, ESR and EIS analyses, respectively. Maximum 99.64% photo-removal yield was obtained for 20 mg/l PBDE-81 and PBDE-82 with 4 mg/l GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, after 120 min photodegradation time, at pH=7.0, at 400 W UV-vis light power, and at 25°C. Langmuir-Hinshelwood kinetic can be presented as a first-order equation for the photo-removals of two PBDEs. k_{app} values for PBDE -81 and PBDE-82 were found as 0.019 min⁻¹ and 0.017 min⁻¹, respectively. The μ values was found as 1.234 cm⁻¹ and 0.987 m⁻¹ for 4 and 20 mg/l Ag@Ag₃PO₄/g-C₃N₄ nanocomposite concentrations, respectively.

Key-Words: - Graphene oxide-silver loaded silver phosphate doped graphitic carbon nitride (GO-Ag@Ag₃PO₄/g-C₃N₄) nanocomposites; Kinetic models; Nanoparticles; Organo-bromine; 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82); Photo-removal; Polybrominated diphenyl ethers (PBDEs); Polychlorinated biphenyls (PCBs); Polychlorinated diphenyl ethers (PCDEs); 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81).

Received: March 6, 2026. Revised: May 22, 2026. Accepted: August 11, 2026. Published: October 29, 2026.

1 Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used since the 1970s as brominated flame retardants in polyurethane foam used in furniture, casings of electrical and electronic equipment, construction materials, and the textile industry, [1], [2], [3], [4], [5]. Until 2005, the global production of these compounds had reached between 1.3 and 1.5 million tons, [6]. Total consumption of commercial PBDEs from 1970 to 2020 was estimated at ~46,000 (Penta-BDE), ~25,000 (Octa-BDE), and ~38,000 (Deca-BDE) tons in the U.S. and Canada, respectively, [4]. Because of their persistence, bioaccumulation, and potentially toxic effects, Penta-BDE and Octa-BDE are now included in the Stockholm Convention. The Deca-BDE mixture has been withdrawn from the U.S. market at the

end of 2013, but it is still the dominant commercial product in some Asian countries, [7]. Due to their ubiquity and high toxicity, the elimination of PBDEs attracts increased attention and concern.

PBDEs are one of highly toxic and recalcitrant environmental pollutants that bioaccumulate across trophic levels of food webs, which was included in the United States Environmental Protection Agency's (USEPA) "Chemicals of Concern" list and the United Nations (UN) Persistent Organic Pollutants (POPs) list, [8]. PBDEs was not composited with other materials by chemical bonding, they are readily released into the ambient air, ash, [9], sediments, and aquatic environments, [10], during their production, use, and disposal, [11]. The main routes of human exposure to PBDEs are ingestion, inhalation and skin absorption,

[12]. Among these, ingestion via food intake is the most common route of PBDEs into the human body, [13]. It has been reported that PBDEs can cause serious negative effects to human health, such as neurotoxicity, immunotoxicity, reproductive deficiency and so on, [8], [14].

On account of the strong intractability of PBDEs to oxidative degradation, their reductive debromination has been widely studied, including anaerobic bio-reduction, [15], [16], electrochemical reduction, [17], [18], zerovalent metal reduction, [19], [20], [21], [22], and photocatalytic reduction, [14], [23], [24], [25], [26], [27]. TiO₂-mediated photocatalysis is a promising method for the degradation of PBDEs. It has been reported that low brominated diphenyl ethers such as 2,2',4,4'-Tetrabromodiphenyl ether (BDE-47) are inflexible and degrade 2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (BDE-209) in anoxic BDE-209/TiO₂ dispersions under UV irradiation, [14]. To achieve complete debromination of PBDEs, several TiO₂-based composites, including Ag/TiO₂, [23], CuO/TiO₂ [24], Cu₂O/TiO₂, [26] and graphene/TiO₂, [27], were fabricated to treat lower-BDEs. By improving the charge separation and weakening the C-Br bond, the photocatalytic reduction of BDE-47 was rapidly occurred, but its complete debromination was rather difficult because the intermediates were more resistant to the photocatalytic reduction. Recently, we found that during the photocatalytic reductive debromination, the reaction rate constant of BDE-47 was about 500 times larger than that of 4,4'-dibromodiphenyl ethers (BDE-15), because the phenyl ring substituted by more Br atoms is more reactive for the one-electron transfer process, [28]. Unluckily, these lower brominated PBDEs are known to be more toxic as bio-accumulative congeners, [29], [30]. For this reason, it is still necessary to develop methods for the complete debromination of PBDEs.

The concentration of PBDEs in biota and environmental compartments could increase due to bioaccumulation effect. Among all the congeners of PBDEs, BDE-47 is one of the most prevalent congeners that can be detected in both abiotic and biotic environment attributed to higher water solubility and bioaccumulation than other high brominated congeners, [27], [31]. In the ecosystem, BDE-47 can be transformed by microorganisms through anaerobic reduction debromination and aerobic degradation, by mammals through oxidative metabolism, and by ultraviolet light through reductive debromination, [32]. However, these transform strategies are still full of several drawbacks, such as low transform efficiency, long transform cycle and toxicity bioaccumulation. Thus, searching for a novel method to remove PBDEs in ecosystem has been urgent. In recent years, solar energy driven photocatalysis technology has been

applied in various fields, especially in the treatment of robust contaminants and energy conversion, [33], [34], [35].

Reduced graphene oxide (rGO) formed through reduction of GO has been proved to facilitate charge pair separation and migration due to excellent electronic conductivity, strong optical absorbance capacity and chemical stability, [36], [37]. The large surface area is favourable for the attachment of inorganic nanoparticle and provide abundant number of active sites, [38]. In addition to, it has been reported that graphene material can tailor the size and distribution of photocatalyst, [39]. Considering these remarkable properties, rGO can function as an ideal cocatalyst to participate in the photocatalysis reaction. Up to now, a large number of ternary composites that exhibit enhanced photocatalytic activity with rGO serving as cocatalyst have been constructed, such as g-C₃N₄/CdIn₂S₄/rGO, [40], g-C₃N₄/BiOBr/rGO, [41], CdS/rGO/g-C₃N₄, [42], and so on.

Silver phosphate (Ag₃PO₄) with quantum efficiency of over 90% has been proven to be a promising VLD photocatalyst in the environment pollution treatment, [39], [43], [44], [45], [46]. Furthermore, as a semiconductor with relative narrow band gap (~2.4 eV), Ag₃PO₄ NCs may couple with graphitic carbon nitride (g-C₃N₄) NCs to form heterojunction composite to achieve ultra-fast charge transfer and separation. It has been reported that Ag₃PO₄/g-C₃N₄ hybrid nanocomposites exhibited higher photocatalytic activity than pristine catalysts. For example, Z-scheme Ag₃PO₄/g-C₃N₄ nanocomposites with enhanced photocatalytic activity in converting CO₂ into fuel was produced, [47]. A core-shell structured Ag₃PO₄/g-C₃N₄ nanocomposites with impressive photodegradation activity was reported, [48]. Despite these promises, several challenges and obstacles still exist in the g-C₃N₄/Ag₃PO₄ nanocomposites Z-scheme system: (1) some defects formed between g-C₃N₄ nanocomposites and Ag₃PO₄ nanocomposites can serve as recombination center, [49]; (2) the low electron storage results in relatively weak reduction ability; (3) molecular oxygen activation is not strong enough, [45]; (4) lattice mismatch and relatively low structure elements is not favourable for charge pair separation, [50]. In order to overcome above drawbacks, it may be feasible to introduction of another cocatalyst, further affecting the synthesis and photoreaction process.

Graphitic carbon nitride (g-C₃N₄) is a promising stable, active, metal free photocatalyst with excellent visible light activity. g-C₃N₄ nanocomposites possesses a band gap of ~ 2.7 eV, and its conduction and valence band edges are about -1.1 V and 1.6 V (versus normal hydrogen electrode), respectively, [51]. On the other hand, g-C₃N₄ nanocomposites has other unusual features: (1) g-C₃N₄ nanocomposites has a typical two-

dimensional (2D) nanosheet structure, which is propitious to disperse and stabilize noble-metal nanoparticles, increasing the availability of noble-metal atoms; (2) the high stability of g-C₃N₄ nanocomposites against chemical attacks from acids, bases and organic solvents enables its direct use for sustainable chemical reactions, [52].

2D metal-free g-C₃N₄ nanocomposites material with π -conjugated systems, has been designed as a promising substance in the field of photocatalysis, such as hydrogen (H₂) production, carbon dioxide (CO₂) conversion and pollutants oxidative degradation owing to tuneable electronic structure, relatively high thermal stability and extensive availability, [53]. Nevertheless, weak optical absorbance capacity and fast electron-hole recombination still restrict its real application, [54], [55]. To enhance photocatalytic performance of pristine g-C₃N₄ nanocomposites material, designing heterojunction system by coupling with well-matched bandgap semiconductor is the most popular topic in the past decades and still continues to be vital strategy. Among them, construction of g-C₃N₄ nanocomposites based artificial Z-scheme system is undoubtedly the most effective strategy, which can simultaneously possess highly-efficient charge separation and strong redox activity. For instance, it has been reported that BiOI/g-C₃N₄ hybrid nanocomposites based on Z-scheme mechanism has been synthesized, which shows excellent photoconversion activity in transferring CO₂ to fuel energy, [56]. The light-induced electrons remaining in the conduction band (CB) of g-C₃N₄ nanocomposites are responsible for the conversion of CO₂ to carbon monoxide (CO), H₂ and methane (CH₄).

Recent research indicate that graphene could be employed to construct the Z-scheme photocatalytic systems due to its excellent electrical conductivity. Specifically, the addition of rGO may enhance heterojunction performance. GO/Ag₃PO₄ nanocomposites can remove 97.33% BDE-209 after 8 h of visible light irradiation time, [16], [46]. Besides, an Ag@Ag₃PO₄/g-C₃N₄/rGO nanocomposites based to Z-scheme system with excellent photocatalytic activity could remove 93.40% of BDE-47 after 2 h of visible light irradiation time, [34]. A Z-scheme system based on rGO-Cu₂O/Bi₂WO₆ NCs was fabricated for tetracycline degradation, [57].

In this study, 3,4,4',5-Tetrabromodiphenyl ether (C₁₂H₆Br₄O) (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (C₁₂H₅Br₅O) (PBDE-82) photo-removal process was examined with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites under different experimental conditions. The effect of increasing pH values (3.0, 4.0, 6.0, 7.0, 8.0 and 11.0), increasing photodegradation times (30, 60, 90, 120 and 150 min), increasing GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites concentrations (2, 4, 6, 8 and 10 mg/l) on the

photodegradation process of 3,4,4',5-Tetrabromodiphenyl ether (C₁₂H₆Br₄O) (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (C₁₂H₅Br₅O) (PBDE-82) were investigated with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites. The characteristics of the synthesized nanocomposites were assessed using XRD, SEM, TEM, DRS, XPS, ESR and EIS analyses, respectively.

2 Materials and Methods

2.1 Chemicals

Disodium phosphate dodecahydrate (Na₂HPO₄·12H₂O), nitric acid (HNO₃), sodium sulfate (Na₂SO₄), ethanol absolute (CH₃COOH), melamine (C₃H₆N₆), silver nitrate (AgNO₃) and N,N-dimethylacetamide (DMF) were purchased from Merck, Germany. All the chemical agents are analytical and used without any further purification. The ultrapure water used in the whole experiments was obtained from Milli-Q ultrapure (18.25 MΩ cm) system.

2.2 Preparation of g-C₃N₄ Nanocomposites

The substance sample of g-C₃N₄ nanocomposites was obtained according to literature with modification, [43]. The bulk g-C₃N₄ nanocomposites was dispersed into a certain amount of nitric acid (HNO₃), 3 M solution with ultrasonic treatment for 3 h. Then, the suspension was stirred vigorously and then transferred to Teflon-lined stainless-steel autoclave for heat treatment. After, cooling up to the ambient temperature (at 25°C), the sample was collected and washed with ultrapure H₂O for several times until the pH was of natural. Then, the collected sample was heated to 520°C for 4 h in air and named as g-C₃N₄ NCs.

2.3 Synthesis of Ag₃PO₄/g-C₃N₄ Nanocomposites

g-C₃N₄ nanosheets (0.1 g) were added to 100 ml of deionized water and ultrasonicated for 20 min. Different amounts of [Ag(NH₃)₂]⁺ solution was then added to the g-C₃N₄ mixture and magnetically stirred for 30 min. Finally, NaH₂PO₄ was added to the mixture solution under vigorous stirring. After 3 h, the product was collected by filtration, washed with deionized water, and dried in an oven at 70°C for 10 h. The obtained samples were denoted as Ag₃PO₄/g-C₃N₄ nanocomposites, where Ag₃PO₄/g-C₃N₄ nanocomposites (10%, 20%, 30%, or 40%) represents the molar ratio of Ag₃PO₄ to g-C₃N₄ in Ag₃PO₄/g-C₃N₄ nanocomposites. The Ag₃PO₄ nanocomposites sample was prepared following the same procedures, excluding the addition of g-C₃N₄ nanocomposites.

2.4 Preparation of GO/Ag@Ag₃PO₄/g-C₃N₄ Nanocomposites

GO was synthesized based on the modified Hummer's method, [58]. Firstly, 0.012 g GO and 0.37 g silver nitrate (AgNO₃) nanocomposites were dispersed into 100 ml of N,N-dimethylacetamide (DMF) with ultrasonic treatment for 1 h (Suspension A). 0.3 g of g-C₃N₄ NCs was added into 30 ml of ultrapure H₂O containing disodium phosphate dodecahydrate (Na₂HPO₄·12H₂O) (molar ratio of Ag⁺/HPO₄²⁻ = 3.06) with vigorous stir to get uniform suspension (Suspension B). Secondly, the suspension B was slowly added dropwise to suspension A, and then stirred for 4 h in a dark room. Then, the forming sample was collected and dispersed into mixed solution of ultrapure H₂O and methanol (CH₃OH), and then illuminated under 400 W Xe lamp for 1 h. The forming sample was collected, and then washed with ultrapure H₂O as well as ethanol absolute (CH₃COOH), to remove residue ions. Finally, the sample was dried at 80°C overnight and denoted as GO/Ag@Ag₃PO₄/g-C₃N₄ nanocomposites.

2.5 Photodegradation Measurements

The UV irradiation treatments were created using eight 50 W Xe lamp for UV-A vis light (Total: 400 W) emitting in the 150–650 nm range ($\lambda_{\text{max}} = 400$ nm; FWHM = 17 nm; Actinic BL TL-D 18W, Philips). At given different photodegradation time intervals, the suspension of 10 ml was sampled and separated by centrifuge, then analysed according to the absorbance between $\lambda_{\text{max}}=200$ nm and $\lambda_{\text{max}}=500$ nm by a UV-vis spectrometer (Cary 5000 UV-Vis Spectrophotometer from Varian, Siemens, Germany) with a Quartz cuvette. BDE-81 and BDE-82 mixed solution (5 mg/l, 100 ml, methanol/ultrapure H₂O = 20/80) containing 50 mg of catalysts was stirred vigorously in the dark for 30 min to achieve adsorption-desorption equilibrium between catalyst and BDE-81+BDE-82 mixed solution. Methanol (CH₃OH) in the BDE-81+BDE-82 mixed solution functions as both co-solvent and holes scavenger. After that, a suitable amount of sample was collected and filtrated through 0.22 μm glass fibre filter to remove remaining nanoparticles from solution.

2.6 Characterizations

Powder XRD patterns were recorded on a Shimadzu XRD-7000, Japan diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å, 40 kV, 40 mA) at a scanning speed of 1°/min in the 10–80° 2 θ range. Raman spectrum was collected with a Horiba Jobin Yvon-Labram HR UV-Visible NIR (200–1600 nm) Raman microscope spectrometer, using a laser with the wavelength of 512 nm. The Raman spectrum was collected from 10 scans at a resolution of 2 /cm. The zeta potential was measured with a SurPASS Electrokinetic Analyzer

(Austria) with a clamping cell at 300 mbar. The morphological features and structure of the synthesized catalyst were investigated by SEM (FESEM, Hitachi S-4700). To investigate the composition of the elements, present in the synthesized GO-Ag@Ag₃O₄/g-C₃N₄ nanocomposites; SEM images were used. The size and structure of the GO-Ag@Ag₃O₄/g-C₃N₄ nanocomposites samples were identified with TEM analysis. The obtained GO-Ag@Ag₃O₄/g-C₃N₄ nanocomposites were collected and harvested by centrifugation (8000 rpm, 5 min), washed twice with deionized water and resuspended in ethanol (C₂H₅O) and dripped onto a carbon-coated copper (Cu) TEM grid. Vacuum drying then occurred to the GO-Ag@Ag₃O₄/g-C₃N₄ nanocomposites for 24 h at 25°C room temperature. The dry samples on the Cu grid were viewed and examined by TEM analysis recorded in a JEOL JEM 2100F, Japan under 200 kV accelerating voltage. Diffuse reflectance UV-vis spectra (DRS) in the range of 200–800 nm was recorded on a Cary 5000 spectrophotometer from Varian. The valence state of the GO-Ag@Ag₃O₄/g-C₃N₄ nanocomposites samples were investigated and was analyzed using XPS (ESCALAB 250Xi, England). XPS used an Al K α source and surface chemical composition and reduction state analyses was done, with the core levels recorded using a pass energy of 30 eV (resolution $\approx$ 0.10 eV). The peak fitting of the individual core-levels was done using XPS-peak 41 software, achieving better fitting and component identification. All binding energies were calibrated to the C 1s peak originating from C–H or C–C groups at 284.6 eV. The free radical signals were analyzed with electron spin resonance (ESR) (ESR, Bruker A300, Billerica, MA, USA) under UV-vis light for 10 min. Electrochemical impedance spectroscopy (EIS) and photocurrent measurements were employed by an electrochemical workstation (CHI Instruments, CHI 760E, Shanghai, China) using a conventional three electrode system.

The BDE-81 and BDE-82 experimental samples WERE analyzed by gas chromatography–mass spectrometry (GC-MS) and gas chromatograph (GC) (Agilent Technology model 6890N) equipped a mass selective detector (Agilent 5973 inert with MSD). Mass spectra were recorded using a VGTS 250 spectrometer equipped with a capillary SE 52 column (HP5-MS 30 m, 0.25 mm ID, 0.25 μm) at 220°C with an isothermal program for 10 min. The initial oven temperature was kept at 50°C for 1 min, then raised to 220°C at 25°C/min and from 200 to 300°C at 8°C/min, and was then maintained for 5.5 min. High purity helium gas [He(g)] was used as the carrier gas at constant flow mode (1.5 ml/min, 45 cm/s linear velocity).

2.7 Photodegradation Mechanism

Both hydroxyl and superoxide radicals (OH $\cdot$ and O $_2^{\cdot-}$)

were generated from photocatalysts under UV irradiation, which was confirmed by the quantitative investigation of the intensity of active oxidative species, investigated by the ESR. Compared with GO, Ag@Ag₃PO₄, g-C₃N₄ and GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites showed a stronger signal with characteristic peaks of OH• and O²⁻• under irradiation. In the photocatalytic process, the production of O²⁻• was assigned to the reaction between photo-electrons and surface-adsorbed oxygen, while OH• and corresponded to the photo-holes, which could react with OH•. Meanwhile, the existence of O²⁻• could contribute to the conversion of OH•. The target organic molecules could be degraded by OH•, O²⁻• in the process of oxidation-reduction, [59].

From the result of the trapping experiment, OH, O²⁻• and h⁺ were all responsible for ROS during the photocatalytic processes, from the result of ESR analysis, O²⁻• and OH• radicals were indeed generated and played an important role during the reaction. Generally, there are two types of electron separation processes for the photogeneration electron-hole pairs during the photocatalytic reaction. From the result of the trapping experiment, OH, O²⁻• and h⁺ were all responsible for reactive oxygen species (ROS) during the photocatalytic processes, from the result of ESR, O²⁻• and OH• radicals were indeed generated and played an important role during the reaction. Generally speaking, there are two types of electron separation processes for the photogeneration electron-hole pairs during the photocatalytic reaction, one is a double-transfer mechanism and the other is a Z-scheme mechanism. The double-transfer mechanism is a common separation process for a large amount of composite photocatalysts, such as Ag₂O/g-C₃N₄ nanocomposites, [60]. If the Ag₃PO₄/g-C₃N₄ heterojunctions follow this mechanism, the schematic diagram of Ag₃PO₄/g-C₃N₄ nanocomposites can be seen in Fig. 1, as the potentials of the conduction band (CB) and valence band (VB) edges of the g-C₃N₄ nanocomposites are -1.30 eV and +1.40 eV (vs. NHE), respectively, (Fig. 1a) and the CB and VB edge potentials of the Ag₃PO₄ nanocomposites are +0.45 eV and +2.90 eV (vs. NHE), respectively, [61]. Electrons in the CB of g-C₃N₄ nanocomposites would transfer to that of the Ag₃PO₄ nanocomposites, and the holes accumulate on the VB of g-C₃N₄ nanocomposites. However, as the CB of the Ag₃PO₄ nanocomposites (+0.45 eV, vs. NHE) is more positive than the potentials of the O₂/O²⁻• (-0.33 eV, vs. NHE), [62], the photogenerated electrons on the CB of the Ag₃PO₄ nanocomposites cannot reduce the O₂ to yield O²⁻•. In addition, due to the potentials of the OH•/OH⁻ (+2.38 eV, vs. NHE) and one is a double-transfer mechanism and the other is a Z-scheme mechanism.

* Figure 1 can be found in the Appendix section.

The double-transfer mechanism is a common separation process for a large amount of composite photocatalysts, such as Ag₃PO₄/g-C₃N₄ nanocomposites, [60]. If the Ag₃PO₄/g-C₃N₄ heterojunctions follow this mechanism, the schematic diagram of Ag₃PO₄/g-C₃N₄ nanocomposites can be seen in Fig. 1b, as the potentials of the CB and VB edges of the g-C₃N₄ nanocomposites are -1.30 eV and +1.40 eV (vs. NHE), respectively, and the CB and VB edge potentials of the Ag₃PO₄ nanocomposites are +0.45 eV and +2.90 eV (vs. NHE), respectively, [63]. Electrons in the CB of g-C₃N₄ nanocomposites would transfer to that of the Ag₃PO₄ nanocomposites, and the holes accumulate on the VB of g-C₃N₄ nanocomposites. However, as the CB of the Ag₃PO₄ nanocomposites (+0.45 eV, vs. NHE) is more positive than the potentials of the O₂/O²⁻• (-0.33 eV, vs. NHE), [62], the photogenerated electrons on the CB of the Ag₃PO₄ nanocomposites cannot reduce the O₂ to yield O²⁻•. In addition, due to the potentials of the ·OH•/OH⁻ (+2.38 eV, vs. NHE) and OH•/H₂O (+2.72 eV, vs. NHE), [63], which are more positive than the VB of g-C₃N₄ nanocomposites (+1.4 eV, vs. NHE), the holes on the VB of g-C₃N₄ nanocomposites cannot react with the OH⁻ and H₂O to form an OH• radical. As this result contradicts the results in the reactive species-trapping experiments, the double-transfer mechanism played a minor or negligible role.

In contrast, the electron transfer might follow a direct Z-scheme on the Ag₃PO₄/g-C₃N₄ nanocomposites. During the photocatalytic reactions, Ag⁰ could be formed through the reduction of Ag₃PO₄ nanocomposites by the photoexcited electron that is deposited on the Ag₃PO₄ nanocomposites surface. In this scheme, the Ag⁰ nanoparticles could act as a charge transmission bridge to form the Ag₃PO₄/g-C₃N₄ nanocomposites Z-scheme system, which is shown in Fig. 1b. The Ag had a relatively low Fermi level (EF=0.4 V vs. NHE), which could serve as the electron acceptor for the photoexcited electrons. The photogenerated electrons in the Ag₃PO₄ nanocomposites could be rapidly transferred to the g-C₃N₄ nanocomposites through Ag⁰ nanoparticles that promote the effective separation of photogenerated electron-hole pairs and suppress the Ag₃PO₄ nanocomposites reduction. Simultaneously, the holes in the VB of the g-C₃N₄ nanocomposites could move to the Ag⁰ nanoparticles and combine with the electrons. The type of charge transmission could efficiently enhance the electron-hole pairs separation and enable the electrons and holes to remain on the CB of the g-C₃N₄ nanocomposites and VB of Ag₃PO₄ nanocomposites, respectively.

On the other hand, the surface plasmon resonance (SPR) endowed in the Ag nanoparticles could effectively promote the visible-light absorption ability of the $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ nanocomposites. Furthermore, under this scheme, as the CB of $\text{g-C}_3\text{N}_4$ nanocomposites (-1.30 eV, vs. NHE) was more negative than the potentials of $\text{O}_2/\cdot\text{O}^{2-}$ (-0.33 eV, vs. NHE), and the VB of Ag_3PO_4 nanocomposites (2.90 eV, vs. NHE) was more positive than the potentials of the $\text{OH}\cdot/\text{OH}^-$ (2.38 eV, vs. NHE) and the $\text{OH}\cdot/\text{H}_2\text{O}$ (2.72 eV, vs. NHE), the photogenerated electrons on the CB of $\text{g-C}_3\text{N}_4$ nanocomposites could reduce the O_2 to yield $\cdot\text{O}^{2-}$. The enriched holes on the VB of Ag_3PO_4 nanocomposites could react with the OH^- or H_2O to form $\text{OH}\cdot$ radicals, which is consistent with the trapping experimental results.

2.8 Computational Methods

Theoretical calculations used several quantum mechanics models such as the Hartree–Fock self-consistent field method based on one-electron approximation, the Hubbard–Mott model, [64], introducing the effects of electron correlations on the Hamiltonian, Peierls mechanism, [65], involving electron–phonon interactions, or the density function theory (DFT), [66]. One of the most important parameters with regard to the properties of materials is the bandgap energy (E_g). Generally, the E_g of a semiconductor or an insulator has been found to decrease with increasing temperature. The variation of the fundamental E_g with temperature is very important for both basic science and technological applications.

In fact, for all the mentioned application, a proper assessment of the ionization potential (IP) and electron affinity (EA) as well as the energy gap is crucial, not only as a basic characterization of newly synthesized materials but also to conceive the combination of materials to be used to assemble the device. To cite an example, the energy offsets play a key role in the charge separation in OPVs, [67]. Since the advent of the new electron acceptors, commonly called non-fullerene acceptor (NFA), an intense debate is taking place regarding the need (or not) of an IP offset between the donor and acceptor materials for the charge transfer process when the acceptor is excited by the absorption of a photon, [68]. Additionally, a simplistic comparison of energy levels measured for the isolated materials cannot fully describe the charge transfer process, [69]. Concerning the energy gap, different techniques are used to measure it both as a direct measurement, such as UV-vis absorption, or as an indirect measurement, such as cyclic voltammetry (CV). In CV measurements both the reduction and oxidation processes are accessible so that the energy gap will be defined as the difference between the reduction and oxidation potentials multiplied by the fundamental electron

charge. Finally, the energy gap can be evaluated by spectroscopic measurements if one has access to ultraviolet photoelectron spectroscopy (UPS), [70], to directly measure the HOMO energy and inverse photoemission spectroscopy, [71], to probe the LUMO energy (then the energy gap is determined by the HOMO–LUMO difference).

Regarding data correlation, there is little consensus in the literature on how the energy gap determined through reflection electron energy loss spectroscopy (REELS) is physically related to the ones determined through other methodologies, such as CV, UV-vis, or photoemission. In optical measurements, for instance, the energy gap is the lowest incident energy for photon absorption, i.e., the onset of the absorption band. In this case, there is an additional information due to the interaction between the electron and the hole (exciton), which should affect the gap obtained through this method. The exciton binding energy may range from few meV to 1.5 eV depending on the material, [72].

Theoretical estimation of energy gaps also has challenges of its own. It can be determined as an energy difference between the frontier orbitals (HOMO and LUMO), which is analogy to the photoemission assessment of the gap. It can also be determined by the difference between the calculated redox potential obtained by properly preparing the ionic states and computing all the thermodynamic contributions to the Gibbs free energy, [73], which should be more comparable to CV based measurements. Another way is to calculate the energy of the first electronic excitation via time-dependent calculation which is the theoretical analogy of a UV-vis measurement. According to our experience, a comparative analysis of these quantities is not often seen in the literature.

Besides the non-trivial correlation of those different techniques commonly used to probe the energy gap, a lack of standardized nomenclature is also a clear issue. Usually, the terminology bandgap is used, perhaps borrowed from the inorganic semiconductor field. This sounds inappropriate for organic semiconductors as for most of them the intermolecular interaction is rather weak, resulting in more molecular-like electronic structure without the formation of bands. In those cases, the term energy gap is more appropriated. Another point is the proliferation of many specifications associated to the term “gap” like transport gap, optical gap, and electrochemical gap, which raises an important question on which of them should be used to describe a general physical process or what is the meaning of them. That is a crucial discussion since those terms do not denote simple nomenclature differences, but they represent distinct physical concepts that are related to specific information about the energetics of the material. These subtle differences should be considered for a sound

interpretation of the desired physical/chemical phenomena.

2.8.1 Density Functional Theory (DFT)

The redox potential and the Gibbs free energies associated to oxidation and reduction processes were also assessed theoretically by means of DFT. The procedure to obtain the Gibbs free energy variation, associated to the oxidation and reduction reactions for the redox pair $P^+/P^0(E_{ox})$ and $P^0/P^-(E_{red})$ was as follows: First the structures were optimized using M06, [74], as exchange–correlation functional and 6-311++G(d,p) as basis-set, [75], followed by frequency calculations to get the Gibbs free energies for the neutral and ionic species. The Gibbs free energy was calculated as Eq. (1):

$$G_{solv} = E_{elect} + E_{ZPE} + PV + U_{298} - TS_{298} \quad (1)$$

where E_{elect} stands for the total energy of the molecule, E_{ZPE} for the zero-point energy and the last two terms represents the finite temperature contribution to the internal energy and the entropic contribution.

The solvation free energies were introduced by using Born–Harber thermodynamic cycle using the dichloromethane. Then, the theoretical electrochemical energy gap (EE^{Calc}_G) was obtained through is Eq. (2):

$$EE^{Calc}_G = E_{red} - E_{ox} \quad (2)$$

Additionally, the HOMO–LUMO energy gaps (EE^{SCF}_G) were obtained directly from self-consistent field DFT calculations.

Finally, the electronic transitions were calculated within the TD-DFT framework, by considering the first 100 singlet electronic transitions at the same theory level described before. These calculations provided the optical energy gap (OE^{Calc}_G) by considering the energy of the first electronic transition. All the calculations were performed using the Gaussian16 code, [74].

Essentially it classifies the gaps in two major groups: [77], (i) The first group is formed by the techniques that quantifies the optical gaps (E_{opt}) (Fig. 2). Here it corresponds to the experimental gaps given by Reflection Electron Energy Loss Spectroscopy (REELS) and UV-vis and the theoretical gap calculated by TD-DFT (OE^{Calc}_G). The methods in this group are characterized by very fast electronic transitions so that the geometry of the molecules is essentially frozen (vertical transition) during the gap quantification. (ii) The second group is constituted by the techniques that evaluate the fundamental gap (E_{fund}). Here it corresponds to the cyclic voltammetry measurements and the theoretical gap (EE^{Calc}_G). The methods in this group are characterized by slow adiabatic processes that allow nuclear relaxation.

* Figure 2 can be found in the Appendix section.

Fig. 2 can be used as a guide to clarify the basic physics behind each kind of energy gap, and it will be very helpful for the discussions below. The basic distinction illustrated in this scheme should always be remembered before any direct inference from the numerical results reported in the next section.

2.9 Electronic Structures and Optical Analysis

The theoretical basis of optical properties results from Maxwell's equations. From optical spectra, the complex dielectric function $\varepsilon(\omega)$ is derived, [78], in Eq. (3):

$$\varepsilon(\omega) = \varepsilon_1 - i\varepsilon_2 \quad (3)$$

where ω is angular frequency of light ($\omega=2\pi\nu$), ε_1 and ε_2 represent real and complex parts of ε , and i is the imaginary unit, in Eq. (4) and in Eq. (5).

$$\varepsilon_1 = n^2 - \kappa^2 \quad (4)$$

and

$$\varepsilon_2 = 2n\kappa \quad (5)$$

where n and κ are real and imaginary parts of the refractive index.

Measurement of light absorption is one of the most important techniques used to determine the optical properties of solids. In absorption measurements, the intensity of light ($I(d)$) after it has travelled through a certain thickness of a material is compared with the incident intensity (I_0), thereby defining the absorption coefficient (α) is shown in Eq. (6):

$$I(d) = I_0 \exp[-\alpha(\omega)d] \quad (6)$$

The dependence of the absorption coefficient on frequency is shown in Fig. 3.

* Figure 3 can be found in the Appendix section.

Since $I(d)$ depend on the square of the field variables, it immediately follows that in Eq. (7):

$$\alpha(\omega) = 2 \frac{\omega\kappa}{c} = 4 \frac{\pi\kappa}{\lambda} \quad (7)$$

where the factor of 2 results from the definition of $\alpha(\omega)$ in terms of light intensity, which is proportional to the square of the optical fields. This expression entails that the absorption coefficient is proportional to $\sim \kappa(\omega)$, the imaginary part of the complex index of refraction

(extinction coefficient), so that κ is usually associated with power loss.

It can be concluded from Eq. (4), Eq. (5) and Eq. (7) that either set- $(\varepsilon_1, \varepsilon_2)$ or (n, α) -represents the wavelength-dependent constants characterizing the optical properties of a studied solid. Many efforts have been devoted to the determination of the refractive index (n), but there is so far no universal approach. Various assumptions were used in these methods, and the results are often subjective/debatable and ambiguous.

Parameter (n) decreases with wavelength. This dependence may be verified using the theoretical equation proposed by Cauchy, [79], in Eq. (8):

$$n(\lambda) = A + \frac{B}{\lambda^2} \quad (8)$$

where A and B are independent of λ .

The experimental points are consistent with the theory postulated by Cauchy. The analysis of the dependence of the absorption coefficient on light frequency is very significant from the view point of the semiconducting properties of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites and its subsequent areas of application. Generally, the frequency dependence of the absorption coefficient ($\alpha(\omega)$) is rather different for various physical processes which occur during the interaction of light with the solid. In particular, the following cases can be observed, [78]: 1. Free carrier absorption; (a) typical semiconductor is Eq. (9):

$$\alpha(\omega) \sim \omega^{-2} \quad (9)$$

(b) metals at low frequencies are shown in Eq. (10):

$$\alpha(\omega) \sim \omega^{\frac{1}{2}} \quad (10)$$

2. Direct interband transition (conservation of crystal momentum): (a) allowed transition is Eq. (11):

$$\alpha(\omega) \sim \frac{(\hbar\omega - E_g)^{\frac{1}{2}}}{\hbar\omega} \quad (11)$$

(b) forbidden transition is shown in Eq. (12):

$$\alpha(\omega) \sim \frac{(\hbar\omega - E_g)^{\frac{3}{2}}}{\hbar\omega} \quad (12)$$

3. Indirect interband transition (change in crystal momentum); (a) allowed transition is shown in Eq. (13):

$$\alpha(\omega) \sim \frac{(\hbar\omega - E_g \pm \hbar\omega_{phonon})^2}{\hbar\omega} \quad (13)$$

(b) forbidden transition is shown in Eq. (14):

$$\alpha(\omega) \sim \frac{(\hbar\omega - E_g \pm \hbar\omega_{phonon})^3}{\hbar\omega} \quad (14)$$

The $\hbar\omega_{phonon}$ factor is generally omitted in Eq. (13) and Eq. (14) because of the fact that phonon energy is several times lower than the energy of electron transition.

Eq. (11), Eq. (12), Eq. (13), and Eq. (14), known as Tauc equations, are applied to determine the bandgap (E_g) of semiconductors. Fig. 4 shows the mechanisms of electron interband transition for direct and indirect semiconductors.

* Figure 4 can be found in the Appendix section.

A direct transition corresponds to the photon-electron interaction process in which the k-vector does not change. The crystal momentum of electrons and holes is the same in both the CB and the VB. In an indirect transition photon, electron and phonon of the lattice take part. This process is accompanied by a change in the k-vector. The allowed transitions remain in agreement with particular selection rules, assuming a dipole model. On the other hand, if this model is not valid, the transition is called forbidden. More complex models can then be taken into account (involving, for instance, a magnetic dipole, electric quadrupole, etc.).

Optical transmittance and reflectance spectra were measured over a wide wavelength range from 180 to 3200 nm with a Lambda 19 Perkin-Elmer double beam spectrophotometer equipped with a 150 mm integrating sphere. The reflectance (R), transmittance (T) and absorbance (A) spectra recorded for one of the thin films were determined for series 1, series 2 and series 3. The transparency region of Ag@Ag₃PO₄/g-C₃N₄ nanocomposites is limited by the fundamental absorption edge at ca. 1000 nm. The reflectance values vary in the range of 10–20% for the Series 1 sample (mostly amorphous), in the range of ca. 0–10% for the Series 2 and 3 samples (crystalline). The observed non-monotonic plots of R , T and A may result from additional absorption bands due to the departure from stoichiometry, [80]. The absorption coefficient (α) and photon energy were determined from the following equations are Eq. (15) and Eq. (16):

$$\alpha = \frac{1}{d} \ln \frac{1-R}{T} \quad (15)$$

$$E_{photon}[eV] = \hbar\omega = \frac{1240}{\lambda[nm]} \quad (16)$$

where d represents film thickness. One of the crucial parameters used to evaluate a semi conductor's properties is the bandgap (E_g). The bandgap of a semiconductor can be determined from experimentally

measured transmittance T and reflectance R within the range of fundamental absorption using the following Tauc equation is Eq. (17):

$$(\hbar\omega\alpha)^{\frac{1}{n}} = A(\hbar\omega - E_g) \quad (17)$$

where the A coefficient is constant and n , according to Eq. (11), Eq. (12), Eq. (13) and Eq. (14), assumes values $1/2$, $3/2$, 2 and 3 for direct allowed (DA), direct forbidden, indirect allowed and indirect forbidden transitions, respectively.

The absorption coefficient data experimentally determined for the Series 2 thin film in the coordinate system of $(\alpha\hbar\omega)^{1/n}$ versus $\hbar\omega$ for $n = 1/2$, $3/2$, 2 and 3 , respectively. The bandgap was determined by extrapolating the linear part of the best fit of $(\alpha\hbar\omega)^{1/n}$ vs. $\hbar\omega$ to $\alpha\hbar\omega = 0$. The values of E_g were obtained from the $\hbar\omega$ axis intercepts. Similar plots were computed for the other two Ag@Ag₃PO₄/g-C₃N₄ nanocomposites samples: Series 1 and Series 3.

The analysis of spectrometric results presented in suggests that Ag@Ag₃PO₄/g-C₃N₄ nanocomposites thin films undergo both direct and indirect transitions. However, it is not possible to decide which type of the electron interband transition is predominant in this case. Based on the following evidence, agreement with theoretical band calculations, [81], agreement with recent reports on single crystals, [82], agreement with recent experimental studies based not only on spectrophotometric measurements such as photoluminescence and ellipsometry, [83], the DA transition can be considered the most probable. The best agreement with the theoretically predicted dependence is observed for the DA transition.

The main controversy has been over the ordering of the components of the trigonally split t_{2g} band. Several band schemes have been suggested, [84]. A trigonal distortion causes the splitting of the t_{2g} orbital into a non-degenerate a_{1g} and a doubly degenerate e''_g orbital, [85].

Different procedures to determine the UV-vis optical gap were considered, such as the onset absorption edge, [86], and Tauc plot, [87]. When using the absorption onset edge method, the UV-vis optical gap (OE_G) can be achieved from the offset wavelength (ledge) derived at a low energy absorption band, estimated according to Eq. (18):

$$OE_G(eV) = \frac{1240}{\lambda_{edge}(nm)} \quad (18)$$

By using the Tauc plot method, the OE_G is determined through a linear extrapolation of the observed trend in the spectral dependence of $(\alpha h\nu)^{1/2}$ which intercepts the abscissa axis giving by the photon energies $h\nu$ following the relation, [88], is Eq. (19):

$$(\alpha h\nu)^{1/2} \propto [h\nu - OE_G] \quad (19)$$

where α is the absorption coefficient and $h\nu$ is the photon energy. The OE_G for the three porphyrins are shown in Eq. (19).

As expected, the thin film spectra displayed a redshift in the absorption, when compared to the spectra measured in solution, as well as broadening of the peaks because of solid-state effects as sociated top-stacking and formation of aggregates. For this reason, the OE_G is lower for the films than in solution. Regarding the two different methods (absorption onset and Tauc plot), one can see that they are equivalent since their application only result in minor variations of OE_G . As one could anticipate, the OE_G is slightly smaller than the EE_G . As a matter of fact, this is one important point to be discussed. The EE_G and OE_G are two different quantities in essence since the first is an optical gap whereas the second is a fundamental gap.

2.9 Kinetic Study

The most common kinetic model used for the degradation of organic pollutants is the Langmuir–Hinshelwood equation. This model describes the evolution of concentration of pollutants with time, $C(t)$ (mg/l), in terms of a differential equation, [89], is seen in Eq. (20):

$$C'(t) = - \frac{k_r K_e C(t)}{1 + K_e C(t)} \quad (20)$$

The catalytic reaction may be separated in three different reactions, each with its characteristic equilibrium constant, k_l for adsorption, k_{-l} for desorption and k_r for the reaction that we want to activate. The ratio k_r is always positive, since it is defined as a quotient of powers of concentrations. The global reaction rate r may be written as seen in Eq. (21):

$$r = k_r C_{AS} = k_r \theta C_S \quad (21)$$

where, C_A : Concentration of adsorbate (mol/m³); C_{AS} : Surface concentration of occupied sites (mol/m²); C_S : Surface concentration of total sites (occupied by adsorbate or not) (mol/m²); and θ : Surface coverage; fraction of occupied sites C_{AS}/C_S . When the steady state is reached in Eq. (22):

$$\frac{dC_{AS}}{dt} = 0 \quad (22)$$

Then, in Eq. (23):

$$k_1 C_A C_S - k_{-1} C_A C_{AS} - k_r C_{AS} - k_{-1} C_{AS} = 0 \quad (23)$$

where, the different terms refer to the different processes taking place: $k_1 C_A C_S$, adsorption of adsorbates onto all sites; $k_1 C_A C_{AS}$, adsorption taking account that only empty sites are available for adsorption; $k_r C_{AS}$, reaction between adsorbate and sites; and $k_{-1} C_{AS}$, desorption. In terms of coverage $\theta = C_{AS}/C_S$, we can rewrite the equation as Eq. (24):

$$\theta = \frac{k_1 C_A}{k_1 C_A + k_{-1} + k_r} \quad (24)$$

Considering that in steady state $r = k_r \theta C_S$ and as seen in Eq. (25):

$$r = \frac{k_1 k_r C_A C_S}{k_1 C_A + k_{-1} + k_r} \quad (25)$$

Two scenarios in terms of the limiting step. If the limiting step is the adsorption (Eq. 26):

$$k_r \gg k_1 C_A; k_{-1} \rightarrow r \approx k_1 C_A C_S \quad (26)$$

If the limiting step is the reaction of adsorbed species, and setting $K_e = k_1/k_{-1}$ (which is also positive as a quotient of positive ratios), we obtain the equation of Langmuir isotherms (Eq. 27):

$$k_r \ll k_1 C_A; k_{-1} \rightarrow r \approx \frac{K_1 k_r C_A C_S}{K_1 C_A + 1} \quad (27)$$

Now, adsorption and desorption must be considered for both species and the corresponding equilibrium constants will be k_1 and k_{-1} for A, k_2 and k_{-2} for B, and k_r for the reaction towards the final products, as in the simple Langmuir case. The reaction rate will be Eq. (28):

$$r = k_r \theta_A \theta_B C_S^2 \quad (28)$$

Following the same reasoning as for the Langmuir isotherm is Eq. (29):

$$\theta_A = \frac{k_1 C_A \theta_E}{k_{-1} + k_r C_S \theta_B} \quad (29)$$

where, the fraction of empty sites, θ_E so that is Eq. (30):

$$\theta_A + \theta_B + \theta_E = 1 \quad (30)$$

The probability that two adsorbates A and B adsorb on adjacent sites is low. Then, considering that the adsorption is the limiting step for the global reaction, it follows that:

$$\begin{aligned} \theta_A &= K_{e,1} C_A \theta_E \\ \theta_B &= K_{e,2} C_B \theta_E \quad \text{being } K_{e,i} = \frac{k_i}{k_{-i}} \end{aligned}$$

and is seen in Eq. (31):

$$r = k_r C_S^2 \frac{K_{e,1} K_{e,2} C_A C_B}{(1 + K_{e,1} C_A + K_{e,2} C_B)^2} \quad (31)$$

This expression in two limiting cases. The term CA will be denoted by C; and $K_{e,1}$ will be simplified to K_e . Finally, the Langmuir–Hinshelwood equation can be rewritten as follows (Eq. 32):

$$\frac{dC}{dt} = -r = -\frac{k_r K_e C}{1 + K_e C} \quad (32)$$

where k_r (mg/l.min) is the reaction constant, K_e is the adsorption constant of the reactant (l/mg) and C the reactant (pollutant) concentration. Two standard approximations can be made:

For $K_e C \ll 1$, this equation may be simplified to an apparent first-order equation in Eq. (33):

$$\frac{dC}{dt} = -k_{app} C \rightarrow C = C_0 e^{-k_{app} t} \quad (33)$$

and, k_{app} may be easily determined from the slope of the graph $\ln(C_0/C)$ versus t .

• For $K_e C \gg 1$, the equation can be simplified to a zeroth-order equation in Eq. (34):

$$\frac{dC}{dt} = -k_r \rightarrow C = C_0 - k_r t \quad (34)$$

The main disadvantage of approximating in these ways is the impossibility of obtaining these two constants, k_e and k_{app} , at the same time. Assuming that the concentration of pollutant is a continuous function, its derivative is also continuous for all $t > 0$ by virtue of the Langmuir–Hinshelwood kinetics equation and the non-negativeness of C. Joining the initial condition, it can be checked that the function is seen in Eq. (35):

$$C(t) = \frac{1}{K_e} W(K_e C_0 e^{K_e(C_0 - k_r t)}) \quad (35)$$

satisfies the Langmuir–Hinshelwood kinetics equation with initial condition $C(0) = C_0$. $W(x)$ is the principal branch of the Lambert function. This is an analytical, monotone injective defined as the inverse of $f(x) = xe^x$, [90].

As the approximations of Eq. (33) and Eq. (34) rely on the value of $K_e C$ versus 1, let us calculate the solution of the equation $K_e C(t) = 1$. This value is the intersection of the red line of Fig. 1 with the Lambert function graph. The result is as follows in Eq. (36):

$$t_c = \frac{1}{k_{app}} (K_e C_0 + \ln\{K_e C_0\} - 1) \quad (36)$$

Table 1 summarizes the mathematical formulation of the Langmuir-Hinshelwood kinetics problem and its approximations yielding zeroth-order and first-order regimes, their respective solutions and the assumptions made to arrive at them.

* Table 1 can be found in the Appendix section.

After all, the solution C described by the W function is the generalization of the first order or zeroth-order regime depending on the value of $K_e C(t)$. The more we approach the assumptions validating a certain regime, the more the values of k_{app} (for first order) and k_r (for zeroth order) obtained from the general solution and the approximated solution should coincide, as they are the limit cases of it. A small relative error between these constants might be an indicator of how close we are to a particular regime, but the main test for ascribing an experiment to a regime should be the calculation of the critical time, as it is a direct translation of the value $K_e C(t)$. Similarly, other nonphysical results, such as obtaining negative k_r and K_e ratios in a particular regime, would be indicative for discarding it.

2.10 Measurements of Transmitted and the Reflected Photons

The transmitted and the reflected photons and ambient dose equivalent (Sv/photon) were evaluated by Monte Carlo simulation (PHITS code, [18]) for several commonly used shielding materials. This outcome enabled us to shield properly the photons that transmitted and reflected by the material in our facility. For verification of our Monte Carlo code with theory and literature data, we calculated the percentage of transmitted photon for all the main photon's interaction, such as photoelectric absorption, Compton scattering (including Rayleigh scattering), and pair productions were considered in our calculation. The scattered photons that penetrate the material were ignored for comparison with the attenuation coefficients generated by XCOM, [19]. For verification of our Monte Carlo code with theory and literature data, we calculated the percentage of transmitted photon from for single-photon energy of 400 keV photons.

2.11 Relative Reactivity Index

The hard soft acid-base (HSAB) principles classify the interaction between acids and bases in terms of global softness. In last few years the reactivity index methodology is well established and had found its application in a wide variety of systems. The electronegativity χ , defined by Mulliken as the average of ionization potential I and electron affinity A , as seen in Eq. (37):

$$\chi = \frac{1}{2(I+A)} \quad (37)$$

It is such a parameter; it is a useful measure of the tendency of a species to attract electrons. Another such conception is the idea of hardness or softness, introduced by Pearson in studying acid-base chemical reactions of the type $A + B \rightarrow A/B$, where A , the acceptor of electrons, is the acid, B , the donor of electrons, is the base. Acids and bases are classified as hard or soft. The principle of hard and soft acids and bases states that hard acids prefer to react with hard bases and soft acids prefer to react with soft bases (both thermodynamically and kinetically). This principle has been valuable for classifying a wide variety of chemical facts. Thus, the electronegativity χ has been identified as the negative of the chemical potential μ , which is the Lagrange multiplier in the Euler-Lagrange equation in DFT, and in Eq. (38):

$$\mu = (\delta E / \delta N) v(r) = -\chi \quad (38)$$

where, E is the total electronic energy, N is the number of electrons, and $v(r)$ is the external electrostatic potential an electron at r feels due to the nuclei. Mulliken's formula $-1/2(I+A)$ is no more than the finite-difference approximation for Eq. (37).

Which, has the finite-difference approximation $I - A$. It is remarkable that chemists sensed the importance of the quantities and before their quantitative definitions as first and second derivatives of the E versus N curve were realized. The hardness/softness/acid/base principle has been derived using Eq. (38) as the definition of hardness. On the other hand, the frontier electron densities proposed by Fukui are local properties that depend on r ; they differentiate one part of a molecule from another and serve as reactivity indices. In density functional theory, hardness (η) is defined as, [91], in Eq. (39):

$$\eta = \frac{1}{2} (\delta^2 E / \delta N^2) v(r) = \frac{1}{2} (\delta \mu / \delta N)_v \quad (39)$$

Where E is the total energy, N is the number of electrons of the chemical species and the chemical potential. The global softness, S , is defined as the inverse of the global hardness, η , and shown in Eq. (40):

$$S = \frac{1}{2\eta} = (\delta N / \delta \mu)_v \quad (40)$$

Using the finite difference approximation, S can be approximated as defined in Eq (41):

$$S = \frac{1}{(IE - EA)} \quad (41)$$

where, IE and EA are the first ionization energy and electron affinity of the molecule, respectively. The Fukui function $f(r)$ is defined by, [92], in Eq. (42):

$$f(r) = [\delta\mu/dv(r)]_N = [\delta\rho(r)/\delta N]_v \quad (42)$$

The function ' f ' is thus a local quantity, which has different values at different points in the species. Since $\rho(r)$ as a function of N has slope discontinuities, Eq. (37) provides the following three reaction indices, [92]:

$$f^-(r) = [\delta\rho(r)/\delta N]_v^- \text{ (governing electrophilic attack)}$$

$$f^+(r) = [\delta\rho(r)/\delta N]_v^+ \text{ (governing nucleophilic attack)}$$

$$f^0(r) = \frac{1}{2}[f^+(r) + f^-(r)] \text{ (for radical attack)}$$

In a finite difference approximation, the condensed Fukui function, [91], of an atom, say x , in a molecule with N electrons are defined as Eq. (43):

$$f_x^+ = [q_x(N+1) - q_x(N)] \text{ (for nucleophilic attack)} \quad (43)$$

$$f_x^- = [q_x(N) - q_x(N-1)] \text{ (for electrophilic attack)}$$

$$f_x^0 = [q_x(N+1) - q_x(N-1)]/2 \text{ (for radical attack)}$$

where q_x is the electronic population of atom x in a molecule. The local softness $s(r)$ can be defined as Eq. (44):

$$s(r) = (\delta\rho(r)/\delta\mu)_v \quad (44)$$

Eq. (39) can also be written as Eq. (45):

$$s(r) = [\delta\rho(r)/\delta N]_v [\delta N/\delta\mu]_v = f(r)S \quad (45)$$

Thus, local softness contains the same information as the Fukui function $f(r)$ plus additional information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner, as stated in HSAB principle. Atomic softness values can easily be calculated by using Eq. (40), namely as seen in Eq. (46):

$$s_x^+ = [q_x(N+1) - q_x(N)]S \quad (46)$$

$$s_x^- = [q_x(N) - q_x(N-1)]S$$

$$s_x^0 = S[q_x(N+1) - q_x(N-1)]/2$$

We further explained the interaction energy scheme as follows. This is known that A & B interacts in two steps: (1) interaction will take place through the equalization of chemical potential at constant external potential and (2) A and B approach the equilibrium state through changes in the electron density of global system generated by making changes in the external potential at constant chemical potential. That means within DFT we can write as seen in Eq. (47):

$$\Delta E_{inter} = E[\rho_{AB}] - E[\rho_A] - E[\rho_B] \quad (47)$$

where, ρ_{AB} , ρ_A , ρ_B are the electron densities of the systems AB at equilibrium and of the isolated systems A and B , respectively. Or in terms of the potentials, we can write as Eq. (48), Eq. (49) and Eq. (50):

$$\Delta E_{inter} = \Delta E_v + \Delta E_\mu \quad (48)$$

where,

$$\Delta E_v = -1/2[(\mu_A - \mu_B)^2/(S_A + S_B)](S_A S_B) \quad (49)$$

$$\Delta E_\mu = -1/2 N_{AB}^2 k[1/(S_A + S_B)] \quad (50)$$

N_{AB} total no. of electrons, k the proportionality constant between S_{AB} and $S_A + S_B$, product of N^2 and K is λ , as shown in Eq. (51):

$$\Delta E_\mu = (-1/2)\lambda/(S_A + S_B) \quad (51)$$

If the interaction is taking place through j site of A , is seen in Eq. (52):

$$\lambda_{Aj} = q_{Aj}^{eq} - q_{Aj}^0 \quad (52)$$

Where, q_{Aj}^{eq} is density of j^{th} atom of A in complex AB & q_{Aj}^0 is the density in isolated system. This new definition proved to be more accurate while proposing the interactions, in compared to the well-established interaction energy.

We have plotted the binding energy per atom vs. cluster size. The binding energy per atom is calculated using the expression is in Eq. (53):

$$EB = [ET - mE_{atom}]/m \quad (53)$$

where, m is the number of atoms present in the Ag cluster.

The binding energy for metals over the $g\text{-C}_3\text{N}_4$ nanocomposites surface is calculated as the following is Eq. (54):

$$E_{binding} = (ME_{metal} + E_{slab} - E_{total})/M \quad (54)$$

Where, E_{binding} is the binding energy per metal atom binded to the alumina surface, E_{metal} is the energy of isolated metal atom, M is the number of metal atoms, E_{Slab} is the energy of the slab and E_{total} is the total energy of the metal adsorbed alumina system. Hence, the binding energy is defined as positive if the total energy decreases when the metal atom is brought from infinity and placed onto the surface. We have as well calculated the interaction energy (λ) in terms of which is based on reactivity at a certain external potential within a specific chemical potential.

3 Results and Discussions

3.1 XRD Results

The results of XRD analysis of as prepared for g-C₃N₄ NCs, GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, GO and Ag@Ag₃PO₄ nanocomposites, respectively, after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) (Fig. 5).

* Figure 5 can be found in the Appendix section.

The characterization peaks of g-C₃N₄ nanoparticles were observed at 2θ values and corresponding of 28.12° (004) (Fig. 5). The XRD patterns of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites showed the 2θ values and corresponding of 27.50° (003), 33.43° (007), 37.26° (112) and 55.19° (133), respectively (Fig. 5). The XRD peaks of GO NPs obtained at 2θ values and corresponding of 34.18° (100), 37.85° (002), 54.67° (101) and 58.14° (103), respectively (Fig. 5). The XRD peaks of Ag@Ag₃PO₄ nanocomposites obtained at 2θ values and corresponding of 33.78° (100), 37.55° (002), 53.47° (101), 54.92° (120) and 58.84° (103), respectively (Fig. 5).

There are two characteristic peaks at 13.1° and 27.5° in the XRD pattern of g-C₃N₄ nanocomposites, which correspond to the (100) and (002) planes, respectively, (JCPDS files: 87-1526). All diffraction peaks of the as-prepared Ag₃PO₄ coincide with the cubic Ag₃PO₄ nanocomposites (JCPDS No. 06-0505). The Ag₃PO₄/g-C₃N₄ nanocomposites exhibited diffraction peaks corresponding to g-C₃N₄ and Ag₃PO₄ nanocomposites. By increasing the content of the Ag₃PO₄, its diffraction peaks gradually intensified at the expense of the g-C₃N₄ peaks, thus reflecting their contents in the Ag₃PO₄/g-C₃N₄ nanocomposites hybrids. The XRD analysis also confirmed the high purity of the Ag₃PO₄ and g-C₃N₄ nanocomposites.

3.2 SEM Results

The morphological features of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites were characterized through SEM

image and was also performed to investigate the composition of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites after photodegradation process of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) (Fig. 6).

* Figure 6 can be found in the Appendix section.

The morphology and microstructure of Ag₃PO₄/g-C₃N₄ nanocomposites were investigated by SEM. As shown in Fig. 6, the C, N, O, P, and Ag elements were all detected in the Ag₃PO₄/g-C₃N₄ nanocomposites by the element mapping results, which indicated Ag₃PO₄ nanocomposites were deposited on the surface of g-C₃N₄ nanocomposites and the heterojunction was formed.

3.3 TEM Results

The TEM images of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites were observed in micromorphological structure level after photodegradation process of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) (Fig. 7).

* Figure 7 can be found in the Appendix section.

The TEM images of g-C₃N₄ and Ag₃PO₄/g-C₃N₄, nanocomposites, respectively. According to previous research, the light part is g-C₃N₄ nanocomposites, and the dark part is Ag₃PO₄ nanocomposites which further demonstrates that Ag₃PO₄ nanocomposites was well-deposited on the surface of g-C₃N₄. The TEM images of Ag₃PO₄, Ag₃PO₄/g-C₃N₄ (20%), Ag₃PO₄/g-C₃N₄ (40%) nanocomposites are shown in Fig. 7. With the increasing ratio of Ag₃PO₄ nanocomposites in the composites, the size of Ag₃PO₄ nanocomposites increased slightly following an aggregation.

3.4 DRS Results

The DRS spectrums of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, Ag@Ag₃PO₄ nanocomposites, GO and g-C₃N₄ nanocomposites were obtained after photodegradation process of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) (Fig. 8).

* Figure 8 can be found in the Appendix section.

Compared with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites (Fig. 8, black curve), Ag@Ag₃PO₄ nanocomposites (Fig. 8, green curve), GO nanoparticles (Fig. 8, blue curve) and g-C₃N₄ nanocomposites (Fig. 8, red curve) was exhibited a strong photo-degradation in the UV region with 275 nm, 230 nm, 250 nm and 400

nm respectively. The band gaps of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, Ag@Ag₃PO₄ nanocomposites, GO nanoparticles and g-C₃N₄ nanocomposites might be 4.51 eV, 5.39 eV, 4.96 eV and 3.10 eV, respectively.

The optical properties of the prepared GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites were measured with UV-vis DRS. The absorption edge of pure g-C₃N₄ and Ag₃PO₄ is approximately 460 and 505 nm, respectively, indicating that both the g-C₃N₄ and Ag₃PO₄ could absorb solar energy. Based on the Kubelka-Munk function, the plots of $(Ah\nu)^{1/2}$ vs. $h\nu$ for g-C₃N₄, Ag₃PO₄, and Ag₃PO₄/g-C₃N₄ nanocomposites (30%) are shown in Fig. 8. The indirect band gap energies of the g-C₃N₄ and Ag₃PO₄ are 2.70 and 2.45 eV, respectively, which is consistent with previous results. Compared to g-C₃N₄, the Ag₃PO₄/g-C₃N₄ nanocomposites show an intense and broad background absorption in the visible light region from 300 to 500 nm, which means that the visible-light absorption ability of the Ag₃PO₄/g-C₃N₄ nanocomposites was improved.

3.5 XPS Results

The XPS images of g-C₃N₄ nanocomposites, GO-Ag@Ag₃PO₄ nanocomposites and GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites were observed in micromorphological structure level after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) (Fig. 9).

* Figure 9 can be found in the Appendix section.

Absorption peaks were observed at binding energy of 401.14 eV for g-C₃N₄ nanocomposites (Fig. 9, black spectra), at 420.63 eV for GO-Ag@Ag₃PO₄ nanocomposites (Fig. 9, red spectra) and at 397.82 eV for GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites (Fig. 9, purple spectra), respectively, after photodegradation 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82). The survey spectra of g-C₃N₄ NCs sample exhibited O, N, C element signals. The Ag, O, C and P element signals were attributed to GO-Ag@Ag₃PO₄ NCs, and Ag, O, N, C as well as P element signals belonged to GO-Ag@Ag₃PO₄/g-C₃N₄ NCs, respectively (Fig. 9). Two new forming peaks at 286.6 eV and 288.9 eV belonged to C-O and O=C-O bonds, respectively, because of presence of GO material, [36].

Surface chemical states of the Ag₃PO₄/g-C₃N₄ nanocomposites were studied by XPS. Fig. 9 shows the XPS spectrum of Ag₃PO₄/g-C₃N₄ (30% and Ag₃PO₄ nanocomposites. All signals of C, N, Ag, P, and O₂ were detected in the Ag₃PO₄/g-C₃N₄ nanocomposites, which is consistent with the XRD and DRS results. The typical high resolution XPS spectra of C 1s, Ag 3d, and

P 2d in the composite are shown in Fig. 9. C 1s has two peaks at 284.6 and 287.4 eV that are separately attributed to the adventitious carbon and the sp²-hybridized C of N-C=N in g-C₃N₄ nanocomposites. The Ag 3d_{5/2} and 3d_{3/2} of Ag₃PO₄ nanocomposites were located at 367.8 and 373.8 eV, which are consistent with the value of Ag⁺ in the Ag₃PO₄. The P 2p has a peak at 132.4 eV, corresponding to P⁵⁺ in the Ag₃PO₄ nanocomposites.

3.6 EIS Results

The EIS result of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites after photodegradation process of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) (Fig. 10). The EIS analysis of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites was implied that the size of arc radius was based on the following order: g-C₃N₄ > GO > Ag@Ag₃PO₄ > AGP/CN > GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites.

* Figure 10 can be found in the Appendix section.

Therefore, the prepared GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites indirect Z-scheme showed enhanced surface charge separation and migration. As is well known, photoluminescence (PL) spectroscopy is an effective technology and usually adopted to study transfer and separation efficiency of charge pairs. One semi-conductor was induced by light with no less than the band gap, the electrons in the valence band transferred to the conduction band to be photo-electrons and formation of photo-holes in the valence band. However, a large number of photo-electrons came back to the valence band and then combined with holes.

To better illustrate the separation of photogenerated electrons and holes, EIS and photoelectrochemical measurements were carried out, [93], [94]. EIS was performed to investigate charge migration and interfacial reaction capacity in photocatalytic materials.

3.7 Effect of pH Values during Photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ Nanocomposites

Increasing pH values (3.0, 4.0, 6.0, 7.0, 8.0 and 11.0) were examined during photodegradation process for 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at 400 W UV-vis light power, at 25°C (Fig. 11).

* Figure 11 can be found in the Appendix section.

57.42%, 83.63%, 91.54%, 82.19% and 74.35% photo-removal efficiencies were measured at pH=3.0, pH=4.0, pH=6.0, pH=8.0 and pH=11.0, respectively, after photodegradation process for 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at 400 W UV-vis light power, at 25°C (Fig. 11). The maximum 99.27% photo-removal yield was obtained after photodegradation process for 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at pH=7.0, at 400 W UV-vis light power, at 25°C, respectively (Fig. 11).

With the pH increased in the range of 8.0–11.0, photodegradation efficiency decreased. Excellent photodegradation performance at the optimal pH value of 7.0 was found. The decrease in photocatalytic performance was mainly due to that GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites was partly dissolved in the strongly acidic and base solvent, resulting missing quality of catalyst, [46].

ANOVA test statistics showed that a linear significant regression was detected between pH and PBDE yields until a pH value of 7.0 ($p=0.0065$, $R^2=99$). As the pH was increased from 7.0 to 8.0–11.0, and the PBDE yields decreased. Therefore, it was not found a significant linear regression between pH and PBDE yields for pH values greater than 7.0 ($p=7.89$, $R^2=0.56$).

3.8 Effect of Photodegradation Time during Photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ Nanocomposites

Increasing photodegradation times (30, 60, 90, 120 and 150 min) were operated to photodegradation process for 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at 400 W UV-vis light power, at 25°C (Fig. 12).

* Figure 12 can be found in the Appendix section.

45.74%, 61.13%, 84.49% and 95.01% photo-removal yields were obtained after 30 min, 60 min, 90 min and 150 min, respectively, after photodegradation process for 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at 400 W UV-vis light power, at 25°C (Fig. 12). The maximum 99.58% photo-removal efficiency was observed after 120 min photodegradation time after photodegradation process for 3,4,4',5-

Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at pH=7.0, at 400 W UV-vis light power, at 25°C, respectively (Fig. 12).

ANOVA test statistics showed that a significant linear regression was detected between photodegradation time and PBDE yields until 150 min ($p=0.0064$, $R^2=99$). As the time was increased from 120 min to 150 min the PBDE yields decreased. Therefore, it was not found a significant linear regression between time and PBDE yields after 120 min photodegradation durations ($p=8.99$, $R^2=0.44$).

3.9 Effect of GO-Ag@Ag₃PO₄/g-C₃N₄ NCs Concentrations during Photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ Nanocomposites

Increasing GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites concentrations (2, 4, 6, 8 and 10 mg/l) were examined during photodegradation process for 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at pH=7.0, after 120 min photodegradation time, at 400 W UV-vis light power, at 25°C, respectively (Fig. 13).

* Figure 13 can be found in the Appendix section.

75.05%, 81.43%, 60.51% and 42.37% photo-removal yields were measured after 2 mg/l, 6 mg/l, 8 mg/l and 10 mg/l GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites concentrations, respectively, after photodegradation process for 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at pH=7.0, after 120 min photodegradation time, at 400 W UV-vis light power, at 25°C, respectively (Fig. 13). The maximum 99.64% photo-removal efficiency was obtained at 4 mg/l GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites concentration after photodegradation process for 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at pH=4.0, after 120 min photodegradation time, at 400 W UV-vis light power, at 25°C, respectively (Fig. 13).

It was owing to lower photon adsorption of catalyst was obtained along with initial concentration increasing, which would make less electrons generation during photocatalytic process, [95].

ANOVA test statistics showed that a significant linear regression was detected between GO-

Ag@Ag₃PO₄/g-C₃N₄ and PBDE yields until a GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites concentration of 6 mg/l ($p=0.0045$, $R^2= 99$). As the nanocomposite concentration was increased from 6.0 to 10 mg/l the PBDE yields decreased. Therefore, it was not found a significant linear regression between GO-Ag@Ag₃PO₄/g-C₃N₄ and PBDE yields for nanocomposite concentration greater than 4 mg/l ($p=7.89$, $R^2= 0.56$).

3.10 Langmuir-Hinshelwood Kinetics for PBDE Photodegradations

As aforementioned in Eq. (35), in this study since $K_c C \ll 1$, the Langmuir-Hinshelwood kinetic can be presented as a first-order equation. From this plot k_{app} values for PBDE -81 and PBDE-82 were found as 0.019 min⁻¹ and 0.017 min⁻¹, respectively. Fig. 14 shows the results of plotting experiments with high R^2 values.

* Figure 14 can be found in the Appendix section.

Fig. 14 shows the calculation of transmitted photons as a function of material thickness for a pencil beam of 150 keV photon. From this graph, it can be seen that the percentage of calculated transmitted photon decreased exponentially with increasing thickness of material. Then, the data were fitted with an exponential equation to obtain the value of the linear attenuation coefficient (μ ; cm⁻¹). Overall, the calculated μ value has a good agreement, within 1% with the XCOM as illustrated in Table 2. This indicates that the μ value calculated by the simulation was reliable and verified to be used for the study of photon interactions between radiations and energy within the material.

* Table 2 can be found in the Appendix section.

3.11 Calculated Transmitted Photons versus Ag@Ag₃PO₄/g-C₃N₄ Nanocomposite Concentration

Fig. 15 exhibited the transmitted photons are functions of nanocomposite concentration. From this graph, it can be seen that the percentage of calculated transmitted photon decreased with increasing of Ag@Ag₃PO₄/g-C₃N₄ nanocomposite dose from 2 up to 12 mg/l. Then, the data were fitted with an exponential equation to obtain the value of the linear attenuation coefficient (μ ; cm⁻¹). Overall, the calculated μ value has a good agreement, within 1% with the XCOM. The μ values was found as 1.234 cm⁻¹ and 0.987 m⁻¹ from Fig. 15 for 4 and 20 mg/l Ag@Ag₃PO₄/g-C₃N₄ nanocomposite concentrations. This indicates that the μ value calculated by the simulation was reliable and verified to be used for the study of photon interactions between radiations and energy within the nanocomposite.

* Figure 15 can be found in the Appendix section.

3.12 Transmitted Photon Dose of GO and Ag@Ag₃PO₄/g-C₃N₄ Nanocomposite

The transmitted dose from GO is higher about 5% compared to GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposite. In the case of an Nanocomposite show almost similar ability in photon attenuation as their Z number are close each other (Fig. 16). At 400 keV, the transmitted dose for 4 mg/l GO-Ag@Ag₃PO₄/g-C₃N₄ Nanocomposite is 480 sv/inc/cm²/s while 20 mg/l GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposite has a transmitted photon dose is 320 sv/inc/cm²/s.

* Figure 16 can be found in the Appendix section.

GO-Ag@Ag₃PO₄/g-C₃N₄ has the least amount of transmitted dose among other materials as it has the highest atomic number. As photoelectric effects is more dominant in materials with higher atomic number, it can be trap more photons than other materials. Hence reducing the number of transmitted photons.

3.12 Variation of Reflected Photon Dose versus Incident Photon Energy

Reflected photons are scored as a result of Compton scattering photons with a large angle within the materials. The probability occurs the scattered photons depends on the incident photon energy and the atomic number of the materials. As the reflected scattered photons can be a source of unnecessary additional radiation dose to the patients and workers that may stay inside the irradiation room, or close to the shielding material, therefore it is important to evaluate the reflected photons in terms of their dose and energy.

Fig. 17 shows a graph of reflected dose as a function of incident photon energy for shielding materials. Based on the graph in Figure 4, it can be seen that the reflected dose from all studied materials increased until a maximum then decreased versus increasing of incident photon energy.

* Figure 17 can be found in the Appendix section.

This means that the higher the energy of the incident photon, the lower the amount of photon that can be trapped or absorbed by the shielding materials until a maximum. The highest amount of reflected dose among the materials occurred since low energy photon is unable to penetrate far within the nanocomposite, which means most of photon interactions will occur only at the surface of the nanocomposites. Therefore, the Compton scattered photons could easily exit the nanocomposite material as reflected photons. It was expected that the reflected dose from nanocomposite will be higher for lower incident photon energy. low Z element such as go

and 20 mg/l GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites which commonly used as a shielding material show higher reflected dose among other material, in wide energy range. As the concentration of GO-Ag@Ag₃PO₄/g-C₃N₄ increased to 20 mg/l material increase the intensity of reflected dose, hence a thin layer of suitable material is enough to reduce the backscatter. In conclusion, the intensity of scattered and backscattered radiation is affected by both concentration and the energy of the incident photon.

When photons impinge on shielding materials, most of the incident photon energy is absorbed within the material. The shielding materials must be studied both for its transmitted and reflected photons particularly if the shielding compound has a higher Z element or the source is higher energy photons. From a radiation protection point of view, the reflected photon component is important to be evaluated.

3.13 Quantitative Structure–Reactivity Relationships

We use the well-understood chemical space of PBDE-81 and PBDE-82 as examples to demonstrate the functionality of our approach and the performance of the resulting quantitative structure–reactivity relationships (QSRRs). Our results suggest that it is straightforward to build low-cost QSRR models that are accurate, interpretable, and transferable to unexplored systems within a given scope of application. Moreover, our QSRR approach suggests that Hammett σ parameters are only approximately additive.

Mayr and his team found that the Mayr–Patz equation (Eq. 55) is also valid for many other classes of nucleophiles and electrophiles. To date, reactivity parameters have been determined for 352 electrophiles (E) and 1281 nucleophiles (N, sN), which can be accessed via Mayr’s Database of Reactivity Parameters, [96], [97].

$$\log k (20^\circ \text{C}) = s_N (N + E) \quad (55)$$

Here, E, N, and s_N represent electrophilicity, nucleophilicity, and a nucleophile-specific sensitivity parameter, respectively. Attempts, have been made to determine reactivity parameters by thermochemical calculations based on density functional theory (DFT). However, they have not yet prevailed over the experimental approach also because of accuracy issues. In a recent uncertainty quantification study, [98], we confirmed that the average accuracy of experimental rate constants corresponding to reactions of olefins with PBDE-81 is higher deviation in k below 1 order of magnitude than that achievable with standard DFT calculations. Even high performing functionals result in average barrier height errors of at least 2 kcal/mol, [99], translating to a deviation in k of 1 to 2 orders of

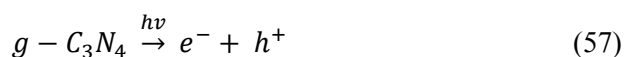
magnitude at 20°C assuming validity of the Eyring equation, [100]. Ultimately, DFT is not suitable for the efficient prediction of the reactivity parameters. This is one reason why data-driven or machine-learning (ML) algorithms have gained much attention in this context as they are capable of yielding fast predictions by interpolating between available data, [101]. In supervised ML, relationships between descriptors (input variables) and targets (output variables) are learned by means of regression (continuous target) or classification (discrete target). Aside from the expensive acquisition of targets (i.e., experimental reactivity parameters), the generation of descriptors can constitute a critical bottleneck in the ML workflow. For instance, previous data-driven studies have mostly relied on quantum molecular properties (QMPs) as descriptors, [102], [103], [104], [105], [106], [107], [108], [109], [110], [111], [112], meaning that each prediction is preceded by quantum chemical (mainly DFT) calculations, which occupy almost 100% of the overall prediction time. This applies less to semiempirical electronic-structure methods, as recently applied in a related context, [113], which can much more efficiently generate QMPs and other electronic descriptors. While QMPs are among the most informative descriptors, [108], we target descriptors that can be both generated quickly and interpreted intuitively. For this purpose, we focus on structural descriptors in this work. Structural descriptors are direct representations of the connectivity/graph or the three-dimensional (3-D) structure of a molecule, [114]. There are two principal types of structural descriptors: General (application-agnostic) descriptors, which are applicable to a broad range of structure classes but rather difficult to interpret. On the other hand, application-specific descriptors are rather simple to interpret but not generalizable to cases outside the domain of application. We are particularly interested in the latter type of descriptors but will investigate the merits and drawbacks of both types. In general, structural descriptors are much higher in dimensionality than QMPs. As a rule of thumb, the greater the dimensionality of a descriptor, the more data are needed to uncover the underlying QSRR. However, the number of reactivity parameters in Mayr’s database is limited. Therefore, we hypothesize that the structural descriptors examined here are too high-dimensional to be directly linked to the relatively small number of available reactivity parameters. To meet this challenge, we propose a two-step workflow for building QSRR models from structural descriptors (Fig. 16). Assume a set of K available reactivity parameters that is too small to build an accurate QSRR model based on a high dimensional structural descriptor. Further, assume that a set of L $\gg$ K reactivity parameters would be necessary to achieve the desired accuracy. Then, if we could

identify a less expensive surrogate quantity that correlates well with the reactivity parameter of interest, it would be possible to build such a twostep QSRR model. However, given a set of M molecules of interest, only $L \ll M$ of which are equipped with QMPs, we have avoided (multiples of) $M - L$ quantum chemical calculations, leading to substantial computational savings.

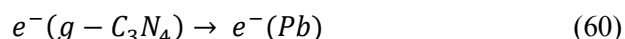
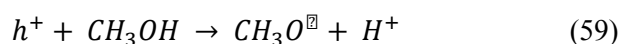
Mechanism for photocatalytic debromination of PBDE-81 on GO-Ag@Ag₃PO₄/g-C₃N₄ was sufficient for the photocatalytic reduction of PBDE-81, and the loading of Ag nanoparticles able a complete debromination of PBDE-81. It is clear that an evident induction period was required for a subsequent debromination of PBDE-81 over GO-Ag@Ag₃PO₄/g-C₃N₄. The presence of an induction period implied that before the PBDE-81 reduction takes place, GO-Ag@Ag₃PO₄/g-C₃N₄ needs time to accumulate electrons for stretching the C-Br bond. Ag has affinity interaction with halogen atom because Ag is an electron rich metal, which results in preferable adsorption of PBDE-81 molecules on the surface of Ag nanoparticles (Eq. 56).



When GO-Ag@Ag₃PO₄/g-C₃N₄ is exposed to visible light irradiation in anoxic atmosphere, g-C₃N₄ is excited to produce holes (h^+) and electrons (e^-) (Eq. 57), then parts of electrons and holes were easy to recombine through light or heat (Eq. 58):

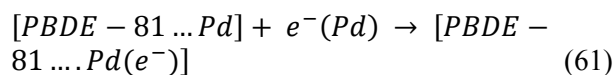


A portion of photogenerated holes is captured by methanol to yield $CH_3O^\bullet$ and H^+ (Eq. 59), [115], while the electrons in conduction band of g-C₃N₄ are transferred to Pd nanoparticles (Eq. 60) and stored there.



PL measurements provide information on the interfacial electron transfer between g-C₃N₄ and Ag nanoparticles. The relative PL intensity was rapidly decreased after Ag nanoparticles were loaded on g-C₃N₄ (data not shown). This is because that the interfacial electrons transfer from g-C₃N₄ to Ag reduced the charge recombination of g-C₃N₄. After the Ag nanoparticles stored enough electrons, the C-Br bond was further stretched as similar as we observed in Ag₃PO₄/g-C₃N₄, and the strong Ag (e^-)-Br interaction would result in the

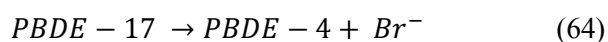
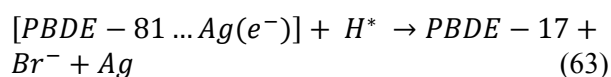
formation of an activated transition complex [PBDE-81 Ag(e^-)] (Eq. 61):



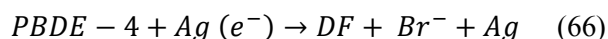
In addition, the loaded Ag nanoparticles would provide interface electron transfer from the metal surface to proton (H^+) generated from methanol (Eq. 59), which leads to the form of active H atom species ($H^\bullet$) on the Ag nanoparticles (Eq. 62).



Subsequently, the active $H^\bullet$ continues to attack the activated transition complex [PBDE-81 Ag(e^-)], which promotes the debromination and hydrogenation of [PBDE-81 Ag(e^-)] to generate PBDE-17, then PBDE-4 (Eqs. 63 and 64).



It is worth noting that the formed PBDE-4 have two routes to produce bromine-free products, which are clarified as DE and DF. In route 1, the PBDE-4 is further reacted with active $H^\bullet$ by the hydrodebromination process (Eq. 65), while the coupling reaction directly occurred on the surface of Ag nanoparticles with rich electrons to generate DF, [116], (Eq. 66):



The generation of active H atom species ($H^\bullet$) and other active species in the photocatalytic system was evidenced by ESR technique. As shown in Fig. 18, the adducts of DMPO- $H^\bullet$ and DMPO- $CH_3O^\bullet$ were observed after an irradiation of 120 min.

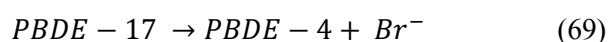
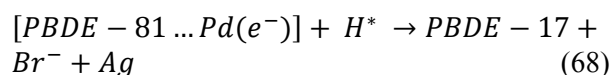
* Figure 18 can be found in the Appendix section.

The ESR spectrum of DMPO- $H^\bullet$ showed characteristic nine peaks with an intensity ratio of 1:1:2:1:2:1:2:1:1, whose splitting pattern is well reproduced by hyperfine splitting constants of $\alpha_N = 16.6$ G and $\alpha_H^\beta = 22.6$ G. In addition, we also got the DMPO- $CH_3O^\bullet$ signal with peak intensities of 1:1:1:1:1:1, which was characteristic of DMPO- $CH_3O^\bullet$ according to the hyperfine splitting constants of $\alpha_N = 15.7$ G and $\alpha_H^\beta = 22.6$ G. Magnetic parameters determined for DMPO- $H^\bullet$ are in good agreement with

those reported in literature, [119], [118], [119]. Especially, the spectrum obtained from experiment was almost perfectly matches the adduct spectrum of DMPO-H* and DMPO-CH₃O*, which confirmed the generation of active H* atom and CH₃O* during the photocatalytic reductive process, Eq. (67):



Subsequently, the active H* continues to attack the activated transition complex [PBDE-81 Ag(e⁻)], which promotes the debromination and hydrogenation of [PBDE-81 Pd(e⁻)] to generate PBDE-17, then PBDE-4 (Eqs. 68 and 69).



It is worth noting that the formed PBDE-4 have two routes to produce bromine-free products, which are clarified as DE and DF. In route 1, the PBDE-4 is further reacted with active H* by the hydrodebromination process (Eq. 70), while the coupling reaction directly occurred on the surface of Ag nanoparticles with rich electrons to generate DF, [116], (Eq. 71):



Indeed, both CH₃OH and H₂O may react with holes to generated H*. In order to identify the source of H*, the reductive degradation of PBDE-81 was carried out by using D₂O instead of H₂O. Figure 19 showed the mass spectra of DE and DF produced with various solvents.

* Figure 19 can be found in the Appendix section.

By comparing with the mass-to-charge ratio (m/z) and peak intensity, the mass spectra of both DE and DF were found to be no obvious change when the H₂O was replaced by D₂O. Therefore, CH₃OH was considered as the prominent hydrogen donors, while H₂O functioned only as a solvent. It roughly contains four steps. In step 1, the strong interaction between Ag nanoparticles and bromine atoms of PBDE-81 form an adsorbed PBDE-81 ([PBDE-81 Ag]). In step 2, the photogenerated electrons in g-C₃N₄ transfer to Ag and GO nanoparticles to form an activated transition complex ([PBDE-81...Ag GO(e⁻)]), and this process require an induction time. In step 3, the methanol molecules react with photogenerated holes to provide H+, thereby forming

active H* on the surface of Ag and GO nanoparticles. In step 4, the [PBDE-81...Ag GO(e⁻)] is attacked by the active H* to generate PBDE-4. In step 5, the formed PBDE-4 is transformed to DE and DF by the hydrobromination process and the coupling reaction on Ag GO nanoparticles, respectively.

Reactivity parameters for M compounds are requested. In step 1, high-dimensional structural descriptors are linked with a small number of QMPs. The training set size of step 1 is L << M. In step 2, the same QMPs are linked to the actual reactivity parameters. The training set size of step 2 is K << L. Step 1 is based on Gaussian process regression (GPR), [120], [121], [122], a powerful nonlinear ML method that we have found to be particularly effective when there are limited data available, [123], [116], [124]. Step 2 is based on multivariate linear regression (MLR), a method that has experienced a revival in physical organic chemistry where MLR models are better known as linear free energy relationships, [125], owing to the work by Sigman and coworkers, [126]. The Sigman-type MLR method was adapted by Orlandi et al., [110], for predicting and understanding Mayr's nucleophilicity parameter N. To facilitate interpretation of results, MLR is additionally applied in step 1 of our workflow (i.e., GPR for prediction, MLR for understanding). In this work, we apply the novel two-step QSRR workflow to a data set of M=3570 PBDE-4, for only K=27 of which an electrophilicity parameter E is available (see Fig. 20 and Table 3).

* Figure 20 can be found in the Appendix section.

* Table 3 can be found in the Appendix section.

At the same time, these 27 systems cover a wide range of reactivity, -10.04 < E < 8.02, spanning almost 20 orders of magnitude. Their electrophilic center, a Br ion, can be tuned by distant substituents. As a result, the reactivity of PBDE ions can be dominantly attributed to electronic effects, leading to unambiguous E parameters. These electrophiles are therefore particularly well suited for building quantitative nucleophilicity scales for a variety of organic compounds, [127]. After an overview of the data and methods used in this work, the potential of our two-step workflow, in terms of real-time reactivity prediction, is evaluated. In particular, the MLR and GPR models are analysed with respect to performance (GPR in step 1, MLR in step 2) and interpretability (MLR in both steps). Finally, we analyse the relationship between Mayr's electrophilicity E and (the sum of) Hammett σ parameters, [128].

Fig. 20 PBDE -81 and 82 scaffold has substituents Y and Z, which are specified in Table 3.

Mayr's database, [96], [97], comprises electrophilicity parameters for, [108], PBDE ions, six of which are annulated and therefore removed for the following analysis. Table 3 show the remaining K=27 electrophiles.

For this study, a combinatorial data set of PBDE derivatives was generated based on the unsubstituted ion, [108]. Its four meta (*m*) and two para (*p*) positions, which are shown in Fig. 20, are suitable substitution sites. By avoiding substitution of the ortho positions, the steric situation at the PBDE ion is preserved, and hence, its electrophilicity is predominantly caused by electronic substituent effects. We considered only substituents of PBDE ions available in Mayr's database (see Table 3), [129], in total: -F, -Cl, -Me, -OMe, -OPh, -dma, -mpa, -dpa, -pyr, -mor, -mfa, -pfa, Br, Cl and -CF₃. Only -Br and -Cl were selected as possible m-substituents to avoid steric hindrance with the substituents, while all of the above-mentioned substituents were selected as possible p-substituents. Next, all possible substitution combinations of these functional groups were generated, leading to $34 \times 142 = 15876$ structures (counting hydrogen as third m-substituent and 14th p-substituent, respectively).

In general, structural descriptors are much higher in dimensionality than QMPs. As a rule of thumb, the greater the dimensionality of a descriptor, the more data are needed to uncover the underlying QSRR. However, the number of reactivity parameters in Mayr's database is limited. Therefore, we hypothesize that the structural descriptors examined here are too high-dimensional to be directly linked to the relatively small number of available reactivity parameters. To meet this challenge, we propose a two-step workflow for building QSRR models from structural descriptors (Fig. 21).

* Figure 21 can be found in the Appendix section.

If structures could be converted into each other by the C2 rotation axis, shown as a gray solid line in Fig. 21, only one of them was kept. In addition, tests have shown that assuming a symmetry axis passing through the bond between the Br ion and the aromatic rings (dashed gray lines in Fig. 21) is a reasonable approximation. The resulting duplicate molecules were removed, as well. The final data set therefore consists of M=3570 structures, in which the K=27 aforementioned reference structures are present.

Schematic description of our two-step workflow for predicting reactivity parameters from molecular structures. In step 2 of the workflow, the relationship between a suitable quantum molecular (QM) property and the reactivity parameter of interest is learned. Since QM properties require expensive quantum chemical calculations, we seek to replace their calculation in step 1 of the workflow. For this purpose, the three

dimensional (3D) molecular structures are initially transformed into machine-learnable descriptors before the relationships between these descriptors and the QM property are learned (Table 4).

* Table 4 can be found in the Appendix section.

The metrics taken into account in this work are specified with respect to N observations $\{y\}$ and corresponding predictions $\{y_i\}$. An observation y_i refers to either the electrophilicity parameter E or a QMP of the i th molecule. The mean values of $\{y\}$ and $\{y_i\}$ are denoted y and y_i , respectively. The root-mean-square error (RMSE) is defined as Eq. (72):

$$RMSE = \sqrt{N^{-1} \sum_{i=1}^N (y - y_i)^2} \geq 0 \quad (72)$$

The $F2B$ split descriptor outranks the other two descriptors in all categories, making it the descriptor of choice for prediction tasks. Consequently, $F2B$ split not only surpasses $F2B1$ in terms of interpretability but also in terms of performance. This finding also holds for CFG versus $F2B1$; with the exception of HOMO, where both descriptors yield the same test set accuracy. Moreover, the $F2B$ split descriptor can reproduce the LUMO energy of benzhydrylium ions exactly (up to the third decimal in R^2), and the corresponding GPR predictions (Fig. 22).

* Figure 22 can be found in the Appendix section.

Closely resemble those of the rMLR model of step 2 (Fig. 23).

* Figure 23 can be found in the Appendix section.

Finally, we would like to know if we really need $M - K = 3543$ systems to obtain a good prediction of E or whether a substantially smaller number L is sufficient to identify a QSRR.

They describe the distribution of electrons within a molecule and play a key role in determining how molecules interact with each other. The Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are particularly important, as they are involved in the formation of new bonds during chemical reactions.

The energy gap between the HOMO and LUMO, also known as the HOMO-LUMO gap, is a significant factor in determining a molecule's reactivity. A smaller HOMO-LUMO gap indicates that a molecule is more reactive, it requires less energy to excite an electron from the HOMO to the LUMO.

Quantum mechanical calculations provide detailed insights into the electronic structure of molecules and

transition states, enabling a deeper understanding of reactivity.

The partial rate factors for debromination based on kinetic measurements are presented in Table 5 along with computed Ea values and alternative re-activity indices (EPN and NBO charges at the re-acting carbon) for comparison.

* Table 5 can be found in the Appendix section.

Fig. 24 shows the excellent correlation of Ea with the experimental partial rate factors ($\log f$) for chlorination of benzene and the methylbenzenes at various positions.

* Figure 24 can be found in the Appendix section.

Fig. 24 shows the excellent correlation of Ea with the experimental partial rate factors ($\log f$) for chlorination of PBDEs at various positions. Textbook explanations of the reactivity and regiospecificity of aromatic substitution reactions usually consider the partial atomic charges at the different arene positions. Therefore, the performance of electronic parameters associated with charge density distribution were evaluated, namely, the EPN index (VC) and the NBO atomic charges (qC) at the reacting carbon atoms. B3LYP/6-311+G(2d,2p) EPN and NBO values are given in Table 5. The correlation coefficients (r) of plots with the partial rate factors show that the EPN index reflects the initial arene reactants satisfactorily ($r=0.972$), although not quite as well as Ea ($r=0.992$). However, essentially no correlation exists between qC (NBO) and $\log f$ ($r=0.095$). Although, π complex formation shifts the electron densities at the different ring positions, VC of the initial reactants may, nevertheless, be related to reactivity. In this regard, a recent, [130], theoretical interaction energy decomposition analysis of the S E Ar reaction found that intrinsic properties of both the aromatic reactant and the electrophile can be used as reactivity and regioselectivity indicators.

The electrophile affinity-based quantitative reactivity and regioselectivity relationships for the bromination of an extended series of mono- and poly-substituted phenyl derivatives, yielded spectacular accord with experimental relative rate constants (k_{rel}), [131], (see Fig. 25). The PBDE derivatives included methoxy-, chloro-, fluoro-, iodo-, and methyl substituents at various positions. The σ complexation energies were computed at B3LYP/6-311+G(2d,2p). IEFPCM methodology modeled the bulk solvent effects. The excellent correlation with experimental $\log (k_{rel})$ values (Fig. 25) underlines the effectiveness of the computed Ea approach in quantifying both Reactivity and regiospecificity for the SE Ar bromination of arenes.

* Figure 25 can be found in the Appendix section.

The electrophile affinity (Ea), a new theoretical construct, has been applied successfully to account for the reactivity and regioselectivity of electrophilic bromination, and alkylation of aromatic compounds. The easily computed Ea quantities are based on the stabilization energies associated with the formation of σ complex intermediates (or the corresponding transition states) in SE Ar reactions. Both Ea and the rates of electrophilic substitutions at different positions in the aromatic ring depend on the thermodynamic stability of these σ complex species. Ground-state EPN indices also may be used to analyze the reactivity of arenes in SE Ar processes.

Reactivity index was introduced to mathematically support claims about structure–reactivity relationships and it was that a strong correlation between reactivity index and structure of PBDE -81 and PBDE-82.

4 Conclusions

In the present study, 3,4,4',5-Tetrabromodiphenyl ether ($C_{12}H_6Br_4O$) (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether ($C_{12}H_5Br_5O$) (PBDE-82) photo-removal process was investigated with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites under different experimental conditions. Maximum 99.64% photo-removal yield was obtained after photodegradation of PBDE-81 and PBDE-82 with 44 mg/l GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposite, after 120 min photodegradation time, at pH=7.0, at 400 W UV-vis light power and at 25°C. The photo-removal of PBDE-81 and PBDE-82 followed the pseudo-first-order kinetic model.

GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites was found to have good stability and excellent photocatalytic performance for PBDE-81 and PBDE-82 reductive degradation. Morphological characterization of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites was carried out via XRD, SEM, TEM, DRS, XPS, ESR and EIS. Moreover, the optical characteristics of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites were analysed via UV-vis, DRS spectrum. The addition of GO increased the photocatalytic activity of the GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites. Ag nanoparticles worked as charge transfer mediator, further remaining excellent redox ability. GO, as a co-catalyst, was favourable for charge pair separation, and enhanced photocatalytic activity. The as-prepared GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites was exhibited high photodegradation activity. The electrons played a critical role in the photodegradation process. The environmental effects, such as different pH, increasing photodegradation time, increasing GO-Ag@Ag₃PO₄/g-

C₃N₄ nanocomposites concentrations affect significantly the photocatalytic activity.

The enhanced photocatalytic performance of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites was contributed to the Ag nanoparticles in promoting the charge separation of GO-g-C₃N₄ nanocomposites and the subsequent formation of active H atom species, and providing a high affinity interaction with GO for assisting the C-N cleavage of PBDE. Before initiating the PBDE, Ag nanoparticles need an induction period to enrich a critical number of electrons to decrease the dissociation energy of C-N bond. These findings not only explained the important role of Ag nanoparticles on the enhancement of photocatalytic reduction of PBDE over GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, but also provide a new insight into the design and fabrication of advanced photocatalysts for removing toxic halogenated pollutants.

Acknowledgement:

Experimental analyzes in this study were performed at the Laboratories of the Canada Research Center, Ottawa, Canada. The authors would like to thank this body for providing financial support.

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APPENDIX

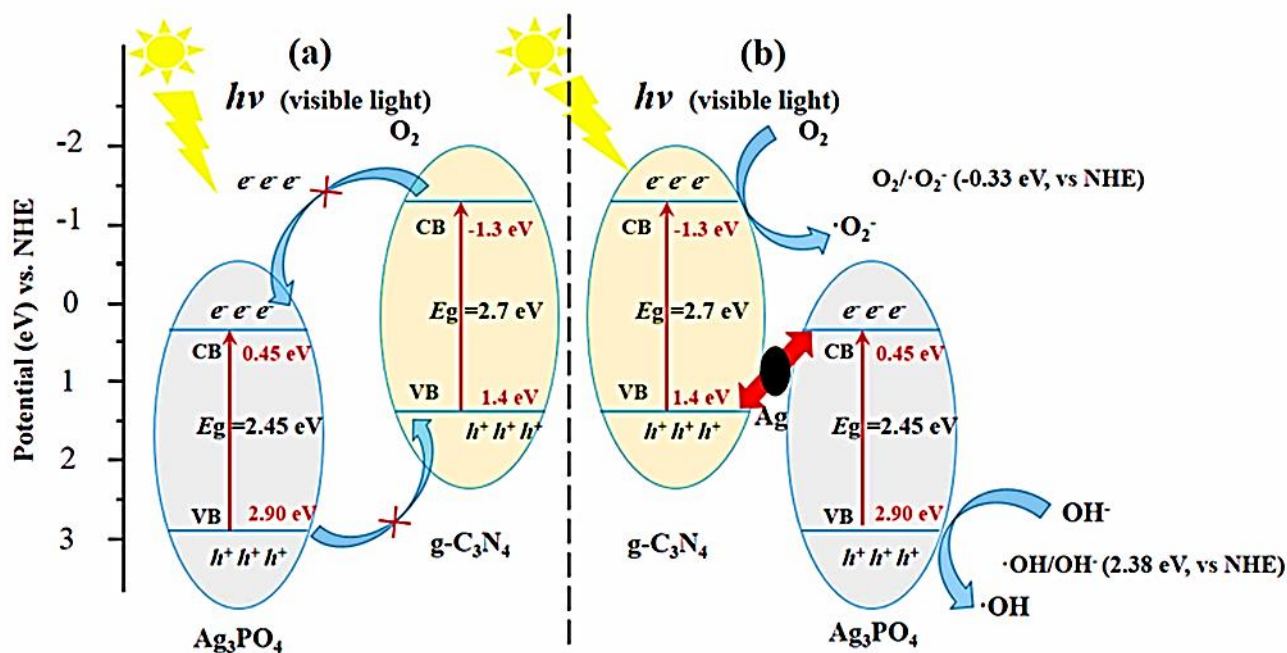


Figure 1. Schematic diagram of the photoexcited electron-hole transfer process (a) Double-transfer mechanism; and (b) Z-scheme mechanism.

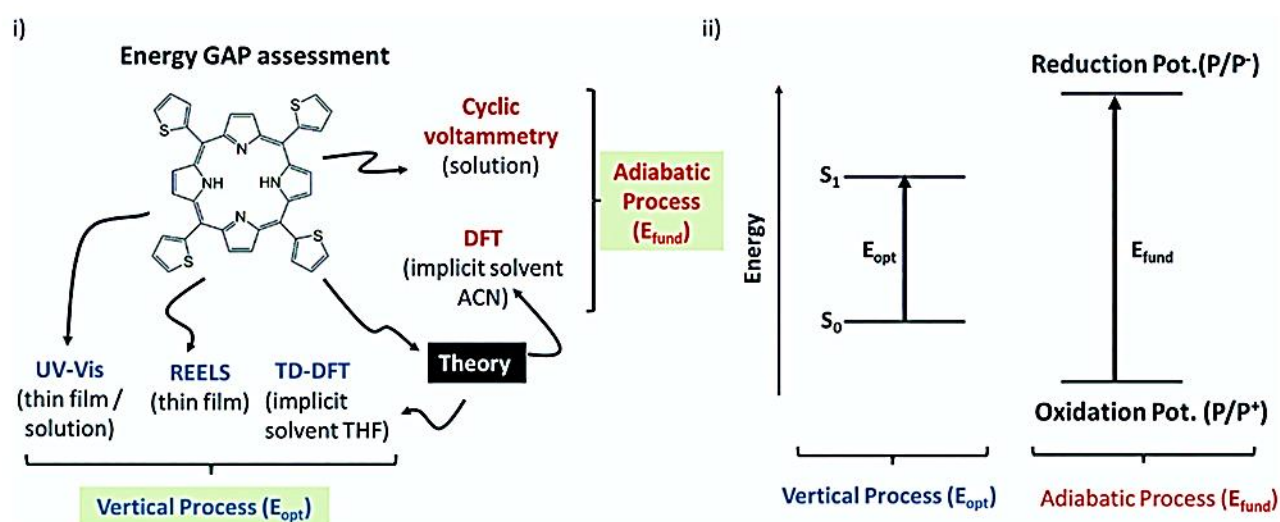


Figure 2. (i). A representative scheme of the energy gap assessment using different experimental and theoretical approaches discussed in this article; **(ii)** illustrative representation of optical (E_{opt}) and fundamental energy gap (E_{fund}) highlighting the conceptual differences between these two quantities.

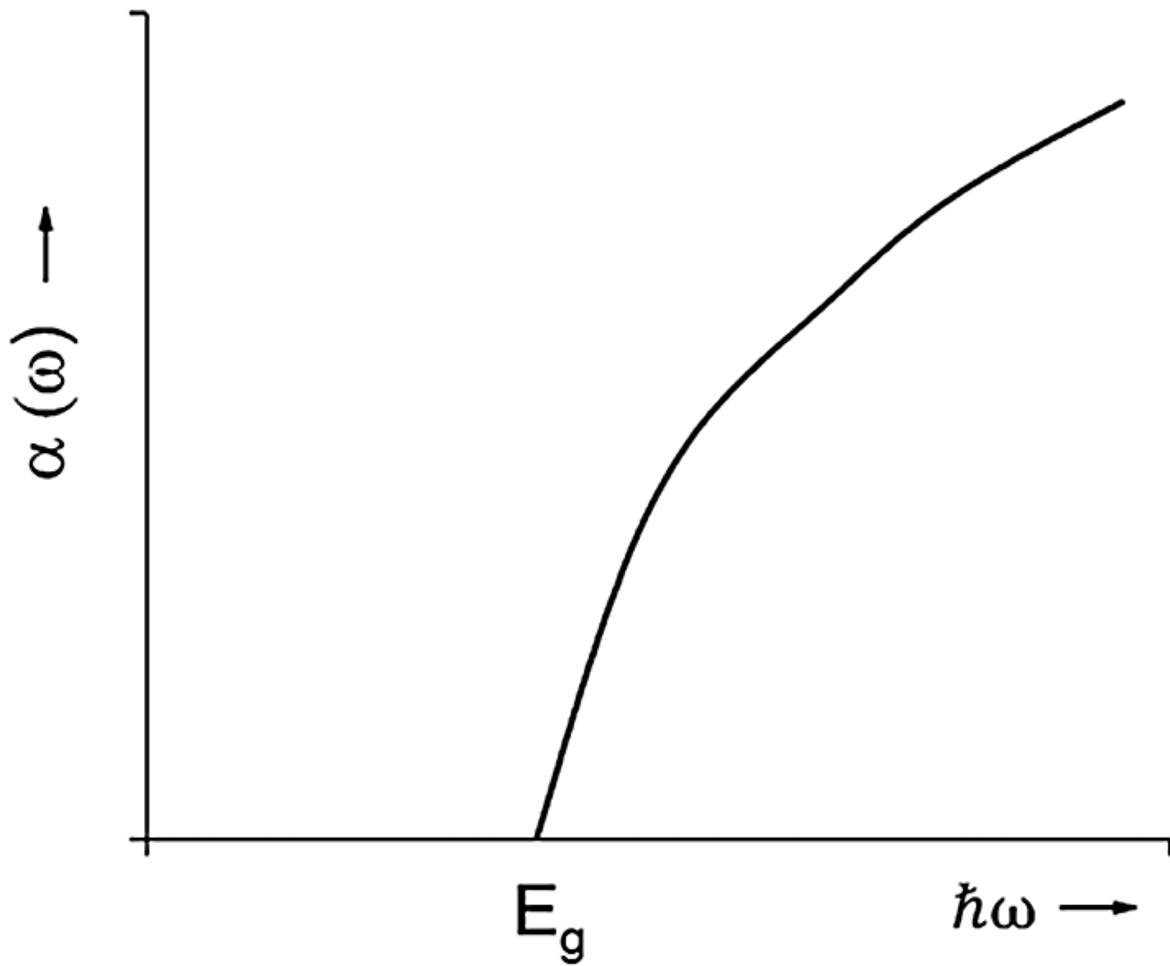


Figure 3. Frequency dependence of the absorption coefficient (α) near the threshold for inter band transition.

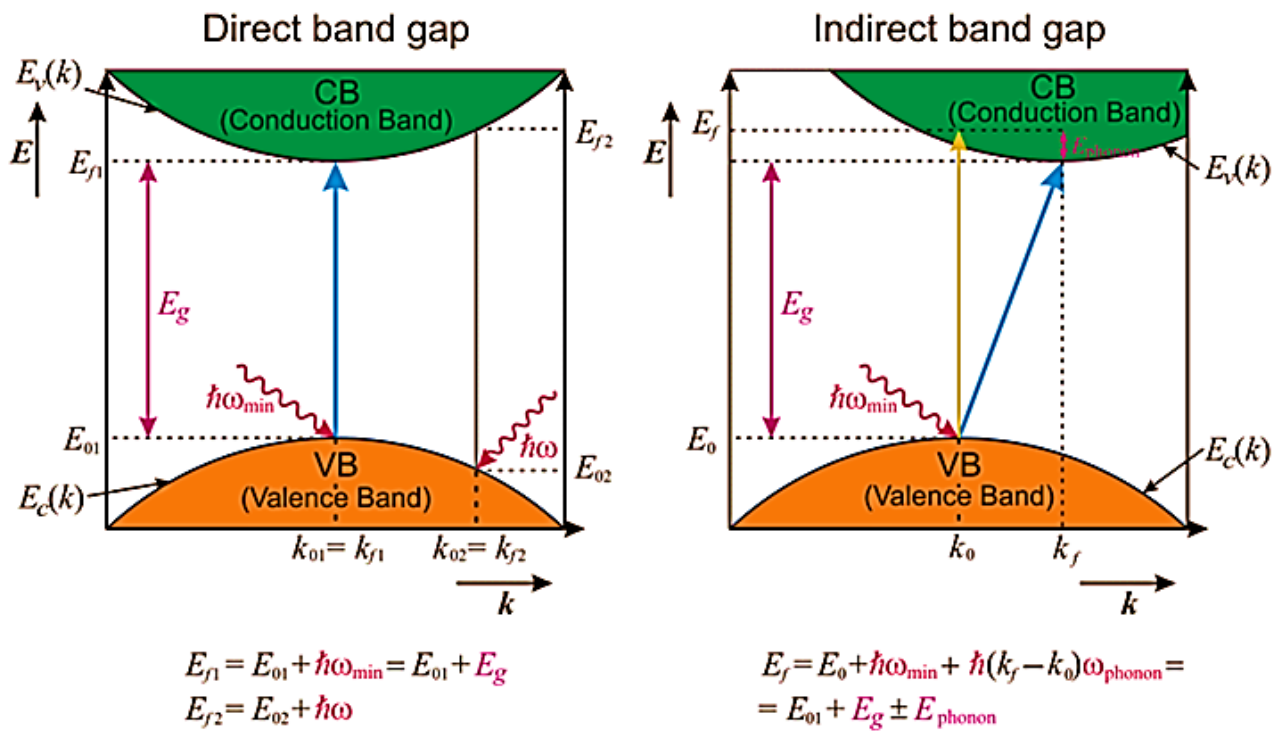


Figure 4. Direct and indirect mechanisms of electron inter band transition.

Table 1. Mathematical formulation of the Langmuir Hinshelwood kinetics problem and its approximations, their respective solutions and the hypothesis assumed to arrive at these approximations.

Regime	Cauchy Problem (Differential Equation with Initial Condition)	Analytic Solution of C(t)	$K_e C(t)$ Hypothesis	t_c Hypothesis
Zeroth-order	$\{C'(t) = -k_r$ $\{C(0) = C_0$	$C_0 - k_r t$	$K_e C(t) \gg 1$	$t \ll t_c$
First-order	$\{C'(t) = -k_r C K_e C(t)$ $\{C(0) = C_0$	$C_0 e^{-k_{app} t} - k_r t$	$K_e C(t) \ll 1$	$t \gg t_c$
General solution	$\{C'(t) = -\frac{k_r K_e C(t)}{1 + K_e C(t)}$ $\{C(0) = C_0$	$\frac{1}{K_e} W(K_e C_0 e^{K_e(C_0 - k_r t)})$		

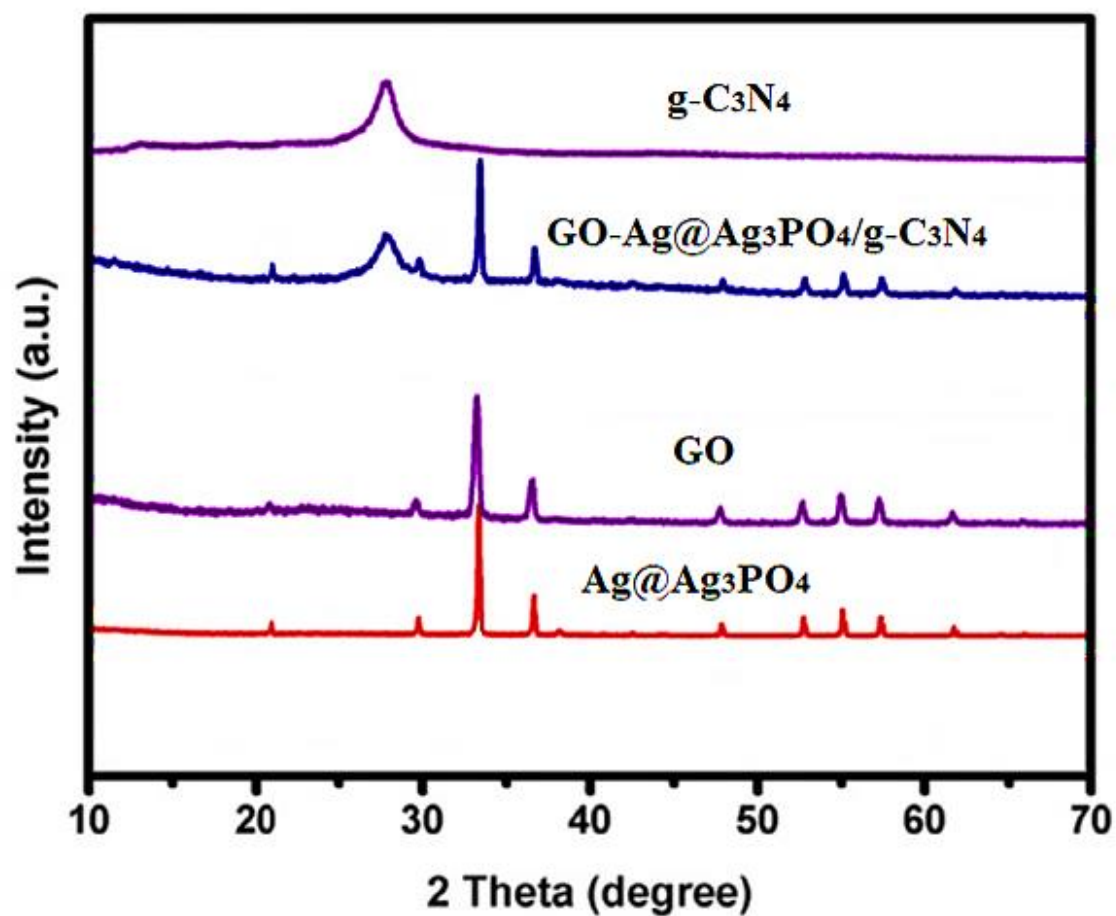


Figure 5. XRD spectrum of g-C₃N₄, GO-Ag@Ag₃PO₄/g-C₃N₄, GO and Ag@Ag₃PO₄ nanocomposites after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82).

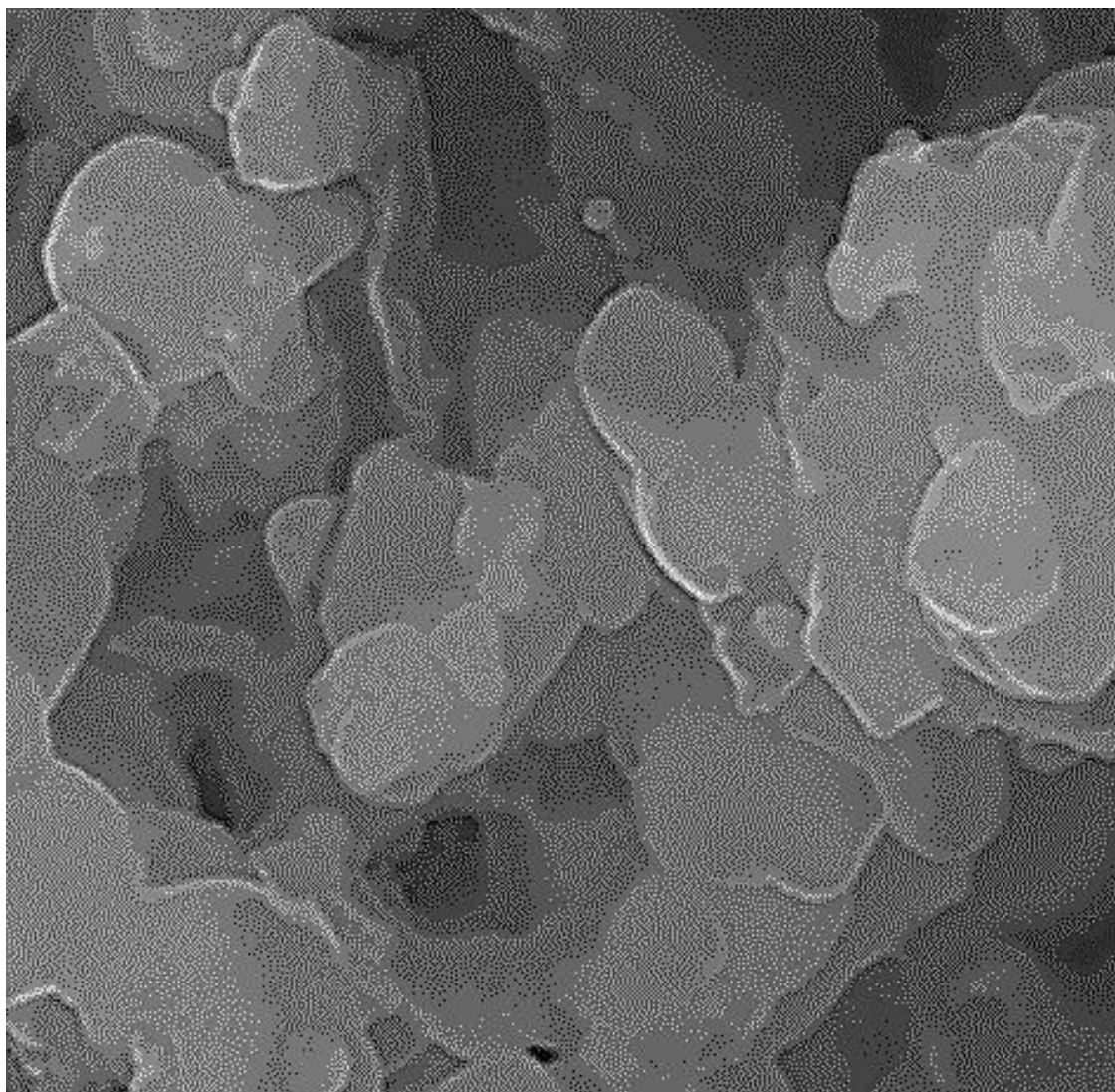


Figure 6. SEM image of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) (SEM size: 500 nm).

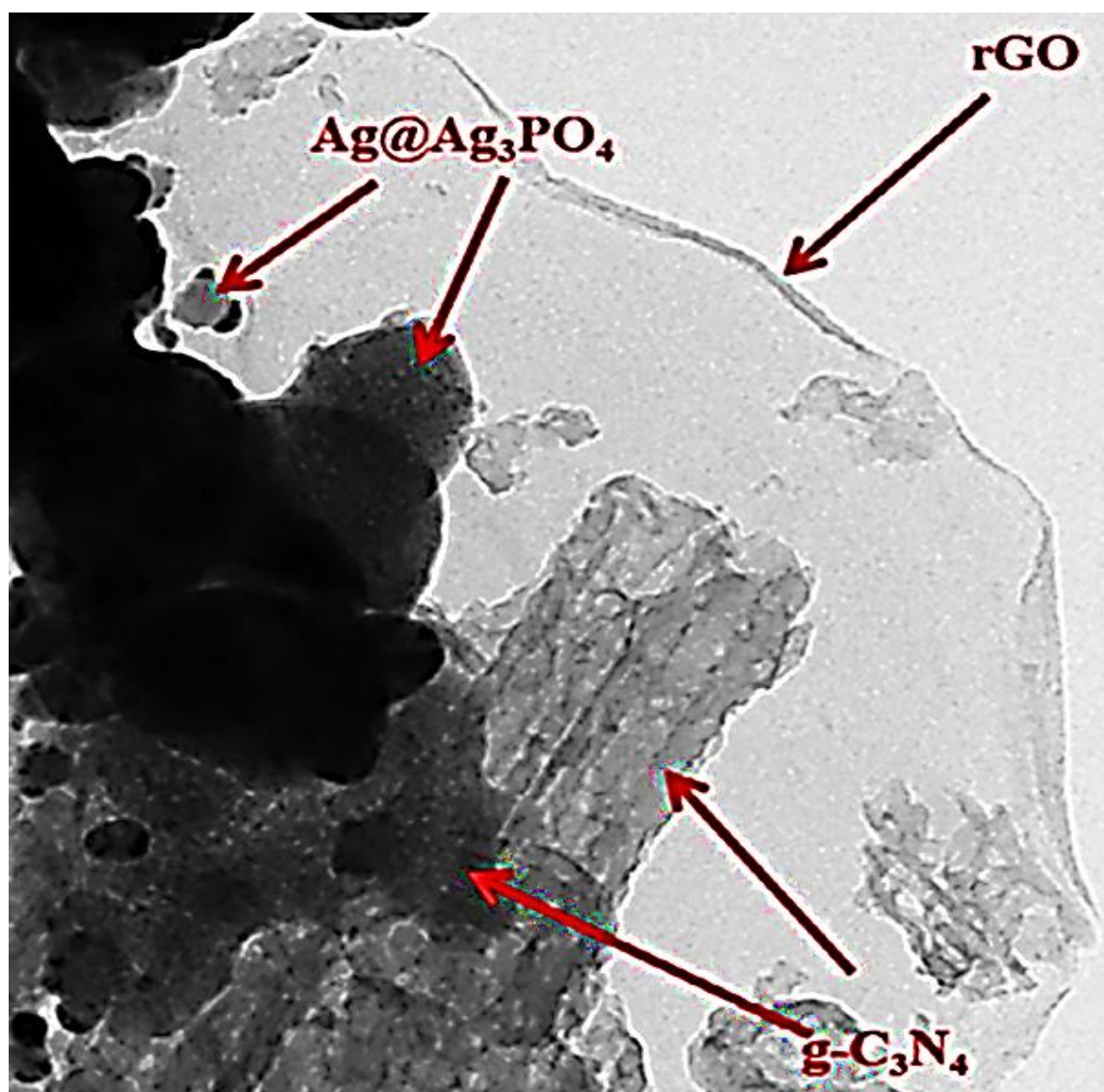


Figure 7. TEM image of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) (TEM size: 100 nm).

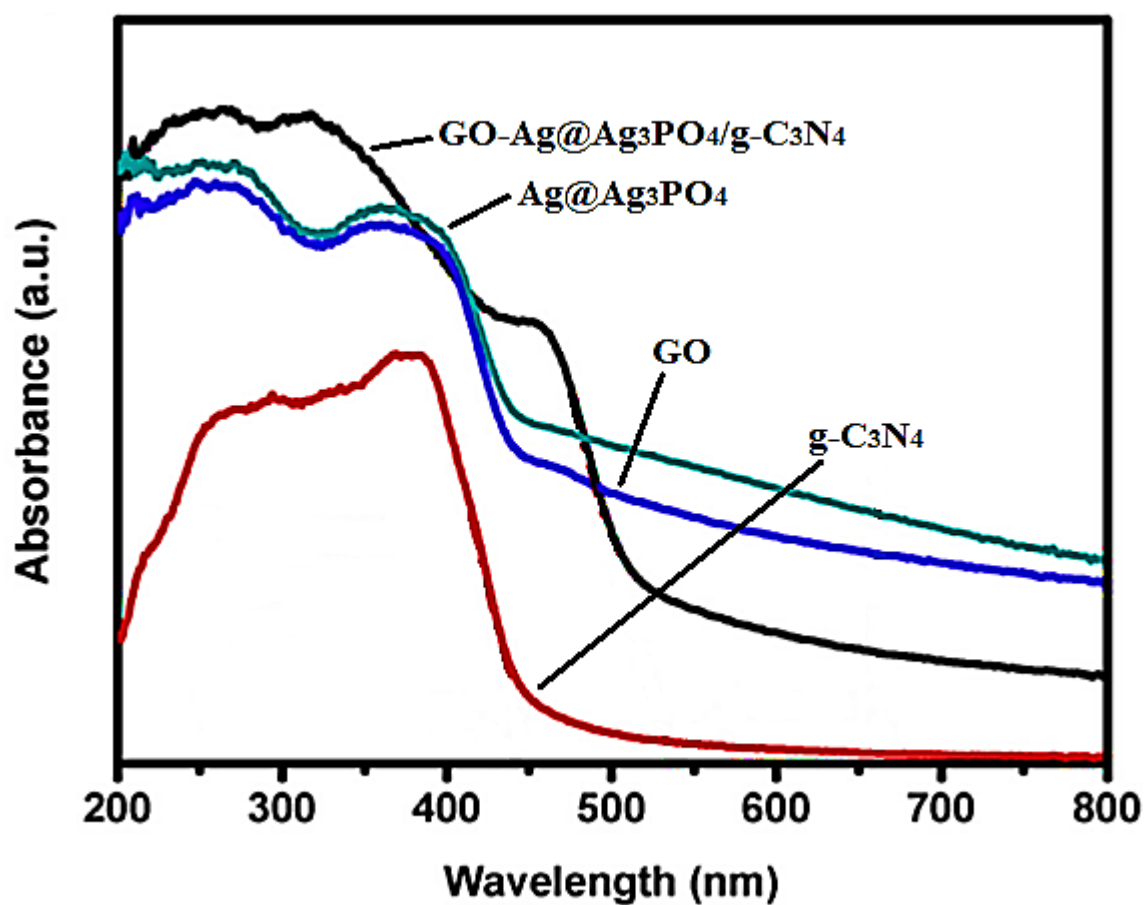


Figure 8. DRS spectrum of GO-Ag@Ag₃PO₄/g-C₃N₄, Ag@Ag₃PO₄, GO and g-C₃N₄ nanocomposites after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82).

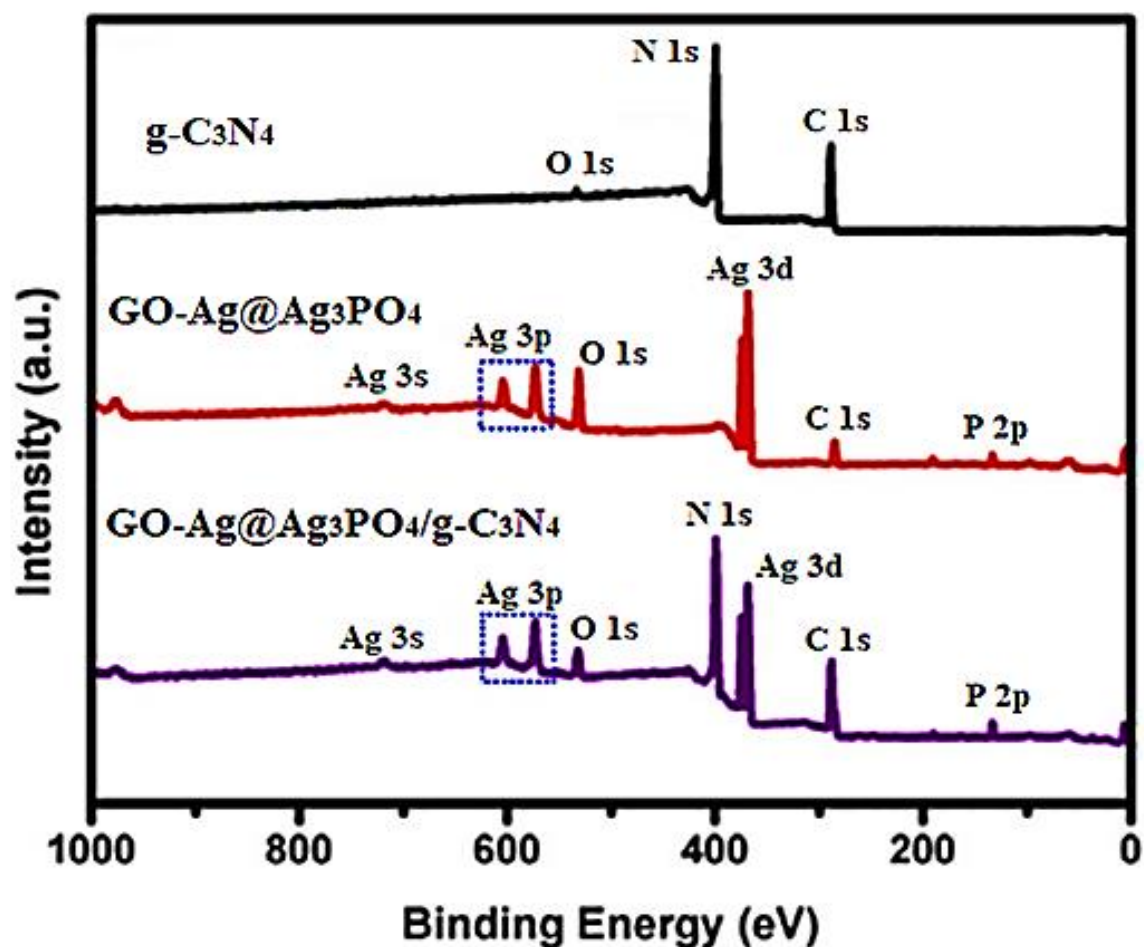


Figure 9. XPS spectrum of $g\text{-C}_3\text{N}_4$, $\text{GO-Ag@Ag}_3\text{PO}_4$ NCs and $\text{GO-Ag@Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4$ nanocomposites after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82).

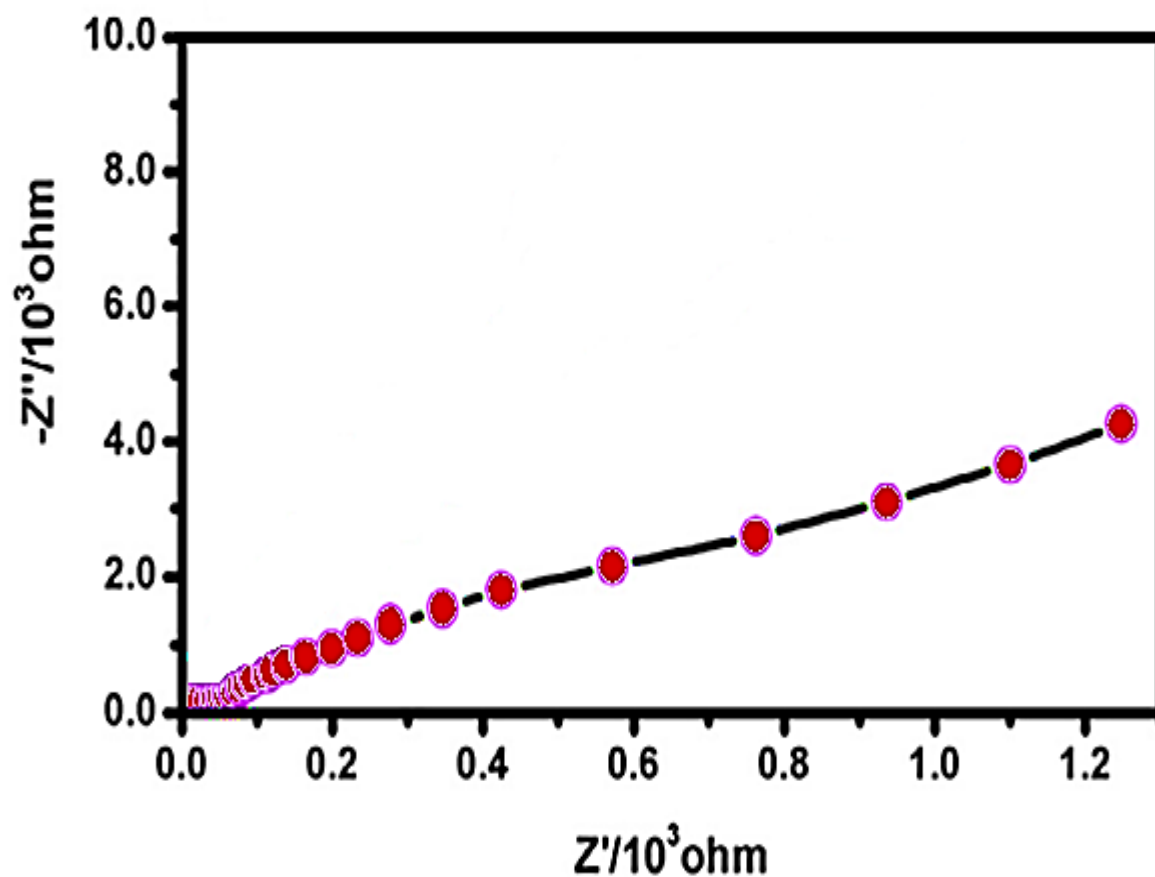


Figure 10. EIS result of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82).

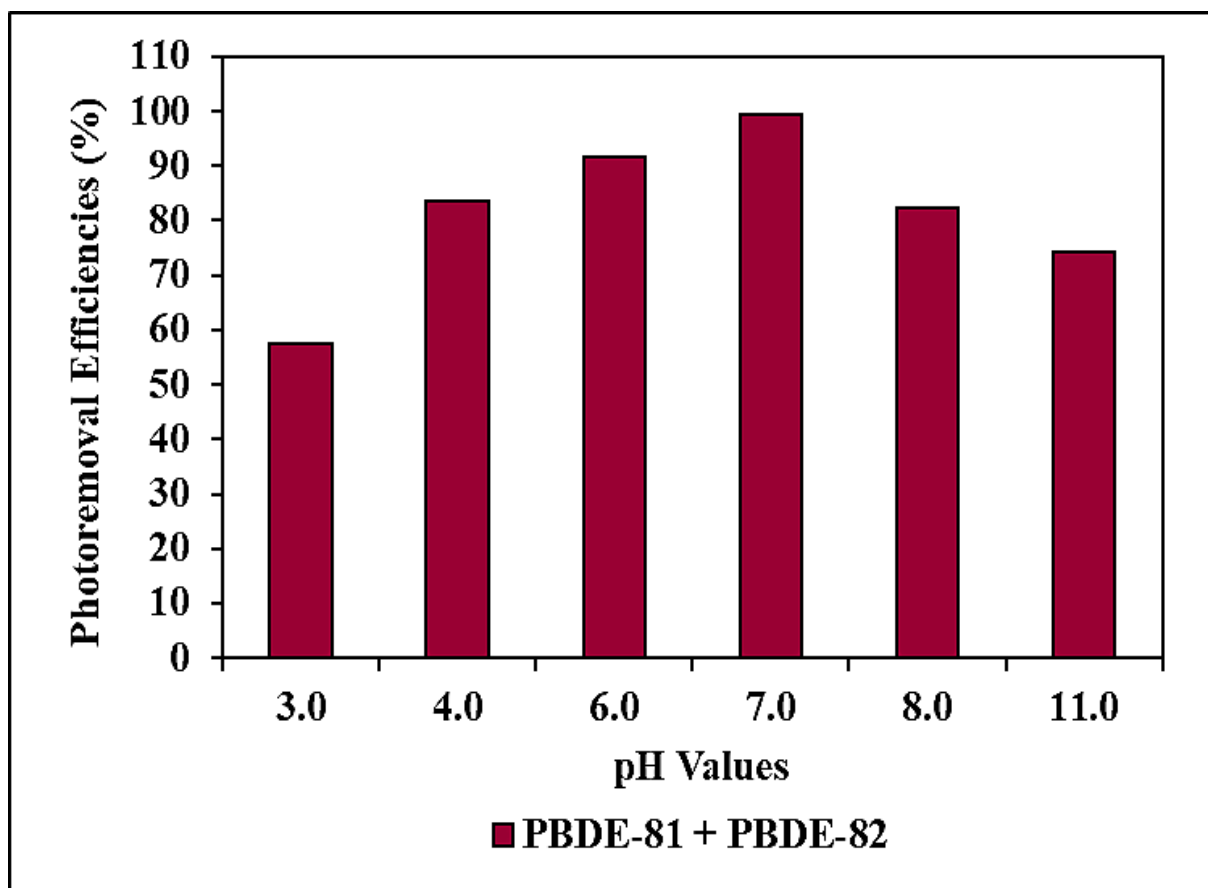


Figure 11. Effect of pH values after photodegradation of 3,4,4',5-Tetrabromodiphenyl ether (PBDE-81) and 2,2',3,3',4-Pentabromodiphenyl ether (PBDE-82) with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites at 400 W UV-vis light power and at 25°C.

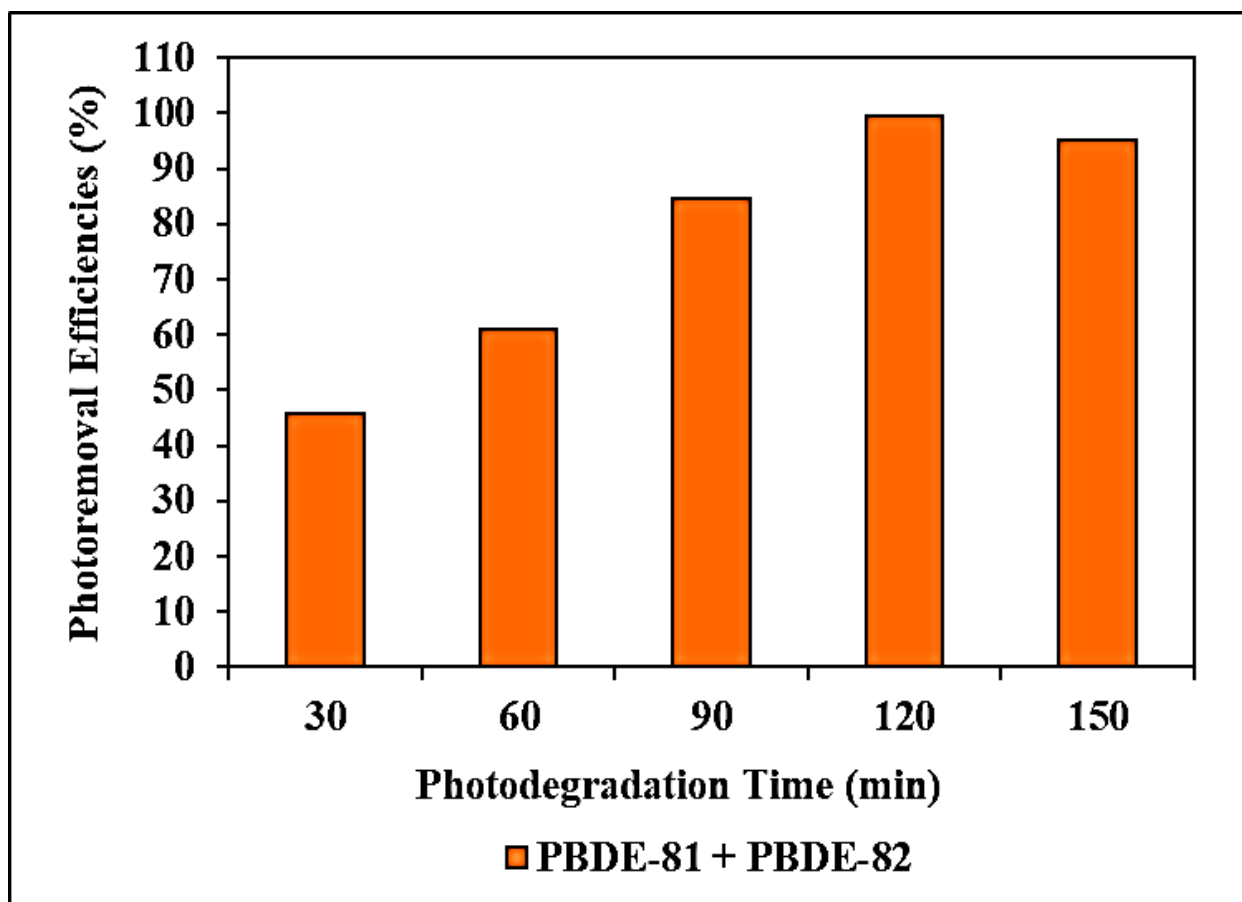


Figure 12. Effect of increasing photodegradation times after photodegradation process for PBDE-81 and PBDE-82 with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites at pH=4.0, at 400 W UV-vis light power and at 25°C.

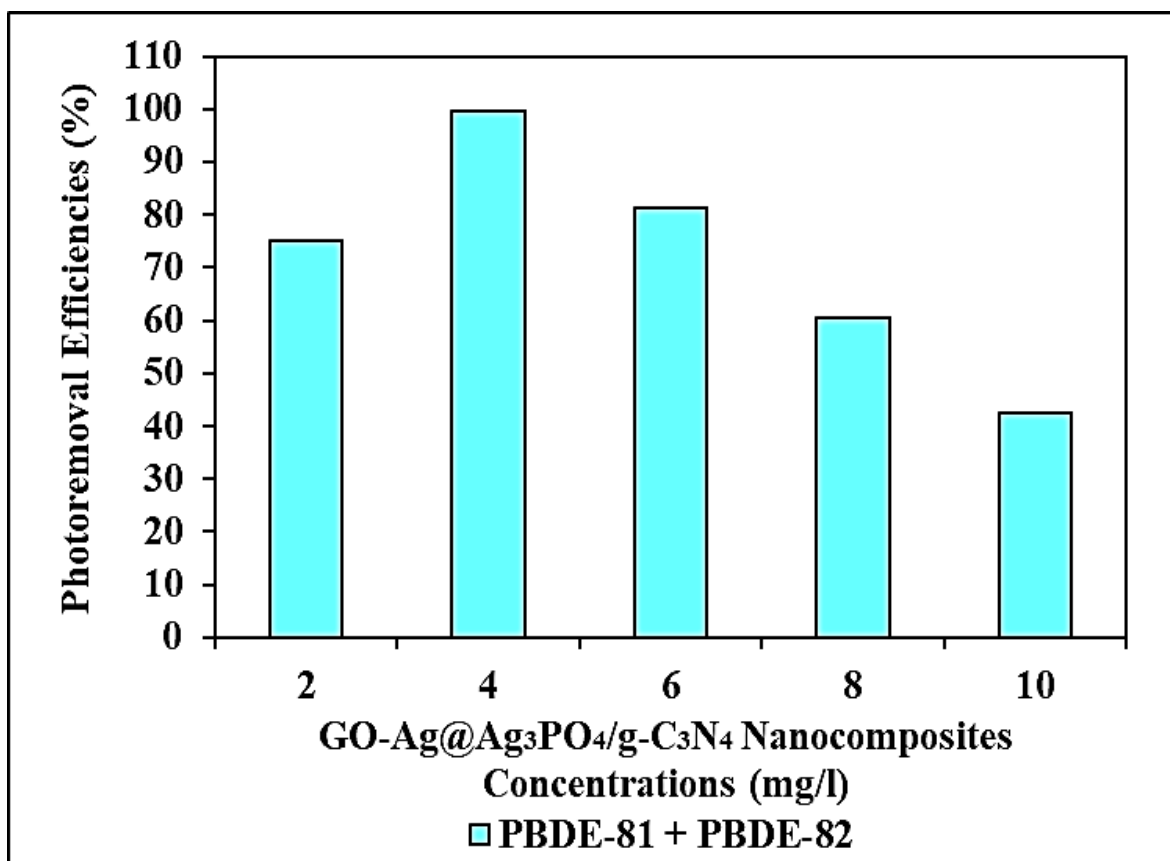


Figure 13. Effect of increasing GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites concentrations after photodegradation process for PBDE-81 and PBDE-82 with GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposites, at pH=4.0, after 120 min photodegradation time, at 400 W UV-vis light power and at 25°C.

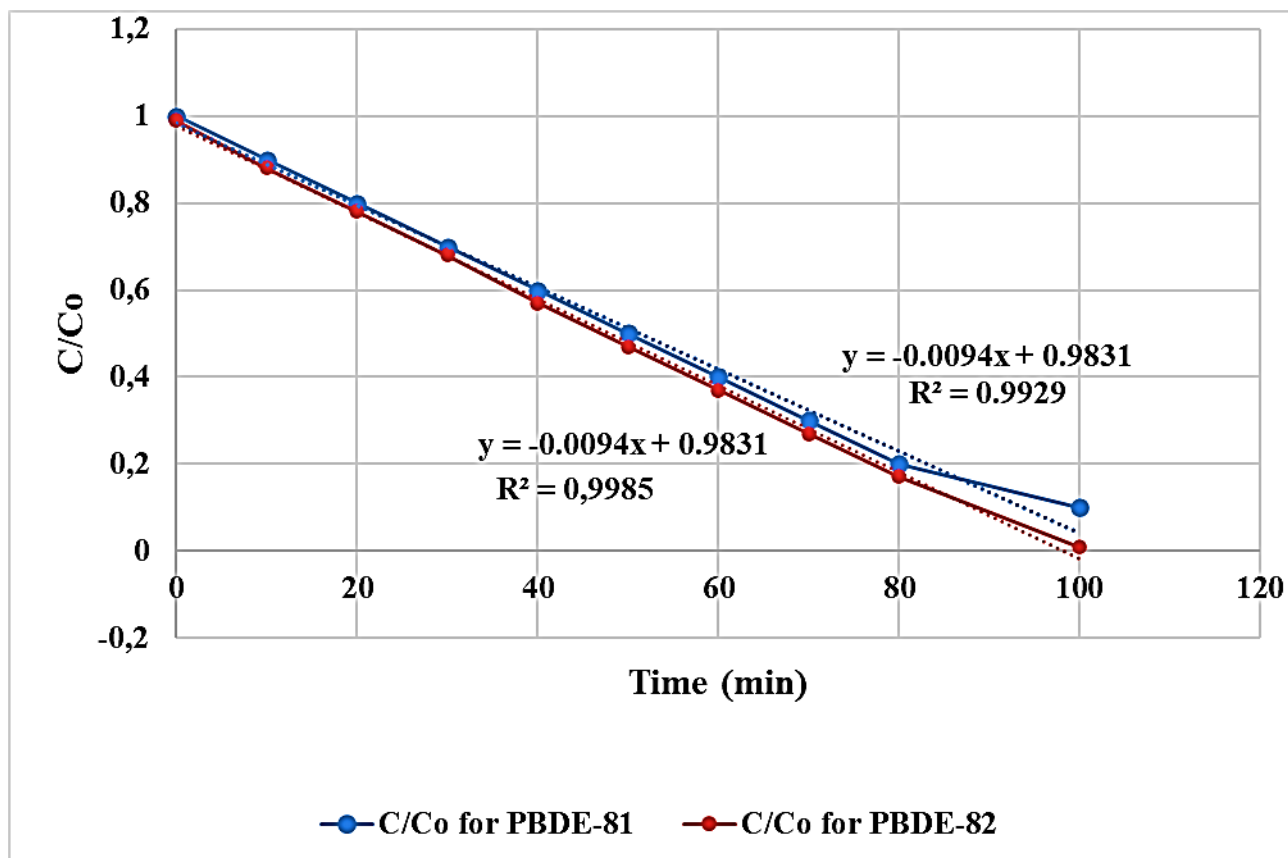


Figure 14. First order photodegradation kinetic of PBDE -81 and PBDE-82.

Table 2. PBDE derivatives of Mayr's Database considered in this work^a

ID	Y	Z	E ¹	ID	Y	Z	E ¹
1	<i>p-pyr</i>	Y	-7.69	15	<i>p-Me</i>	H	4.43
2	<i>p-dma</i>	Y	-7.02	16	<i>p-F</i>	Y	5.01
3	<i>p-mpa</i>	Y	-5.89	17	<i>p-F</i>	H	5.20
4	<i>p-mor</i>	Y	-5.53	18	3- <i>F</i> , <i>p-Me</i>	Y	5.24
5	<i>p-dpa</i>	Y	-4.72	19	<i>H</i>	Y	5.47
6	<i>p-mfa</i>	Y	-3.85	20	<i>p-Cl</i>	Y	5.48
7	<i>p-pfa</i>	Y	-3.14	21	3- <i>F</i>	H	6.23
8	<i>p-OMe</i>	Y	0.00	22	<i>p-(CF₃)</i>	H	6.70
9	<i>p-OMe</i>	p-OPh	0.61	23	3,5- <i>F₂</i>	H	6.74
10	<i>p-OMe</i>	p-Me	1.48	24	3- <i>F</i>	Y	6.87
11	<i>p-OMe</i>	H	2.11	25	3,5- <i>F₂</i>	3- <i>F</i>	7.52
12	<i>p-OPh</i>	p-Me	2.16	26	<i>p-(CF₃)</i>	Y	7.96
13	<i>p-OPh</i>	H	2.90	27	3,5- <i>F₂</i>	Y	8.02
14	<i>p-Me</i>	Y	3.63				

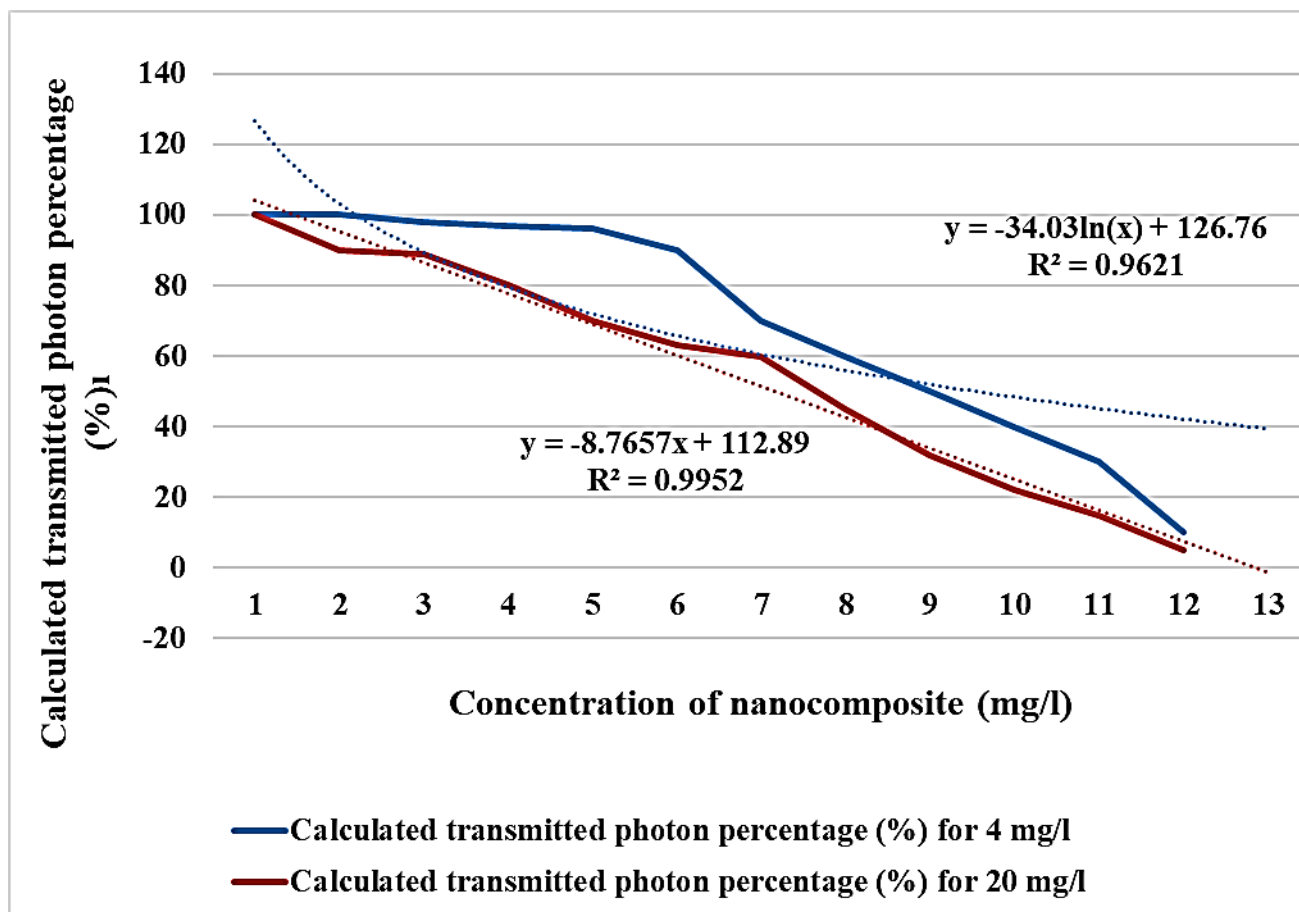


Figure 15. Calculation of transmitted photons as a function of nanocomposite concentration.

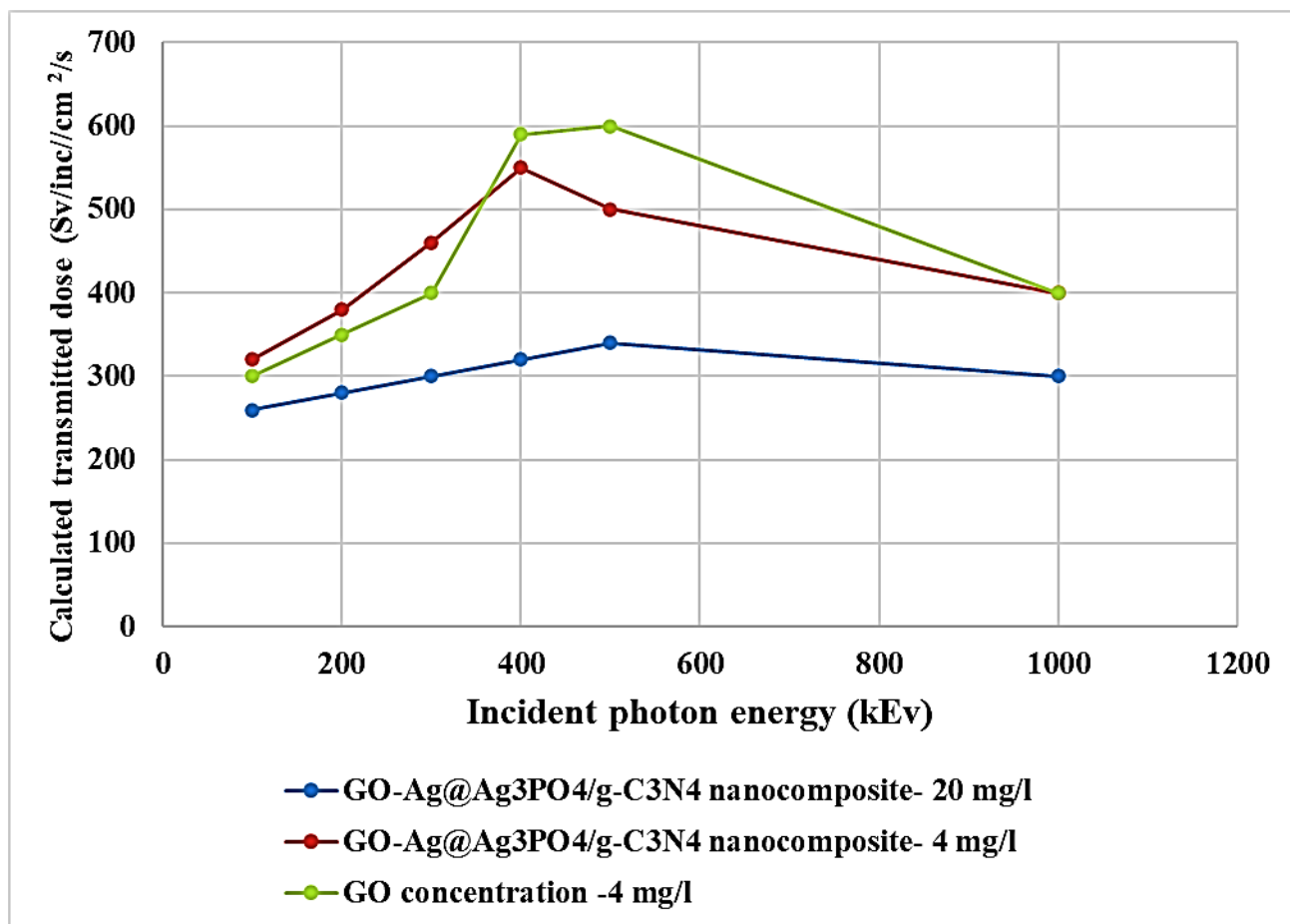


Figure 16. Calculation of transmitted photons as a function of GO-Ag@Ag₃PO₄/g-C₃N₄ nanocomposite concentrations.

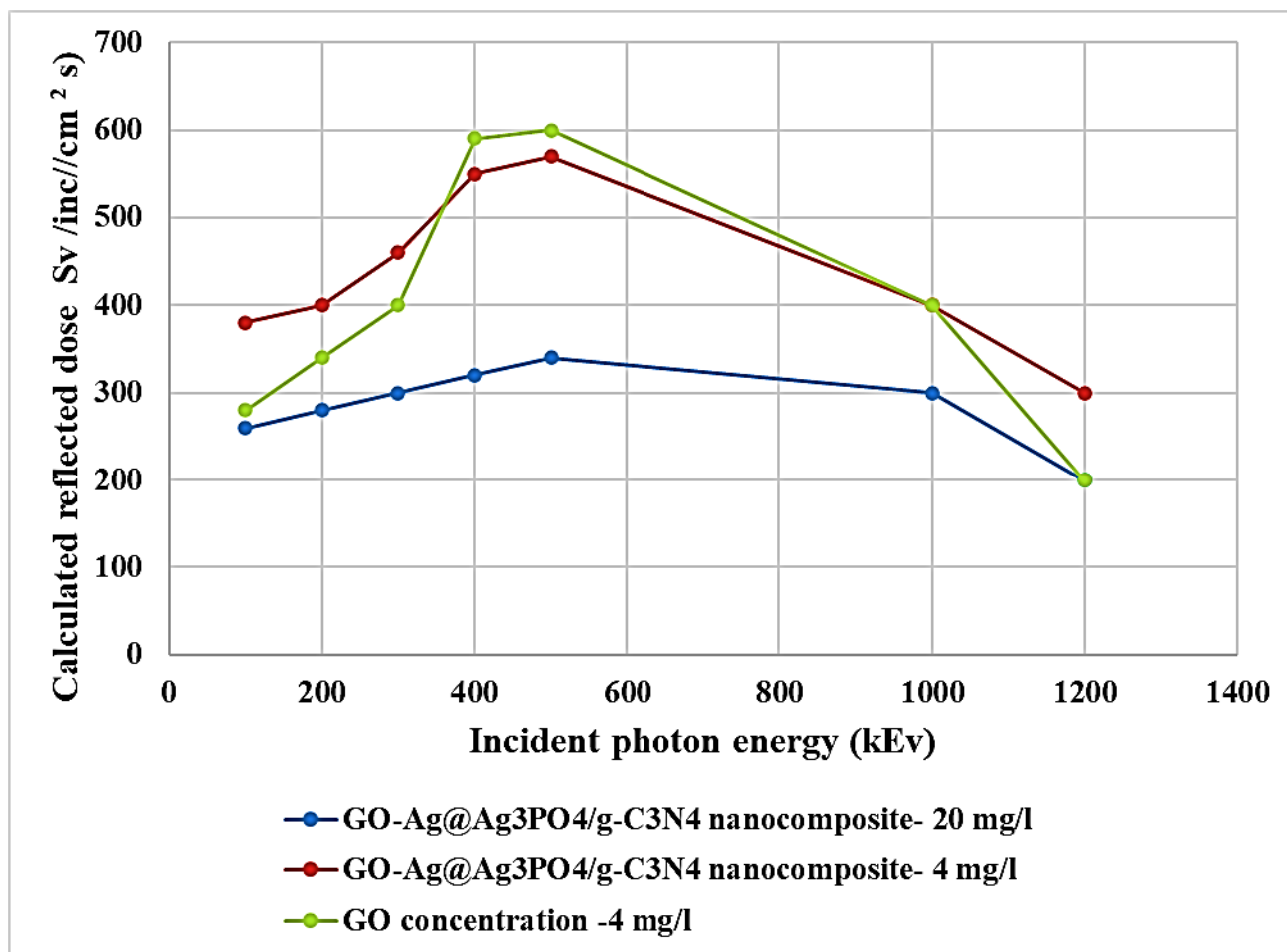


Figure 17. Variation of reflected photon dose versus incident photon energy varying between 200 keV and 1200 keV.

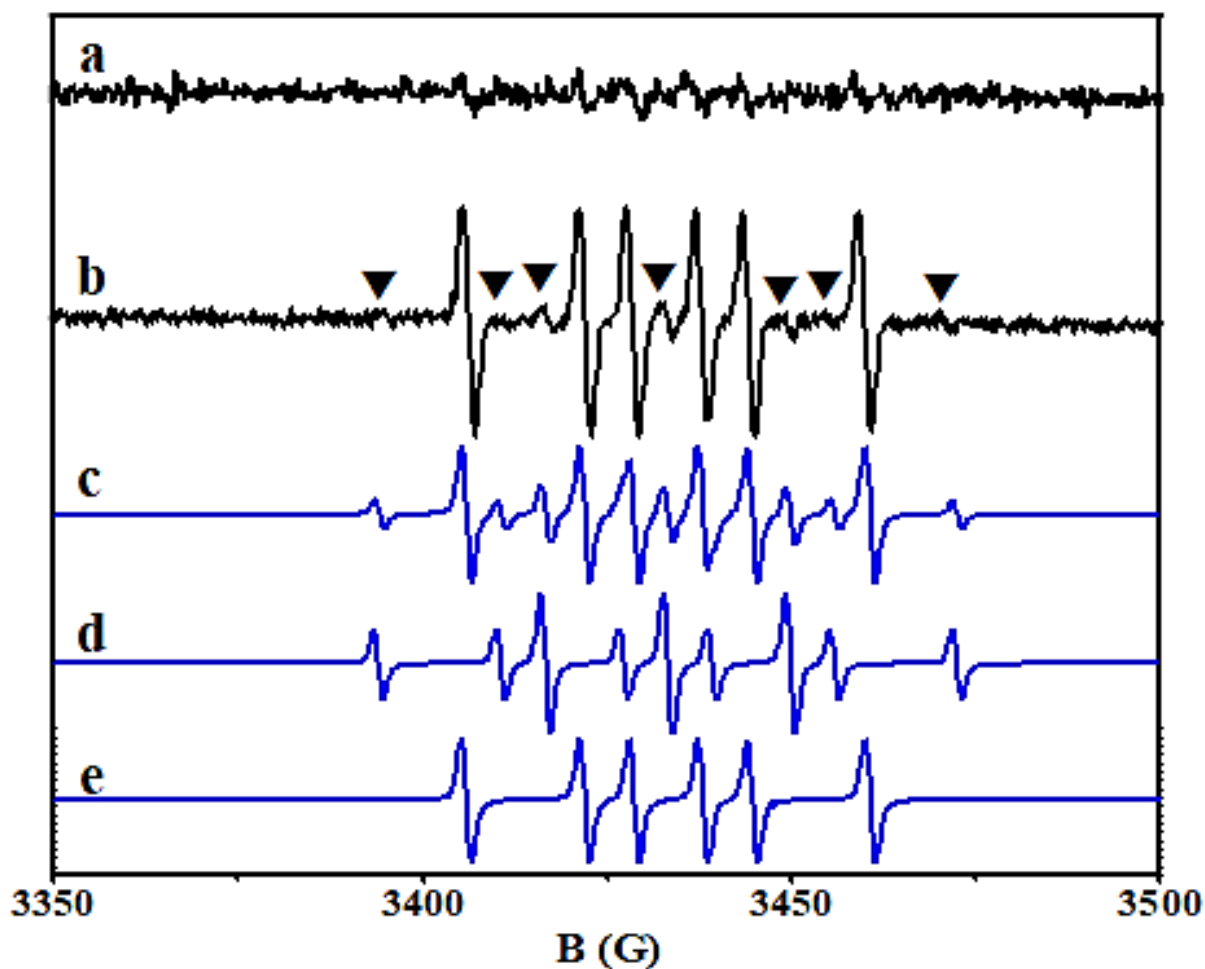


Figure 18. ESR spectra trapped by DMPO (a) before and (b) after 120 min of irradiation in the photocatalytic system with GO-Ag@Ag₃PO₄/g-C₃N₄ as catalyst and Ar-saturated methanol-water (v:v, 70:30) mixture as solvent. (c) The adduct spectra of DMPO-H* and DMPO-CH₃O*, and the individual spectra of (d) DMPO-H* and (e) DMPO-CH₃O* obtained from the software.

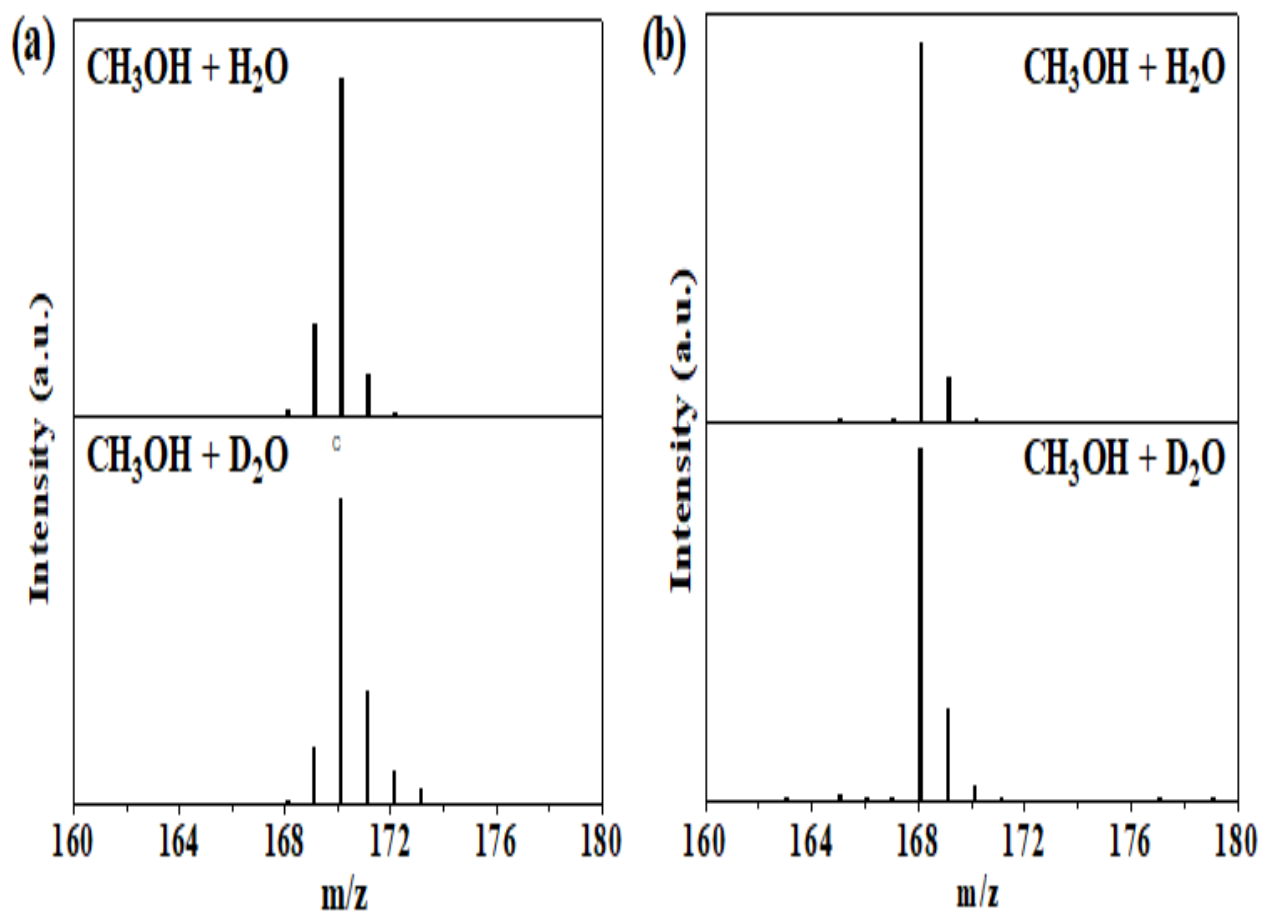


Figure 19. Mass spectra of (a) DE and (b) DF produced in the photocatalytic degradation of PBDE-81 on Pd/g- C_3N_4 with using $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (v:v = 7:3) or $\text{CH}_3\text{OH}-\text{D}_2\text{O}$ (v:v = 7:3) as solvents, respectively.

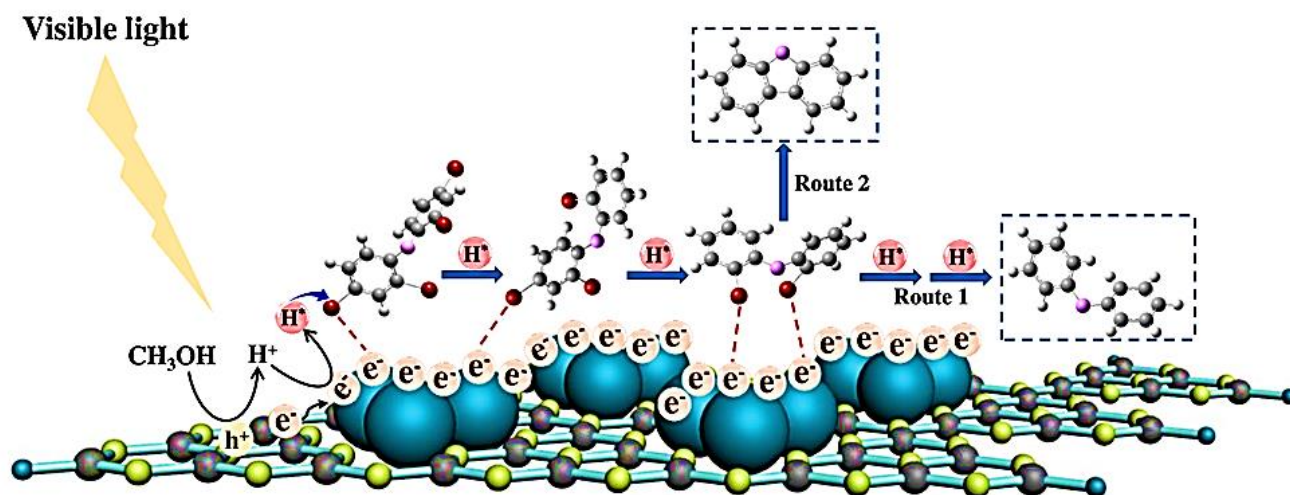


Figure 20. A mechanism for the photocatalytic degradation of PBDE82 on Pd/g-C₃N₄ composites.

Table 3. PBDE -81 and 82 scaffold has substituents Y and Z.

Abbreviaton	Formula	Chemical name
PBDE-1	C ₁₂ H ₉ BrO	2-bromodiphenyl ether
PBDE-2	C ₁₂ H ₉ BrO	3-bromodiphenyl ether
PBDE-3	C ₁₂ H ₉ BrO	4-bromodiphenyl ether
PBDE-4	C ₁₂ H ₈ Br ₂ O	2,2'-dibromodiphenyl ether
PBDE-5	C ₁₂ H ₈ Br ₂ O	2,3-dibromodiphenyl ether
PBDE-6	C ₁₂ H ₈ Br ₂ O	2,3'-dibromodiphenyl ether
PBDE-7	C ₁₂ H ₈ Br ₂ O	2,4-dibromodiphenyl ether
PBDE-8	C ₁₂ H ₈ Br ₂ O	2,4'-dibromodiphenyl ether
PBDE-9	C ₁₂ H ₈ Br ₂ O	2,5-dibromodiphenyl ether
PBDE-10	C ₁₂ H ₈ Br ₂ O	2,6-dibromodiphenyl ether
PBDE-11	C ₁₂ H ₈ Br ₂ O	3,3'-dibromodiphenyl ether
PBDE-12	C ₁₂ H ₈ Br ₂ O	3,4-dibromodiphenyl ether
PBDE-13	C ₁₂ H ₈ Br ₂ O	3,4'-dibromodiphenyl ether
PBDE-14	C ₁₂ H ₈ Br ₂ O	3,5-dibromodiphenyl ether
PBDE-15	C ₁₂ H ₈ Br ₂ O	4,4'-dibromodiphenyl ether
PBDE-16	C ₁₂ H ₇ Br ₃ O	2,2',3-tribromodiphenyl ether
PBDE-17	C ₁₂ H ₇ Br ₃ O	2,2',4-tribromodiphenyl ether
PBDE-18	C ₁₂ H ₇ Br ₃ O	2,2',5-tribromodiphenyl ether
PBDE-19	C ₁₂ H ₇ Br ₃ O	2,2',6-tribromodiphenyl ether
PBDE-20	C ₁₂ H ₇ Br ₃ O	2,3,3'-tribromodiphenyl ether
PBDE-21	C ₁₂ H ₇ Br ₃ O	2,3,4-tribromodiphenyl ether
PBDE-22	C ₁₂ H ₇ Br ₃ O	2,3,4'-tribromodiphenyl ether

PBDE-23	$C_{12}H_7Br_3O$	2,3,5-tribromodiphenyl ether
PBDE-24	$C_{12}H_7Br_3O$	2,3,6-tribromodiphenyl ether
PBDE-25	$C_{12}H_7Br_3O$	2,3',4-tribromodiphenyl ether
PBDE-26	$C_{12}H_7Br_3O$	2,3',5-tribromodiphenyl ether
PDDE-27	$C_{12}H_7Br_3O$	2,3',6-tribromodiphenyl ether
PBDE-4	$C_{12}H_7Br_3O$	2,3',4-tribromodiphenyl ether
PBDE-81	$C_{12}H_6Br_4O$	3,4,4',5-Tetrabromodiphenyl ether
PBDE-82	$C_{12}H_5Br_5O$	2,2',3,3',4-Pentabromodiphenyl ether

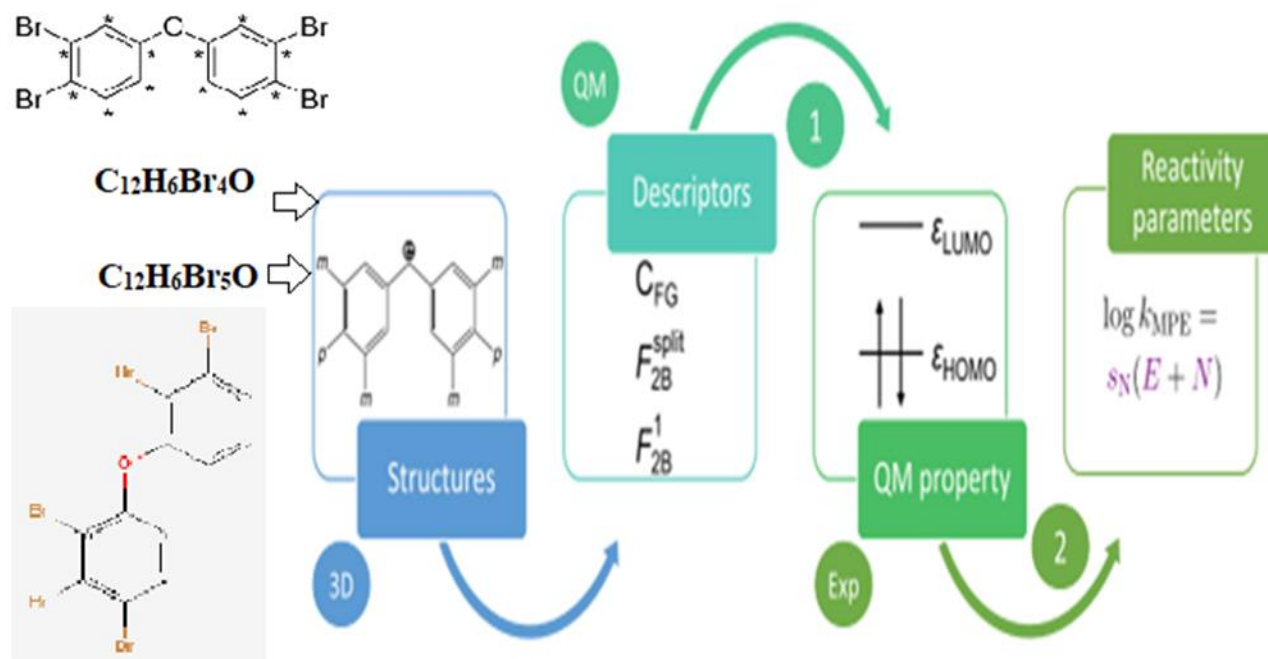


Figure 21. Br scaffold in bizimxx nanocomposite with emphasized *meta* positions *m* and *para* positions *p*. Rotation axes leading to approximately isoenergetic structures are displayed in gray.

Table 4. List of QMPs examined in this study, including mathematical definitions

Name	Mathematical definition
Ionization potential, [132]	$\mu_{FMO}^- = \varepsilon_{HOMO}$
Electron affinity, [132]	$\mu_{FMO}^+ = \varepsilon_{LUMO}$
Global molecular hardness, [133]	$\eta_{FMO} = \varepsilon_{LUMO} - \varepsilon_{HOMO}$
Electronic chemical potential, [115], [134]	$\mu_{FMO} = \frac{\mu_{FMO}^+ - \mu_{FMO}^-}{2}$
Electrophilicity index, [117]	$\omega_{FMO} = \frac{\mu_{FMO}^2}{2\eta_{FMO}}$
Electro-accepting power, [118]	$\omega_{FMO}^+ = \frac{(3\varepsilon_{LUMO} + \varepsilon_{HOMO})^2}{16\mu_{FMO}}$
Electro-donating power, [118]	$\omega_{FMO}^- = \frac{(\varepsilon_{LUMO} + 3\varepsilon_{HOMO})^2}{16\mu_{FMO}}$
Net electrophilicity, [119]	$\Delta\omega_{FMO}^+ = \omega_{FMO}^+ - \omega_{FMO}^-$

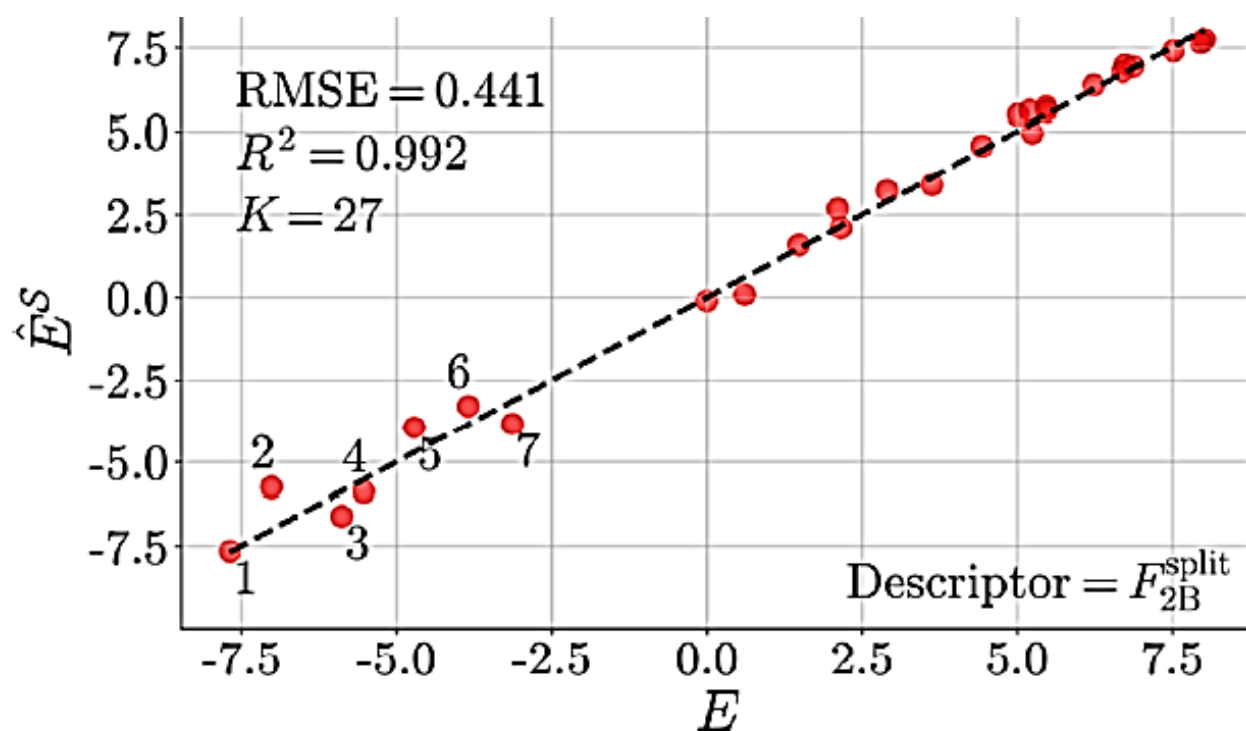


Figure 22. Predicted E (F_{2B}) split versus Mayr's E for $K=27$ reference structures. The results are based on quantum chemical FMO energies for $M - K = 3543$ PBDE -81 and PBDE-82 ions.

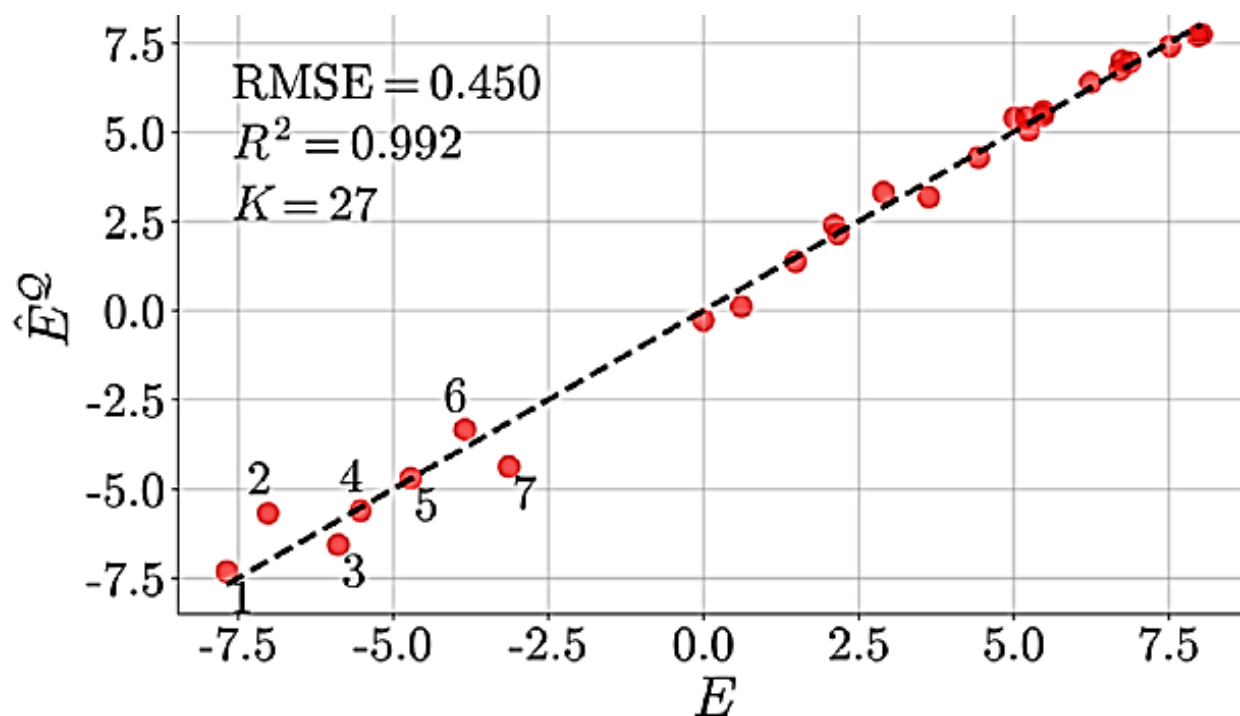


Figure 23. Predicted E versus Mayr's E for $K=27$ reference structures. The coefficients of the rMLR model yielding E were optimized with respect to E for the same set of structures. FMO energies obtained from quantum chemical calculations served as input.

Table 5. Electrostatic potentials at the reacting carbon atoms (V_C) and NBO charges (q_C) of PBDE types with experimental $\log f$ Values for M. All computations were performed at the B3LYP/6-311+G(2d,2p) Level.

Reactants	Potential of chlorination	E_a (kcal/mol)	V_c (reactant) + 401 (volts)	Q_c (NBO) €	$\log f^1$
PBDE 1	2	183.7	-1.069	-0.204	0
PBDE 1	4	192.0	-1.225	-0.206	2.8
PDBE 2	3	193.6	-1.210	-0.213	2.9
PBDE 2	4	194.6	-1.310	-0.199	3.4
PBDE 1	2	196.7	-1.298	-0.205	3.6
PBDE 1	4	199.0	-1.372	-0.209	5.5
PBDE 2	2	200.9	-1.359	-0.216	5.6
PBDE 2	2	195.8	-1.307	-0.197	3.5
PBDE 1	3	206.9	-1.500	-0.218	7.8
PBDE 2	6	203.5	-1.521	-0.194	6.7
PBDE 2	4	210.9	-1.686	-0.201	8.9
Correlation coefficient (r) ²		0.992	0.972	0.095	

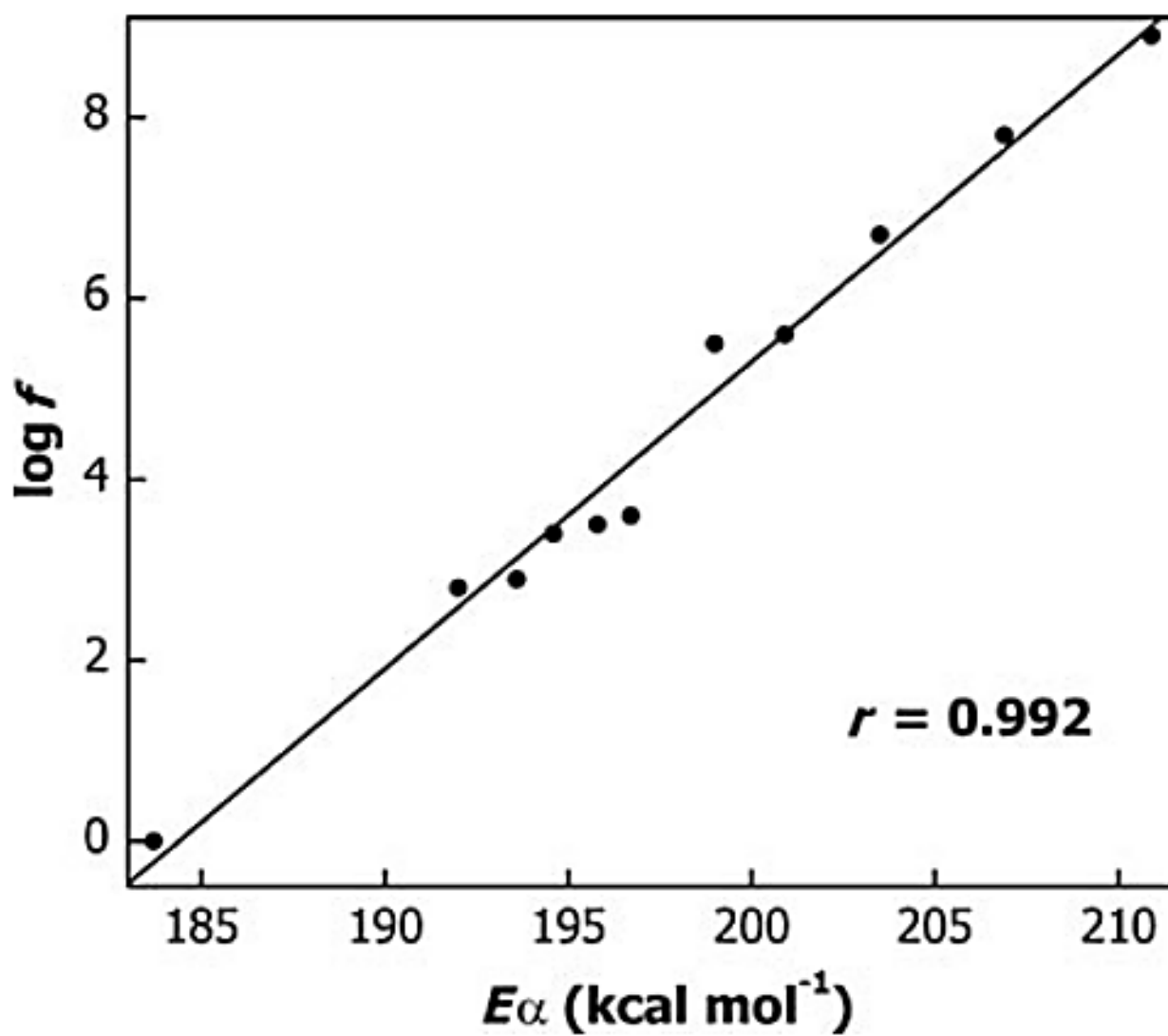


Figure 24. Partial rate factor ($\log f$) versus electrophile affinity($E\alpha$) for the debromination of PBDE.

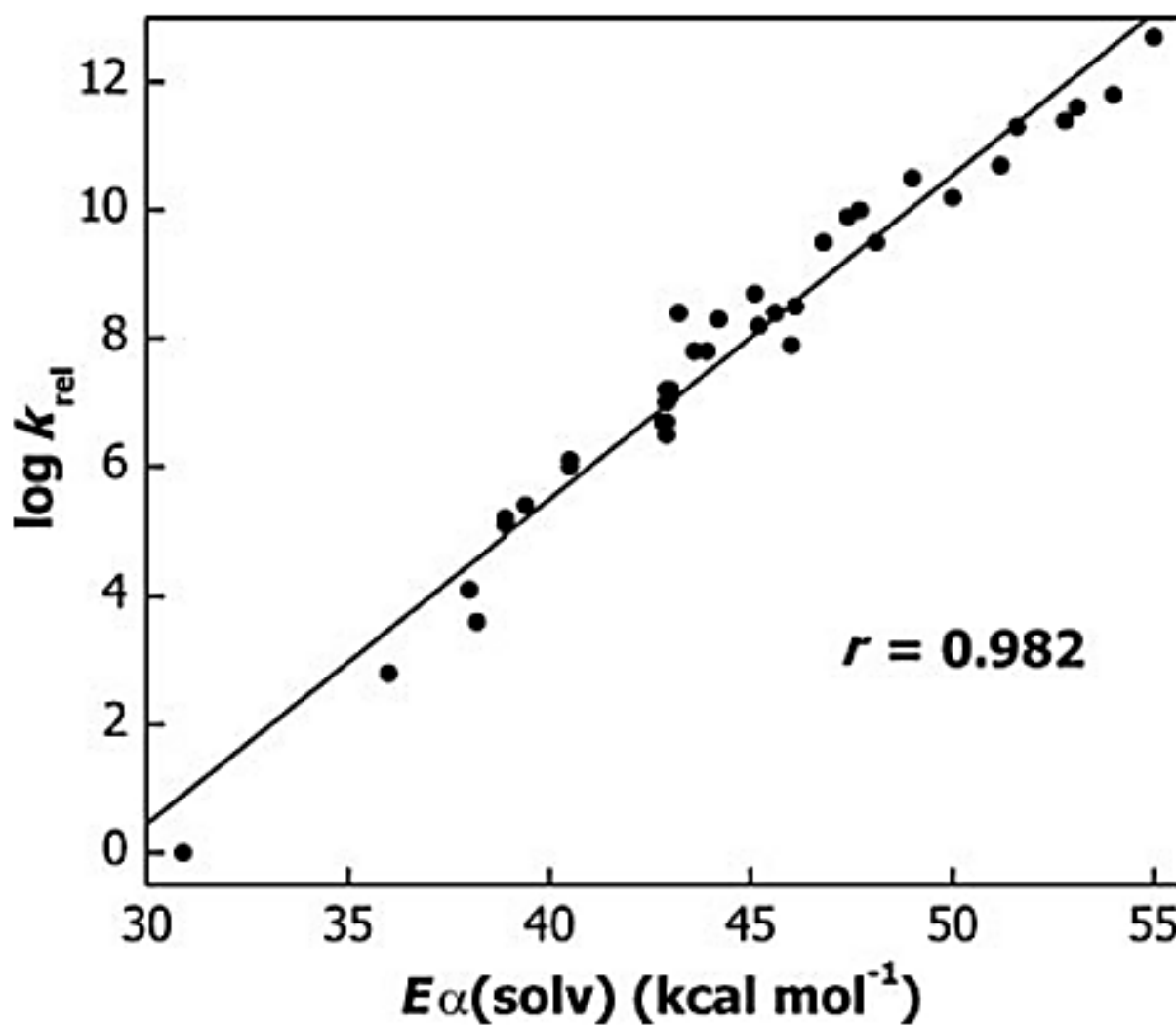


Figure 25. Electrophile affinities $E\alpha(\text{solv})$ versus experimental $\log k_{\text{rel}}$ kinetic data 84 for a set of 37 bromination reactions of PBDE variously substituted derivatives.