

Preparation of polyphenol-coated CoFe_2O_3 nanoparticles for magnetic solid-phase extraction and preconcentration of lawsone by high-performance liquid chromatography –DAD

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ABSTRACT

A novel polyphenol-coated CoFe_2O_4 system was synthesized as a magnetic adsorbent by chemical oxidative polymerization process for magnetic solid-phase extraction of lawsone. The synthesized nanoadsorbent showed a spherical morphology with diameters under 50 nm by scanning electron microscopy images. The extraction efficiency of this adsorbent was studied towards the extraction of lawsone from saline aqueous solution in dispersion mode. Major parameters including the type and volume of desorption solvent, amount of sorbent, desorption time, extraction time, extraction temperature, ionic strength and pH were optimized. Under the optimum conditions the relative standard deviation in $0.005 \mu\text{g mL}^{-1}$ (inter-day $n = 6$; intra-day: $n = 6$; and adsorbent to adsorbent $n = 4$) were obtained as 5.2, 8.07 and 11.7%, respectively. A linear calibration curve in the range of $0.003\text{--}0.5 \mu\text{g mL}^{-1}$ with $R^2 = 0.993$ was obtained. The limit of detection and limit of quantification of the method were $0.001 \mu\text{g mL}^{-1}$ and $0.003 \mu\text{g mL}^{-1}$, respectively. The relative recovery percentages were in range of 90-96.4% for henna leaves, henna shampoo, and henna dermal lotion real samples.

Keywords: Magnetic solid-phase extraction, CoFe_2O_3 Nanoparticles, Polyphenol, Lawsone, High-performance liquid chromatography

Introduction

The leaves of *Lawsonia inermis* have a natural pigment as Lawsone (2-hydroxy-1, 4-naphthaquinone), has been used as a skin and hair dye since 1400 (Babula et al., 2005). Depending upon many of the environmental factors the lawsone concentration varies from place to place, the highest quantity reported so far is about 1% of the dry mass (Saeed et al., 2013).

Plumbagin shown activities of cell cycle arrest and apoptosis in numerous cancer cell lines including melanoma, lung and breast (Castro, Mariani, Panek, Eleutherio, & Pereira, 2008). The plant derivatives have various advantages in cancer therapy including, their potential to be used in an edible form and lower side effects (Rates, 2001). Persian henna that is found in Asia, Australia and Mediterranean coasts of Africa is a bushy and flowering tree (Muhammad & Muhammad, 2005). Henna crude extracts have many biological activities such as antibacterial, antioxidant, anti-inflammatory and anticancer properties (Hosein & Zinab, 2007). Lawsone, the major constituent of henna plant, using in the synthesis of some anticancer drugs, like dichloroallyl lawsone and lapachol (Ali, Jülich, Kusnick, & Lindequist, 2001; McKelvey, Lomedico, Lu, Chadwick, & Loo, 1979; R. P. Singh & Narke, 2015) that anticancer effect of which one has been approved (D. K. Singh & Luqman, 2014). Therefore, the extraction of lawsone of henna leaves is necessary for cancer therapy.

In the past years, different kinds of nanometer-sized materials have been introduced as alternative potential adsorbents in the field of sample preparation methods for trace-level analysis (Lucena, Simonet, Cárdenas, & Valcárcel, 2011; Tian et al., 2013). Among introduced nanomaterials, magnetic nanoparticles (MNPs) due to their outstanding properties, such as the high surface area to volume ratio, tunable magnetic properties, excellent mechanical strength and surface

modifiability are shown high performance towards chemical compounds adsorption (Hemmati, Rajabi, & Asghari, 2018). The MNPs have an important feature, collected from the sample solution easily using an external magnetic field and when the magnetic field removes, they can be rapidly re-dispersed. Therefore, the combination of solid-phase extraction (SPE) methods with MNPs can offer another mode of extraction as magnetic solid-phase extraction (MSPE) (Faraji, Yamini, & Rezaee, 2010; C. Huang & Hu, 2008; Ji et al., 2009).

The MSPE have numerous dominate advantages, such as convenience, quickness, reduced solvent consumption (Van Eijkeren, Heringa, & Hermens, 2004), high preconcentration factors (Oomen, Mayer, & Tolls, 2000) (PFs) and possible miniaturization and automation (Q. Li, Lam, Wu, & Jiang, 2010; Rios, Zougagh, & Bouri, 2013). The naked MNPs can't adsorb analyts selectively and also aggregate in the aqueous solutions. Therefore, chemical functionalization of MNPs surface can be considered as a good strategy to solve these issues (Filik & Avan, 2019; D. Huang, Deng, & Zhang, 2014).

Recently, a great deal of researches on nanomaterials as coating of MNPs in order to use them as sorbent in solid-phase extraction have been examined (H. Li et al., 2012; Xiao et al., 2012; Yantasee et al., 2007). These nanomaterials including polymers (S. Wang et al., 2012), molecularly imprinted polymers (MIPs) (Thibert, Legeay, Chapuis-Hugon, & Pichon, 2012), carbon nanotube (CNTs) (Chen et al., 2011) and MIP-CNTs (Z. Zhang et al., 2011) can adsorb drugs and other biomolecules by forming stable covalent or non-covalent bonds between nanomaterials and analyts. Among these nanomaterials, polymers are the best candidate not only for drug delivery system in therapeutics but also for SPE in drug analysis (Ahmadi, Shahsavari, & Rahimi-Nasrabadi, 2008; Silva, Lanças, & Queiroz, 2009).

Phenol as a chemical compound, a benzene ring and a hydroxyl group, has been electrochemically polymerized due to its hydroxyl groups. Some applications such as metal corrosion prevention and its use in biosensors have been reported (Hu, Wang, Zhou, Xue, & Luo, 2016; J. Wang, Jiang, & Lu, 1998). Phenols and their derivatives can be polymerized in aqueous and non-aqueous environments depending on the pH of the solution. In acidic solution, the carbon-carbon bond is the main reaction product, but in alkaline solution the carbon-oxygen bond is formed mainly. So far, no chemical synthesis of polyphenol has been reported.

In this study, for the first time we design and synthesis CoFe_2O_4 magnetic nanoparticles modified with a polyphenol (Pph) shell to obtain an inorganic-organic nanoparticle ($\text{CoFe}_2\text{O}_4@\text{Pph}$) for lawsone extraction in various types of samples. Cobalt ferrite is displayed some advantages than other MNPs, it offers higher thermal and chemical stability than Fe_3O_4 magnetite and shows a better magnetic response than other ferrites (MFe_2O_4) in the same size (Kooti, Saiahi, & Motamedi, 2013; Kraus, Jainae, Unob, & Sukpirom, 2009). The phenol was selected as coating layer of MNPs because it plays important roles, preventing the aggregation of nanoparticles or their oxidation and acts as active sites for extraction of lawsone.

2. Experimental

2.1. Synthesis of CoFe_2O_4 nanoparticles

The CoFe_2O_4 nanoparticles was synthesized by a simple co-precipitation method. Briefly; 3.785 g of $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ and 2.52 g of $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ were dissolved in 200 mL deionized water under nitrogen atmosphere. Then 50 mL of NaOH solution (6 N) was added to this solution slowly. The obtained solution was continuously stirred at constant temperature of 85 °C. After 30 min, the produced nanoparticles were magnetically collected, washed with distilled water, and dried at

60 °C. A detail on materials and instrument is given in supporting information ([Section S1&S2](#)) file

2.2. Coating of CoFe₂O₄ NPs with polyphenol

The magnetic NPs was coated with polyphenol by a chemical polymerization method of phenol monomer in acidic medium. Briefly, 1 g of magnetic NPs was added to 10 mL ACN and ultrasound for 10 min until NPs completely dispersed, also 0.2 g phenol monomer added to the resulted suspension. In order to increasing of stability and polarity of system, 0.04 g of sulfur was added to this sample suspension. Then, 0.250 g ammonium persulfate as initiator dissolved in 6 mL of concentrate sulfuric acid in a centrifugal tube separately and the mentioned solution added to stirring resulted suspension dropwise. The resulted nanoparticles (CoFe₂O₄@Pph) were magnetically collected, washed with deionized water, and dried at 60 °C.

[Figure 1 A](#) is briefly shown the synthesis process of CoFe₂O₄@Pph NPs including (i) the preparation of CoFe₂O₄ NPs, and (ii) the immobilization of polyphenol shell onto surface of CoFe₂O₄ NPs.

2.3. Procedure of MSPE

20 mL of lawsone solution (0.05 µg/mL) was taken and 0.05 g of magnetic adsorbent was added to it in a 50 mL beaker and ultrasound for 14 min at room temperature to facilitate adsorption of lawsone onto the system. Then, the magnetic adsorbents were collected at the bottom of the beaker by applying an external magnetic field. The supernatant was separated by decantation and 2.0 mL of methanol as desorbing solvent was added to decanted sample. The resulted suspension was ultrasound for 3 min. After desorption, the magnetic adsorbents were removed by applying an external magnetic field and then desorption solvent was evaporated under nitrogen atmosphere. Finally, extracted lawsone was dissolved in 100 µL of methanol and filtered by a 0.45 mm

membrane filter and injected into the HPLC system for analysis. A detail on procedure of real samples collection is given in supporting information (Section S3).

3. Results and discussions

3.1. Nanoparticle characterization

3.1.1. XRD analysis

The XRD patterns of CoFe_2O_4 and $\text{CoFe}_2\text{O}_4@\text{Pph}$ were recorded before and after loading of phenol, and analyzed (Figure 2 A, curve a&b). The pattern obtained on CoFe_2O_4 shows several peaks, which are attributed properly to the system phases. Thus, The observed characteristic peaks (220), (311), (400), (422), (511), (440), and (533) in the XRD pattern of cobalt ferrite (Ghiasi & Malekpour, 2020) (curve a). These data were matched to the standard XRD data of CoFe_2O_4 crystal (Reference code. 22-1086). The characteristic XRD of $\text{CoFe}_2\text{O}_4@\text{Pph}$ is not significantly changed by grafting of polyphenol onto CoFe_2O_4 NPs (curve b), supporting stability of the fabricated system structure upon immobilization of polyphenol.

3.1.2. FT-IR analysis

The FT-IR spectroscopy measurements were performed to support the formation of CoFe_2O_4 and $\text{CoFe}_2\text{O}_4@\text{Pph}$ (Figure 2 B&C). The spectrum obtained on CoFe_2O_4 (panel B) shows two characteristic peaks at 500 and 593.46 cm^{-1} corresponding to the Co-O and Fe-O bond (Rao, Choudary, Rao, & Sujatha, 2015), also the two common peaks at 1620 and 3405.5 cm^{-1} attributed to the O-H stretching of water onto magnetic nanoparticles (Ghiasi & Malekpour, 2020).

The peaks observed for $\text{CoFe}_2\text{O}_4@\text{Pph}$ system (panel C) are assigned as follows; 594 cm^{-1} to the stretching vibration of Fe-O in CoFe_2O_4 , 752.2 and 844.4 cm^{-1} to bending vibration of C-H in the phenol, also 2853, 2921 and 3026 cm^{-1} to C-H stretching (Y. Zhang et al., 2016) in CH_2 and CH_3

groups, and 1172.7 and 1224.9 cm^{-1} to C-O groups of Pph (H. Wang, Chen, Weng, Zhang, & Shen, 2014), supporting formation of Pph onto naked nanoparticles.

3.1.3. SEM images and magnetic properties

The morphologies of as-synthesized CoFe_2O_4 and $\text{CoFe}_2\text{O}_4@\text{Pph}$ NPs analyzed using SEM analysis (Figure 3 A). The CoFe_2O_4 nanoparticles are shown spherical and aggregated particles mostly. Upon immobilization of polyphenol onto CoFe_2O_4 NPs, the nanoparticles more dispersed (Figure 3 B), supporting formation of polyphenol onto naked nanoparticles.

VSM analysis was used for measuring of magnetic properties of CoFe_2O_4 and $\text{CoFe}_2\text{O}_4@\text{Pph}$ NPs at room temperature. The paramagnetic properties of cobalt ferrite nanoparticles were proved (Figure 3 C). The magnetic saturation of CoFe_2O_4 and $\text{CoFe}_2\text{O}_4@\text{Pph}$ were obtain 34.5 and 27.7 emu g^{-1} , respectively. Upon the naked nanoparticles coated with polyphenol the magnetic saturation (Ms) of CoFe_2O_4 decreased which can be attributed to nonmagnetic properties of polyphenol shell.

3.2. Optimization of MSPE conditions

3.2.1. Effect of type and volume of desorption solvent

Desorption solvent is an essential parameter for desorbing of analyte in extraction process. For this purpose, lawsone was desorbed from $\text{CoFe}_2\text{O}_4@\text{Pph}$ NPs (Figure 4 A) with some common solvents such as methanol, ethanol, acetonitrile and chloroform that indicated ethanol had the most extraction recovery among other solvents. Also the volume of desorption solvent was studied as an effective factor on the extraction efficiency. Thus, the volumes in the range of 0.5 to 5.0 mL of ethanol was studied to desorb lawsone of system. The highest recovery was obtained when the volume of ethanol was 4 mL (Figure 4 B).

3.2.2. Effect of time

The effect of adsorption/desorption time on the extraction and desorption of lawsone was studied. The sample solutions were exposed to the various ultrasonic times of 2, 5, 10, 15, 20 and 25 min. It showed that CoFe₂O₄@Pph NPs adsorbed lawsone efficiently within first 5 min and longer ultrasonic time had negative effect on the extraction recoveries (Figure 4 C). Therefore, in this study an ultrasonic time of 5 min was selected.

Moreover, desorption time in range of 2 to 7 min was studied. The results showed an ultrasonic time of 4 min was sufficient for complicating of desorption process and effective desorption of lawsone by ethanol (Figure 4 D)

3.2.3. Effect of adsorbent dosage

Amount of extracted lawsone can be affected by content of the adsorbent. While the excessive dosage of the adsorbent increases the volume of desorption solvent, insufficient amount of the adsorbent cannot provide enough active sites for complete adsorption of the analyte. In the present work, different amounts of adsorbent (0.01, 0.03, 0.06, 0.09 and 0.12 mg) was added to lawsone solution and the effect of adsorbent dosage on the extraction of lawsone was studied (Figure 4 E). The extraction recoveries enhanced with increasing of added adsorbent from 0.01 g to 0.09 and then became almost constant. It should be noted that, the number of available functional groups involved in the adsorption process was increased as the adsorbent dosage increased. It was found, effective adsorption of lawsone can occur in 0.09 g of system in 20 mL of lawsone aqueous solution.

3.2.4. Effect of temperature

the solutions were putted under different temperatures (10, 20, 25, 30, 35 and 40 °C) before performing the MSPE process to study the effect of temperature on extraction process. The results (Figure 4 F) showed the extraction efficiency was increased as the temperature increased from 10 °C to 25 and then extraction efficiencies were decreased, because adsorbing process is a pyrogenic process.

3.2.5. Effect of salt

Addition of salt to water samples might be affected the extraction efficiency of analytes (Sereshti, Ghiasi, Naderloo, Taghizadeh, & Astaneh, 2014). The extraction recoveries were studied in different concentrations of NaCl (0, 5, 10, 20, and 30 W/V %) and the results were plotted in Figure 4 G. The extraction recoveries were enhanced as salt content increased from 0% to 5% and then decreased. The solubility of analyte in the aqueous phase can be decreased with increase in amount of salt. On the other hand, diffusion rates of analyte from aqueous solution to the adsorbent surface can decrease with increase of salt. Thus, the salt content for this study was kept at 5% (W/V).

3.2.6. Effect of pH

The appropriate adjustment pH of the aqueous solution may improve the extraction recovery of analyte. The pH affects the stability and hydrolysis of the analytical targets in the aqueous phase and also the adsorption features of adsorbent. So, the influence of pH on extraction recoveries of lawsone was studied in different pHs of solution (3, 7, 10 and without buffer). The highest recovery was obtained in solution without adjustment of pH (Figure 4 H). Two types of π - π interaction and hydrogen bonding between analyte and adsorbent can be suggested. The hydrolysis of the analyte may be occurred in the acidic (pH, 3) and basic environment (pH, 10). The extraction recovery at

pH 7 decreased toward the solution without pH adjustment, because the viscosity of solution with pH adjustment is more than that for without pH adjustment solution. Therefore, solution without pH adjustment was chosen in this study.

In this study, the content of sulfur and phenol monomer was optimized and the results obtained were 0.033 and 0.15 g for which one, respectively.

3.3. Evaluation of the method

Some crucial features for samples with $0.005 \mu\text{g mL}^{-1}$ like RSD (inter-day $n = 6$; and intra-day: $n = 6$; and adsorbent to adsorbent $n = 4$), limit of detection (LOD as $3S_b$), limit of quantification (LOQ as $10S_b$) and linear dynamic range (LDR) were evaluated for investigating the effectiveness of method under optimum conditions (Table 1). Calibration curve was achieved by plotting the peak area against various concentration of the lawsone (Figure S1). This method displayed a high determination coefficient ($R^2 > 0.99$), confirming acceptable linearity of current method.

3.4. Real samples analysis

Various real samples (henna leaves, henna shampoo, and henna dermal lotion) was analyzed for practicality studying of the developed method based on the $\text{CoFe}_2\text{O}_4@\text{Pph}$ for extraction of lawsone. For this purpose, a saline aqueous solution (100 ml, 5% NaCl) with concentration $0.1 \mu\text{g/mL}$ of lawsone was prepared. 0.5, 4, 5 ml of real samples henna leaves, henna shampoo and henna dermal lotion (Section S3) was added to a 20 mL volumetric flasks, respectively, diluted with abovementioned solution. Finally, the extraction process was performed, the recovery percentages were calculated and summarized in Table 2.

The obtained detection limit and linear range for the current MSPE method was compared to other reported methods for the extraction and identification of lawsone (Section S4, Table S1). Also, typical HPLC-DAD chromatograms of different samples are displayed in Figure S2.

Conclusion

In the present study, Pph-coated CoFe_2O_4 nanospheres were successfully synthesized, and applied as the absorbent to extract and concentrate lawsone in different samples. The adsorbent could extract and enrich lawsone from sample in a short time of 5 min with a high efficiency due to the intense bonding between polyphenol and the lawsone. It should be note that, the adsorbent can be removed from sample and the eluent because of the magnetic property of the CoFe_2O_4 core. The experiment results showed that the suggested method based on Pph-coated CoFe_2O_4 nanoparticles was a fast, simple and convenient method to extract lawsone from sample.

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Caption of Figures and Tables

- Figure 1.** The procedure of synthesizing polyphenol-coated magnetic nanoparticles (A), and the procedure of magnetic solid phase extraction (B)
- Figure 2.** The XRD patterns of CoFe_2O_4 (a) and $\text{CoFe}_2\text{O}_4@\text{Pph}$ (b) nanoparticles (A). The FT-IR spectra of CoFe_2O_4 (B) and $\text{CoFe}_2\text{O}_4@\text{Pph}$ (C) nanoparticles.
- Figure 3.** The SEM images of CoFe_2O_4 NPs (A) and $\text{CoFe}_2\text{O}_4@\text{Pph}$ NPs (B). The VSM (C) curves of CoFe_2O_4 (a) and $\text{CoFe}_2\text{O}_4@\text{Pph}$ NPs (b).
- Figure 4.** The effect of desorption solvent type (A) and volume (B), desorption (C) and absorption (D) time, adsorbent content (E), adsorption Temperature (F), salt content (G) and solution pH (H) on the extraction recovery of lawsone.

Table 1. Quantitative features of the established method for the lawsone

Table 2. The recoveries of different real samples

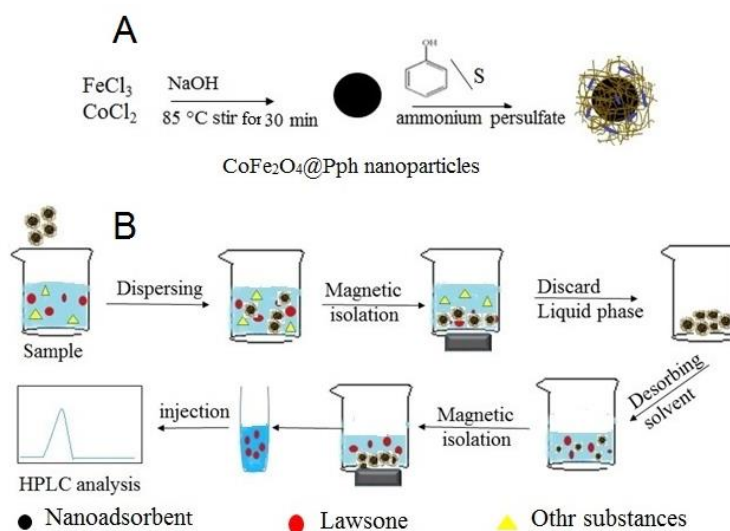


Figure 1.

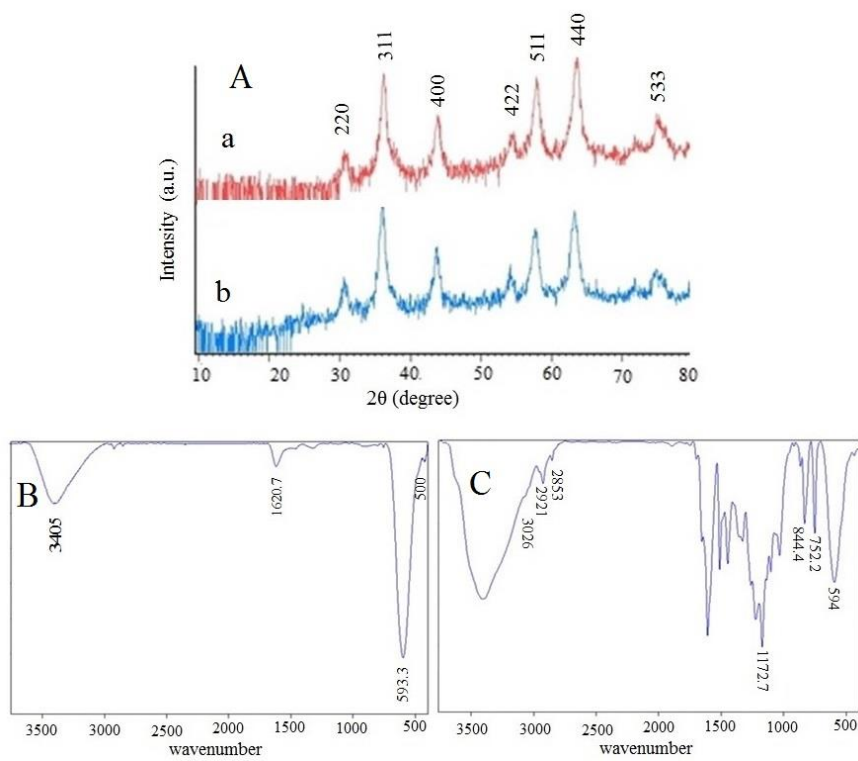


Figure 2.

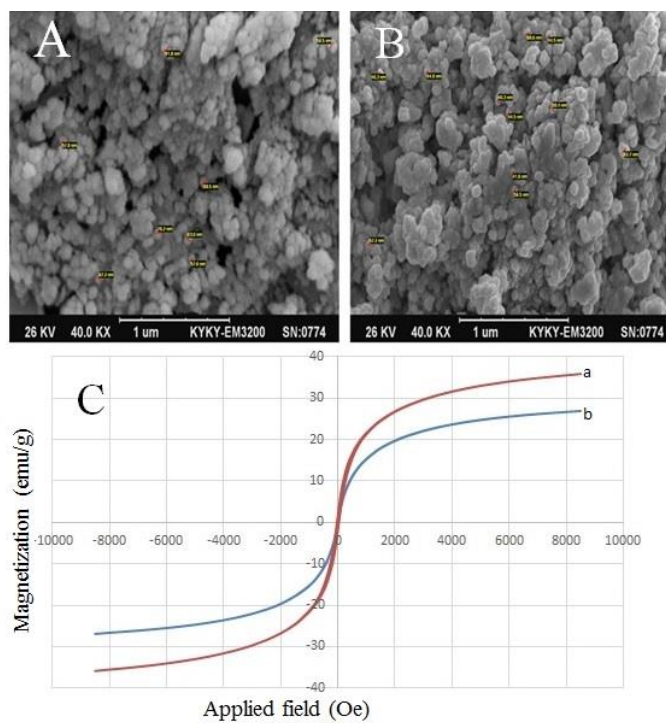


Figure 3.

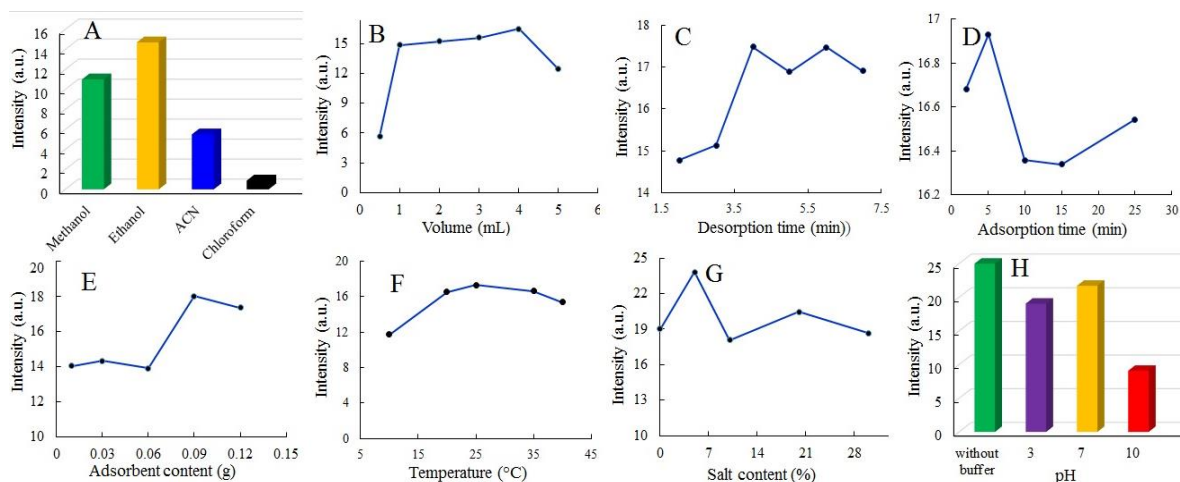


Figure 4.

Table 1.

RSD _{interday}	RSD _{intraday}	RSD _{adsorbent to adsorbent}	Linearity range	LOD	LOQ
5.2%	8.07%	11.7%	0.003-0.5 µg/mL	0.001 µg/mL	0.003 µg/mL

Table 2.

Real sample	Lawson concentration (µg/mL)	Added standard concentration (µg/mL)	Measured concentration (µg/mL)	Recovery (%)
Henna leaves	0.01	0.1	0.099	91.91
Henna shampoo	0.014	0.1	0.11	96.40
dermal lotion	0.073	0.1	0.159	90.00