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PHOTOELECTROCATALYTIC DEGRADATION OF ENDOCRINE DISRUPTING CHEMICAL FROM AQUEOUS SOLUTION USING ZnO NANOCATALYST

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The watery arrangement by Photoelectrocatalytic oxidation utilizing ZnO nanocatalyst was examined. The most astounding 65% of COD evacuation was accomplished with NaCl at 60 min of treatment time where as it was 53% and at 41% with Na_2SO_4 and $NaNO_3$, individually. The aftereffects of CV, UV– Vis and HPLC show that at the amid the PECO treatment BPA mixes were expelled from fluid arrangement. It could be inferred that PECO utilizing ZnO is a promising treatment for the expulsion of BPA from fluid arrangement. Nanomaterials can possibly considerably advantage ecological quality and manageability through contamination anticipation, treatment and remediation.

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Keywords: Endocrine disrupting chemical; Bisphenol–A (BPA); Photoelectrocatalytic Oxidation; Degradation, COD removal

1. Introduction

As of late, Endocrine Disturbing Chemicals (EDCs) have turned out to be a standout amongst the most important issues in the fields of natural science and innovation because of their capability to cause negative consequences for the endocrine frameworks of people and untamed life [3]. Bisphenol A [BPA, 2,2-(4,4-dihydroxydiphenyl)] is a run of the mill endocrine disturbing compound, utilized as a part of the creation of polymers, for example, epoxy, unsaturated polyester– styrene pitches and polycarbonates, as a forerunner of fire retardants or as coreactant in warm papers and other strength items [2]. BPA is mostly discharged into nature by means of wastewater from plastic delivering mechanical plant and landfill locales [5]. BPA is every now and again found in wastewater, sewage muck, water, and silt. The potential hindering impacts of BPA have been accounted for on untamed life and human generation by changing their endocrine capacities and estrogenic action [1],[4]. Appropriately, there is a dire requirement for creating viable advances for the fast expulsion of BPA from oceanic condition.

Lately, there have been escalated endeavors toward the improvement of productive innovations for the expulsion of relentless xenobiotics from fluid lattices. In the course of recent years, heterogeneous photocatalysis has gotten gigantic consideration for the treatment of different classes of natural contaminants found in waters and wastewaters. Of the different semiconductors, ZnO has solely been utilized in ecological applications. PECO utilizing a semiconductor, for example, ZnO is enlightened by light beams with wavelength underneath 380nm, the photons energize valence band electrons over the bond jabber into conduction band, abandoning openings in the valence band. The gap in ZnO will respond with water particles or hydroxide particles (OH^-) and afterward deliver hydroxyl radicals (OH^o).

Many researchescome about proof of BPA causing unfriendly wellbeing impacts; even low measurements can bring about perpetual character changes in and develop living creatures [5]. High grouping of BPA can be contained in wastewater from its generation manufacturing plants

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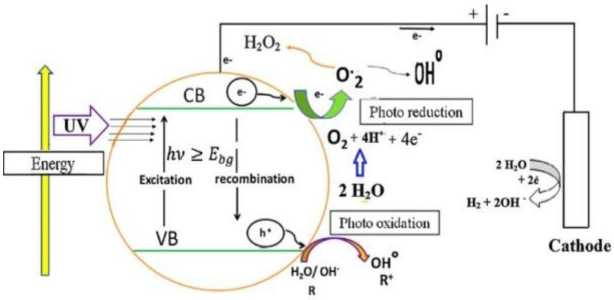
since it is mostly expelled amid wastewater treatment.The wastewater containing BPA can be wellspring of sullying in amphibian condition. In spite of the fact that BPA is promptly debased by microorganisms, natural techniques normally require long circumstances for the wastewater containing BPA at high fixation [6]. In like manner, there is a dire requirement for creating compelling innovations for the quick expulsion of BPA from oceanic condition.



Scheme. 1 Photo-Electrochemical Reactor

In the course of recent years, extensive endeavors have been committed to evacuation and treatment of BPA, incorporate microbial corruption, adsorption, sonochemical debasement, photo–Fenton, Fenton's reagent, ultrasonic cavitations, photocatalytic corruption, ozonation and electro enzymatic catalyzed oxidation. In spite of the fact that these techniques demonstrated high expulsion effectiveness and furthermore had a few disadvantages, for example, high cost, the age of auxiliary items those are much more dangerous than the first materials. In this manner, it is critical to build up a basic, protected and viable technique for the corruption of BPA. Be that as it may, there are few examinations managing photoelectrocatalytic corruption of watery BPA in writing [7].

The extent of this work was to examine BPA debasement by photoelectrocatalysis corruption on ZnO. The impact of different working conditions, for example, connected current, BPA focus, arrangement pH has been analyzed.

The point of the exploration work was to contemplate the attainability of the treatment of BPA from watery arrangement by consolidated electrocoagualtion took after by electrochemical oxidation treatment forms. The procedure was analyzed under various current thicknesses, with a specific end goal to set up ideal working conditions. The evacuation productivity of the treatment was controlled by checking the rate expulsion of COD.

2. Experimental

2.1 Materials

In the present study, BPA stock arrangement was set up by dissolving BPA (Merk Chem, Mumbai, India), without advance filtration, with twofold refined water and 1N NaOH has been included for increment dissolvability on the grounds that BPA has awesome solvency at soluble pH condition and included fitting measure of supporting electrolyte. All chemicals utilized as a part of the trials were of logical review. The arrangement pH was balanced by 0.1 M of H_2SO_4 or NaOH and doubly refined water was utilized as a part of the considerable number of examinations [8].

2.2 Photoelectrocatalytic oxidation reactor

The photoelectrocatalytic oxidation tests were performed in a 750 mL photoelectrocatalytic oxidation reactor furnished with UV light connected with a quartz jacketed 15W drenching low weight mercury circular segment light (Philips, display TUV) as illumination at 254 nm source and anode get together inside a solitary compartment barrel shaped glass cell. The reactor is associated with a cooling water dissemination shower for controlling temperature at

27±2 °C. In the highest point of the reactor there is an arrangement for holding the UV light, cathodes, gas outlet and thermometer. An inner light source encompassed by a quartz coat and the light source is UV light. Graphite sheets each with expansiveness 3.8 cm and length 12.5 cm and it's thickness of 0.8 cm was utilized as terminals for photoelectrocatalytic oxidation reactor. Schematic graph of exploratory setup for photoelectrochemical reactor are appeared in the Fig.1

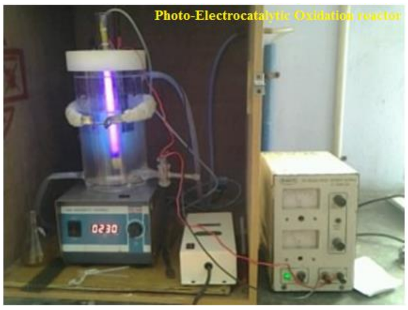


Fig.1.Experimental setup for photo-electrochemical reactor

The holes between the plates were kept up at 7 mm to limit the ohmic misfortunes. A dynamic aggregate anodic surface region of graphite plates was 102 cm^2. Electric power was provided by a managed DC control supply was acquired from M/s. Forceful Electronics Equipments Corporation Pvt. Ltd., Coimbatore, India. An arrangement of four terminals (two for anode and two for cathode) are on the other hand circled inside. The UV light and cathodes are associated with the particular terminals of the power source.

The known amount of the fluid BPA arrangement is coursed to the photoelectrocatalytic oxidation reactor at control stream rate utilizing peristaltic pump. 50 mg/L of nano materials ZnO is blended with arrangement. The arrangement is mixed with an attractive stirrer at 200 rpm. After the investigation, the power was turned off and the anodes were disengaged. The treated resorcinol test was centrifuged at 2000 rpm for 5 min and afterward supernatant fluid was taken for examination.

2.3 ZnO nanomaterial Preparation methodology and attributes

Zinc nitrate hexahydrate (200 mL) 0.5M arrangement was first arranged in refined water and refluxed at 100 °C in a 500mL reflux carafe fitted with a condenser. When warm balance was accomplished, hexamethylene tetramine arrangement of particular focus was included gradually. HMTA fixation was changed as 0.25, 0.5 and 0.75M to accomplish Zn:HMTA molar proportions 1:0.5, 1:1 and 1:1.5, separately. Refluxing time was additionally shifted and isolate clusters were refluxed for 2 and 4 h. To examine the impact of surfactants on the ZnO morphology, another arrangement of response blends was refluxed with various convergences of surfactants. The Zn:HMTA proportion was kept up at 1:1 for all arrangements utilizing surfactants. Arrangements were finished utilizing CTAB and Span-80 surfactants. CTAB focus was fluctuated as 0.05, 0.10 and 0.15Mand that of Span-80 as 1, 5 and 10 wt%, individually. After reflux, a white crystalline powder was gotten in all cases and was gathered and washed with refined water and ethanol, trailed by radiating filtration before drying at 70 ◦C.

Powder X-beam diffraction designs were gathered utilizing a Philips, X'Pert Pro X-beam diffractometer (Cu Kα radiation, λ= 1.54178å and 2θ = 20– 60°). Powder X-beam diffraction designs picture is appeared in Fig. 2.

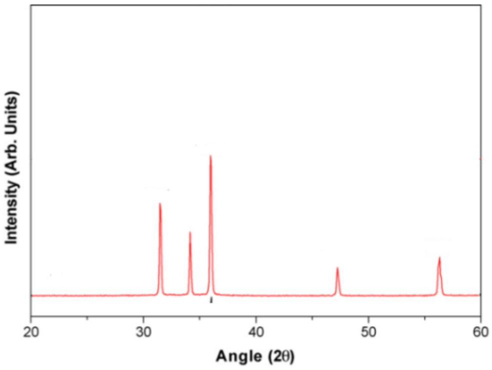


Fig. 2. Powder X-ray diffraction patterns

Fourier change infrared spectroscopy (FTIR) examination was completed utilizing a FTIR-Bruker-EQUINOX-55 spectrometer at encompassing conditions in the area 4000– 400cm^{-1}. The FTIR spectra picture of ZnO nanomatrial is appeared in Fig. 3. Molecule estimate dissemination was measured utilizing photograph relationship spectroscopy [PCS] (a Zetasizer 3000 HS framework, Malvern, UK). The morphological highlights and dimensional changes were seen under a checking electron magnifying instrument [JEOL, JSM-6700F]. The SEM picture of ZnO nanomatrial is appeared in Fig. 3. Transmission electron microscopy pictures were recorded utilizing a JEOL, 200CX, TEM contraption. Room temperature photoluminescence (PL) spectra were recorded utilizing a Fluoro Log-4 (Horiba Jobin Yvon, USA) framework and was energized by a Xe light at 380 nm.

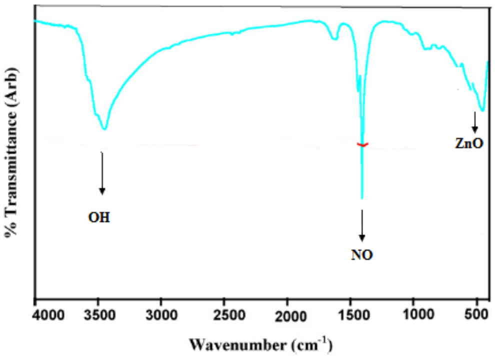


Fig. 3. FTIR spectra of ZnO nano material

The UV source in the reactor was 15 W, Philips G15 T8 tubes emitting radiation in the range 200–400nm (photon energy, 3.07–6.14 eV).

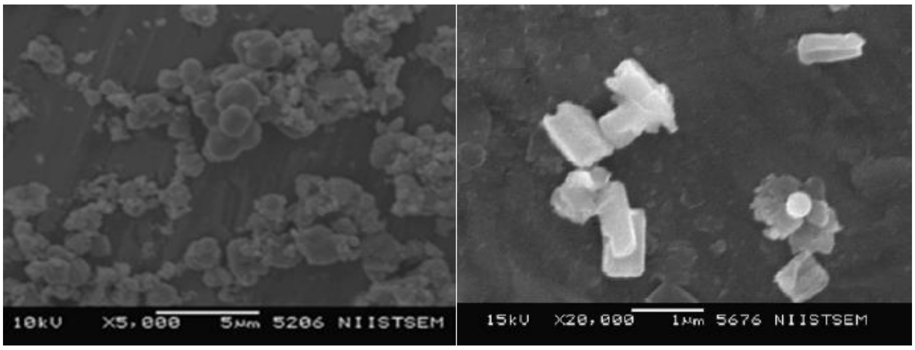


Fig. 4. SEM image of ZnO nano material

A suspension (500 mL) was set up by scattering 50mg/500mL of the ZnO powder in fluid BPA arrangement. The suspension was equilibrated oblivious for 1 hr to finish the adsorption of the color on the ZnO particles. The suspension was then presented to UV radiation under mixing.

2.4 Analytical Techniques

As is known, COD esteem mirrors the general grouping of organics in arrangement and has been broadly used to assess the level of corruption or mineralization of natural species amid the response. The fluid arrangements coming about because of photoelectrochemical treatment were broke down for COD as per standard techniques endorsed by American Public Health Association (APHA, 2005). Evacuation or debasement effectiveness of BPA was additionally checked utilizing HPLC. The pH of the arrangement was fluctuated by including 0.1M HCl or NaOH arrangement according to necessity and measured utilizing ELICO, India, display No. LI–120 pH meter. To test the reproducibility of the outcomes, certain analyses were performed in triplicate.

2.5 Elite fluid chromatography (HPLC) examination

Examination of BPA and its debasement items were additionally completed on a HPLC, (Model – 2489, WATERS, USA) outfitted with a different wavelength UV– obvious locator worked at 276 nm. The identifier yield was handled with top EMPOWER– 2 programming. Detachment was accomplished on a turnaround stage C18 (250mm x 4.6 mm) stainless steel section. For these examinations, tests of 10μL were infused into the chromatograph and a 50:50 (v/v) acetonitrile and water blend was passed at a stream rate of 1 mL/min as versatile stage. The development and corruption of the crests for halfway mixes were taken after at a similar state of segment. It showed a very much characterized crest for BPA at a maintenance time (tr) of 7.06 min at 276 nm. All solvents utilized were Hi– Media HPLC review and HPLC review water was utilized amid the examination, which was provided by RANKEM, New Delhi, India. Prior to every examination, the specimen was separated through a 0.45– µm layer channel (Millex).

3. Results and Discussion

The current research works managing the advancement of photoelectrocatalytic oxidation innovations joining both electrolytic and photocatalytic forms. Consolidating electrochemical and photograph catalysis innovations inside single compartment of the test setup utilized as a part of this exploration work. Impact of trial parameters including electrolyte sorts and focus, arrangement beginning pH and connected current on the photoelectrochemical debasement of BPA was explored.

3.1 Impact of supporting electrolyte sort [10]

In the present work, Gd doped Ceria and Sm doped Ceria were chosen as the nanocatalysts in light of its non–harmfulness and it requires similarly less oxidation potential. Since inorganic particles are broadly present in water assets and wastewater, numerous specialists are quick to know how inorganic mixes influence the photoelectrocatalytic and photocatalytic forms. Inorganic mixes may not exclusively be the harmful reagents or the foragers to the photocatalyst in the photocatalytic procedure, yet in addition be a supporting electrolyte for the electrochemical procedure in the photoelectrocatalytic reactor. In our photoelectrocatalytic tests, the NaCl was picked as a supporting electrolyte; therefore no direct electrochemical response required with the NaCl meddles with the photoelectrocatalytic responses on the grounds that NaCl demonstrated minimal impact on the electrolytic oxidation rate among the electrolytes contemplated some time recently. The impact of the supporting electrolyte on the photoelectrochemical evacuation of BPA is plotted in Fig. 5. The impact of various supporting electrolytes on COD evacuation effectiveness was explored utilizing Na_2SO_4, $NaNO_3$ and NaCl as supporting electrolyte (0.1M) at a connected current thickness of 15 mA/cm^2 and pH 6. Fig.5. demonstrates that the NaCl has the most astounding COD evacuation were seen among the researched supporting electrolytes utilized Gd doped Ceria as nano impetuses prompted the best outcomes. The most astounding 65% of COD expulsion was accomplished with NaCl at 60 min of treatment time where as it was 53% and at 41% with Na_2SO_4 and $NaNO_3$, separately. From the outcomes, it was reasoned that the greatest

COD expulsion was accomplished with NaCl as supporting electrolyte. All resulting photoelectrocoagulation tests were directed with NaCl as supporting electrolyte to explore the impacts of other parameter on the expulsion of the COD.

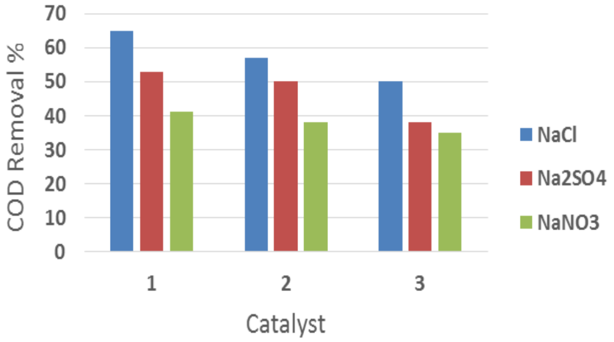


Fig. 5. The COD removal efficiency of BPA as a function of supporting electrolyte

3.2 The effect of solution pH

So as to assess the impact of pH of the arrangement on the rate evacuation of COD, a progression of examinations were directed and the BPA arrangement was acclimated to the coveted pH for each investigation by utilizing sodium hydroxide or sulfuric corrosive arrangements. The impact of arrangement starting pH in the scope of 3– 10 on the COD evacuation of BPA is explored in a progression of arrangements containing 20 mgL^{-1} of the impetus with beginning BPA convergence of 500 mg L^{-1} and the acquired outcomes are introduced in Fig. 6, which demonstrates that the rate of debasement increments with an expansion in pH of up to 7 and after that abatements. Greatest evacuation was accomplished at pH 6 within the sight of Gd doped Ce materials. Most minimal COD evacuation productivity is gotten without impetuses. In the underlying acidic pH, attendant with fermentation of the arrangement by HCl, a high measure of conjugated base adds to the arrangement. Additionally increment in the electrolyte pH past 8.0 does not demonstrate any change on rate evacuation of COD.

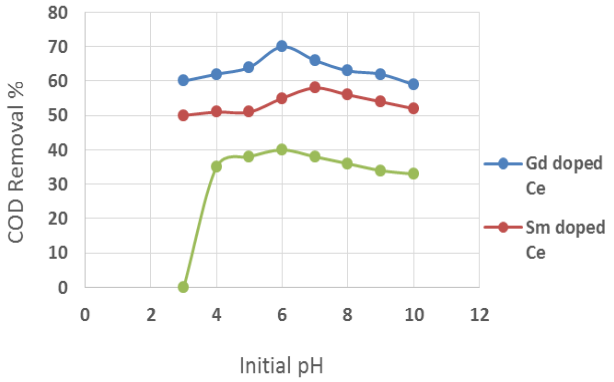


Fig. 6. The COD removal efficiency of BPA as a function of initial pH (treatment time: 60 min, current density of 15mA/cm^{2}and distance between electrodes: 7 mm, supporting electrolyte: NaCl 0.1 M).

The anion Cl^{-} responds with hydroxyl radicals prompting inorganic radical particles (ClO^{-}). These inorganic radical anions demonstrate a much lower reactivity than •OH, with the goal that they don't participate in the BPA debasement. There is likewise a radical rivalry amongst BPA and anions regarding •OH. Thus, an expansion in pH demonstrates an increment in corruption effectiveness. As the outcomes appear, there is a decline in expulsion effectiveness at a pH higher than 7. Creators propose that at a high grouping of $^{-}$OH (pH over 9) two procedures may happen prompting the deactivation of •OH. Initially, the $H_2O•_2$ and $HO•_2$ radicals frame because of the response of •OH with $^{-}$OH. The reactivity of these radicals with natural materials is not as much as •OH. Second, because of the nearness of high measures of •OH radicals, the radical– radical responses occur at higher pH esteems. By and large, deactivation of •OH in high pH esteems has beforehand been accounted for. In this manner, ideal pH sum for photoassisted electrochemical debasement of BPA was picked as 6.

3.3 Electrolyte fixation

Arrangement conductivity increments as the supporting electrolyte fixation builds, so the present going through the circuit increments in the potentiostatic mode. In light of preparatory trial comes about, the impact of supporting electrolyte fixation has been investigated inside the scope of 0.01M and 0.15M. In this way, with a specific end goal to decide the impact of supporting electrolyte fixation on the COD evacuation and the outcomes are introduced in Fig. 7. The expansion of NaCl marginally expanded the photoelectrocatalytic expulsion proficiency of BPA. At the diverse fixations, the evacuation effectiveness of oxalic corrosive comparably diminished at later response runs, despite the fact that the photoelectrocatalytic expulsion proficiency changed little at the primary run. Additionally, Fig. 8.Demonstrated that the groupings of NaCl likewise displayed a little impact on the photoelectrocatalytic response rate. It was apparent that the COD expulsion esteems expanded with the expansion of NaCl focuses in photoelectrocatalytic response; correspondingly, the measure of BPA evacuated additionally expanded. Therefore, the COD evacuations esteem expanded with the expansion of supporting electrolyte focuses.

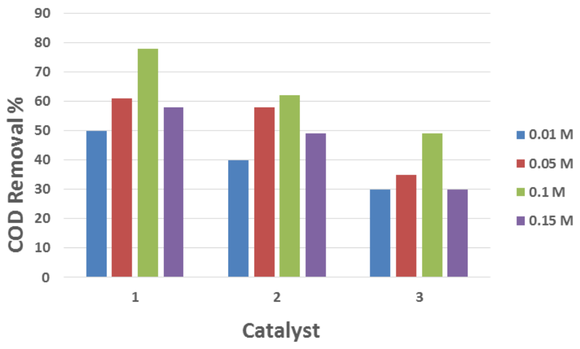


Fig. 7. The COD removal efficiency of BPA as a function of supporting electrolyte concentration (treatment time: 60 min, current density of 15 mA/cm^2).

After 60 min of treatment, when the convergence of the supporting electrolyte expanded from 0.01 to 0.05, and 0.1M, the COD expulsion productivity enhanced altogether from 48%, 63%, and 73.5%, separately. This is because of chlorine which produces solid oxidants that can oxidize resorcinol compound and advance cathode responses. Additionally increment the centralization of supporting electrolyte up to 0.15M with orders the COD expulsion (63.5%). It can be inferred that the most noteworthy expulsion rate are the point at which the direct convergence of supporting electrolyte of 0.1M within the sight of Gd doped Ce material.

3.4 Impact Current thickness

In any electrocoagulation procedure current thickness (mA/cm^2) and time of treatment are imperative operational parameters setting a definitive evacuation and characterizing the electrical vitality and power utilization so in the long run a definitive working expense for the procedure. Decision of cathode material is likewise essential influencing the cell voltage (diverse oxidation potential for various terminal materials) and the division accomplished. The impact of connected current thickness on the corruption of BPA by photoelectrochemical process is appeared in Fig. 8. Clearly the corruption rate of BPA expanded drastically as the present thickness expanded. For instance, when the connected current thickness expanded from 3 to 21 mA/cm^2, the corruption proficiency of BPA expanded quickly from 51.7 to 87.9 % within the sight of Gd doped ceria doped nanoparticles, 45.9 to 75.3% by Sm doped ceria and 33.4 to 54% without impetus. From the outcomes, it can be inferred that greatest expulsion is accomplished within the sight of Gd doped ceria material. At to begin with, the utilization of an outside electric field gives a potential slope to head out the photogenerated openings and electrons effectively in various ways.

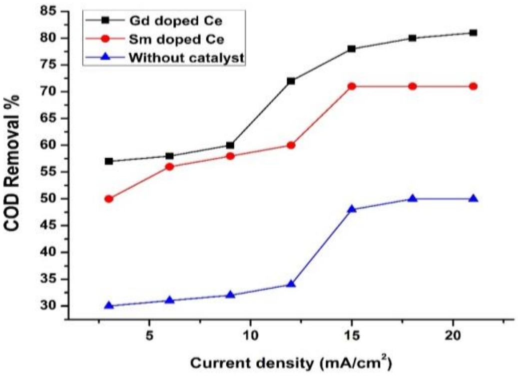


Fig. 8. The COD removal efficiency of resorcinol as a function of applied current density

Therefore, the recombination rate of photogenerated openings and electrons can be fundamentally perished, permitting numerous more photoelectrogenerated gaps to oxidize the natural species that are available in arrangement. This procedure guarantees that most intermediates are oxidized totally before dissemination happened from the impetus into the mass arrangement. In any case, the connected anodic inclination potential is dependably lower than that of target natural contamination in most photoelectrocatalytic tests, so no direct electrochemical oxidation confounds the photocatalysis. These examinations just viably introduced a proof-of-idea of the upgraded impact on photocatalytic debasement of natural toxins by lessening the electron gap recombination at outside electric field. Nonetheless, it merits calling attention to that electrochemistry is likewise a sort of compelling strategy for expelling natural poisons from water. Specifically, the electrochemical innovation in light of three-dimensional anode has pulled in more consideration as of late on the grounds that the three-dimensional terminal innovation is described by extensive particular surface territories and superior in contrast with regular two-dimensional plate cathodes. It is clarified by the way that the outside electric field couldn't just reduction the rate of recombination of electron-opening sets, yet could likewise enhance the direct or potentially roundabout electro-oxidation responses of anodes under higher connected current thickness.

3.5 Impact of blending

The rate of photodegradation is influenced by the anode response itself as well as by the vehicle of species to and from mass arrangement. This vehicle can happen by dissemination, convection or relocation. Relocation is a basic electrostatic impact that emerges because of the utilization of voltage which makes a charged interface on the terminals. Any charged species close to the interface will either be pulled in or repulsed from it by electrostatic powers. In this examination, the impact of movement can be ignored. This is because of the nearness of supporting electrolyte (0.1M NaCl), which acts to transport all the current in the cell and lessen the cell protection. Thus, the impact of the electrical field is constrained to a little separation from the cathode. Consequently, mass transport because of the dissemination and convection of the BPA atoms to the interface may influence the general effectiveness.

3.6 Electrical vitality utilization

Since the electric vitality has noteworthy extent of the working expenses in treatment forms. The impact of connected current thickness on vitality utilization was contemplated as appeared in Fig. 9. The vitality utilization expanded from 0.34 to 4.6 kWh/m^3 with expanding treatment time from 5 to 60 min. The vitality utilization was 4.16 kWh/m^3 utilizing Gd doped ceria nano impetuses at 15 mA/cm^2 of connected current thickness.

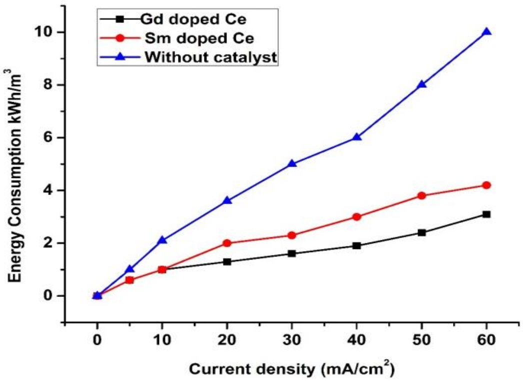


Fig. 9. The Energy consumption (kWh/m^3) of BPA.

3.7 HPLC analysis of before and after PCO treatment

From Fig. 10.Crude example shows a top at 7.03 min of maintenance time. For the second specimen (the example got after 60 min of electrolysis time tops range were moved to 4.49 min and 6.52 min. After 120 min of treatment time, the pinnacle was moved to 4.46 min and 6.83 min amid the electrochemical debasement One– ring fragrant mixes, for example, hydroquinone and benzoquinone, have been accounted for as vital intermediates of electrochemical corruption of phenolic chemicals. These one– ring items can be shaped through cleavage of the isopropylidene connect. In the present investigation, the measures of hydroquinone and p– benzoquinone created by electrochemical oxidation.

In the greater part of the proposed systems of the electro catalytic corruptions of natural poisons on metal oxide terminals, the very oxidizing hydroxyl radical, which begins from the oxidation of chemisorbed OH^- or H_2O by the connected anode potential, is viewed as the fundamental oxidative species in charge of the degradation[9]. Both fragrant mixes and aliphatic acids were distinguished by HPLC as the imperative intermediates of BPA electrolysis. In the underlying phase of BPA devastation and vanished through and through with BPA evacuation. It is very much recorded that sweet-smelling rings are promptly assaulted by hydroxyl radicals amid oxidation to shape hydroxylated subsidiaries through a middle of the road cyclohexadienyl radical response [11].

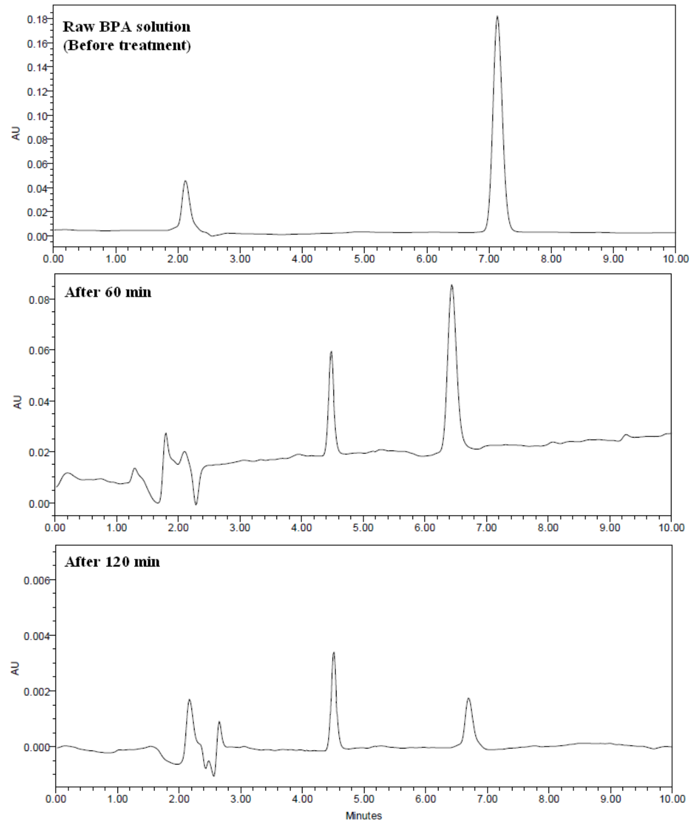


Fig. 11. HPLC analysis of before and after PECO treatment

To screen the debasement of BPA amid the photo assisted electrochemical process, the COD estimations were done under the diverse working parameters. Results show that 93.24% of COD was disposed of after 120 min of the procedure. Be that as it may, a few other got chromatographic pinnacles couldn't be recognized in view of their low match factor. PECO processes for corruption of BPA, as a model contamination from BPA wastewater, was contrasted and coordinate photolysis and electrochemical procedures. All procuress's take after the pseudo-first arrange energy. The outcomes demonstrated that the composed PECO framework had proper capacity for debasement of the BPA.

4. Conclusions

Among the electrolytes utilized, NaCl was seen to be exceptionally powerful contrasted with Na_2SO_4 and $NaNO_3$. Higher CD and [NaCl] quicken the PECO debasement. Among the electrolytes utilized, NaCl was seen to be extremely compelling contrasted with Na_2SO_4 and $NaNO_3$. Higher CD and [NaCl] quicken the PECO corruption. Most extreme BPA evacuation of 93% was accomplished at under the advanced condition, for example, pH: 7.0, CD:16 mA/cm2, d: 0.6 cm and r.s: 300 rpm [NaCl]:0.05M and inside 120 min tPECO.

The aftereffects of CV, UV– Vis and HPLC demonstrate that at the amid the PECO treatment BPA mixes were expelled from fluid arrangement. From the above confirmation, it could be inferred that PECO utilizing ZnO is a promising treatment for the expulsion of BPA from watery arrangement. Nanomaterials can possibly significantly advantage ecological quality and maintainability through contamination anticipation, treatment and remediation.

Acknowledgements

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References

[1] H.H. Le, E.M. Carlson, J.P. Chua, S.M. Belcher, Toxicol. Lett, **176,**149 (2008).
[2] B. Seyhia, Patrick Droguia, Gerardo Buelnab, Jean Franc¸ Chemical Engineering Journal **172,**61 (2011).
[3] Z.H. Liu, Y. Kanjo, S. Mizutani, Sci. Total Environ**407,**731(2009)
[4] Jing Xua, Tiantian Tangb, Kun Zhanga, Shiyun Aia, Hongxia Dub, Process Biochemistry **46,** 1160 (2011).
[5]Jin Zhang, Qian Li a, Miaojing Chena, Hong Li a, Zhenghe Xub, Sensors and ActuatorsB, **160,**784 (2011).
[6] Zacharias Frontistis, Vasileia M. Daskalaki, Alexandros Katsaounis, Ioannis Poulios, Dionissios Mantzavinos, water research,**45** ,2996e3004(2011).
[7] M. Govindaraj, S. Pattabhi, Desalin. Water Treat.**53**(10), 2664 (2015).
[8] M. Govindaraj, R. Rathinam, C. Sukumar, M. Uthayasankar, S. Pattabhi, Environ. Technol. **34**(4), 503 (2013).
[9] Brillas, E., I. Sires, M.A. Oturan, Chem. Rev,**109**(12), 6570 (2009).
[10] P. Ju, H. Fan, D. Guo, X. Meng, M. Xu, S. Ai, Chem. Eng. J. **179,** 99(2012).
[11]Mehmet A. Oturan, Jean Pinson, J. Phys. Chem. **99** (38), 13948 (1995).