Silver nanoparticles and Griess reaction in determination of bisphenol A

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Research Article

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Abstract

In this work, we introduced two colorimetric methods to determine Bisphenol A (BPA) in water samples using silver nanoparticles (AgNP) prepared by walnut carbon dot and Griess reaction. Therefore, firstly the optimal medium was selected based on acidic, neutral and alkaline media. In determination by AgNPs, the optimal order of addition of the reagents was obtained as: sample containing BPA, sodium hydroxide and AgNP. In the presence of 100 microliter of synthesized AgNPs, the highest variation in the AgNP spectrum while BPA is added was observed. In the presence of BPA, the yellow color of AgNP is faded. In this method, a linear range of 1.0–16.0 ppm and LOD of 0.68 ppm was obtained. In Griess method, nitrite and 2-nitroaniline were used as reagents and BPA act as analyte. In the method, for reaction and observing the color, sample containing BPA was added to the reaction mixture (nitrite and 2-nitroaniline with concentrations of 0.60 M and 0.072 M, respectively). Response surface methodology was used to investigate the Griess reaction. According to the results, the lower the concentration of 2-Nitroanilin and the higher the concentration of nitrite the better the response and the clearer the color change. With Griess reaction, linear range and LOD were 3.0–25.0 ppm and 0.65 ppm of BPA, respectively. Real water sample and spiked samples were analyzed by proposed method which results were satisfactory.

1. Introduction

Estrogen-like endocrine disrupting chemicals (EEDCs) have attracted increasing attention due to occurrence in aquatic environments such as surface and groundwater, sewage, runoff and landfill discharges and their potential detriment to the system of reproduction of organisms [1].

Exposure to low concentration of EEDCs for long-terms can result in adverse effects on the systems of reproduction and endocrine of aquatic organisms [2, 3]. Therefore, these chemicals are recognized as emerging contaminants and endocrine disrupting chemicals [4]. BPA as one of the EEDCs (Fig. 1), acts as a monomer primarily in the production of polycarbonate and epoxy resins. Because of their resistance to heat and chemicals, epoxy resins are used as paints, adhesives, protective coatings for food and beverage containersand electronic laminates [5]. BPA can easily migrate from products to food during their use [5–8].

Because of the similarity of BPA structure to that of diethylstilbestrol and estradiol, cellular response can be stimulated by its binding with the estrogen receptors. Adverse health effects of BPA even at low dosage has been observed in laboratory animals [9].

Effect of BPA on human beings includes reproductive effects, mammary gland developmental problems, cardiovascular problems, fetal growth restriction, obesity, anxiety and depression, low sperm production, hormone-related diseases like breast and prostate cancer [10].

Mainly, extraction and chromatographic methods followed by different detection systems have been used to determine BPA [11–15]. These methods are very accurate and sensitive, but they are time-consuming and need well-trained technicians. Therefore, these methods are unsuitable for routine analysis. Moreover,

reports of using spectrophotometry and fluorimetry can be found for determination of BPA [16–19]. Karrat and Amine [18] developed a spectrophotometric method for determination of BPA by producing a colored compound after solid phase extraction by MIP. Mei et al. [19] synthesized AuNP-aptamer complex and used to detect BPA colorimetrically.

Development of adequate methods for monitoring of the pollutants is an analytical challenge. One of the ideal characteristics of these methods is simplicity and environmental friendliness.

In this work, two colorimetric methods consist of using silver nanoparticles (AgNPs) and a diazotization reaction were used to determine BPA. AgNPs have been synthesized by green method. Herein, it is tried to propose simple methods which are based on color changes. This enables the analyst to distinguish and determine BPA by naked eye.

2. Experimental

2.1. Materials and instruments

All chemicals were of analytical reagent grade. Ammonia 25% concentrated solution, ethanol, sodium nitrite, hydrochloric acid and silver nitrate were purchased from Merck (Darmstadt, Germany). Bisphenol A was prepared from Sigma-Aldrich. 3-Nitroaniline was supplied by BDH Chemicals Ltd (Poole, England). For preparation of all solutions, distilled water was used.

Water samples include tap waters poured in polyethylene terephthalate (PET) bottle.

An Agilent spectrophotometer (model 8453) with diode array detector was used for recording spectra. Design and analysis of the experiments were carried out by MINITAB (Minitab Inc. Release 18.0) statistical package.

2.2. Synthesis of walnut carbon dots (CDs) and Synthesis of AgNP

In a single-step hydrothermal method CDs were prepared using walnut [20, 21]. 15 g of walnut was weighed and boiled for 10 min in 100 mL distilled water. After filtering the mixture, 20 mL of ethanol was added to the filtrate and heated at 150°C for 3 hours. Now, the obtained dark brown solution was filtered through a Whatman filter paper. The solvent of the resultant filtrate containing CD can be evaporated for obtaining solid state CD.

Prepared CDs were used as reducing and stabilizing agent in the preparation of AgNPs. To a 100 mL distilled water when boiling, 125 µL of the prepared CDs (50 mg mL^{-1}) was added and boiled for 15 min while stirring. Now, 1 mL ammonia (10%) and 5 mL of silver nitrate (3.42 mg mL^{-1}) were added successively. After development of the reaction for 45 min, the reaction mixture containing AgNP was cooled to room temperature [22].

3. Results And Discussion

3.1. Transmission electron microscopy (TEM)

For investigation about the shape and sized of the prepared AgNP, its transmission electron micrograph was recorded (Fig. 2). As can be seen from Fig. 2, the prepared AgNP is spherical in shape. Estimation based on the micrograph showed that the average size of the prepared AgNP is 16.3 ± 3.6 nm. Solution of the synthesized AgNP is yellow in color and stable.

3.2. Optimization of medium

In order to explore about the best media, color changes of 1000 µL of AgNP in the presence BPA with concentration of 5.0 mg L^{-1} was followed in acidic, neutral and alkaline solutions. The results have been shown in Fig. 3.

The results showed that disappearance of the color and difference between the blank and the sample is more pronounced in alkaline medium (sodium hydroxide with concentration of 0.01 mol L^{-1}).

3.3. Optimizing the order of addition of the reagents

According to Table 1, six different order for addition of five components were applied to find the best order in determination of BPA using AgNPs. According to the results seen in Fig. 4 and Table 1, the second order in terms of color change and the difference between absorbance of blank and sample was selected as optimal order for addition of the components in determination of BPA using AgNPs. Therefore, in the determination of BPA using AgNP, sodium hydroxide is added to the sample containing BPA followed by addition of AgNP.

Table 1

Different order of addition of the components.

No.	Order of addition of components			Absorbance change at 585 nm
1	BPA	AgNP	NaOH	0.298
2	BPA	NaOH	AgNP	0.786
3	NaOH	AgNP	BPA	0.424
4	AgNP	NaOH	BPA	0.149
5	NaOH	BPA	AgNP	0.191
6	AgNP	BPA	NaOH	0.203

3.4. Optimization of sodium hydroxide concentration

In this experiment, five different concentrations of sodium hydroxide were examined. Based on the results (Fig. 5), the optimal concentration of sodium hydroxide was 0.01 mol L^{-1}. With this concentration of sodium hydroxide, variation in the spectrum of the sample with respect to the blank and its color changes were higher. In the presence of high concentration of sodium hydroxide, the color of AgNP itself turns from bright yellow to brown and the mixture with BPA changes to a dusky green color.

3.5. Optimizing volume of silver nanoparticle

Effect of BPA on spectral variation and color changes of different volumes of AgNP was explored. The results have been shown in Fig. 6. It can be seen clearly that the higher the volume of AgNP, the greater the extent of color and spectral variation. Since there exist a limit for the total volume of the sample, as optimal volume of AgNP, 1000 µL was selected.

3.6. Griess reaction for determination of BPA

In Griess method for determination of BPA, a diazotization reaction is performed [23]. Here, instead of nitrite, BPA acts as analyte. Therefore, 2-nitroaniline and nitrite were used as the reagents.

Firstly, the order of the addition of the components were optimized. Different orders (Fig. 7) were examined and it was observed that addition of the mixture of hydrochloric acid, nitrite and 2-nitroaniline to the solution of BPA and vice versa, results in the highest color and absorbance variations.

In the next step, amount of the reagents were optimized. For this purpose, response surface methodology was employed [24]. In Table 2, designed experiment with three factors using central composite design has been shown (A, B and C are volume of hydrochloric acid, nitrite and 3-nitroaniline, respectively in µL). Correspondingly, response which is absorbance at 500 nm has been reported.

ANOVA results have been reported in Table 3 and Figs. 8 and 9. As can be seen in Table 3, hydrochloric acid (A) and nitrite (B) are significant factors at 95% significance level in the studied system with p values lower than 0.05. Among the second order interactions, the term B×B is important. Pareto chart shows these results, too (Fig. 8). Surface plots (Fig. 9) which show the variation of response with simultaneous variation of two factors indicate that in higher levels of nitrite (B), the response can be higher. In the same time, moderate amounts of hydrochloric acid are necessary to achieve favorite response.

Analysis of the experiment showed that the optimal volume of the reagents are 150, 690 and 16 µL of hydrochloric acid (0.1 mol L^{-1}), nitrite (0.6 mol L^{-1}) and 2-nitroaniline (0.072 mol L^{-1}), respectively.

Table 2 Designed experiment for optimization of the reaction between BPA, hydrochloric acid (A), nitrite (B) and 3-nitroaniline (C). the values for the factors are volume in µL.

Run	A	B	C	Absorbance at 500 nm
1	40	300	50	0.051
2	80	550	100	0.311
3	120	800	150	0.295
4	120	300	150	0.311
5	40	800	100	0.160
6	80	550	50	0.462
7	40	800	100	0.278
8	80	550	50	0.309
9	120	300	16	0.289
10	80	550	100	0.297
11	13	550	100	0.173
12	80	550	100	0.277
13	147	550	100	0.331
14	80	970	100	0.270
15	80	130	100	-0.100
16	80	550	100	0.250
17	40	300	150	0.112
18	80	550	184	0.241
19	120	800	50	0.373
20	80	550	100	0.307

Table 3. Results of ANOVA of the designed experiment reported in Table 2.

Term	Coefficient	t value	*p* value
Constant	0.3177	10.80	0.000
A	0.0684	3.51	0.006
B	0.0707	3.62	0.005
C	-0.0153	-0.78	0.451
A×A	-0.0154	-0.81	0.435
B×B	-0.0744	-3.92	0.003
C×C	-0.0095	-0.50	0.628
A×B	-0.0260	-1.02	0.332
A×C	0.0001	0.00	0.998
B×C	-0.0348	-1.37	0.201

3.7. Calibration

In order to find the relation between concentration of BPA and responses, different concentrations of BPA were examined in the presence of AgNP and in the Griess reaction in optimal conditions. Calibration curves can be seen in Fig. 10 and corresponding statistical results have been reported in Table 4.

For calibration, wavelengths 585 and 500 nm were chosen with AgNP and Griess method, respectively because the highest variations in absorbances were observed in these wavelengths. Correlation coefficient of the relations are close to unity which indicates that the calibration curve are linear. Moreover, high values of calculated *F* statistics for the calibrations confirm the linearity of the calibration.

Relatively a wide linear range was obtained in calibrations. With AgNP, calibration is more extended to lower concentrations. Comparison of slopes of the calibration curves shows that the method by AgNP is more sensitive.

Table 4

Statistical parameters of the calibrations using AgNP and Griess reaction.

	Slope	Wavelength (nm)	Linear range (mg L^{-1})	Intercept	DL (mg L^{-1})	R^2	F
AgNPs	0.062(0.002)	585	1.0–16.0	0.187(0.018)	0.68	0.9849	650.6
Griess	0.0135(0.0006)	500	3.0–25.0	-0.041 (0.009)	0.65	0.9940	574.5

In Table 5, results of the analysis of bottled water have been collected. The analysis was performed in different times after filling the bottle. In order to evaluate the accuracy of the method, an amount of the standard BPA solution was added to the water samples and the spiked samples were analyzed.

Table 5

Results of the analysis of the real samples by proposed methods.

Method	Added (mg L^{-1})	Found (mg L^{-1})	Percent Relative Error	RSD%
AgNP				
After 13 days	5.00	3.70	16.2%	2.7%
After 37 days	5.00	4.80	4.4%	10%
Griess method				
After 13 days	14.00	13.45	-3.9%	0.2%
After 37 days	14.00	13.94	-0.4%	13.8%

4. Conclusions

Green synthesized AgNP was successfully used to detect and determine BPA in water samples. Different variables in the method were explored and optimized. Moreover, Griess method was modified and used for detection and determination of BPA. Response surface methodology was employed to explore the reaction of BPA as a component in Griess method.

The methods are colorimetric and simple which highly reduce the expense of the analysis.

Declarations

Funding No funding was received for conducting this study.

Ethics Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication All authors have read and approved the final manuscript.

Conflict of Interest Masoud Shariati-Rad declares that he has no conflict of interest. Asma Ebrahimi declares that she has no conflict of interest.

Data availability All data generated or analyzed during this study are included in this published article.

Author Contribution Masoud Shariati-Rad Conceptualization, Initial Study, Experimental design, Analysis of the results, Review of the initial draft of the manuscript. Asma Ebrahimi Initial study, Experiments, Writing the initial draft of the manuscript.

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Figures

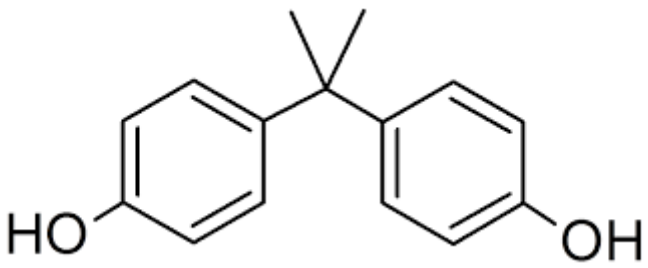

Figure 1

Chemical structure of BPA.

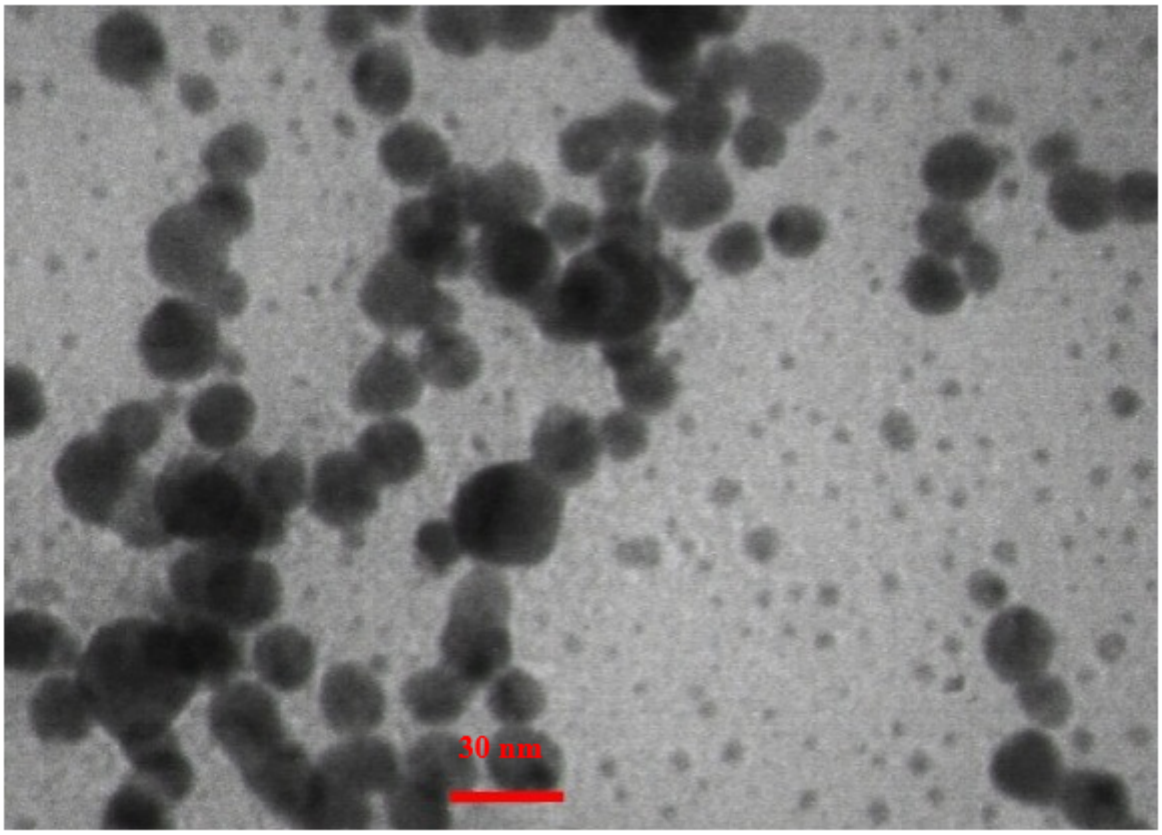

Figure 2

TEM image of the prepared AgNP.

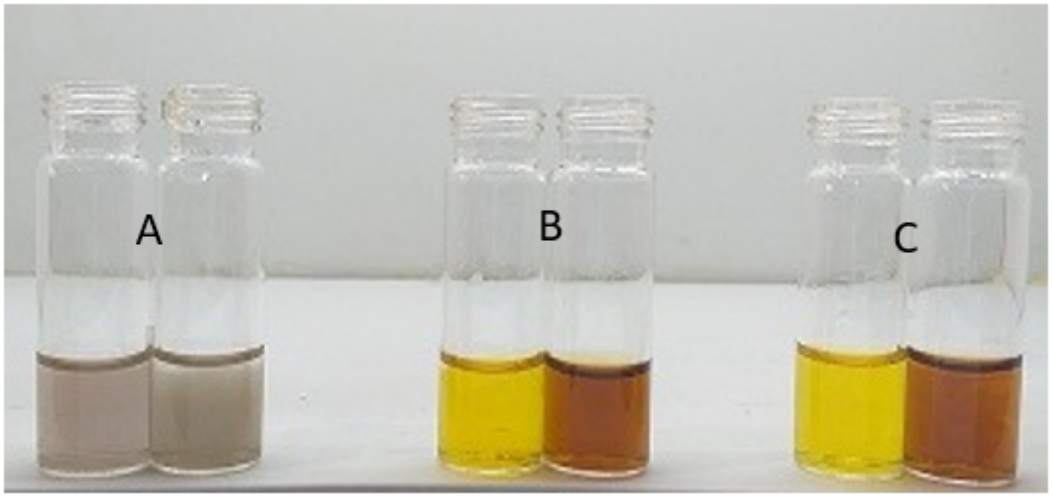

Figure 3

Optimization of the medium, A (pH< 7), B (pH =7), C (pH>7)

Figure 4

Color variations of the mixture of BPA, AgNP and sodium hydroxide with different order of addition of the components (Table 1). The left hand side sample tubes contain blank and the right hand side tubes contain sample.

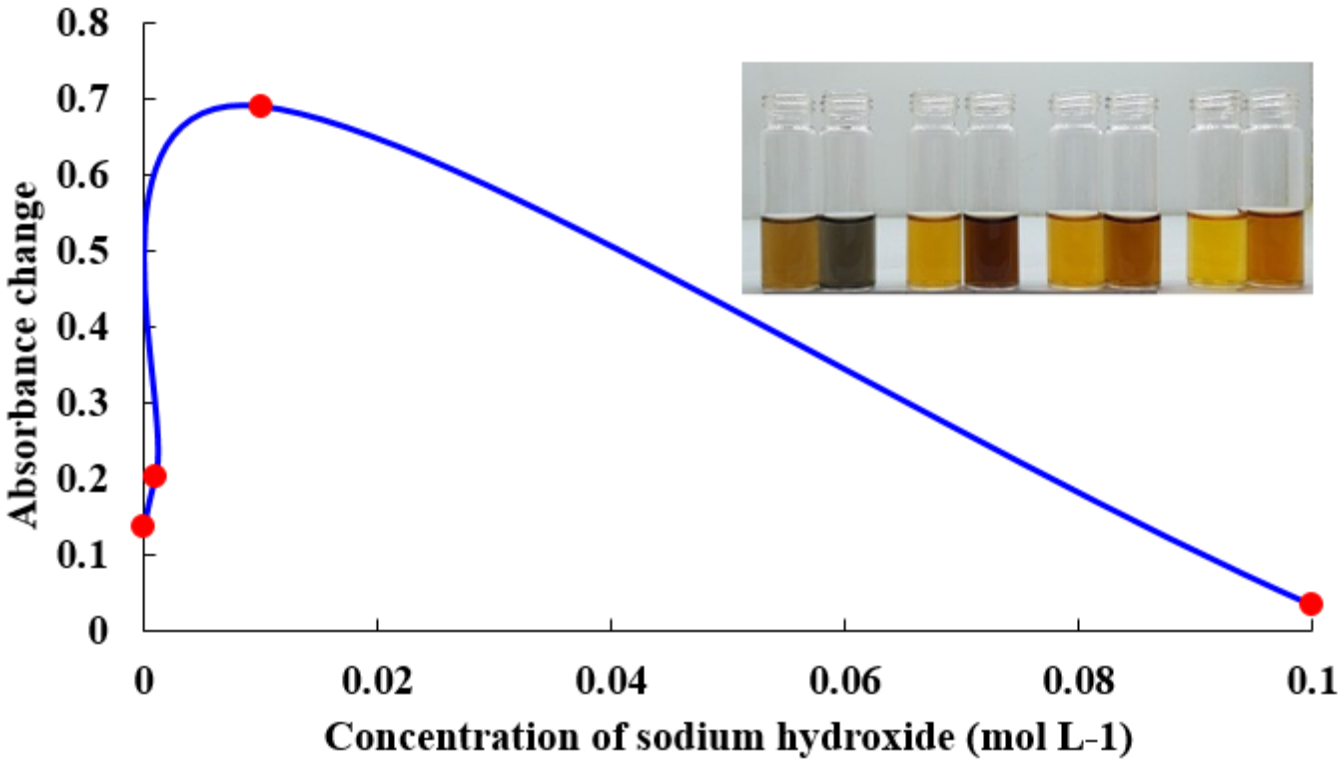

Figure 5

Curve of Optimization of NaOH concentration at 585 nm. Concentration of BPA is 5.0 mg L^{-1} and the volume of AgNP is 1000 microliter. Inset shows the corresponding images of the solutions.

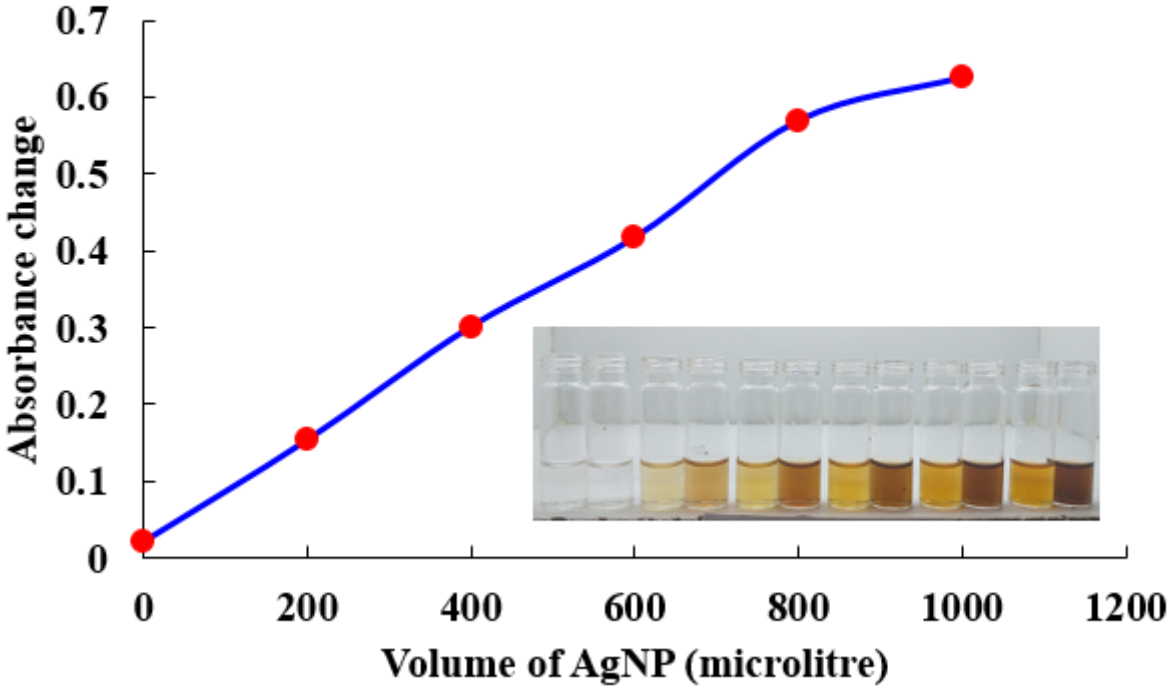

Figure 6

Absorbance variation of different volumes of AgNP in the presence of BPA (5.0 mg L^{-1}) at 585 nm. Inset shows the corresponding images of the solutions. The left hand side sample tubes contain blank and the right hand side tubes contain sample.

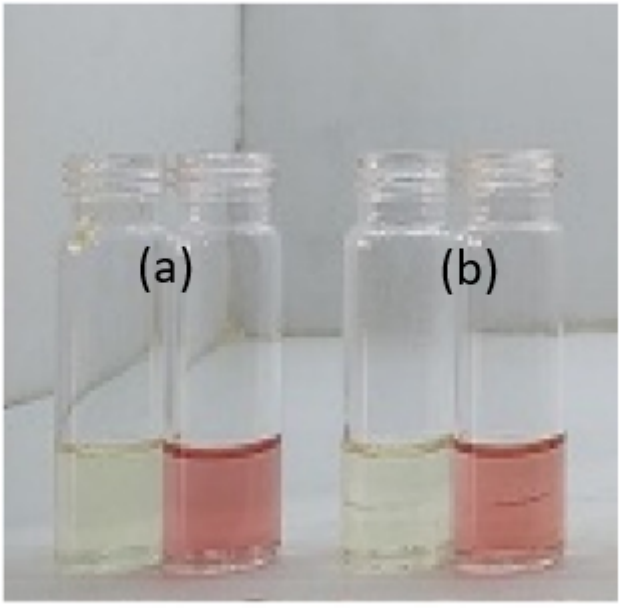

Figure 7

Order of the addition of components in Griess reaction. (a) Addition of the mixture of hydrochloric acid, nitrite and 2-nitroaniline to the solution of BPA and (b) addition of solution of BPA to the mixture of hydrochloric acid, nitrite and 2-nitroaniline.

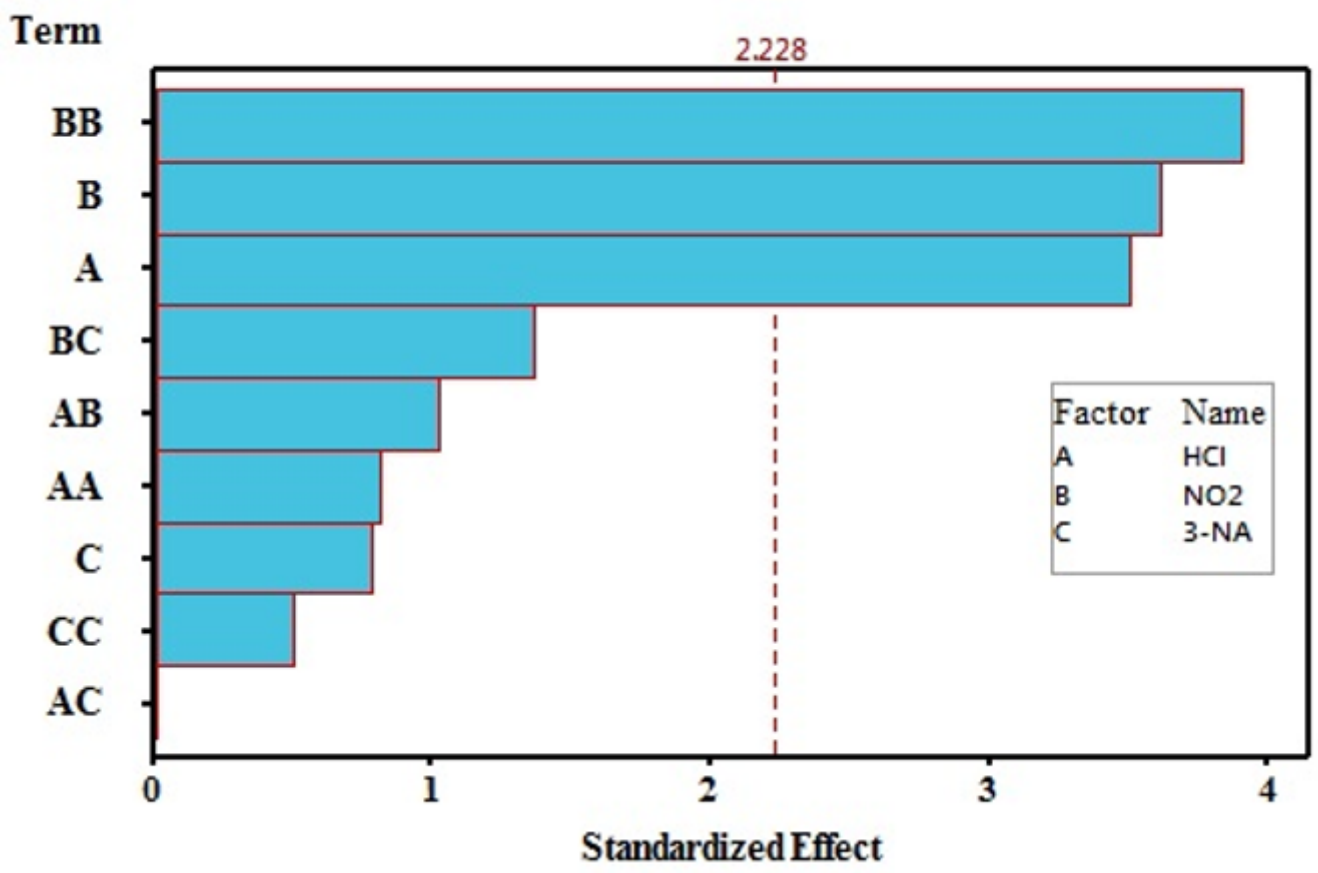

Figure 8

Pareto chart obtained by ANOVA of the designed experiment reported in Table 2.

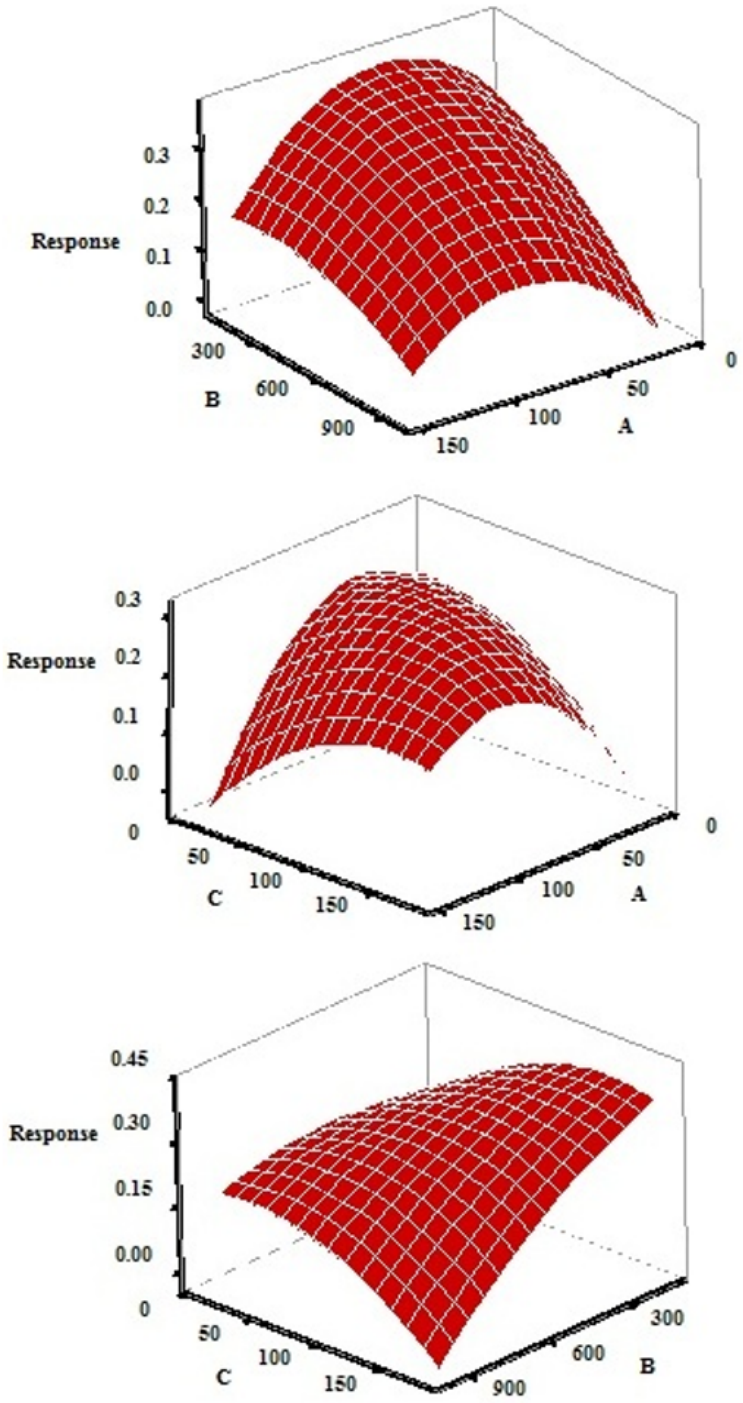

Figure 9

Response surfaces calculated based on the results of ANOVA.

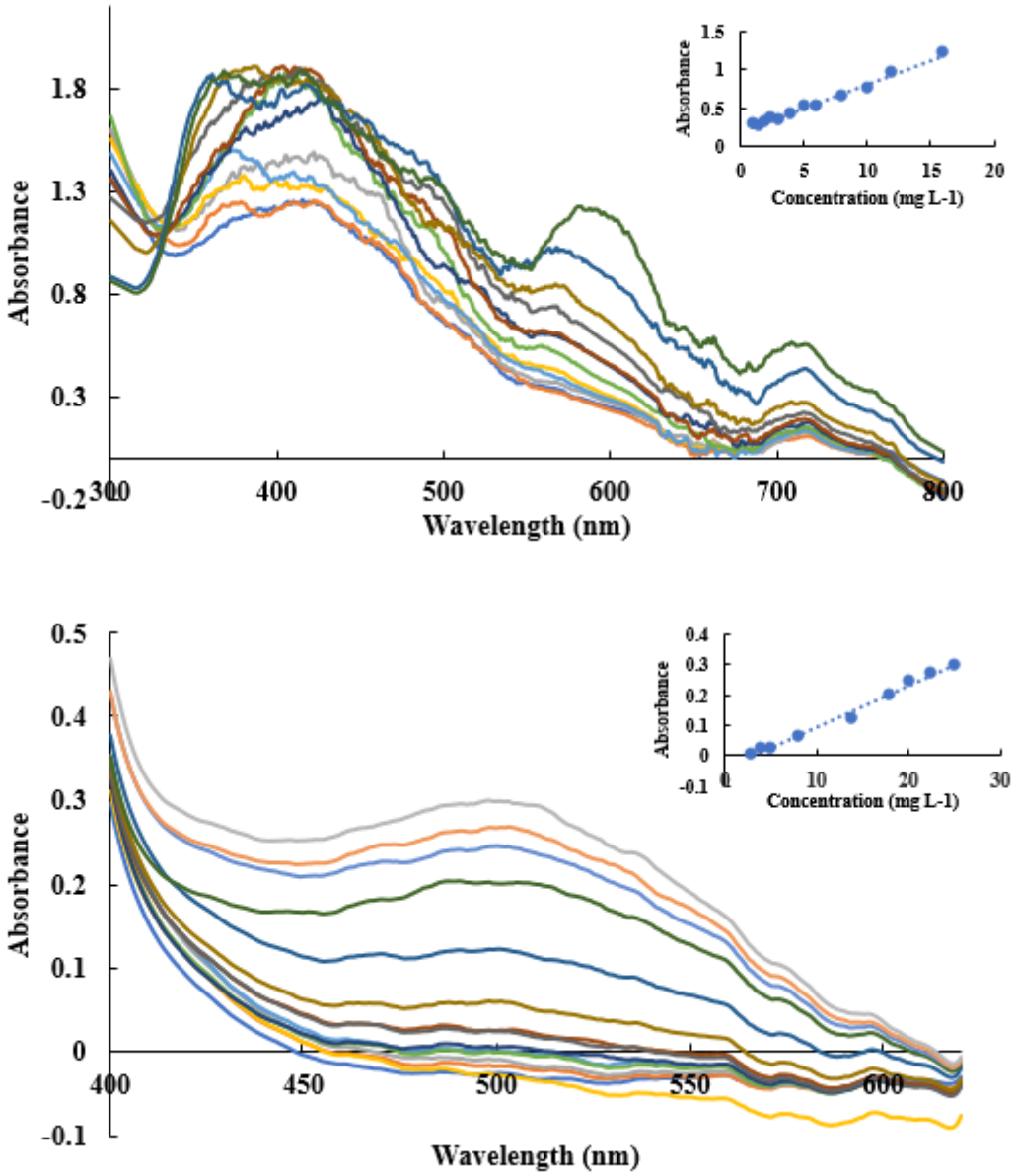

Figure 10

Spectra for calibration of BPA using AgNP (a) and Griess reaction (b) in optimal conditions. Insets are the obtained calibration curves.