Sensors and Actuators B 245 (2017) 541–550

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Simple and selective detection of pendimethalin herbicide in water and food samples based on the aggregation of ractopamine-dithiocarbamate functionalized gold nanoparticles

Jigneshkumar V. Rohit, Suresh Kumar Kailasa *

Department of Applied Chemistry, S. V. National Institute of Technology, Surat 395007, India

ARTICLE INFO

Article history:
Received 13 September 2016
Received in revised form 28 January 2017
Accepted 1 February 2017
Available online 2 February 2017

Keywords:
Pendimethalin
RAC-DTC-Au NPs
Colorimetric sensor
DLS
TEM

ABSTRACT

In this work, a simple, selective and sensitive colorimetric method was developed for the detection of pendimethalin herbicide using ractopamine-dithiocarbamate capped gold nanoparticles (RAC-DTC-Au NPs) as a probe. The pendimethalin was effectively induced the aggregation of RAC-DTC-Au NPs *via* various interactions (donor-acceptor, π-π, van der Waals and hydrogen-bonding), resulting a color change from red to blue. As a result, the linear graph was plotted between the absorption ratio at A_{650}/A_{522} and the pendimethalin concentration in the range of 5.0–500 μM. The detection limit was found to be 0.22 μM, which is very close to the maximum residue limit (MRL) of pendimethalin that was established by European Commission. The proposed method was successfully applied to detect pendimethalin in environmental water and food samples with good recoveries.

1. Introduction

Pendimethalin (*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine) is a class of dinitroaniline herbicide that was widely used in the various crops to control broadleaf weeds and grassy weed species [1]. It is listed in the K1-group and used as herbicide to protect various crops including cereals (wheat, barley, rye, triticale), soybeans, corn, potato, rice, fruits, legumes, vegetables, nuts as well as lawns and ornamental plants. However, it causes chromosome separation, and inhibits the cell division steps and cell wall formation [2]. It is widely distributed in soil, food, water and air due to excess use in agriculture [3]. Therefore, pendimethalin is classified as a possible human carcinogen (Group C) by U.S. Environmental Protection Agency (USEPA) [4], which exhibits endocrine effects [5]. It shows cytotoxicity by altering mitochondrial respiration in rat hepatocytes [6]. In this connection, several analytical methods, including chemiluminescence [7], voltammetry [8,9], gas chromatography [10,11] and high performance liquid chromatographic [12,13] techniques have been so far developed for detection of pendimethalin in various sample matrices, offering good sensitivity. However, they are time-consuming, expensive and rely on complicated instrumentation, which limits their application for on-site screening of pendimethalin. For example, specific reagents or electrolyte and electrochemical cell are need for the analysis of pendimethalin. Despite the progresses have been made in the development of analytical methods for pendimethalin, there are still of significance to design colorimetric sensor for rapid, facile detection of pendimethalin in environmental and food samples.

In recent years, Au NP-based colorimetric methods have received tremendous interest in assaying of various chemical species (metal ions, biomolecules and drugs) because of their size depended properties, which can also improve the selectivity and sensitivity of simple UV–vis spectrophotometer just like as sophisticated instrument [14,15]. To tune analytical applications of Au NPs, the functionalization of Au NPs plays key role for the specific interaction (donor-acceptor, π-π, H-bonding, ligand exchange, electrostatic and covalent) with target analyte, yielding the aggregation of Au NPs induced by specific analyte, which results a red-shift and a color change [16,17]. In this connection, a wide variety of organic molecules has been functionalized on the surfaces of Au NPs and used as probes for colorimetric detection of various analytes including amino acids [18,19], metal ions [20,21], and small organic molecules [22,23]. Apart from these, molecular assembly was carried out on the surfaces of Au NPs for colorimetric assay of various pesticides such as ethyl parathion, atrazine, imidacloprid, glyphosate, carbaryl, methyl parathion and cyhalothrin in environmental samples [24–30]. By taking the inspiration from the

* Corresponding author.
E-mail addresses: sureshkumarchem@gmail.com, skk@ashd.svnit.ac.in, skk@chem.svnit.ac.in (S.K. Kailasa).

http://dx.doi.org/10.1016/j.snb.2017.02.007
0925-4005/

above reports, our group also developed metal (Ag and Au) NPs-based colorimetric sensors for the detection of various pesticides, including mancozeb [31], tricyclazole [32], thiram and paraquat [33,34], carbendazim [35], glyphosate [36], quinalphos [37] and metsulfuron-methyl [38] in environmental water and food samples at minimal volume of samples.

Herein, we synthesized RAC-DTC-Au NPs and used as a probe for colorimetric assay of pendimethalin in environmental and food samples. The pendimethalin was promoted the aggregation of RAC-DTC-Au NPs *via* various interactions (electron donor-acceptor, π-π, van der Waals and H-bonding), causing a color change and a red-shift (Scheme 1). This method easily allows us to observe a color change upon the addition of pendimethalin even at 7.5 μM. The proposed method was successfully employed to detect pendimethalin in water and food samples.

2. Materials and methods

2.1. Chemicals and reagents

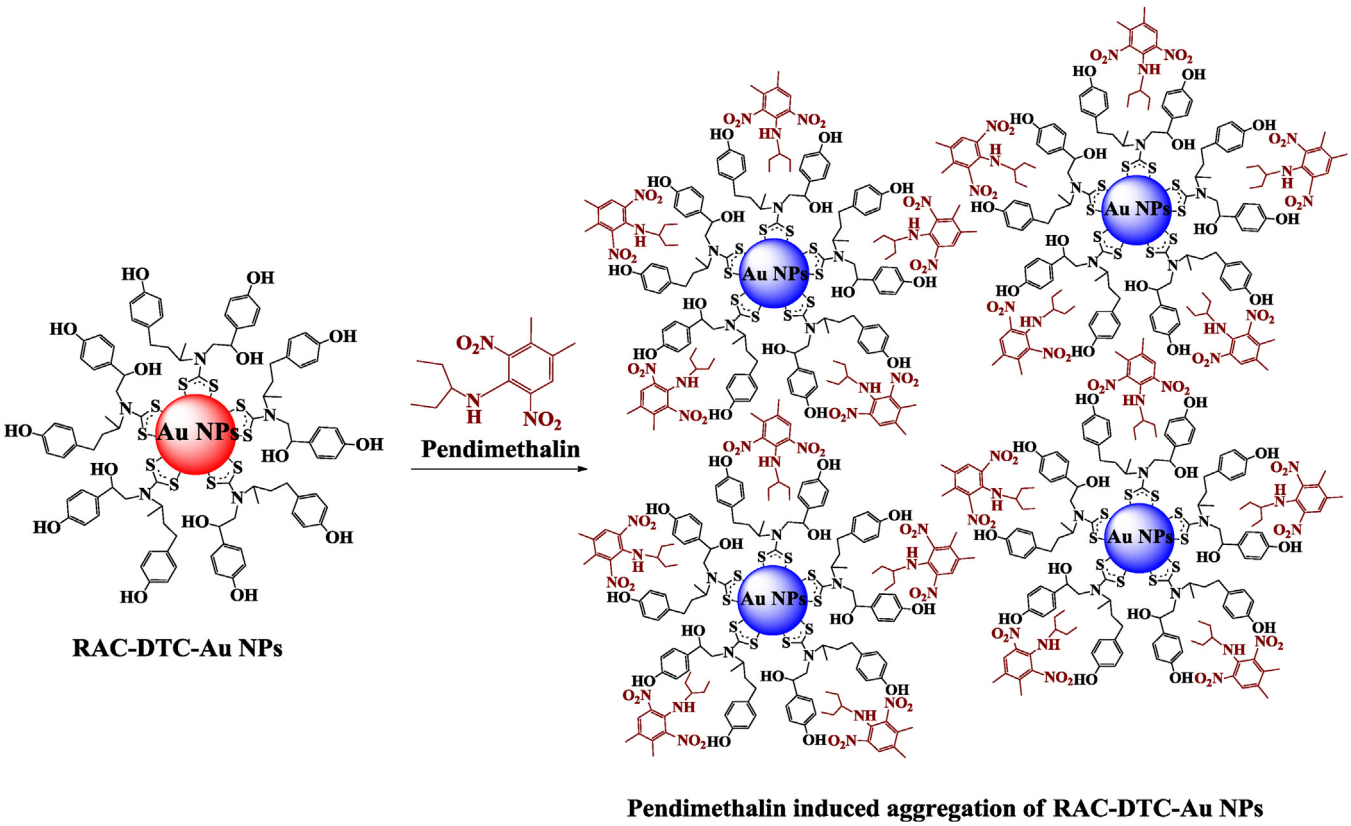
Technical grades of pesticides were received from United Phosphorus Ltd, Cheminova India Ltd, Coromandel International Ltd, Crop Life Science Ltd, Gujarat Insecticides Ltd, Super Crop Safe Ltd, Atul Ltd and Vallabh Pesticides Ltd, India. Hydrogen tetrachloroaurate hydrate ($HAuCl_4{\cdot}xH_2O$) was purchased from Sigma-Aldrich, USA. Ractopamine hydrochloride was obtained as a gift sample from Thinq Pharma, India. Carbon disulfide (CS_2), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), sodium acetate and glacial acetic acid were obtained from Merck Ltd, India. Methanol, disodium phosphate, hydrochloric acid and dipotassium phosphate were purchased from Finar Chemicals Ltd, India.

2.2. Instrumentation

Maya Pro 2000 (Ocean Optics, USA) UV–vis spectrophotometer was used for measuring absorption spectra. Nuclear magnetic resonance (NMR) ^1H spectra were recorded on Avance-II 400 MH_Z (Bruker, Switzerland). FT-IR 8400S (Shimadzu, Japan) was used to measure FT-IR spectra. Transmission electron microscopic images were measured on Tecnai 20 (Philips, Holland). Zetasizer Nano ZS90 (Malvern, UK) was used for measuring of average size distribution data of NPs.

2.3. Preparation of ractopamine-dithiocarbamate-Au NPs

Briefly, 25 mL of $HAuCl_4$ solution (1.0 mM) was taken into a reaction flask and boiled for 25 min. To this, trisodium citrate (38.8 mM, 5.0 mL) was added and stirred for another 15 min. The formation of Au NPs was confirmed by color change of solution from yellow to cherry red [39]. Then, dithiocarbamate (DTC) derivative of rectopamine (RAC) was synthesized according to reported method in the literature with some modification [40]. Briefly, CS_2 (0.06 mL, 0.001 M) was added to an equimolar mixture of sodium hydroxide (0.04 g, 0.001 M) and RAC (0.337 g, 0.001 M) in 25 mL of methanol. The above mixture was stirred for 6.0 h at 0–5 °C, leading to form RAC-DTC. Then, 15 μL of 1.0 mM RAC-DTC solution was added into 5.0 mL of Au NPs solution and then stirred for 2.0 h at room temperature to ensure the assembly of RAC-DTC on Au NPs surfaces. The obtained RAC-DTC-Au NPs were stored at 4.0 ± 2.0 °C in the refrigerator for further use. Supporting information of Fig. S1a illustrates the synthesis of RAC-DTC and their assembly on the surfaces of Au NPs.



Scheme 1. Schematic illustration of RAC-DTC-Au NPs as a probe for colorimetric detection of pendimethalin.