Chemical Engineering Journal 313 (2017) 283–292

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Electrochemical sensing and remediation of 4-nitrophenol using bio-synthesized copper oxide nanoparticles

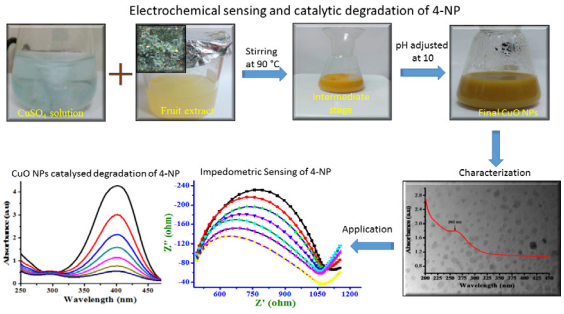
Suman Singh [a,*,1], Nishant Kumar [a,1], Manish Kumar [a], Jyoti [a], Ajay Agarwal [b], Boris Mizaikoff [c,*]

[a] CSIR-Central Scientific Instruments Organisation (CSIR-CSIO), Sector 30-C, Chandigarh, India
[b] CSIR-Central Electronics Engineering Research Institute (CSIR-CEERI), Pilani, Rajasthan, India
[c] Institute of Analytical and Bioanalytical Chemistry, Ulm University, Germany

HIGHLIGHTS

- Biosynthesis of copper oxide (CuO) nanoparticles their characterization.
- Functionalization of screen printed electrodes (SPE) using CuO nanoparticles.
- Detection of 4-nitro phenol (4-NP) using functionalized SPE.
- Used impedance spectroscopy and square wave voltammetry for detection.
- The linear detection range was from 10 nM to 10 mM of 4-NP.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 September 2016
Received in revised form 29 November 2016
Accepted 12 December 2016
Available online 19 December 2016

Keywords:
Biosynthesis
Copper oxide
4-Nitrophenol
Impedance
Catalytic activity

ABSTRACT

The present work reports impedance based electrochemical sensing and remediation of 4-nitro phenol (4-NP) using biosynthesized (CuO) copper oxide nanoparticles. The synthesis of CuO nanoparticles is achieved using fruit extract of plant *Fortunella japonica* as reducing and stabilizing agent. The CuO nanoparticles were characterized using various analytical techniques like UV–Visible spectroscopy, Atomic force microscopy (AFM), High resolution transmission electron microscopy (HR-TEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and X-ray diffraction (XRD). For electrochemical sensing of 4-NP, the CuO nanoparticles were drop casted on screen printed electrode (SPE) and electrode is referred at SPE/CuO_{NPs} sensor. The mechanism of 4-NP redox reactions was examined using cyclic voltammetry (CV). The electrochemical sensing of 4-NP has been done using square wave voltammetry (SWV) and impedance spectroscopy. In SWV, the oxidation peak current increased with increase in the concentration of 4-NP from 10 nM to 10 mM having regression coefficient of 0.996. In impedometric sensing, change in charge transfer resistance (R_{ct}) with change in 4-NP concentration was used as a signal. The R_{ct} decreased with increase in 4-NP concentration which is in accordance with SWV results. The effect of solution pH on impedometric response of SPE/CuO_{NPs} sensor was also evaluated. The SPE/CuO_{NPs} sensor exhibited good reproducibility and selectivity towards the analyte and is able to perform real sample analysis. The CuO nanoparticles act as a catalyst and showed good degradation percentage of 4-NP pollutant.

1. Introduction

The 4-nitrophenol (4-NP) is widely used in the industries as an intermediate for the production of various pharmaceuticals,

* Corresponding authors.
E-mail addresses: sumansingh01@gmail.com (S. Singh), boris.mizaikoff@uni-ulm.de (B. Mizaikoff).
[1] Equal contribution for first authorship.

http://dx.doi.org/10.1016/j.cej.2016.12.049
1385-8947/

pesticides and dyestuffs [1]. As a result, it is inevitably released into the environment as an industrial effluent and contributes to the deterioration of the environment. It has been detected not only in industrial wastewater, but also in marine and fresh water. It can act as a mutagen, teratogen, and carcinogen [2]. The onset symptoms of its ingestion or inhalation by human include headache, nausea, drowsiness and cyanosis [3]. The U.S.A. Environmental Protection Agency (EPA) has cited 4-nitrophenol (4-NP) in the list of priority pollutants due to its persistence and toxicity [4]. It is therefore highly desired to keep monitoring of 4-NP and find a solution for its remediation as well.

Various techniques have been extensively used by the researchers for the detection of 4-NP such as spectrophotometry [5], high-performance liquid chromatography (HPLC) [6], fluorescence [7], gas chromatography [8], capillary zone electrophoresis [2]. But these conventional techniques get easily interfered by related compounds, require expensive reagents and expertise for handling them. These shortcomings urge a great demand for the development of new analytical technique having simple operation, low cost instrument, time saving and real time detection of 4-NP. The electrochemical method easily overcomes these shortcomings and allow a very sensitive determination of analyte [9]. Considering the fact that the selectivity and sensitivity of electrochemical detection are strongly dependent on microstructures and properties of electrode materials, researchers are now focusing on the use of nanostructured materials or chemically modified electrodes [10–12]. In the present work, the copper oxide nanoparticles were used for the modification of electrode surface. CuO is a p-type semiconductor with a narrow band gap of 1.2 eV and is promising for the development of electrochemical sensor due to its high specific area, good electrochemical activity and possess the ability of promoting electron transfer reactions [13,14]. These CuO nanostructures also posses strong adsorption capability, being biocompatible facilitates the immobilization of biomolecules for improving biosensing characteristics [15].

There are various methods reported for the synthesis of CuO nanomaterials such as microwave irradiation [16], thermal decomposition of precursor [17], sono-chemical [18], precipitation pyrolysis [19], alkoxide based route [20], electrochemical method [21] and biological method [22]. But most of these traditionally used synthesis processes either require costly and toxic chemicals or are dependent on sophisticated apparatus/equipments, requiring controlled environment. Sometimes the toxic chemicals leach into soil and water and result in environmental contamination which often leads to the health hazards. The biological synthesis on other hand, is nowadays gaining momentum as the synthesis protocol does not involve use of any toxic chemicals. Moreover, this biogenic synthesis of nanomaterials is cheap, facile, rapid and biocompatible [23–25]. There are various plants which have been reported for the biosynthesis of CuO nanoparticles such as *Gloriosa superba* [26], *Carica papaya* [27], *Tabernaemontana divaricate* [28], *Calotropis gigantea* [29]. Plants and fruits are very rich in phytochemicals like phenolic compounds which act as anti-oxidants and have reducing properties. Phenolic compounds possess hydroxyl and ketone groups which are able to bind to metals and show chelate effect. The chelating ability of phenolic compounds arises from the highly nucleophilic character of the aromatic rings present within the molecule. In this study, fruit extract of *Fortunella japonica* plant has been used for biosynthesis of CuO NPs. This plant possess proteins/biomolecules which act as a reducing as well as capping agent for the synthesis of CuO NPs [30]. The synthesized copper oxide nanoparticles were thoroughly characterized for their morphology, optical and electrochemical properties, etc. These CuO nanoparticles were then used for the modification of screen printed electrode surface. The copper oxide nanoparticles modified electrode was then used for electrochemical sensing of 4-nitrophenol which is one of the toxic chemical found as environmental pollutant.

2. Experimental

2.1. Materials

Fruits of *Fortunella japonica* were acquired from institutional campus garden. Copper sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$) was obtained from S. D. Fine-Chem Ltd. Mumbai, India, 4-nitrophenol was acquired from Loba Chemie Pvt. Ltd. Mumbai, India. Sodium borohydride ($NaBH_4$) was obtained from Spectrochem Pvt. Ltd. Mumbai, India and sodium hydroxide (NaOH) was purchased from Merck Pvt. Ltd. Mumbai, India. All chemicals were used as received.

2.2. Instrumentation

Biosynthesis of CuO nanoparticles by fruit extract of *Fortunella japonica* was monitored using UV–Vis spectrophotometer (Hitachi, U 3900 H) in absorbance mode. The crystal structure of copper oxide nanoparticles was studied by recording their diffraction pattern on X-ray diffractometer (XRD) from Rigaku Ultima IV Type II. The sample was analyzed from 20° to 80° (2 theta) angles. The Raman spectrum of CuO nanoparticles was attained using Raman analyzer from Renishaw (UK). The atomic force microscope (AFM) images of CuO nanoparticles were recorded on Bruker Table Top AFM. The FTIR spectra of CuO nanoparticles and fruit extract were recorded on Varian FTIR system (600 series, USA). The size and morphology of CuO nanoparticles was determined using High Resolution Transmission Electron Microscopy (HR-TEM), from JEOL, USA, Model No. JEM-2100F. For HR-TEM imaging, a drop of CuO nanoparticles colloidal solution was put on copper grid and solvent was evaporated. All the electrochemical studies were executed on CHI 660 C electrochemical analyzer (CHI Instruments Inc., USA) using screen printed electrode (SPE). The SPE consists of Ag/AgCl as a reference electrode, carbon as a working as well as counter electrode which are printed together. The SPE was further modified with biosynthesized CuO nanoparticles. For impedometric measurements, 10 μL of 4-NP was drop casted on SPE/CuO_{NPs} and recorded the impedance. The impedance spectrum were recorded at the oxidation potential of 4-NP i.e. 0.3 V (vs. screen printed Ag/AgCl) at an amplitude of 5 mV, with the frequency range from 1 Hz to 100 kHz.

2.3. Preparation of fruit extract

The fruit extract of *Fortunella japonica* was prepared in a typical procedure in which fruits were thoroughly washed and cut into small pieces. Subsequently, these small pieces were smashed and crushed using pestle and mortar and diluted to optimized concentration of 25% with deionized water. The fine optimized solution was boiled for 5 min before decanting. The solution was then cooled and filtered using Whatman No. 1. The filtrate obtained was collected and stored at 4 °C for further use.

2.4. Biosynthesis of copper oxide (CuO) nanoparticles

The copper sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$) solution (25 mM) was prepared in 100 mL of deionized water in 250 mL Erlenmeyer flask. The solution was stirred at 90 °C for 5 min and then 20 mL of *Fortunella japonica* fruit extract (5% v/v) was added for the bio-reduction of cuprous ions. A blank sample was also kept with this for comparison. The pH of the solution was maintained at 10 using 0.1 M NaOH solution. The solution was allowed to stir for 1 h and color of the solution initially changed from blue to green and finally to brown. The change in color indicated the formation of CuO nanoparticles, which was later confirmed by recording the absorbance of the solution. The process of synthesis of CuO