Sensors and Actuators B 227 (2016) 373–382

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Label-free surface plasmon resonance detection of hydrogen peroxide; a bio-inspired approach

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ARTICLE INFO

Article history:
Received 12 August 2015
Received in revised form 1 December 2015
Accepted 18 December 2015
Available online 23 December 2015

Keywords:
Silver nanoparticles
Colorimetric detection
Hydrogen peroxide
Biosynthesis
Response surface methodology

ABSTRACT

In this study, silver nanoparticles were synthesized using *Kiwifruit* extract. Response surface methodology (RSM) was successfully used to study the effects of $AgNO_3$ concentration and the quantity of Kiwifruit extract on the production of biosynthesized silver nanoparticles. A suitable model between the factors ($AgNO_3$ concentration and the quantity of *Kiwifruit* extract) and the response (production yield) was statistically developed. Based on the statistical analysis, the first order of extract volume has the most impact on the production yield of silver nanoparticles. Also, the production yield is affected by the second order term of extract volume more significantly than $AgNO_3$ concentration. Further, the interaction between both factors is statistically significant. Under the optimum conditions ($AgNO_3$ concentration $>1.9 \times 10^{-3}$ M and amount of *Kiwifruit* extract ≈1.0 ml); silver nanoparticles in the mean size of 20 nm with stability more than 12 months were synthesized. Also, a localized surface plasmon resonance sensor based on silver nanoparticles was developed for determination of H_2O_2. This sensor has a linear range of 5.0×10^{-5}–5.0×10^{-3} M with a limit of detection value as low as 5.0×10^{-7} M. The applicability of the sensor was demonstrated by analysis of H_2O_2 in packing sterilant solutions and interference study.

1. Introduction

Application of nanoscience in daily life makes it a rapidly growing and cross-disciplinary branch of science. Extraordinary properties of nanomaterials interest chemists, biologists and physicists for applying these advanced materials in versatile applications such as biodiagnostic, medical imaging, cancer therapy and water purification [1–3]. Since industrial demand for using nanomaterials is growing, therefore remarkable synthesis routes have been developed and sacrificing the environmental impact, energy consumption and expenses [4]. Since mid-1990s, combination of the mentioned issues with the bio-applications of nanomaterials led to emerge of a new, environmentally benign and low cost synthesis method, called 'green chemistry' [5].

Many 'green' synthetic methods have been developed for synthesis of metallic nanoparticles using microorganisms (such as bacteria, yeast and fungi) [6], plant extracts [7,8] and other biosources [9,10]. Specific compounds in microorganisms or extracts not only act as reducing agent but also stabilize the colloidal dispersion as a capping agent [6–8]. Since such colloids do not contain any contamination or toxic precursor from reducing agent or solvent, they can be directly used for biological or therapeutic applications. A better therapeutic activity has also been observed for these biological-mediated nanoparticles because of synergistic effects of biological compounds on the metal core [11].

Studying the potential mechanism and effect of suitable factors in a biological-mediated synthesis is as important as its development. Mittal et al [8]. produced silver nanoparticles using *Syzygiumcumini* fruit extract and found pH was the most critical factor. Philip [12] used mushroom extract and explained silver binding through the carboxylate group of the amino acid residues was responsible for stabilizing nanoparticles. Prakash et al. [13] applied leaf extract of *Mimusopselengi* to synthesis antibacterial silver nanoparticles against *Klebsiellapneumonia, Micrococcus luteus* and *Staphylococcus aureus*. Parameshwaran et al. [14] synthesized silver nanoparticles using *Beta vulgaris* and controlled the size of nanoparticles by tuning different parameters such as the concentration of precursors, extract quantity, pH and reaction temperature.

It is well-known that nanostructured noble metals such as gold and silver show localized surface plasmon resonance (LSPR). This phenomenon is generated when light waves trapped within mentioned nanoparticles are smaller than the wavelength of light. In fact, LSPR is a result of the interactions between the incident light

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http://dx.doi.org/10.1016/j.snb.2015.12.062
0925-4005/

and surface electrons in a conduction band of noble metals which produce coherent localized plasmon oscillations [15]. The resonant frequency of gold and silver nanoparticles in visible spectrum is the foundation of recently developed LSPR sensors for detection of various chemical and biochemical substances.

Zargar and Hatamie [16] used LSPR of silver nanoparticles for colorimetric determination of resorcinol. Qi et al [17]. developed a low-cost, simple and fast colorimetric platform for the specific detection of trace Pb^{2+} using silver nanoparticles. Miao et al [18]. have developed a novel label-free colorimetric method for determination of trypsin using silver nanoparticles. Surface plasmon resonance of silver nanoparticles has shown promising results as an analytical tool for detection and measurement of different chemical and bio-chemical species. Also many works on biosynthesis of nanoparticles using plant extracts had been performed mainly because of their ability for tuning over crystal growth and stabilization [19]. This ability of bio-inspired nanoparticles and their surface plasmon resonance make them suitable for development of chemical and bio-chemical sensors. Farhadi et al [9]. used soap-root plant and the extract of hedysarum plant to develop a selective Hg^{2+} colorimetric sensor with detection limit of 2.2×10^{-6} M. Fillipo et al [10]. synthesized silver nanoparticles using glucose and sucralose and developed a fast colorimetric triethylamine sensor. Although plant extracts are free of toxic chemicals and there is no need to use high-pressure and temperature, but time-consuming reactions are the main drawbacks of plant-mediated synthesis of nanoparticles [7–12].

In this study, we developed a green, rapid and straightforward procedure for biosynthesis of silver nanoparticles using *Kiwifruit* extract. To the best of our knowledge, there is no comprehensive parametrical study for biosynthesis of silver nanoparticles using *Kiwifruit* so far and reports in such a rapid biosynthesis are so slender. *Kiwifruit* grows in most climates and according to FAO's (Food and Agriculture Organization) statistics, over 1.4 million tons of *Kiwifruits* produced worldwide in 2012 [20]. So this biosynthesis method holds number of advantages over previously reported biosynthesis procedures [6–14] including: being rapid and easy, using widely available precursor and construction of a proper model between the production yield and the inputted materials.

Most of the parametrical studies for a synthetic method use one-factor-at-a-time methodology, which is inefficient for optimization purposes. Also this method gives no information about possible interactions between factors. Thus, we used factorial design of experiments (DOE), which – with the aid of response surface methodology (RSM) – can simultaneously consider several factors at different levels and gives a suitable model for the relationships between factors and the response [21–23].

In this work, authors focused on the effects of two main factors in biosynthesis of silver nanoparticles including $AgNO_3$ concentration and quantity of *Kiwifruit* extract, using RSM. Also, a central composite design (CCD) was chosen as the design matrix for reliable identification of the possible first order interaction between both factors. CCD also provides a second order polynomial equation which can be used to predict optimum level of the factors. The optimum sample was selected for development of a LSPR sensor for determination of hydrogen peroxide (H_2O_2). In the last decade, there has been a great effort in the precise determination of hydrogen peroxide. The accurate determination of H_2O_2 is important due to its application in food, pharmaceuticals and textiles industries and also in cleaning products [24–26]. In this paper, LSPR-based detection of H_2O_2 presented as a low-cost and rapid method for label-free detection of H_2O_2 in aqueous solution.

2. Materials and methods

2.1. Preparation of Kiwifruit extract

Fully ripped *Kiwifruit*, weighing 50 g was taken and cut into fine pieces and was crushed into 100 ml distilled water in a mixer grinder for extraction. The extract was then separated by centrifugation at 4000 rpm for 10 min to remove insoluble fractions and macromolecules. Then the extract was filtered and used freshly for further experiments.

2.2. Synthesis of silver nanoparticles

Silver nitrate ($AgNO_3$) was purchased from Sigma–Aldrich(USA). For a typical synthesis, 0.2–1.0 ml of *Kiwifruit* extract was added to the $AgNO_3$ solution (5.0 ml of 1.0×10^{-7} M–2.0×10^{-3} M) and the final volume of each sample was maintained at 6 ml by adding distilled water. The samples kept under constant stirring rate of 400 rpm for 60 min. Different colors from white to light reddish brown showed up for samples pointing out the effect of factors on reaction completion (Fig. S1).

2.3. Design of experiments

Eleven experimental runs consisting of 4-starpoints (star distance was 0) and 3 center points were generated with 2 factors and 3 levels by the principle of RSM using MINITAB Release 15. A central composite design (CCD) with multiple linear regression was used to estimate the model coefficient of the selected factors, which believed to influence production yield of silver nanoparticles. Each factor was set at its high level (+1), low level (−1) and medium level (0). The design was involved with two factors, including the concentration of $AgNO_3$ and the quantity of *Kiwifruit* extract and the response is the maximum absorbance of UV–vis spectrum. The levels for these two factors, according to a CCD, and their responses listed in Tables 1 and 2. All the experiments carried out in two replicates and the results for the response reported as a mean value in a randomized order to avoid systematic bias. Finally, a quadratic polynomial regression model (Eq. (1)) was applied to estimate and predict the response value over a range of input factors' values:

$$Y = b_0 + \sum_{i=1}^{2} b_i X_i + \sum_{i=1}^{2} b_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{2} b_{ij} X_i X_j \quad (1)$$

where Y is the dependant response variable (i.e. maximum absorbance of UV–vis spectrum), b_0 is the intercept term, b_i, b_{ii}, and b_{ij} are the measures of the effect of variable X_i, X_i^2 and X_iX_j, respectively. X_i and X_j represent the independent variables. The variable X_iX_j represents the first order interaction between X_i and X_j ($i<j$). The purposes of considering a model such as (Eq. (1)) are:

1. Estimating a relationship between Y and X_i that can be used to predict response value (Y) for a given setting of the control variables.
2. Determination of the significance of the factors whose levels are represented by X_i.
3. Estimation of the optimum settings of X_i that result in the maximum response over a certain region of interest.

The analysis of variance (ANOVA) for quadratic model was performed at 10% confidence level (P-value <0.1). The significance and the magnitude of the effect estimations for each variable and all their possible linear and quadratic interactions were also determined. At last, the model was used to predict main effective factors.