Degradation of bisphenol A: a contaminant of emerging concern, using catalytic ozonation by activated carbon impregnated nanocomposite-bimetallic catalyst

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Abstract
Rampant water pollution events and rising water demand caused by exponential population growth and depleting freshwater resources speak of an impending water crisis. The inability of conventional wastewater treatment systems to remove contaminants of emerging concern (CECs) such as bisphenol A (BPA) beckons for new and efficient technologies to remove them from wastewater and water sources. Advanced oxidation processes such as ozonation are primarily known for their capability to oxidize and degrade organic entities in water, but optimum mineralization levels were hard to achieve. In this study, we synthesized an activated carbon impregnated nanocomposite-bimetallic catalyst (AC/CeO2/ZnO) and used it along with ozonation to remove BPA from water. The catalyst was characterized using BET, XRD, FESEM, Raman spectra, and DLS studies. Catalytic ozonation achieved TOC removal 25% higher than non-catalytic ozonation process. The degradation pathway of BPA was proposed using LC–MS/LC-Q-TOF studies that found six main aromatic degradation byproducts. Catalytic ozonation and non-catalytic ozonation followed similar degradation pathways. The formation of persistent aliphatic acidic byproducts in the treated sample made total organic carbon (TOC) removal above 61% difficult.

Keywords Bisphenol A · Bimetallic catalyst · Characterization · Contaminants · Degradation · Ozonation · Total organic carbon

Introduction

Water pollution is a matter of global concern. Pollution events have aggravated partly due to the ineffectiveness of conventional wastewater treatment plants to remove the rising tide of pollutants. Among them, organic pollutants under the category of contaminants of emerging concern (CECs) are of particular concern due to their ubiquitous nature (Fairbairn et al. 2018).

Bisphenol A (BPA) is an endocrine disrupting compound widely used in the production of epoxy resins and polycarbonate plastics. BPA is associated with reproductive system damage in living organisms. Its presence in the environment and water bodies are ubiquitous due to its wide use. Conventional wastewater treatments were unable to remove them efficiently. At present, it is classified under the larger group of CECs. Dong et al. (2021) studied the photocatalytic removal of BPA using MnO2/UV/persulfate and achieved 90% removal, but mineralization was not achieved. Gan et al. (2021) discusses the removal of BPA with oxidative degradation using delta MnO2 with kenaf carbon fiber (KCF). Complete degradation was achieved with mineralization in water. However, more studies on actual wastewater with a...
mixture of other pollutants than BPA are needed for analyzing the efficacy of the treatment and pilot scale application. In this context it becomes imperative to find an efficient technology to remove CECs such as BPA from water sources (Fürhacker et al. 2000; Amjad et al. 2020).

Advanced oxidation processes (AOP) attracted specific interest from the scientific community because of their high removal, time efficiencies, manual automation capabilities, and zero residue degradation pathways, reducing the need for post-treatment (Garrido-Cardenas et al. 2020). Ozonation produces ozone radicals (∙O₃) that destroy organic molecules and also disinfects drinking water. However, their use to destroy organic chemical molecules had mixed result (Tizaoui and Grima 2011). The introduction of oxygen molecules and hydrogen peroxide in AOP enhances organic pollutant degradation due to the in situ hydroxyl radical (∙OH) production (Duarte et al. 2018). Table 1 discusses about the recent studies and findings on ozonolysis for water treatment.

Ozonation might succeed in completely oxidizing organic pollutants if hydroxyl radicals could be produced in situ. Nanocatalysts enhance photocatalytic removal of organic pollutants from water and wastewater resources. Heterogeneous catalysts were more efficient than homogeneous catalysts because of the larger number of holes, hence, lesser activation energy and broader energy bandwidths. Less costly metal oxides as heterogeneous catalysts are preferred for organic pollutant removals than the costly non-metal oxides (Korotchenkov 2020). Cerium dioxide (CeO₂) provided better organic pollutant removal rates when used along with Fenton processes. When used with other catalysts, they can produce strong oxidants such as superoxide and hydroxyl radicals. The catalytic activity of CeO₂ has a direct correlation with its reducibility and the initiation of oxygen vacancies. According to the literature, the key to increasing the process efficiency of CeO₂-based wastewater treatment is to increase the redox reactions at

| Sl. no | Target compound | Specific technique | Optimal conditions | Contaminant removal | Mineralization | Reference |
|--------|-----------------|--------------------|--------------------|--------------------|---------------|-----------|
| 1      | Bisphenol A in water | Catalytic ozonation using chemicals (O₃/nZrO₂/H₂O₂ and O₃/nTiO₂/H₂O₂) | 1) 4–12 g/L catalyst dosage 2) 20–100 mg/L target compound concentration | ≈100% | 46% using nZrO₂ and 52% using nTiO₂ | Shokoohi et al. (2021) |
| 2      | Bisphenol A in water | Ozonation with 52–82% ozone utilization | 1) Neutral pH 2) 285 mg/L target compound concentration | >98% | >98% | Jabesa and Ghosh (2022) |
| 3      | Bisphenol A in wastewater | Homogeneous catalytic ozonation (ZnSO₄) and heterogeneous catalytic ozonation (ZnO) | 1) Homogeneous catalytic ozonation: pH 6.32, 1 mg/L catalyst dosage, 2400 mg/L ozone dosage, and 12.5 min 2) Heterogeneous catalytic ozonation: pH 6.32, 50 mg/L catalyst dosage, 2400 mg/L ozone dosage, and 20 min | ≈94% for ZnSO₄ ≈99% for ZnO | Not studied | Tanatti (2021) |
| 4      | Metronidazole, copper, and zinc in water | Catalytic ozonation using Mg(OH)₂ | 1) 10–100 mg/L of metronidazole 2) 15 min | ≈100% for metronidazole, copper, and Zinc | Not studied | Sun et al. (2021) |
| 5      | Bisphenol A in Mill-Q water | Catalytic ozonation using AC/CeO₂/ZnO | 1) 500 µg/L of catalyst dosage 2) 5 mg/L of target compound concentration 3) 60 min 4) pH 8 5) 4 g/h ozone dosage | 98% | 61% | Present study |
the catalyst surface. In this regard, CeO₂ nanorods were found to have higher surface redox capacity than CeO₂ nanocubes due to the former’s lesser activation energy requirement for H₂O₂ decomposition (Korotchenkov 2020). Literatures establish zinc oxide (ZnO) as an efficient less costly photocatalyst with ultraviolet (UV) and visible light sources. It has been successfully used to remove organic dyes, persistent organic pollutants, and phenolic compounds from water and wastewater (Lee et al. 2016). ZnO’s efficiency as photo and sonocatalyst is due to its capability to produce higher concentrations of reactive oxygen species such as superoxide radicals and hydroxyl radicals which helps in oxidizing the pollutants in water and wastewater sources (Lee et al. 2016; Khataee et al. 2015). For the use of nanocatalysts in water and wastewater treatments, substrates are needed. Substrates that provide adequate surface and optimal binding for robust structure and stability are preferred. Activated carbon (AC) is found to be a suitable substrate in many nanocatalyst applications. It is cheap and biodegradable. Its production from wood, sugarcane bagasse, and other organic materials makes it environment friendly (Dias et al. 2007; Hernandez-Leal et al. 2011).

In this study, AC produced from sugarcane bagasse was used as the substrate for CeO₂ and ZnO nanocatalysts. The nanocomposite-bimetallic catalyst thus synthesized was used for producing hydroxyl and superoxide radicals from the ozonation process to degrade bisphenol A (a contaminant of emerging concern (CEC)). Bisphenol A was used as the model compound for assessing the efficacy of catalytic ozonation for CEC removal from water. The structure, stability, and morphology of the synthesized catalyst were studied using techniques such as X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). The degradation efficiency and the mechanism of degradation were analyzed using high performance liquid chromatography (HPLC) and liquid chromatography (LC)-mass spectrometry (MS) studies.

Materials and methods

Preparation of activated carbon supported nanocomposite-bimetallic catalyst (ANBCC)

One hundred grams of dried crushed sugarcane bagasse samples were physically activated in a muffle furnace (Genuine Equipment Manufacture, India), at 500 °C for 1 h. Then, the sample was weighed and soaked in 1 M KOH in 1:1 ratio for 24 h. The product obtained was chemically activated at 300 °C for 2 h with a muffle furnace. Free alkalis of the carbonized material were removed by washing it with double distilled water, then dried at 100 ± 5 °C for 2 h, and weighed to calculate the yield of activated carbon. The activated carbon product obtained was used to make the nanocomposite-bimetallic catalyst.

Metal oxides such as zinc oxide (ZnO) and cerium (IV) oxide (CeO₂) were bought from Loba Chemie (Mumbai, India) and prepared the nano-metal oxides with ball milling process (Star Trace Pvt. Ltd, India). Bulk metal oxides were exposed to 200 RPM for 15 h with 8-mm stainless steel balls at a ratio of 20:1 (ball:powder) in a horizontal ball mill. Activated carbon and nano-metal oxides in the ratio of 2:1 were dispersed in 0.5 M HCl for 6 h and evaporated to dryness in an oven for the formation of slurries. The composite material products were washed with Milli-Q water and then dried in a hot air oven (Genuine Equipment Manufacture, India) at 100 °C for 24 h. They were grinded into powder using mortar and pestle. The surface area of the catalysts were analyzed by BET method. Fifty milligrams of BPA (Merck, Bangalore, India) was weighed and dissolved in 1000 mL double distilled water, and 100 mL stock solution was made. Then, the stock solution was diluted to 1000 mL in standard flask with double distilled water to make working standard of 5 mg/L BPA.

Characterization of activated carbon and bimetallic catalysts

The synthesized nanoparticles, activated carbon and the nanocomposite-bimetallic catalyst, were subjected to X-ray diffraction (XRD), so as to understand to what extent the ball milling has influenced the structure. X-ray diffraction patterns were recorded using computer controlled XRD units (PANalytical X-ray diffractometer-XPERT PRO, Netherland). The XRD patterns were recorded between 20 angles, 20–70° at a scan rate of 2°/ min from which d-spacings were calculated. The resulting analysis was described graphically as a set of peaks with intensity on the Y-axis and goniometer angle on the X-axis. If the sample is powdered, it provides, theoretically, all possible orientations of the crystal lattice, the goniometer provides a variety of angles of incidence, and the detector measures the intensity of the diffracted beam. The exact angle and intensity of a set of peaks is unique to the crystal structure being examined. A comparison with patron tables, such as Joint Committee on Powder Diffraction Standards (JCPDS) spectra published by the American Society for Testing and Materials, provides valuable information about composition of the powder. The crystallite sizes were calculated from the X-ray broadening technique as per the Scherrer formula on the best resolved diffraction peak (Cullity and Freda 1958):
where \( D \) is the crystallite size diameter (nm), \( \lambda = 1.54 \text{ Å} \), \( \beta \) is the full width at half maximum (FWHM) of a diffraction peak, and \( \beta_{\text{ref}} \) corresponds to the instrumental FWHM.

Scanning electron micrographs were taken using a field emission scanning electron microscopy (FESEM) (JEOL, JSM-5600, England) attached energy dispersive X-ray (EDX) at 10 kV. The sample powders were deposited on a carbon tape before mounting on a sample holder after sputter coating gold for conduction.

Raman spectra using Horiba Jobin Raman spectrometer, Japan reflection mode, wavelength of 532 nm, and 2mW spectrometer coupled to an Olympus metallographic microscope were used. A 0.1 g of the sample placed on a sample holder and spectra was recorded in 100–1000 cm\(^{-1}\).

### Experimental setup for ozonation process

The experimental setup consists of oxygen concentrator (Sim O2, Italy), ozone generator (Ozonetek Ltd, Chennai, India), and ozonation chamber. Ozone was generated by the oxygen flow (99.7%) from the oxygen concentrator into the ozone generator at a flow rate of 1.5 l/min.

### Table 2 Yield and size of metal oxide nanoparticles prepared by Ball milling process

| Name    | Initial weight (g) | Final weight (g) | Time of ball milling in (h) | Size of nanoparticle (nm) |
|---------|--------------------|------------------|-----------------------------|---------------------------|
| CeO\(_2\) | 20                 | 17.3             | 15                          | 24.89                      |
| ZnO     | 20                 | 17.7             | 15                          | 15.9                       |

### Table 3 BET surface area analysis results of AC/CeO\(_2\)/ZnO nanocomposites bimetallic catalyst

| Compounds                   | BET surface area m\(^2\)/g | Inter particle pore size(Å) | Pore volume cm\(^3\)/g |
|-----------------------------|-----------------------------|------------------------------|------------------------|
| CeO\(_2\) nanoparticle      | 29.7                        | 146.9                        | >0.118                 |
| ZnO nanoparticle            | 6.5                         | 158.1                        | >0.025                 |
| AC/CeO\(_2\)/ZnO nanocomposites | 32.4                        | 88.4                         | >0.071                 |
The reactor (ozonation chamber) had a glass column of 45 cm height, an inner diameter of 6.5 cm with an outlet at the bottom through which the sample was collected after treatment. The teflon tube was used for connecting the ozone generator to the ozone reaction chamber and outlet port. One inlet and one outlet were present at the top of the reactor. During the treatment, the ozone-oxygen mixture was bubbled through diffuser, and ozone was sent to thermal vent before sending it outside. The volume of sample taken for each experiment was 1000 mL. Initial ozone concentration of 4 g/h was maintained throughout the experiment.

For all the experiments, the initial pH was adjusted through addition of 0.1 N NaOH or 0.1 N HCl solutions with the help of pH meter (Susima AP-1 Plus, Chennai, India). The reactor was placed on a magnetic stirring block (Superfit, Coimbatore, India) in order to keep its contents well mixed during the experiment. The schematic diagram of the ozonation process is shown in Fig. 1. After each run, the reactor was washed with distilled water. During the ozonation processes, 20 mL of sample was withdrawn each time at a definite time interval and processed for separation using a centrifuge at 5000 rpm for 15 min. pH of the sample was analyzed before and after treatment. The supernatant of sample was filtered with Millipore filter (0.20 μm) and then analyzed for BPA removal, HPLC, TOC, LC–MS, and LC-Q-TOF.

A closed chamber was used for the ozonation process so that it will not be released to the atmosphere. The excess ozone/half gas coming from the reactor was sent to ozone destruction unit to get dissociated into oxygen molecules in the presence of high temperature. The oxygen molecules were released to the atmosphere.

Degradation studies

TOC was estimated using the procedures adopted from APHA 5310B (APHA 2005). FTIR absorption spectra of the air dry crystal before and after treatment were analyzed using FT-IR spectrometer (Thermo scientific, Model–Nicolet 10, USA). Fifteen milligrams of sample was dispersed in 200 mg of spectroscopic grade potassium bromide (KBr) to record in the range between 4000 and 400 cm⁻¹. The spectra were recorded on KBr discs of the dried sorbent. Before each measurement, the instrument was run to establish the background, which was then automatically subtracted from the sample spectrum. HPLC studies were conducted using procedures adopted from Romani et al. (1994). LC–MS/LC-Q-TOF studies were conducted using procedures adopted from Cordwener et al. (2009).

Results and discussion

Characterization studies

Characterization of the nanoparticles and the nanocomposite-bimetallic catalyst were done by the analysis of the catalyst yield and using BET surface area, XRD, FESEM, Raman Spectra, and DLS studies.

Table 2 shows the yield of nanoparticles after 15 h of ball milling. The yield of CeO₂ was 17.3 g. Yield of ZnO nanoparticle was 17.7 g. The size of nanoparticles was found to be 24.89 nm for CeO₂ and 15.9 nm for ZnO based on the analysis of DLS and XRD. The efficiency of the catalytic ozonation process depends to a large degree on the catalyst and its surface area properties. Thus, the surface area is a crucial factor in catalytic ozonation. The results of surface area analysis are shown in Table 3. It shows that nanocomposite-bimetallic catalyst was having a surface area of 32.39 m²/g (BET surface area). The inter-particle pore size was 88 Å, and pore volume was greater than 0.071 cm³/g. Non-uniform inter-particle porosity occurs in the synthesized nanocomposite-bimetallic catalyst because
of the scarification of the nanoparticle which results in mesoporosity (Neethu et al. 2021).

XRD pattern of the CeO₂ nanoparticles synthesized by ball milling process is shown in Fig. 2. All peaks in the XRD spectra were indexed as (JCPDS-34–0394) of CeO₂. From the analysis of XRD pattern, peak intensity, position, and full width at half maximum (FWHM) data were determined. The diffraction peaks located at 28.54°, 33.08°, 47.48°, 56.34°, 59.09°, and 69.42° belong to CeO₂. This confirmed the synthesized nanoparticle’s purity. There were no other characteristic peaks other than CeO₂ peaks. The synthesized CeO₂ nanoparticle diameter was calculated using Debye–Scherrer formula (Desai et al. 2020). The average particle size of the sample was found to be 24.89 nm.

Figure 2 shows the XRD patterns of the individual metal oxides, AC, and the nanocomposite-bimetallic catalyst. The diffraction peaks at 28.54°, 47.48°, 56.34°, 59.09°, and 69.42° belongs to CeO₂, and diffraction peaks located

![FESEM-images](image1)

![EDX spectra](image2)

**Fig. 3** FESEM-images of a CeO₂ nanoparticles, b ZnO nanoparticles, c AC nanoparticles, and d AC/CeO₂/ZnO nanocomposite-bimetallic catalyst e EDX spectra of AC/CeO₂/ZnO nanocomposite-bimetallic catalyst
at 31.77°, 34.43°, 47.55°, and 69.68° were related to ZnO nanoparticles (JCPDS: 65–3411) (Shi et al. 2014). The peaks at 24° and 42° correspond to activated carbon (Song et al. 2017). The composite peaks found in the XRD analysis mostly corresponds to CeO$_2$. The X-ray diffraction patterns of the activated carbon structure showed diffused peaks at 24° and 42°. They appeared at narrow angles as fingerprint peaks. The AC structures were highly amorphous in nature, and they had heterogeneous surface (Danish et al. 2011).

The structural characterization of pure CeO$_2$ nanoparticle was done using FESEM. Figure 3 shows the FESEM-Image of CeO$_2$, ZnO, AC nanoparticles, AC/CeO$_2$/ZnO nanocomposite-bimetallic catalyst, and EDX image of AC/CeO$_2$/ZnO nanocomposite-bimetallic catalyst. The morphological studies showed that CeO$_2$ nanoparticles had uniform agglomerated nanosphere structure. The morphology of the synthesized ZnO nanoparticle was in the form of triangle-shaped nanorod-like triangle prism, and the pores had been created on activated carbon during the activation process of carbon. The pores were partially opened due to an increase in activation temperature from 500 to 600 °C. CeO$_2$ nanoparticles were evenly distributed, and ZnO was evenly impregnated on activated carbon.

Figure 4a shows the Raman Spectra of AC/CeO$_2$/ZnO nanocomposites. The Raman spectrum of the nanocomposites exhibited an intense band at 453.79 cm$^{-1}$, which is attributed to a symmetrical stretching mode of the CeO$_2$ (Maensiri et al. 2014; Reddy et al. 2007). The peaks for ZnO nanoparticles at 95.71 cm$^{-1}$ and 585.49 cm$^{-1}$ were assigned to the low, high longitudinal optical phonon peak of the ZnO nanoparticles (Song et al. 2019; Damen et al. 1966). The obtained spectra also showed the presence of the band near 1583.56 cm$^{-1}$ (G band) typical of more organized graphitic materials, and band at 1349.55 cm$^{-1}$ (D band) suggested the presence of more defective amorphous carbon structures. The peaks at 1593.55 cm$^{-1}$ and 132.71 cm$^{-1}$ were typical of activated carbon (Nakamizo et al. 1994).

Particle size has a direct influence on material properties such as reactivity and dissolution rate of catalysts. Analyzing the particle size of the catalyst will fetch information on the interaction between catalyst and ozone. Figure 4b represents the graphical representation of dynamic light scattering (DLS) result. The particle size of the nanocomposite-bimetallic catalyst was found to be 453.3 d.nm.

Degradation studies

Catalytic ozonation shows great advantages in removing the refractory organics present in water and is expected to become a powerful and valuable technology in water treatment. The mechanism of catalytic ozonation is based on ozone decomposition reactions followed by the generation of hydroxyl radicals. The metal ions accelerate the decomposition of ozone to produce the •O$_2$, and then electron of •O$_2$ transfers to O$_3$. This is followed by the formation of •O$_3$, and •OH. Figure 5 represents the impact of pH, catalyst dosage, and time on catalytic ozonation of BPA and TOC removal. It was found that when pH increases from 6 to 8 at catalyst dosage of 500 µg/L and ozone rate 4 g/h, the trend of TOC removal in oxidation process increased. When pH was 8, maximum TOC removal was observed within 35 min. Increasing the pH from 8 to 10 showed a decreasing pattern in TOC removal. The possible reason for showing maximum removal at pH 8 was because of the generation of more hydroxyl radicals that randomly reacted with BPA (Thangudu et al. 2020; Rajabi et al. 2020), and a decrease in TOC removal at higher pH was due to the...
conversion of hydroxyl radicals to hydroxide ions (Wang et al. 2019).

Catalyst dosage is a significant aspect in catalytic ozonation. The catalyst surface and type of catalyst also play a key role in heterogeneous catalytic ozonation. The catalyst dosage selected for the study was in the range of 250 to 750 µg/L. When the catalyst dosage increased from 250 to 500 µg/L at pH 8, 60 min and ozone rate 4 g/h, the TOC removal increased. Further increase in catalyst dosage did not show competent increase in TOC removal. At 500 µg/L catalyst dosage, 61% TOC removal was achieved within a time of 60 min.

At pH 8, ozone rate 4 g/h, and 500 µg/L of catalyst dosage, maximum TOC removal was achieved within 60 min. This was because maximum ozone molecules reacted with the catalyst surface within this time. The ozone molecules decomposed to hydroxyl radicals at the catalyst surface and reacted with the BPA.

**Comparison of catalytic ozonation and non-catalytic ozonation**

From Fig. 6, it is evident that the TOC removal efficiency of catalytic ozonation is high compared to non-catalytic ozonation. Non-catalytic ozonation achieved only 36% of TOC removal, while catalytic ozonation achieved 61% TOC removal. The increased efficiency was due to the formation of hydroxyl radicals by ozone decomposition on the surface of the nanocomposite-bimetallic catalyst. The available surface area of AC/CeO₂/ZnO nanocomposites prompted minimization of the diffusion limitations allowing the rapid
adsorption and desorption of ozone molecules dissolved in water.

Figure 7 shows the FTIR spectra of AC/CeO\textsubscript{2}/ZnO nanocomposite-bimetallic catalyst before and after catalytic ozonation. The band due to the stretching frequency of Ce–O is below 785 cm\(^{-1}\) which means that the stretching band at 551.93 cm\(^{-1}\) and 774.23 cm\(^{-1}\) belongs to Ce–O stretch. The “scissor” bending of H–O–H broad absorption band located at 1596.26 cm\(^{-1}\) is associated with water (Jiang et al. 2016). The absorption band located around 3777.69 cm\(^{-1}\) corresponds to the O–H stretching vibration of residual water and hydroxyl groups. The stretching at 1225.23 cm\(^{-1}\) can be attributed to the O–H vibration in absorbed water on the sample surface. The stretching frequency of Ce–O can be seen at 767.83 cm\(^{-1}\), also. The FT-IR peaks at 1589.98 cm\(^{-1}\), 1231.63 cm\(^{-1}\), 1039.71 cm\(^{-1}\), 1064 cm\(^{-1}\), 952 cm\(^{-1}\), and 767.83 cm\(^{-1}\) were similar to those of commercial CeO\textsubscript{2} powders (Shen et al. 2013) and CeO\textsubscript{2} nanoparticles (Phoka et al. 2009). The band at 767.83 cm\(^{-1}\) corresponds to (Ce–O) metal–oxygen bond (Kumar et al. 2013). The small and weak stretching at 1210.83 is ascribed to C-O in carboxylic acid. The weak stretching at 1596.26 is assigned to carbonyl C=O present in esters, aldehydes, ketonic groups, and acetyl derivatives. The small stretching at 2362.32 belongs to weak C≡C band of alkynes (Rother et al. 2016).

In the FTIR spectrum of nanocomposites, the absorption at 1601.28 cm\(^{-1}\) was assigned to the C=C stretching of activated carbon (Allwar et al. 2012; Rother et al. 2016). The absorption curve at 1001.97 cm\(^{-1}\) belonged to the asymmetry vibration of Zn–O. The absorption curve at 812.72 cm\(^{-1}\) was ascribed to the Zn–O stretching of ZnO (Xiong et al. 2006). The FTIR spectra confirmed the presence of nanocomposites and the absence of impurities in both the precursors and the prepared composite materials.

The FTIR spectra of AC/CeO\textsubscript{2}/ZnO nanocomposite obtained after the catalytic ozonation process confirmed the degradation of BPA and the formation of intermediates. The O–H stretching vibration at 3443.35 cm\(^{-1}\) was attributed to the phenolic group. The stretching between the ranges of wave numbers 2800 and 3200 cm\(^{-1}\) were attributed to C-H stretching. The peaks at 1476.45 to 1670.81 cm\(^{-1}\) wave numbers represented C-O and C–OH bonds of carboxylic groups (Ren et al. 2012). The peak at 1013.10 cm\(^{-1}\) is ascribed to the shift of skeletal vibration of C (CH\(_3\))\(_2\) group of BPA (Sahre et al. 2006). The peaks with wave numbers less than 1000 cm\(^{-1}\) represent the para-disubstituted and monosubstituted and/or ortho-disubstituted compounds (Jang and Wilkie 2004). There was also an indication of the formation of polyphenols such as resorcinol (Jyoti et al. 2016). From the above observations, it can be inferred that AC/CeO\textsubscript{2}/ZnO nanocomposites facilitated the production of •OH and degradation of BPA.

The removal of BPA was analyzed using HPLC, and it is presented in the Fig. 8. At 60 min of catalytic ozonation,
BPA concentration decreased about 97%. During catalytic ozonation, the degradation of BPA produced several low molecular weight organic acids which lead to the decrease in the initial solution pH. In order to better understand the BPA degradation during catalytic ozonation, pH of the solution after treatment was estimated with respect to different initial pH. The initial pH of the solutions were 5, 6, 8, 9, and 11, and after treatment, the pH of the solutions were 4.81, 4.12, 5.26, 7.57, and 10.17, respectively. The incomplete removal of TOC indicated the possibility of the formation of intermediates.

LC–MS/LC-Q-TOF analysis was performed by comparing the chromatogram of BPA with those of the aliquots taken at different ozonation times. All samples were subjected to similar derivatization procedure as mentioned in Cordwener et al. (2009). Figure 9c shows the LC–MS/LC-Q-TOF chromatogram of degradation byproducts. Identification of degradation byproducts was carried out based on fragmentation patterns in the mass spectrum and/or by comparing the mass spectrum with the library available in the instrument database. The proposed five aromatic degradation byproducts are
given in Table 4. Researchers had reported the formation of hydroxylated BPA byproducts such as monohydroxylated BPA, dihydroxylated BPA, and their quinones. The phenyl moiety-based compounds such as p-isopropenyl and p-isopropyl phenol and p-hydroxyacetophenone would have formed (Katsumata et al. 2004; Poerschmann et al. 2010; Olmez-hanci et al. 2013). Acidic compounds (responsible for pH decrease) such as formic, acetic, oxalic, succinic, and fumaric acids were also reported (Katsumata et al. 2004; Olmez et al. 2015). Other studies (Poerschmann et al. 2010; Olmez et al. 2015) pointed to the formation of coupling byproducts with higher molecular weight than BPA.

The proposed fragmentation pathway of BPA by catalytic ozonation is displayed in Fig. 9. The •OH radicals ruptured the BPA mainly through two attack sites which were the bond that held the two aromatic rings together and aromatic ring itself. The •OH radicals attacked the methyl bond between the two aromatic rings of BPA, and demethylation occurred by hydrogenation and dehydrogenation. The •OH radicals also attacked aromatic ring structure breaking it through hydroxylation and dehydroxylation. Once the ring structures were broken, further rupture of the ring structure and hydrocarbon bonds occurred through the same oxidation and reduction reactions.

### Conclusion

In this study, a novel activated carbon supported nanocomposite-bimetallic catalyst (AC/CeO2/ZnO) was prepared by wetness impregnation method for the removal of BPA from water sources. The presence of AC, CeO2, and ZnO in nano-bimetallic catalyst was confirmed by yield studies, BET, XRD, FESEM, Raman Spectra, and DLS. The specific surface area and pore size distribution of AC/CeO2/ZnO has played a significant role in catalytic ozonation of BPA. In the alkaline pH condition, ozone decomposition rate increases in water, and the half-life of ozone in water is short; thus, the •OH radical dominates the system as reaction intermediate. Therefore, degradation of BPA occurs due to •OH radicals.

| Molecular Weight | Time (min) | Compound | Proposed structure of Compound |
|------------------|------------|----------|--------------------------------|
| 255              | 7.6        | Hydroquinone | ![OH](image) |
| 209              | 7.02       | 4-Hydroxyacetophenone | ![O](image) |
| 293.5            | 6.2        | 2-(2-(4- Hydroxyphenyl)propan-2-yl)succinaldehyde | ![O](image) |
| 274.99, 273.1, 1.273.1 | 2.7, 5.7, 5.9 | 2-(1-(4-Hydroxyphenyl)vinyl)pent-2-enal | ![O](image) |
| 379.1            | 5.5        | 3-Formyl-4-(4-hydroxyphenyl)-4-methylpent-2-enoic acid | ![O](image) |
Fig. 9 Proposed pathways for the formation of five aromatic byproducts during catalytic ozonation of BPA. a Hydroxyquinone and 4-hydroxyacetophenone, b 2-(2-(4-Hydroxyphenyl)propan-2-yl)succinaldehyde, c 2-(1-(4-Hydroxyphenyl)vinyl)-pent-2-enal, and d 3-Formyl-4-(4-hydroxyphenyl)-4-methylpent-2-enoic acid.
produced on the surface of nanocomposite-bimetallic catalyst not by ozone. pH 8, catalyst dosage of 500 µg/L, and treatment time of 60 min were found to be the optimal conditions for maximum TOC removal (61%) achieved. There was 25% higher TOC removal efficiency for catalytic ozonation compared to non-catalytic ozonation. The FTIR studies of AC/CoO/ZnO nanocomposite-bimetallic catalyst found that degradation of BPA is due to catalytic ozonation and not due to adsorption. The pH changes noticed after catalytic ozonation is due to organic acids formed when BPA was oxidized by ∙OH. LC-Q-TOF analysis found five main aromatic degradation byproducts. They were hydroquinone, 4-hydroxyacetophenone, 2-(4-hydroxyphenyl)propan-2-yl)succinyldehyde, 2-(1-(4-hydroxyphenyl)vinyl)-pent-2-enal, and 3-Formyl-4-(4-hydroxyphenyl)-4-methylpent-2-enolic acid. Future studies would concentrate on finding other catalysts that could achieve higher TOC removal and mineralization. Wider applications of the process require life cycle and cost assessments in actual wastewater and natural water conditions.

Author contribution  HP did the experimental analysis, conceptualization, and preparation of manuscript. SF did the data curation, validation, and preparation of manuscript. SA did the interpretation of results and editing of manuscript. MM supervised, reviewed, and edited the manuscript and gave the overall guidance.

Availability of data and materials We declare that the data and materials supporting the findings of the current study are available within the article.

Declarations

Ethics and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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