

Response Surface Methodology Modeling to Determine of Trace Amounts of Phenolic Compounds Using Silver Modified / Zero Valent Iron/ Fe₃O₄@G Nanocomposite

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Abstract

In this study, a simple and fast magnetic dispersive solid phase extraction methodology was developed G@Fe₃O₄/Fe/Ag nanoparticles for preconcentration and determine of phenolic compounds in water samples. The sorbent was characterized by assorted characterization method. The effects of diverse factor on the extraction process were studied thoroughly via design of experiment and desirability function. This work was showed the G@Fe₃O₄/Fe/Ag NPs was the best sorbent between Graphene, G@Fe₃O₄/Fe and Fe₃O₄, 0.01M HNO₃ in acetonitrile was the most efficiency between eluent types, the best salt content which was 7.5% w/v.

Keywords: Response Surface Methodology, Phenolic Compounds, Silver Modified / Zero Valent Iron/ Fe₃O₄@G, Nanocomposite.

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Introduction

Chemical compounds are important in many industrial and economic activities; they are a significant part of our life. They ready society with a large range of benefits. Chemical substances have many health problems and are hard to removal from the environment [1]. Phenol and phenol compounds are priority pollutants because of their toxicity to human begins at low concentrations [2, 3]. Phenol compounds, a group of organic pollutants have been classified as hazardous pollutants. They should be noted that the pollution of drinking water by 0.005 mg l^{-1} could have about odor and significant taste [4, 5]. Chlorophenols (CPs) are the important organic pollutants that in world because it used widely in industry and agriculture. The big sources containing Chlorophenols are the wastewater from solvent, pesticide, paint, pharmaceuticals, paper and pulp industries.

The general methods used for removal of Chlorophenols include physical treatment use activated carbon adsorption, hyper filtration, solvent extraction, etc. Chemical treatment as chemical oxidation, wet oxidation, hypercritical oxidation, TiO_2 photochemical oxidation, UV/ H_2O_2 oxidation, low temperature plasma method, etc, treatment by biological substance like activated sludge, aerobic or anaerobic method, separation method with membrane, etc. The new chemical and physical methods are limited because they are more expensive [6-9]. Therefore removal analytical methods are required especially for the analysis of CPs owing to their low concentrations. Some methods have been reported for determination of phenol and their products such as adsorption on Chitosan – Calcium [2] extraction [10] and HPLC [11-13].

In this study is determined trace amount of phenolic compounds using zero valent Iron/ magnetic/ Graphene nanocomposite which was produced by Hummer method. Optimization refers to reclaim the efficiency of a system: A process in order to get the best benefit from that. The literacy optimization has been generally used in analytical chemistry as a means of find situation at which to apply a procedure that produces the best possible response [14]. Response surface methodology (RSM) is a collection of mathematical and statistical methods to set the experimental models, in this model, two stages are essential, the estimation of function and the experimental studies. The application of RSM is to check the cost analysis and numerical noise [11,1].

Experimental

Chemical and reagents

4-NP(>99% purity), 4-CP(>99% purity) were purchased from Merck Ltd (Darmstadt, Germany). NaOH, HCl, HNO_3 , H_2SO_4 , H_2O_2 , NaCl, KMnO_4 , Hydrazine, $\text{Fe}_3\text{O}_4 \cdot 6\text{H}_2\text{O}$, NH_4OH (28%w/v), 2-Propanol, Ethanol and Acetone which all were of analytical grade were supplied by Merck

(Darmstadt, Germany). High purity methanol (MeOH) and acetonitrile (ACN) were obtained from Daejeon (Seoul, South Korea). Ultra pure water was obtained by employing a milli-Q system from Millipore (Bedford, MA, USA).

Preparation of solutions

Ten milligram of each phenol was dissolved in 10 ml HPLC grade methanol to prepare the stock solution of each analyte. The solutions were stored at 4°C and brought to ambient temperature prior to use.

Instrumentation

An Agilent 1200 series HPLC instrument consisting of a G1322A solvent degasser, a G1311A quaternary pump, a Rheodyne 7725i (PerkinElmer, USA) injector along with a 100 µL sample loop and a UV –detector (G1314B) was employed for separation and quantification of AAs. An octadecyl silica HPLC column (250×4.6 mm, 5 µm, Agilent Technologies, USA) was used for separation of AAs and data acquisition was performed by ChemStation software (Agilent Technologies, CA, USA). A 250 µL Hamilton microsyringe (Bonaduz, Switzerland) was used for injection to instrument. A MIRA3 TESCAN (Czech Republic) field emission scanning electron microscope (FESEM) was used morphologic survey. The energy dispersive X-ray analysis (EDX) was conducted on a MIRA3 TESCAN instrument. FTIR spectra were obtained using a Bruker IFS-66 spectrophotometer (Bruker Optics, Karlsruhe, Germany). X-ray diffraction pattern (XRD) patterns were recorded on a Philips-PW 12C diffractometer instrument (Amsterdam, The Netherlands) with a Cu K α radiation source.

Synthesis of Ag@magnetite@graphene nanocomposite

Graphene and Graphene oxide were synthesized by Hummer's method [14]. Magnetic graphene was synthesized by chemical co-precipitation of Fe(II) and Fe(II) ions in the presence of graphene nanosheets[15]. For synthesis Ag@Fe₃O₄@Gnanocomposite, 100ml 0.1 mol/lit solution of AgNO₃ was added to 0.5 g graphene / Fe₃O₄ and this and this suspension was stirred for 15 min. Then, 3.5g NaBH₄ was dissolved in 60ml deionized water under nitrogen atmosphere and added drop by drop to the reaction mixture under stirring for about 30 min. The precipitate was then collected using a strong permanent magnet while the solution was decanted and was washed several times by double distilled water and methanol. The washing procedure was continued, until the filtrate become colorless. The achieved nanocomposite was dried in ambient air under vacuum for 24 h.

Extraction procedure

Extraction experiments were performed as follows:

- a) 29.7mg Ag@Fe₃O₄ was dispersed in 52ml of sample solutions containing phenols and NaCl
- b) The pH was adjusted to 8.8 and then the sample was sonicated for 4 min to accelerate the adsorption of phenols onto Ag@Fe₃O₄@G
- c) The adsorbent was separated from the mixture by the external magnetic field
- d) The adsorbent was eluted for 2 min with 135 μ L 0.01 mol/L HNO₃ in acetonitrile using vigorous vortex and then Ag@Fe₃O₄@G was separated from the solution
- e) Finally, the collected eluent was injected to HPLC-UV

Experimental design

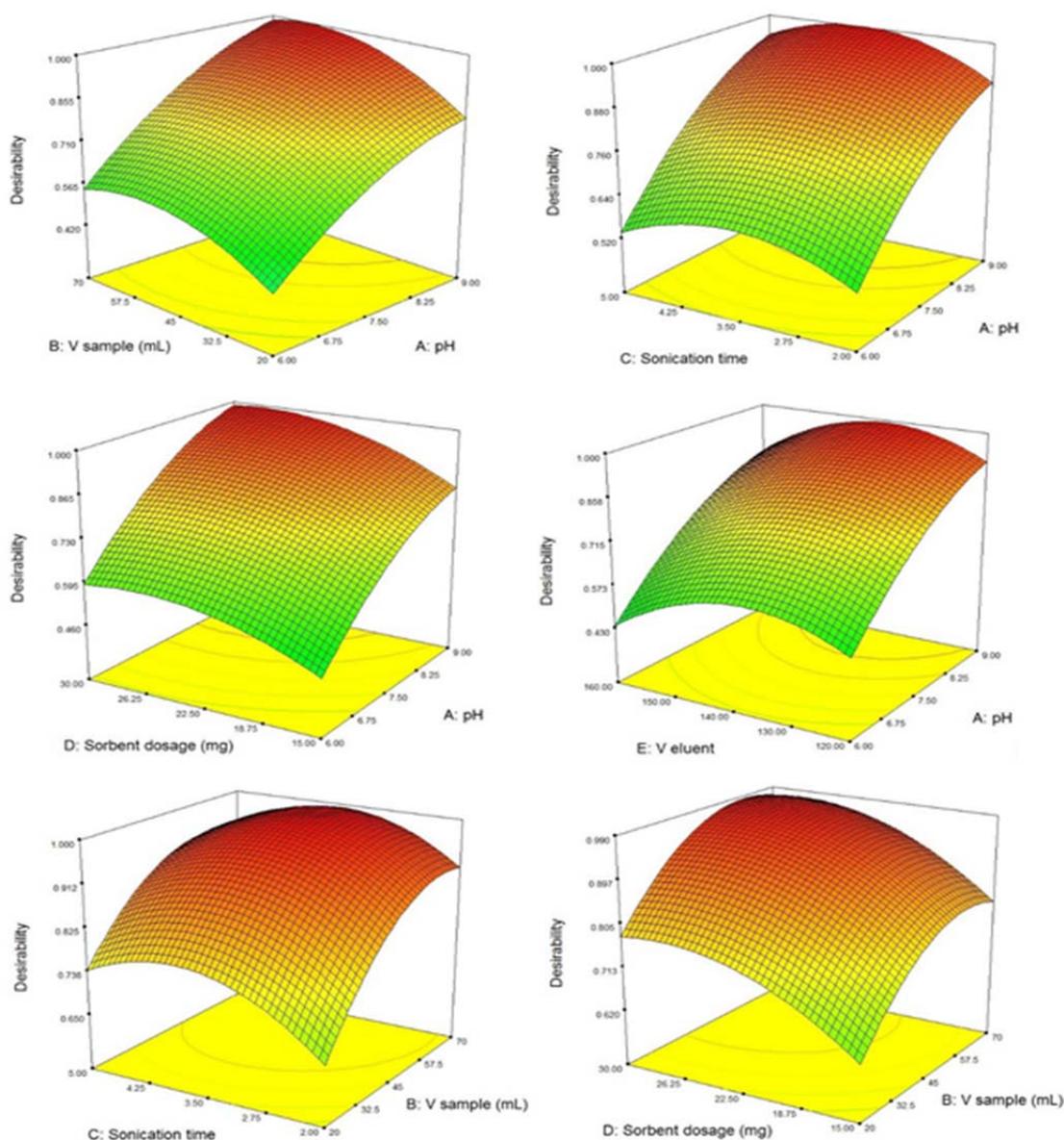
Design-Expert software (7.0.0 trial version) was employed to construct the experimental matrix and to process obtained data. The simplest model which can be used in response surface methodology is based on a linear function. For its application, it is necessary that the responses obtained are well fitted to the following equation:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \varepsilon$$

Design of experimental approach

Herein, the effect of five factors was explored via CCD and desirability function. CCD was employed to optimize the effect of pH, sorbent dosage, sorption time, eluent volume and sample volume. Based on the CCD equation ($N=2f+2f+C_0$, f : the number of variables, C_0 : replicates in center point), f and C_0 were adjusted to 5 and 9, respectively, and hence 51 tests were designed [17]. To take the best extraction condition, simultaneous optimization approach named desirability function (DF) strategy was employed. In this study, geometric mean (Geo mean) was selected as the most appropriate response.

The experimental data showed a good agreement with the quadratic polynomial model. Analysis of variance (ANOVA) was used to investigate the significance of parameters and to create proper model. Hence, the significance of each effect was studied using F-value and p-value. Accordingly, pH, sorbent amount and sorption time exhibited significant effects on extraction efficiency owing the fact that their p-values were lower than 0.05 in 95% confidence level. The model F-value was 35.45 with a p-value lower than 0.0001 that corroborates the suggest model is significant there is only a 0.01% chance that a model with this large F-value could occur owing to the noise. The lack of fit (LOF) p-value was not significant relative to the pure error.



Scheme 1. 3D graphs plots for the effect of pH, sonication time, sorbent dosage and volume of eluent on desirability.

The R_2 and adjusted- R_2 parameters were 0.9607 and 0.9336, respectively which are quite desirable. The response increases by moving from cold “blue” to warm “yellow” colors. Therefore, the highest extraction efficiency was achieved according using: a pH value of 8.8, a sorption time of 4 min, a sorbent amount of 29.7 mg and an eluent solvent volume of 135 μ L. The optimized values of adsorption time and nanoadsorbent amount confirm above statement. The eluent volume is a significant parameter that affects the sensitivity due to the fact that this factor determines the maximum reachable preconcentration factor [18]. The result of CCD gave that the extraction efficiency is promoted by increasing that eluent volume up to 135 μ L. For eluent volumes higher than 135 μ L, preconcentration factor was decreased due to the dilution effect.

Results and discussion

SEM technique was used to study the structure of G@Fe₃O₄/Fe/Ag nanocomposite. As showed in Figure 1, Fe₃O₄@Ag NPs have spherical shape with an average diameter of 15 nm. These NPs have magnetic feature, wide specific surface area and high surface energy.

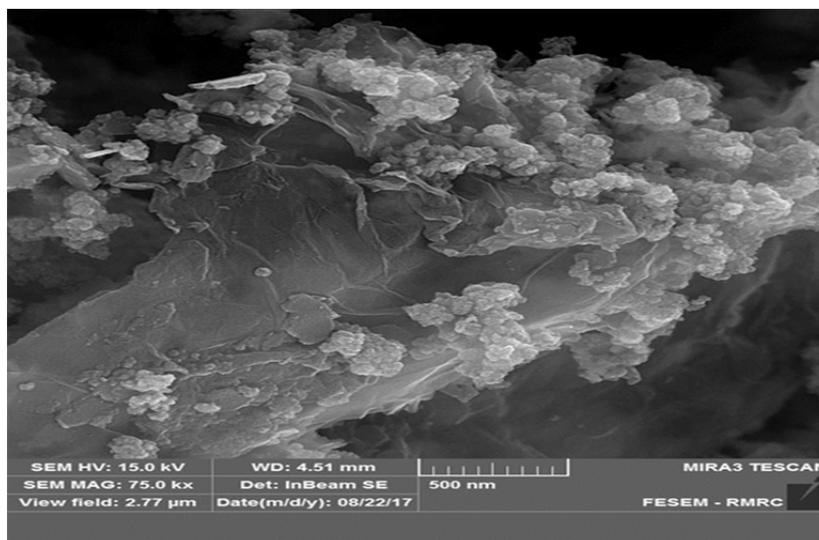


Figure 1. SEM image of G@Fe₃O₄/Fe/Ag nanocomposite.

The Fe₃O₄@Ag NPs are successfully coated onto the graphene surface. The elemental analysis of nanocomposite was defined with EDX method. EDX pattern of composite was confirmed the presence of C, O, Fe and Ag by 9.13, 43.62, 39.43 and 4.89 alliance (Figure 2).

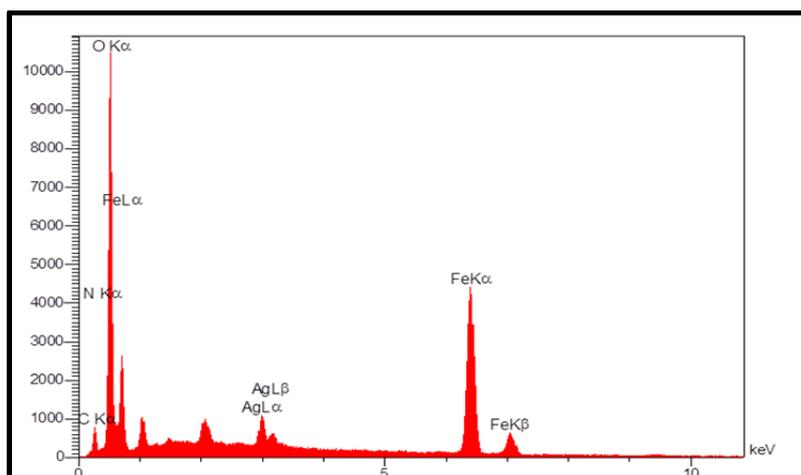


Figure 2. EDX of nanocomposite.

The KBr method was the FTIR spectroscopy of the nanocomposite. The peaks at 3396 cm⁻¹ and 581 cm⁻¹ are correlated with –OH and Fe-O. Besides, the peaks at 1400-1600 cm⁻¹(C=C) showed the presence of graphene on surface the adsorbent (Figure 3).

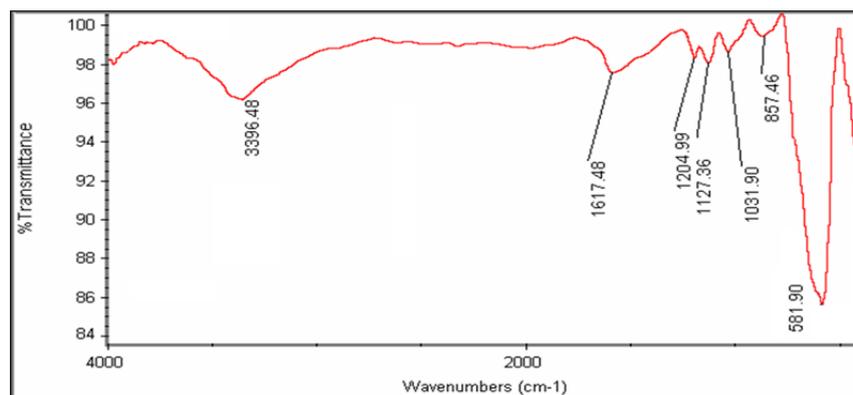


Figure 3. FT-IR spectroscopy of the nanocomposite.

Multiple factors of sorption and desorption such as pH value, sample volume, sorbent type, nanoadsorbent amount, salt addition, adsorption time, eluent type and volume are affecting performance. The sorbent type is a very important factor in the adsorption. Therefore, magnetic graphene was chosen as a support due to the high adsorption property of Fe_3O_4 NPs [16]. The comparison of graphene, Fe_3O_4 NPs, $\text{G@Fe}_3\text{O}_4/\text{Fe}$ NPs and $\text{G@Fe}_3\text{O}_4/\text{Fe}/\text{Ag}$ NPs performance are shown in Figure 4. $\text{G@Fe}_3\text{O}_4/\text{Fe}/\text{Ag}$ NPs has the highest performance compared to the other sorbents. The results can be related to the presence of coordination interaction between the phenolic groups of phenolic compounds and Ag NPs that are present on the surface of $\text{G@Fe}_3\text{O}_4/\text{Fe}$ NPs.

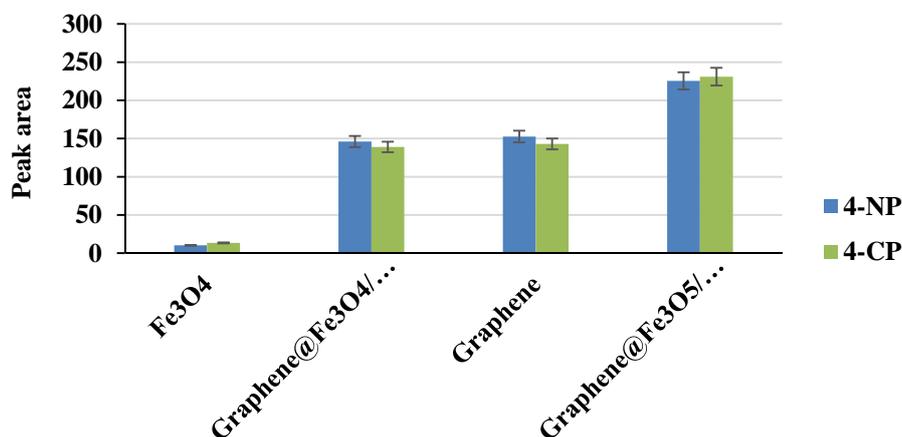


Figure 4. Effect of sorbent type.

The eluent should have high tendency to CPs, NPs and release them from the adsorbent surface to obtain quantitative recovery in short desorption time. Thereby, various eluent such as methanol, ACN, ethanol, 0.01 mol/L HNO_3 in methanol and 0.01 mol/L HNO_3 in ACN were tested to select the best solvent (Figure 5). Therefore, 0.01 mol/L HNO_3 in ACN exhibited the best performance.

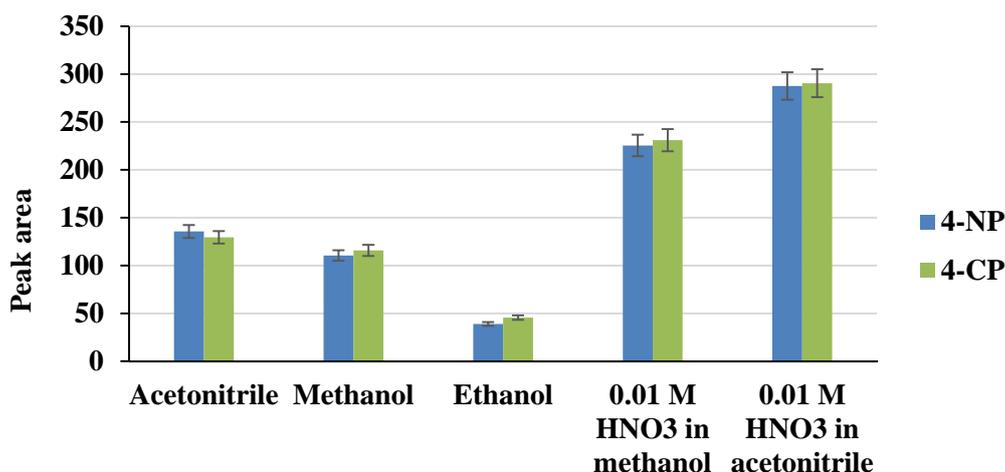


Figure 5. Effect of eluent type.

The effect of salt concentration was investigated. Different concentrations of NaCl ranged between 0 and 15% w/v were added to the sample solution to explore the salt effect. As showed in Figure 6, the extractability of CPs and NPs was enhanced by addition of NaCl up to 7.5% w/v.

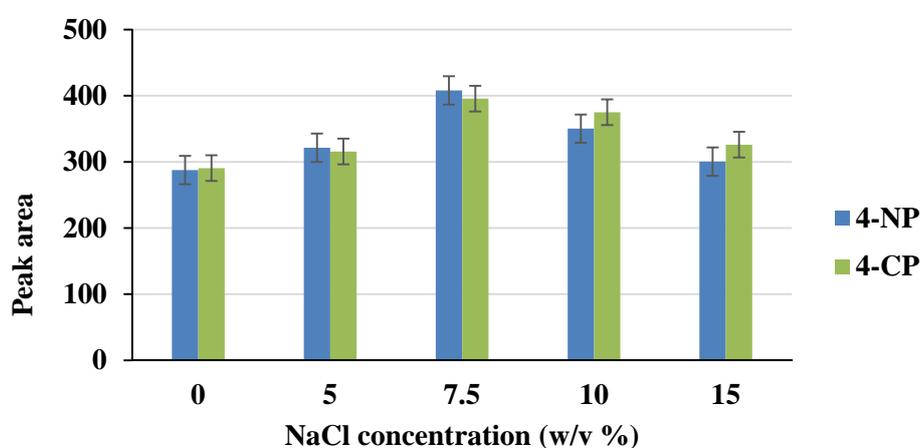


Figure 6. Effect of salt concentration.

Conclusion

In this work, G@Fe₃O₄/Fe/Ag nanocomposite was synthesized for the first time and employed as an adsorbent for the extractive quantification of phenol products as the model analytes in water sample based on MDSPE method. Graphene magnetic coating with AgNPs increases the adsorption capacity. The graphene usage has a very high surface area and excellent adsorption capacity. The method is simply, low LODs, wide LDR and good extraction recovery. The extraction time is short.

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