Development of Bis-Phenol A sensor based on $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ nanoparticles for sustainable environment

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Graphical Abstract

The proposed oxidation reaction of BPA by BPA chemical sensor based on
 $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ /binder/GCE

Research Highlights

1. A versatile nano-molybdenum-iron-zinc-oxide ($\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$) nanoparticles has been synthesized.
2. The nanoparticles were characterized by XRD, SEM, and FTIR and particle size is 20.5 nm.
4. The proposed chemical sensor $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ of Bis-Phenol A (BPA) displays high selectivity with lower detection limit.
5. The calibration plot is linear over the concentration range of 0.1 nM to 1.0 mM of BPA.
6. The calculated sensitivity is $292.7 \mu\text{A mM}^{-1} \text{cm}^{-2}$ with detection limit (DL) of 0.03 ± 0.0015 nM at signal to noise ratio of 3(S/N).

Abstract:

A versatile nano-molybdenum-iron-zinc-oxide ($\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$) nanoparticles (NPs) were prepared by co-precipitation method. The as-synthesized catalyst was characterized by several analytical techniques such as XRD, SEM, and FTIR spectroscopy. From the XRD pattern, particle size of the synthesized nanocomposite was calculated and found to be 20.5 nm. Elemental composition and their homogenies distribution in $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ was confirmed by EDS study. The proposed Bis-phenol (BPA) chemical sensor with active $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs displays good selectivity with lower detection limit (DL) and long-term stability with enhanced electrochemical response. The calibration plot is linear (r^2 : 0.9978) over the concentration range (LDR) of 0.1 nM~0.1 mM of BPA. The calculated sensitivity is $2.2468 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$ with detection limit (DL) of $42.25\pm 2.11\text{pM}$ at signal to noise ratio of 3(S/N). The BPA chemical sensor fabricated with $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs may be a promising with high sensitivity in reliable I-V method. Thus, this novel effort initiates a well-organized way to the development of reliable $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/binder/GCE chemical sensor for efficiently detection of real hazardous toxins in environment as well as health career sector in a broad scale.

Key words: $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ nanoparticles; Bis-phenol A sensor; Glassy carbon electrode; I-V method; Sensitivity; Environmental safety

Introduction

Nanoscience-nanotechnology of new nanostructure material and micro-devices has been attracted attention recently. They played a major role in the development of sensitive and reliable materials. The journey for even more smaller devices capable of nano-level imaging and controlling nanoparticle, biological, chemical, pathological samples and chemi-sensor has lately

gained the focus of attention of the scientific researches, particularly for control monitoring, due to the increasing need for environmental safety and health monitoring.¹⁻³ Some common organic compounds such as dyes, herbicides, pesticides, phenols, and various solvents are widely used in industries. They are the main contaminants and discharged effluents by the industries. These organic pollutants threaten the environment and human health due to their toxicity, carcinogenicity, and other hazardous effect.⁴⁻⁸ Thus, the decontamination of these organic pollutant compounds from the environment has received concentrated investigation. This investigation is aimed to preserve human health and environmental protection. Many conventional techniques such as flocculation, precipitation, adsorption on granular activated carbon, air stripping or reverse osmosis, chemical oxidation, combustion, and biological methods have been used so far for the handling of organic wastes. But they have some boundaries and disadvantages such as high cost, ineffectiveness and incompetence. Sometimes with this technique, organic dye molecules cannot be destroyed totally just to convert the organic pollutions from one phase to another non-toxic phase.⁹ Consequently, there is a vital demand for an efficient method to identify the organic contaminant existed in the environment. Photocatalysis method for efficient treatment of wastewater in the presence of various metal oxides is an exciting technique for the detoxification of organic pollutants, which can solve this problem.¹⁰ So, an optimum band gapped material is needed that would work in low energy abundant light sources.

The toxic BPA is an organic chemical that largely used in plastic industry as a monomer for producing epoxy-resins, polycarbonate, and other necessary polymer materials.¹¹ In daily life, BPA is ubiquitous since it can be unintentionally released and migrated to the environment, food and drinking water due to waste water discharge from the plastic-manufacturing industry and

from a broad assortment of food contact materials mainly resulting from polycarbonates as well as epoxy resins, such as infant feeding bottles, tableware, storage containers, and food can linings,¹²⁻¹⁴ and thus, humans may regularly consume trace amounts of BPA. Extensive research studies have shown that BPA is an environmental endocrine disrupting chemical, which can mimic and interfere with hormonal activities by disrupting growth, development, reproduction and reduction in immune function of humans,^{15,16} and also it can initiate probable cause for various types of cancer,¹⁷ even at very low concentration. To protect the noxious effect and the potential health risk of BPA, the development of sensitive and specific method with reliable, rapid and real time analysis of trace level of BPA is highly significant and desired for safe of human life.

Various conventional techniques have already been investigated to BPA assay including liquid chromatography coupled with electrochemical, ultra-violet and fluorescence detection,¹⁸ liquid chromatography-mass spectrometry,¹⁹ gas chromatography,²⁰ gas chromatography-mass spectrometry.²¹ However, these techniques are expensive and required complicated instruments, skilled operators and time-consuming pretreatment steps, which restrict their usability towards broad applications. Hence, few other methods such as fluorimetry,²² enzyme-linked immunosorbent assay,²³ aptamer based assay,²⁴ flow injection chemiluminescence²⁵ and electrochemical methods²⁶ have been developed for BPA detection towards further significant progress. However, the use of probe molecules based methods such as antibody, enzyme and aptamer as a recognition element for BPA is expensive and complicated due to the risk of stability, multistep immobilization process of biomolecules and non-specific binding of the probe molecules towards BPA analogs.²⁷ Although, somehow electrochemical techniques have attended wide attentions due to the economical approaches of instrumentation, high sensitivity,

and simplicity for operators and portability, however, still there is a need for ultrasensitive detection of BPA with good selectivity. This can be obtained by nanoparticles based modified electrodes. Among various nanoparticles, carbon paste and graphene based electrodes have been used comprehensively because of its high effective surface area and conductivity.^{28,29} Mostly, two dimensional doped material could be an interesting electrode material for the detection of BPA due to its large surface to volume ratio, excellent electronic properties and thermal conductivity.^{30,31} Although, some satisfactory results have been shown, still there is a challenge and need for the ultra-sensitive detection of BPA in real-time analysis, which can be achievable by fabricating a composite electrode based on $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs with other nanoparticles.

BPA has highly hazardous effect on human and this effect can be continued generation to generation. Therefore, it is necessary to develop a proficient detection method to protect the public health care system. In this study, a new platform of electrochemical sensor based on $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs for successfully efficient detection of BPA in the neutral buffer medium has been conferred. To fabricate the working electrode of BPA chemical sensor, a thin layer of $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs are deposited onto the flat of GCE with conducting binder and applied for selective detection of BPA in electrochemical approaches. It should be mentioned that the proposed BPA chemical sensor is extraordinary and recent invention with active $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs onto GCE.

Experimental section

Material and Methods

In this research all the chemicals were used as received without further purification. Followings are some chemicals used in this synthesis and in evaluation of catalysis. Ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Sigma Aldrich, Germany), Zinc Nitrate, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (MERCK, India), Ferric Chloride, FeCl_3 (MERCK, India), Sodium Carbonate, Na_2CO_3 (AR, BDH). The analytical grade toxics chemicals, BPA (bisphenol A), 2-AP (2-aminophenol), 3-CP (3-Chlorophenol), 3-MP (3-methoxyphenol), 4-NP (4-nitrophenol), P-NP (P-nitrophenol), 2,4-DNP (2,4-dinitrophenol), PHyd (phenyl hydrazine), 2-NP (2-nitrophenol), 3-MPHyd (3-methoxyphenylhydrazine), nafion (5% nafion suspension in ethanol), monosodium phosphate and disodium phosphate were purchased from the Sigma-Aldrich company (USA). In this study X-ray diffraction (XRD, Bruker D8 Advance diffractometer, equipped with a graphite monochromator), Scanning Electron Microscope (SEM) equipped with an Energy-Dispersive X-ray Spectrometer (EDS) (JSM-7100F) linked with an EDS (Oxford) device, Fourier transform infrared spectroscopic (FTIR) was carried out using a FTIR spectrometer (Shimadzu, IRPrestige-21). The reliable I-V method was applied to detect BPA in the neutral buffer medium and this electrochemical detection was executed at applied potential ranging from 0 to +1.5 V by Keithley electrometer (6517A, USA).

Preparation of $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ nanoparticles

Mixed metal oxide nanoparticles $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ was synthesized by co-precipitation of carbonates from the aqueous solution of their corresponding metal salts³². Metal carbonates were prepared in-situ to make a homogeneous mixture of them. 0.25 M solutions of three metal salts and a solution of 1 M Na_2CO_3 in distilled water were prepared. $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ was synthesized by thoroughly mixing 0.25 M solutions of

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, FeCl_3 , and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 1:1:1 ratio and adding 1.0 M Na_2CO_3 dropwise until precipitation was complete. The resultant mixture was stirred for further 4 hours at 60 °C with constant stirring. After terminating the reaction, metal carbonate precipitates were separated from the solution by centrifugation, washed several times with deionized water and finally dried at 120 °C in an oven. Then the sample was calcined in muffle furnace at 450 °C, 600 °C, and 900 °C for four hours every time.

Fabrication of GCE with $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs

For the fabrication of working electrode of BPA chemical sensor, a slurry of synthesized $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs was prepared in ethanol and used to coat as a thin layer on GCE. Then, it was allowed to dry at room condition. To improve the binding strength between GCE and $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs, a drop of nafion (5% nafion suspension in ethanol) was added onto the modified GCE. The resultant working electrode was placed inside an oven at 35 0°C for an hour or a time enough to dry the modified electrode completely. An electrochemical cell was assembled with $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/binder/GCE and Pt-wire (dia., 1.5 mm), where the first one was acted as working and Pt-wire as counter electrode. A number of BPA solution based on concentration ranging from 1.0 mM to 0.1 nM was prepared and used as analyte to investigate by fabricated BPA chemical sensor in electrochemical approach. The sensitivity of the BPA sensor was estimated from the slope of calibration curve (plotted as current vs. concentration of BPA relation). Considering the maximum linearity (r^2) of calibration curve, the linear dynamic range (LDR) of the projected chemical sensor was calculated and the detection limit (DL) was obtained from the ratio of 3N/S (ratio of noise*3 vs. sensitivity). It should be noted that, the used Keithley electrometer (6517A, USA) is simple two electrodes system.

Amount of 0.1 M PBS-solution was kept as constant 10.0 mL in the measuring beaker throughout the electrochemical investigation.

Result and discussion

Characterization $Fe_2MoO_4 \cdot Fe_3O_4 \cdot ZnO$ NPs

Structural Analysis:

Cubic (Fd-3m(227)) Iron Molybdenum Oxide (Fe_2MoO_4) formation can be recognized as there are peaks at $2\theta = 18.049^\circ$, 29.901° , 35.194° , and 42.707° in the XRD pattern as shown in Fig 1 (PDF#73-0236). The lattice constants observed are (a, b, c) 8.509, 8.509, and 8.509 where $\alpha\beta\gamma = 90^\circ$, 90° , and 90° respectively and density(c) = 5.856 g/cm³ and volume = 616.1 Å³. Moreover, cubic (Fd-3m(227)) magnetite (Fe_3O_4) in the composite can be established by the peaks arising at 2θ value of 18.049° , 29.901° , 35.194° , and 53.098° (PDF#89-0688). Observed density(c) = 5.18 g/cm³, and volume = 93.7 Å³. They lattice constants are (abc) 8.4045, 8.4045, and 8.4045 where $\alpha\beta\gamma = 90^\circ$, 90° , and 90° . Finally, the hexagonal (P63mc(186)) Zinc oxide or ZnO formation is indicated by 2θ peaks at 31.699° , 36.157° , 47.498° , 56.545° , 66.242° , 67.804° , 68.904° , and 76.798° (PDF#80-0075). The corresponding lattice constants found to be (abc) 3.2539, 3.2539, and 5.2098 where $\alpha\beta\gamma = 90^\circ$, 90° , and 120° . Furthermore, observed density(c) = 5.656 g/cm³ and volume = 47.8 Å³. The volume of the unit cell was calculated from the lattice constant lengths and angles. If the unit cell sides are represented as vectors, then the volume is the dot product of one vector with the cross product of the other two vectors. The volume is represented by the letter V. For the general unit cell

$$V = abc\sqrt{1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma}$$

Moreover, from the XRD pattern, particle size of the synthesized nanocomposite was calculated and found to be 20.5 nm.

Fig. 1: X-Ray Diffraction pattern of $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ nanoparticles

SEM and EDS analysis

Scanning Electron Microscope (Fig. 2) reveals morphology of synthesized nanoparticles. SEM image showed an aggregation of particles; even that aggregation is within nanometer scale. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed to understand the elemental distribution throughout the nanocomposite. It is thus evident from Fig. 3 and Table S1 that NPs are composed of Mo, Fe, Zn, and O with atomic percentage of 2.18%, 11.73%, 22.96%, and 63.13% respectively. An overlapping elemental distribution of Mo, Fe, Zn, and O respectively (Fig. S1) of desired product over the matrix has been observed. The EDS mapping (Fig. S1) also indicated that, elements were not confined in a specific space rather they were distributed throughout the matrix.

Figure 2. SEM image of $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$

Figure 3. EDS of $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$

FTIR spectrum analysis

Fig. 4 shows the FTIR spectrum of $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ nanocomposite in the range of 400-4000 cm^{-1} with KBr. The band centered at 3439 cm^{-1} is assigned to stretching mode of H_2O absorbed from the environment⁹. The O-H in plane and out of plane bonds appears at 1616 cm^{-1} and 871 cm^{-1} , respectively³³. In this FTIR spectrum there is a peak at 1018 cm^{-1} and it arises due to Mo=O bond³⁴. Zn-O bond in the ZnO nanoparticle appeared at 565 cm^{-1} ³⁵. As shown in Fig. 4, the sample exhibited intense peak at 596 cm^{-1} , that is due to the stretching vibration mode associated to the iron-oxygen absorption band (Fe-O bonds in the crystalline lattice of Fe_3O_4)³⁶. Another Fe-O vibration took place at around 438 cm^{-1} . The reason for lower absorbance in this region can be attributed to the fact that some of iron atom formed iron molybdenum oxide. Usually, bulk Fe-O bond vibrates around 570 cm^{-1} , but crystallinity and smaller particle size can cause this higher shift in transmittance. They are characteristically pronounced for all spinel structures and for ferrites in particular. This occurs because, in these regions, the stretching vibration bands are found related to metal in the octahedral and tetrahedral sites of the oxide structure.

Figure 4. FTIR spectrum of synthesized nanocomposite $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$

Applications

Detection of BPA with $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ NPs sensor probe

The BPA chemical sensor based on $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ NPs/binder/GCE was applied to selective detection of BPA in neutral buffer medium. This chemical sensor has exceptional advantages such as inertness in chemical environment, long-term stability in air, enhanced electrochemical activity during the sensing performance, easy fabrication and assemble and above all safe chemo-characteristic. To fabricate the proposed BPA chemical sensor, a thin layer of $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ NPs was deposited on the flat part of GCE conducting binder (5% nafion suspension in ethanol) and the resultant $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ NPs/binder/GCE assembly was implemented as BPA chemical sensor to detect BPA in aqueous medium. In sensing performance of BPA chemical sensor, the applied I-V was measured on the thin film of $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ /binder/GCE. The holding period in the electrometer was set at 1.0 sec. The

proposed oxidation mechanism of BPA is illustrated in **Scheme 1**. According to the oxidation mechanism of BPA, the species of reactive BPA are adsorbed on the surface of $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/binder/GCE and the corresponding oxidation of BPA is occurred to produce electrons. As a result, the enrichment of electrons in measuring neutral buffer medium is observed, which is asked to increase the conductivity of sensing medium. The similar electrochemical oxidation of BPA is observed in previous reports.³⁷⁻³⁹

Scheme 1 The proposed oxidation reaction of BPA by $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/binder/GCE

To estimate the selectivity of $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/binder/GCE, the environmental toxins including BPA, 2-AP, 3-CP, 3-MP, 4-NP, p-NP, 2,4-DNP, PHyd, 2-NP and 3-MPHyd were investigated and obviously, BPA was exhibited the highest I-V response among all toxins, as it is illustrated in **Fig. 5(a)**. The reproducibility performance is an important analytical criteria of a chemical sensor. Therefore, the reproducibility of proposed BPA chemical sensor was tested at $0.01\mu\text{M}$ concentration of BPA solution in neutral butter medium. As it is observed from Fig. 5(b), the projected chemical sensor showed good reproducibility performance and the seven replicated runs are practically indistinguishable. Thus this performance provides the evidence of reliability of this method. The electrochemical (I-V) responses are not changed even washing the electrode after each trail during the testing of the reproducibility performance of BPA chemical sensor. The relative stander deviation provides the precision of a result. The

relative standard deviation of reproducibility performance is calculated at applied potential +1.3 V and it is found to be 1.44%. The response time is another analytical performance of a chemical sensor, which provides the evidence about efficiency of sensor. Thus, the response time of $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/binder/GCE chemical sensor was executed at 0.01 μM concentration of BPA as it is represented in **Fig. 5(c)**. As it is observed from Fig. 5(c), the resulted response time is around 8.0 sec. a result might be high appreciable.

Fig. 5 Optimization of BPA sensor based on $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs. (a) Selectivity study; (b) Repeatability study, and (c) Response time

To evaluate the analytical performances of BPA chemical sensor, a series of BPA solution ranging from 0.1 nM to 1.0 mM was prepared and investigated by $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ NPs/binder/GCE as it is represented in **Fig. 6(a)**. As it is observed in **Fig. 6(a)** and amplified I-V responses **Fig. 6(b)**, the electrochemical (I-V) responses are increased with enrichment of BPA concentration from lower to higher. As it is observed from **Fig. 6(a and b)**, I-V responses are clearly distinguishable from lower to higher concentration. At applied potential +1.3 V, the current data are collected from Fig. 6(a), and plotted as concentration vs. current in Fig. 6(c) and resultant plot is known as calibration curve. The analytical performance sensitivity of projected BPA chemical sensor is calculated from the slope of calibration curve and cross-section area of GCE (0.0316 cm^2) and it is equal to $2.2468 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$, a result is considered as satisfactory. As it is found from Fig. 6(c), the resultant calibration curve is linear over the concentration range (LDR) of 0.1 nM ~ 0.1 mM and obviously, it is a very wide range of concentration to detect BPA in aqueous medium. As it is marked in Fig. 6(c), the current data are fitted with regression coefficient value of $r^2=0.9978$, which verifies the linearity of calibration curve. Therefore, it can be concluded that, the projected BPA chemical sensor based on $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ NPs/binder/GCE is well enough to detect BPA in real field of application. The detection limit (DL) is also calculated at signal to noise ratio of 3 and it is found to be $42.25 \pm 2.11 \text{ pM}$, which is obviously lower.

Fig. 6 The electrochemical (I-V) response of $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ NPs, (a) I-V responses with concentration variation of bisphenol A, (b) the amplified I-V responses at applied potential +1.0 ~ +1.5 V, (c) calibration plot, and (d) calibration plot in logarithmic scale along x-axis (concentration of BPA).

As it is observed from **Fig. 6(a)**, the electrochemical response of BPA chemical sensor based on $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ NPs/binder/GCE varies, with concentration of BPA in measuring buffer medium. At early stage of sensing performance of BPA, the surface coverage of $\text{Fe}_2\text{MoO}_4 \cdot \text{Fe}_3\text{O}_4 \cdot \text{ZnO}$ /binder/GCE film is smaller due to adsorption of few number of BPA

molecules and the oxidation reaction starts progressively. With increasing of BPA concentration, the surface reaction is increased remarkably and the larger surface coverage with the corresponding BPA molecules are observed. Farther enrichment of the analyte (BPA) concentration, a higher oxidation rate is perceived and the corresponding surface coverage approaches to its steady state equilibrium condition. Due to additional increasing of BPA concentration in sensing medium, a steady state equilibrium I-V response is obtained and at this condition, the surface coverage is maximum. Such steady state equilibrium data are represented in Fig. 6(c), the current data are homogeneously distributed along the linear plot. As it is observed from Fig. 5(c), the response time is around 8.0 sec., with additional some data recording time, it can be put as 10.0 sec. Thus, this 10.0 sec. is necessary by the projected BPA chemical sensor to provide the steady state I-V response. Therefore, in conclusion, the projected chemical sensor is reliable and efficient to detect BPA in environmental sample. Considering the analytical performances such as sensitivity, linear dynamic range (LDR), detection limit (DL), reproducibility, and response time, the projected BPA chemical sensor based on $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/binder/GCE is performed qualified performance. A comparison of similar work is represented in **Table 1**.⁴⁰⁻⁴⁴ As it is observed that BPA chemical sensor with active $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs able to perform a very wide range of concentration and detection limit is reasonably lower compare to the previous report. Therefore, this research approach is noble route to develop future prospective of toxic chemical sensor to detect carcinogenic and hazardous chemicals for the safety of environment and healthcare fields in large scale⁴⁵⁻⁵⁶.

Table 1 The performance of earlier invented BPA chemical sensors

Modified Electrode	DL (nM)	Sensitivity ($\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$)	LDR	Ref
PEDOT/GCE	22000.0	1.57	40~410 μM	40
PEDOT/GCE	20.00	2.419	0.1~500 μM	41
ZnO/GCE	1.700	0.05	12.4 nM~1.2 μM	42
Cr ₂ O ₃ - CNT NCs/GCE	0.0643	1.4768	0.01 nM~0.1 μM	43
ZnO.CoO.FeO/GCE	1.200	3.28	0.80 ~7.20 μM	44
Fe ₂ MoO ₄ •Fe ₃ O ₄ •ZnONPs/GCE	0.0422	2.2468	0.1 nM~0.1 mM	This work

* DL (Detection limit), LDR (Linear dynamic range), nM (Nanomole), μM (Micromole)

Recovery test of the sensor in presence of real sample

The recovery test is a kind of reliability measuring performance of the proposed BPA chemical sensor with Fe₂MoO₄•Fe₃O₄•ZnO NPs/GCE sensor probe. To execute this test, a known concentration of BPA solution is added with real environmental sample and resulted data is analyzed to estimate the concentration of BPA again, which is expressed as percentage recovery. The real samples were obtained from various environmental and extracted sources such as sea water, extract from PC-baby bottle, PVC-food packaging bag, PVC-water bottle and waste effluent from industry. The analyzed data are represented in **Table 2** and seem to be quite acceptable and satisfactory.

Table 2. Analyses of real environmental samples with Fe₂MoO₄•Fe₃O₄•ZnO NPs/binder/GCE sensor.

Real samples	Added BPA concentration (μM)	Measured BPA conc. ^a by $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/GCE (μM)			Average recovery ^b (%)	RSD ^c (%) (n=3)
		R1	R2	R3		
Industrial effluent	0.01000	0.01003	0.01016	0.00996	100.52	1.01
PC- baby bottle	0.01000	0.01145	0.01159	0.01139	114.81	0.89
PVC- food packaging bag	0.01000	0.009822	0.009863	0.009974	98.86	0.86
Sea water	0.01000	0.010760	0.010701	0.010682	107.14	0.38

^aMean of three repeated determination (signal to noise ratio 3) with $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs/GCE.

^bConcentration of BPA determined/Concentration taken. (Unit: μM)

^cRelative standard deviation value indicates precision among three repeated measurements(R1,R2,R3).

Conclusions

A nano-molybdenum-iron-zinc-oxide catalyst, $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ was prepared by co-precipitation method. The catalyst was characterized by several techniques such as XRD, SEM, and FT-IR spectroscopy. From the XRD, particle size of the synthesized nanocomposite was found to be 20.5 nm. Elemental composition and their distribution in $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ was confirmed by EDS study. The prepared $\text{Fe}_2\text{MoO}_4\cdot\text{Fe}_3\text{O}_4\cdot\text{ZnO}$ NPs was used to coat on GCE with conducting binder to result a working electrode of a chemical sensor, which was implemented to detect BPA in aqueous medium. The projected BPA chemical sensor is performed with good sensitivity ($2.2468 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$), a very wide linear dynamic range (0.1 nM ~ 0.1 mM), reasonable lower detection lime (42.25 ± 2.11 pM), very short response time (8.0 sec.) and reliable reproducibility. Therefore, this research approach might be a noble way to

develop future chemical sensor to detect toxic chemicals for the safety of healthcare and environment sectors.

Acknowledgements

TWAS research grant 2015 (No. 15-164 RG/CHE/AS_I – FR3240287058) is gratefully acknowledged for funding. MOE (Ministry of Education, Bangladesh) grant 2015-16 (PS 090) is also thankfully acknowledged. Center of Excellence for Advanced Materials Research (CEAMR), Chemistry Department, King Abdulaziz University, Jeddah, Saudi Arabia is highly acknowledged for financial supports and research facilities.

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