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Norfloxacin in biological samples using dispersive solid-phase extraction method with 2-aminopyridine/graphene oxide nano-plates

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***Abstract*---**In recent years, drug use is on the rise, causing environmental pollution. Therefore, drug control is a common practice in many laboratories. This project focuses on increasing the method for determining small amounts of norfloxacin in aqueous and biological samples. Solid-phase extraction of small amounts of norfloxacin in aqueous samples using 2-aminopyridine/graphene oxide nano-plates and visible and ultraviolet spectrophotometric measurements are used in biological samples. These systems include two phases, the aqueous donor phase and the acceptor phase of conjugated carbon nanomaterial. Aqueous phase extraction and norfloxacin adsorption were performed in two experimental steps. First, methanol acidic solvent was used and the adsorbed samples were submitted to Vis-UV spectrophotometry for further analysis. Extraction parameters in this method This cheap and simple method is compatible with most tool analysis methods. These parameters include extraction time, adsorption of organic solvent effect, adsorption time, shaking time, the volume of donor phases, and optimized surfactant effect, and analysis and measurement were performed under optimal conditions. Low consumption of organic solvents, elimination of the effect of previous experiments, short extraction time, low detection threshold, and high concentration coefficient are the advantages of the mentioned technique and also the

concentration factor and detection threshold for Norfloxacin were 16.7 and 8.25. The linear amplitude and relative standard were 1.78%.

***Keywords*---**Norfloxacin, extraction method, 2-aminopyridine/graphene oxide nano-plates, spectrophotometry.

Introduction

In the analysis and measurement of biological samples that contain very complex compounds that often interfere and sometimes even with the strongest detection systems the number of contaminants are not detectable to a small extent or are not compatible with routine analysis systems. Some contaminants have dangerous biological effects in small amounts. Therefore, the introduction of new and sensitive methods to measure the number of such pollutants is necessary. Analytical devices such as chromatography, spectroscopy, microscopic devices, as well as sensors, and microdevices have been developed, although highly accurate and non-destructive methods are not available in most cases. Therefore, to increase the current methods, it is necessary to prepare one or more sample steps [1-5].

The use of improper preparation methods can negatively affect the process of the analysis method. In recent years, little attention has been paid to this issue. Of course, sometimes additional steps in these processes, such as derivation, seem very necessary. The most important common steps in the analysis method include the preparation steps. In this paper, the measurement of the interaction of adsorption of carbon nanomaterials and drugs using measurable and ultraviolet spectrophotometry is considered. This process is based on drug adsorbents and nanomaterials. Important parameters in this method and key parameters in this measurement are evaluated. These advantages include easy analysis, efficient methods, new capabilities, and low-dose analysis of fluoroquinolones Norfloxacin of fluoroquinolones antibiotics with the chemical formula $C_{16}H_{18}FN_3O_3$. Norfloxacin is a broad-spectrum antibiotic that is active against both gram-positive and Gram-negative bacteria. It functions by inhibiting DNA gyrase, a type II topoisomerase, and topoisomerase IV [6-13].

By now, graphene sheets with an extremely special surface (2600 m2/g) have gained specific interest due to their mechanical, thermal peculiar electrochemical features [35]. However, graphene contains a hydrophobic surface that may not suit metal ions' adsorption from water solutions [36]. However, one reputable way to construct the hydrophobic surface of graphene is associated with its oxidation [37]. Hummer's method is usually used for obtaining graphene oxide from natural graphite [38]. The sheets of graphene oxide exhibit a very oxygenated area on the surface containing a group of OH, epoxy, and carboxyl [39]. These functional containing hydroxyl, epoxy, and carboxyl are anticipated to enhance sorption content of the framework of metals [26-29]. Yang et al., [40] displayed that graphene oxide in comparing the active carbon has a high capacity of sorption of 0.733 µmol/mg for heavy metal. In fact, the nature of adsorbent functional groups is associated with the adsorption properties and efficiency of an adsorbent [41]. Besides, the functionalization of graphene oxide may raise its features and in

specifically its highest capacity of sorption. Researchers have shown that the use of nitrogenous agents such as amidoxime, imidazole, amino as ligands in combination with sorbents can be effective in adsorbing heavy metals [42,43]. For example, Chen et al., studied removing heavy metal ions by the graphene oxide sheets was modified with 3-aminopropyltriethoxysilane and 4-aminothiophenol [44]. This research indicated the maximum adsorption capacities of two modified graphene oxide were 10 times higher than graphene oxide. Elimination and separation of ion of heavy metals in water samples is still a challenge. Several pioneer techniques were expanded for the fast detection of ions in water samples neutron activation analysis, mass spectrometry, and absorption spectrometry of flame atomic [45-47].

Unfortunately, Some of the procedures performed are not suitable for determining the concentration of heavy metal ions, for the reason of the usage of the high maintenance cost, expensive equipment, and the application of complex testing procedures [48]. The spectrometry of the UV-Vis technique is noticed as the most convenient technique for the extension of cost-effective, quick, and easy techniques of analytical [49].

The high performance of high-pressure liquid chromatography is increased by HPLC for norfloxacin and its three metabolites in the analysis of plasma, serum and urine. The HPLC method for the extraction of norfloxacin and three metabolites in urine samples was on a polystyrene column, which was quantitatively analyzed using a ultra-violating detector. The current method involves chromatographic extraction, which is suitable for plasma and serum levels and urine levels[2].

In this study, we intend to measure norfloxacin in real samples (plasma, urine) by the interaction between carbon nanomaterials and daronorfloxacin using a UV-Visible spectrophotometer. This method is based on the interaction between norfloxacin and carbon nanomaterials. Important parameters on the interaction and those that affect the measurement are examined.

Experimental

Chemicals and reagents

Norfloxacin($C_{16}H_{18}FN_3O_{3)}$ was prepared from Darmstadt, Germany of Merck, Method and dried for a week over phosphorus pentoxide in a vacuum desiccators before apply. Graphite flake powder (99.55% purity), 2-aminopyridine (99% purity) and cadmium chloride ($CdCl_2{\cdot}2H_2O$, 98% purity) provided by Sigma-Aldrich Co. Potassium chlorate ($KClO_3$, 99.55% purity), sulfuric acid (H2SO4, 97% purity), nitric acid (HNO_3, purity of 63%), hydrochloric acid (purity of 37%), sodium hydroxide (purity of 98%), ethanol (C_2H_6O, 99.9% purity) were acquired from Merck, Germany. All other chemical agents were in analytical grade and applied without further purification.

Instrumentation

Double beam ultraviolet-visible spectrophotometer, Model UV1700, in Razi Laboratory, University of Science and Research. These conditions are tabulated

in. The pH measurements were used by Sartorius model PB-11. Digital scale with 0.1 milligrams accuracy (AND GR-200 model).

Synthesis graphite oxide

Staudenmaier procedure was used to prepare the graphite oxide, for this purpose, the 18 ml of H_2SO_4 and 9 ml of HNO_3 were mixed in an ice bath with vigorous stirring for 30 minutes, then graphite powder (1 g) was poured slowly. After this step, potassium chlorate powder (11 g) was slowly added to this mixture for 1 hour and the temperature was kept at 20 °C. Then, the desired compound was kept for 3 days at room temperature with vigorous stirring. Finally, the black precipitate was washed with deionized water until reached pH=7, and then the obtained precipitate was dried in a vacuum oven at 60 °C [50].

Synthesis GrO

To prepare GrO, a certain amount of graphite oxide powder (0.1 g) was placed in 100 mL of water and ethanol solution (50/50%, v/v) under ultrasonic power of 140 W for 2 h. The resulted powder was dried in a vacuum desiccator [51].

GrO functionalized with 2-aminopyridine

The 0.1 g of GrO powder was poured in 200 mL of deionized water, then 0.2 g of 2Ap was poured and the mixture was placed in a homogenizer for 30 min at 13000 rpm. Then, the 0.2 g KOH was added to the homogeneous mixture and was subjected to ultrasonic power of 140 W for 30 min. The precipitate was refluxed at 80 °C and then washed with water and ethanol and dried at 25 °C (Fig. 1) [52].

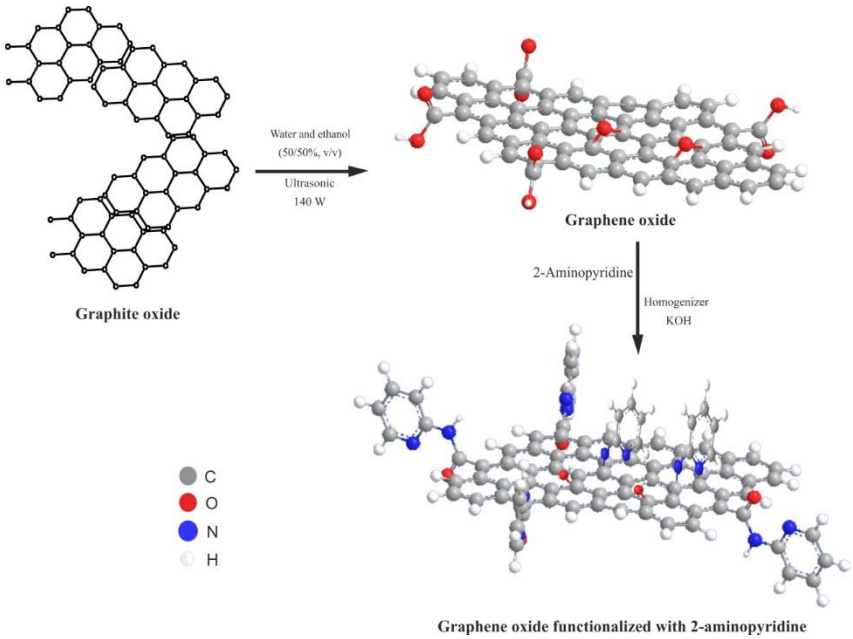

Fig. 1. Preparation of graphene oxide functionalized with 2-aminopyridine

Optimizing wavelength in the extraction of norfloxacin

This medication with 2-aminopyridine/graphene oxide nano-plates and 2-10 range of buffer undergoes quantitative analysis with UV-vis spectrophotometer, after being shaken and centrifuged Fig1.

pH effect on norfloxacin extraction

To assess the effect of pH in norfloxacin extraction, the following steps were performed initially. For each container, the desired tampon is added, since the goal is to determine the appropriate pH. The lowest absorption is considered the best value.

50 ml of the drug with 500 pm concentration for norfloxacin was taken. 1.15 g of 2-aminopyridine/graphene oxide nano-plates absorbent, 5 ml of buffer in the 2-10 range were taken and added to a 50 ml balloon, and delivered to volume with distilled deionized water. Then the balloon is shaken for 15 minutes, centrifuged for 15 minutes, and then passed through syringe filters and finally, quantitative analysis of norfloxacin took place.

Absorbent amount in norfloxacin extraction

In this step, optimized pH and absorbent were used in the optimized wavelength based on previous experiments, and different amounts of absorbent (3, 5, 10, 12, 15, and 20) were used for each medication. 5 ml of the drug was taken. 0.15 g of 2-aminopyridine/graphene oxide nano-plates, 5 ml of buffer in 2-10 range were taken and added to a 50 ml balloon and delivered to volume with distilled deionized water. Then the balloon is shaken for 15 minutes, centrifuged for 15

minutes, and then passed through syringe filters and finally, quantitative analysis of norfloxacin took place. Quantitative analysis of filtered solutions for norfloxacin was performed in 272 nm wavelength in a UV-vis spectrophotometer.

Salt effect

The other important parameter is the salt, due to paired ion function between reactants which leads to a better reaction between the substances. It is also very important in absorption intensity. 0.20 g was selected as the optimum value for norfloxacin.
In this step of the experiment, optimum pH, absorbent, and wavelength were used. Different amounts of salt were used for the drug.

Effect of time of drug absorption in solution

Another important parameter on absorption system and drug measurement based on their extraction is reaction rate. 5 solutions were prepared with optimum properties and shaking was performed at different times. Then they were centrifuged and passed through a filter and their absorption rate at maximum wavelength was checked.

Effect of elusion solvent type

The type of elusion solvent is one of the most important parameters affecting the absorption system. In this study, for each medication, methanol, ethanol, acetonitrile, acidic and basic methanol, acidic and basic ethanol were used and the optimum solvent was detected for each medication. After choosing the optimum solvent, the acidic or basic form of the solvent was assessed. 7 balloons were used (by considering optimum conditions) and the upper water was removed after centrifuging and the solvents were added. After shaking for 20 minutes and centrifuging for 15 minutes, the solutions were filtered and their absorption at maximum wavelength was recorded and resorption took place. Due to resorption, the highest absorption should be selected.

Effect of elusion solvent volume

The volume of elution solvent is another effective parameter on the absorption intensity of the system. In this study, different volumes of selected solvents have been assessed. 5, 7, 10, 12, 15, and 18 ml of the solvent have been added to the absorbent in optimum conditions. Absorption intensity was recorded with a UV-Vis spectrophotometer, after shaking for 20 minutes and centrifuging for 15 minutes.
2.13. Determining limit volume and condensation factor
To determine limit volume, desperate solutions of norfloxacin were prepared with 50, 100, 150, and 200 ml volume. Then, 100 ml was selected as the limit volume [15].

Analytical properties

After optimizing all effective parameters on absorption intensity, a calibration curve of the method was drawn. For this purpose, a 10 ml volumetric flask was filled with different concentrations of the medication. Then sodium choroid salt was added to 0.12 g norfloxacin in percentage form and 2-aminopyridine/graphene oxide nano-plates absorbents were added to the volumetric flask with optimum pH. Finally, it was delivered to volume by adding distilled deionized water. Then elusion and … steps were performed. Finally, the absorption intensity of the solutions was recorded in laboratory temperature and the calibration curve was drawn.

Calculation of limit of detection (LOD)

Generally, the limit of detection of a laboratory substance is considered as the concentration whose device response is significantly different from control or background. The common definition of a limit of detection in analytical chemistry is a concentration of a substance with a response equal to three times of control standard deviation (S_b) according to the following equation:

$$LOD = \frac{\mathbf{3}Sb}{m}$$

To calculate the limit of detection for norfloxacin measurement, four control solutions with the optimum situation were prepared without adding the medication and absorption intensity was recorded at medication absorption peak wavelength:

$$LOQ = \frac{\mathbf{10}Sb}{m}$$

Accuracy of %RSD method
This parameter is used to evaluate experiment accuracy and closeness of study data. To assess the accuracy of this method (based on relative standard deviation), measuring absorption intensity for 4 solutions of norfloxacin were measured in one day. For this purpose, 4 standard solutions with optimum concentrations were prepared exactly based on the purposed method:

Evaluating disturbing species and selectivity

Effects of disturbing species in the measurement of norfloxacin were evaluated based on biological matrix under optimum conditions. For this purpose, the medication sample was mixed with different concentrations of disturbing species and measurement was performed one hour later and absorption intensity was compared with pure medication same. Fluoxetine drug was a disturbing species.

Preparation of biologic samples for norfloxacin measurement

A blood sample is taken from the patient and put into EDTA-containing tubes with 3.9 ml volume. Samples were centrifuged at 3000 RPM for 30 minutes. The yellow fluid above the sample is plasma and is taken. To make sure that there is

no protein in the plasma, 10 ml of acetone is added to 10 ml of plasma and centrifuged 3000 RPM for 10 minutes so that excess proteins coagulate. For measurement with the purposed method, a definite volume of plasma is taken and measurement steps are performed.

Urine Sample for norfloxacin measurement

Huma urine samples s taken and filtered. It is stored in a black glass container. To measure with the purposed method, a definite volume of urine is taken and measurement steps are performed.

Discussion and Results

Assessment of results of FT-IR spectrum of GrO and Gr2Ap

We synthesized Gr2Ap with the process of grafting of 2Ap on GrO. The recognition of the 2Ap group on the GrO surface via reaction of amination was demonstrated with the FT-IR test **(**Fig. 2c**)**. Also seen, the spectrum of the GrO (Fig. 2a) shows two absorption bands in 1055 and 1401 cm^{-1} related to the C-O stretch bond from the carboxylic acid. Also, the band of tensile vibration bond of C–O–C was seen in the area of 1207 cm^{-1}. Moreover, a vibration band in 1629 cm^{-1} relating to the C=C bond belonging to unoxidized carbons. Finally, the strong band in 3443 cm^{-1} belongs to the O–H vibration [21,56].

In the FT-IR spectrum of 2Ap (Fig. 2b), the absorption band in 1630 cm^{-1} indexed to the C=N bond of the pyridine ring. The peak of 1558 cm^{-1} corresponds to the C=C of the aromatic ring. The peak of 1273 cm^{-1} ascribed to the C-N bond in the ring and also the peak of 3444 cm^{-1} related to N-H tensile vibrations [56].

Fig. 2c displays FT-IR spectra of Gr2Ap, this sample has an absorption band in 3448 cm^{-1} which originated from the group of OH from GrO. Two peaks at 2858 and 2923 cm^{-1} indicate asymmetric and symmetric vibrations of the CH_2 group [55]. The weak peak in 1162 cm^{-1} is related to the grafting of the amine group to GrO. Also, the peak intensity of the C-O at 1074 cm^{-1} decreased compared to the spectra of GrO. The peak in 1629 cm^{-1} is related to the C=N bond of the pyridine ring on the GrO surface. The band of 1207 cm^{-1} indexed to the bond of C-N in the ring of pyridine on GrO. The results obtained from the FT-IR analysis confirm the functionalization of GrO.

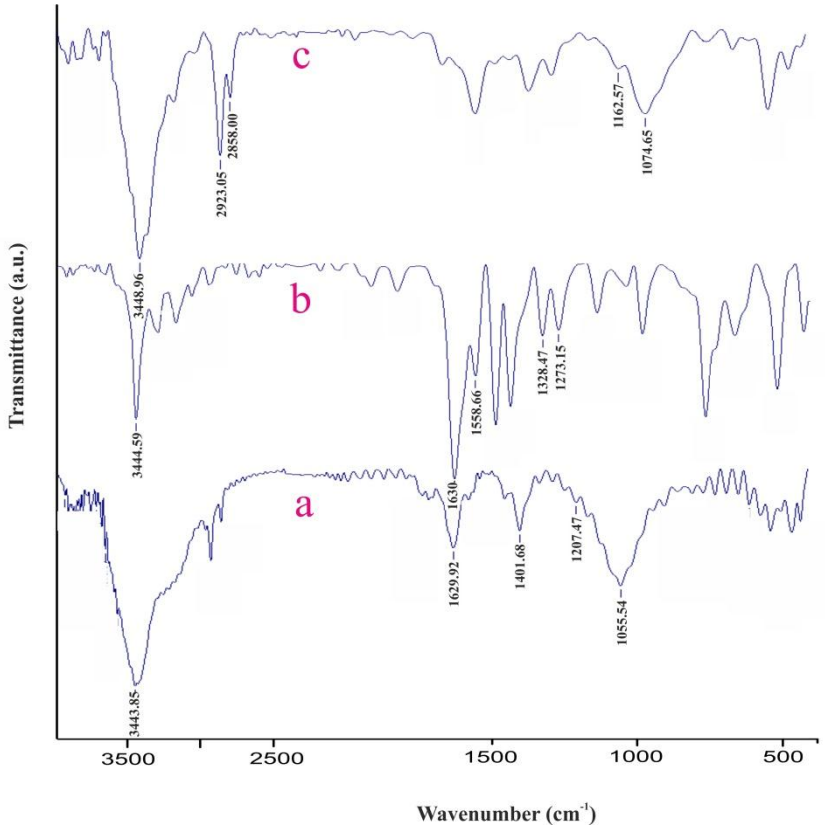

Fig. 2. FTIR spectra of GrO (a), 2Ap (b), and Gr2Ap (c)

Fig. 3 represents X-ray diffraction patterns of synthesized GrO and Gr2Ap. Regarding the results, GrO shows a drastic peak at 2θ=11.6° demonstrating severe oxidation of graphite sheets and crystalline structure of GrO nano-plates (Fig. 3a) [55,56]. After functionalization with 2Ap, a new broad peak has appeared at 2θ ranging from 23 to 37, and also was decreased the intensity of the main peak (Fig. 3b). These results are respectively related to the disordering of the regularity of GrO nanoplates due to the incorporation of 2Ap groups between them as well as concurrent reduction of its oxygenated groups.

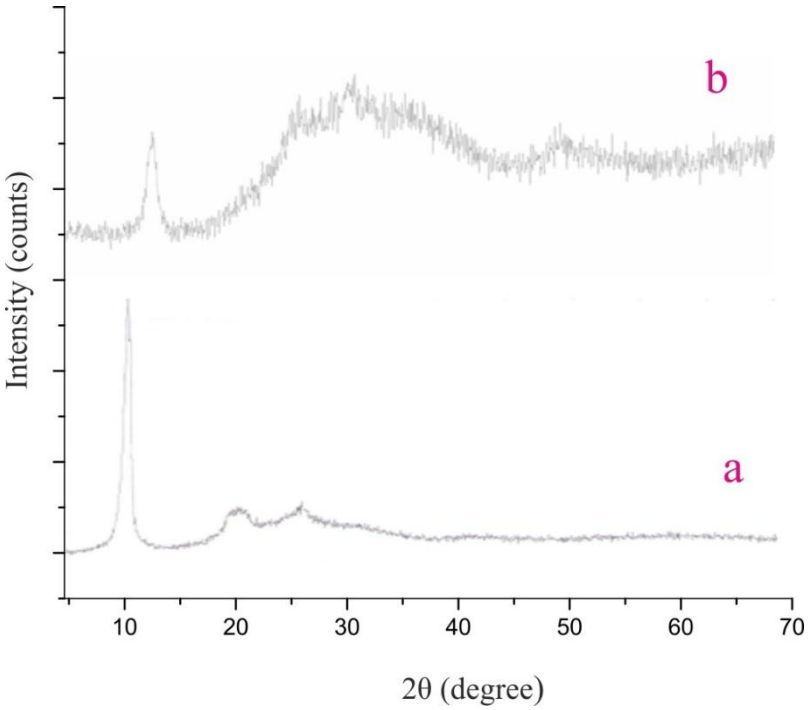

Fig. 3. XRD patterns of GrO (a) and Gr2Ap (b)

The morphology of GrO and Gr2Ap and the surface changes after functionalization was surveyed with SEM images. Fig. 4a is related to synthesized GrO through the improved Staudenmaier procedure. As is evident, the synthesized GrO has a finite number of layered structures with a flat surface. Fig. 4b1 implies that the GrO nano-plates retain their structure of layered while functionalizing process, but the structural regularity of the layers has been considerably decreased. Moreover, the 2Ap functional group is seen as spherical shapes on the GrO surface in sizes of 29-53 nm (Fig. 4b2). The width of GrO pores was distributed in the range of 2-10 nm according to the synthesis method in the reference, which can be classified as mesoporous.

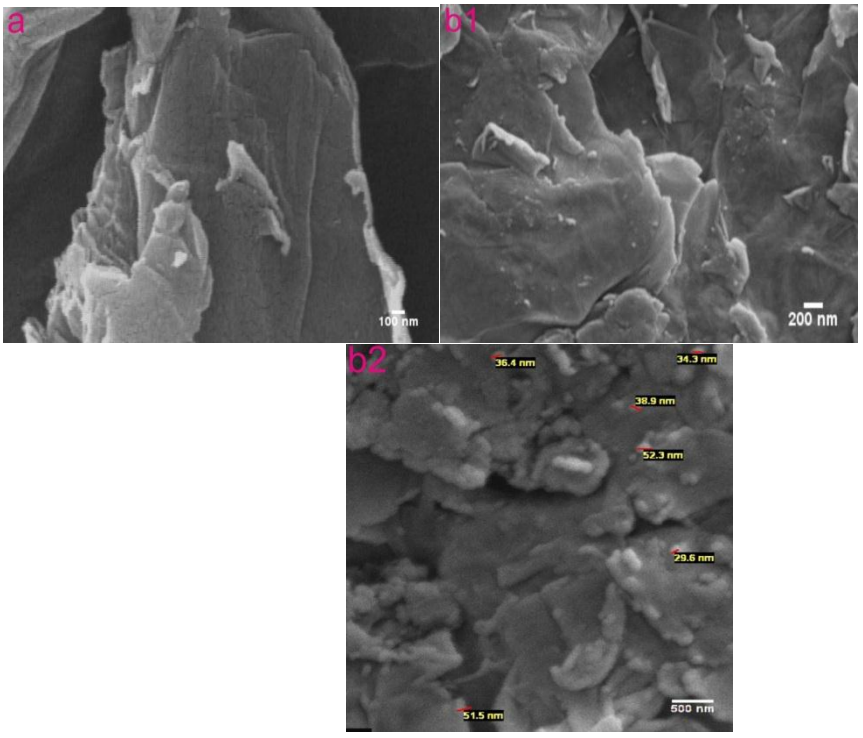

Fig. 4. SEM images of (a) GrO and (b1-2) Gr2Ap.

pH effect on norfloxacin extraction

This chart shows that pH=6 is appropriate for protonating 2-aminopyridine/graphene oxide nano-plates which is associated with higher norfloxacin absorption on 2-aminopyridine/graphene oxide nano-plates . Thus, the best electrostatic situation for absorbent and the drug for surface attraction are present at pH=6 [17].

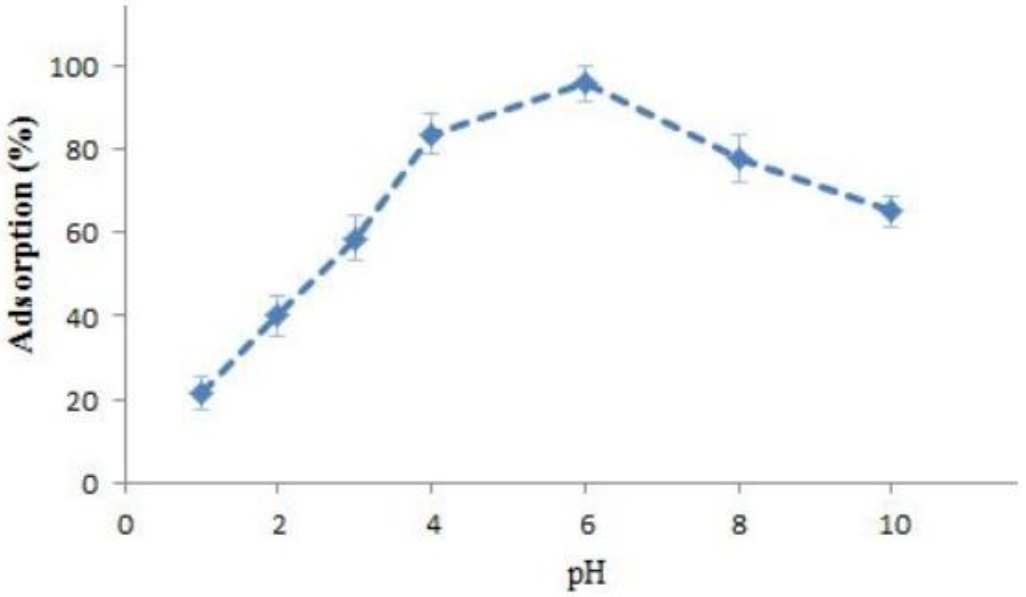

Figure 5. The curve of changes in the norfloxacin absorption in relation with pH

Absorbent amount in norfloxacin extraction

Another parameter affecting absorption, is the amount of absorbent. 0.12 g was selected for norfloxacin. Reported results indicate that din lower amount of absorbent, some substances may enter the solution since absorption may happen in drug maximum wave length [18].

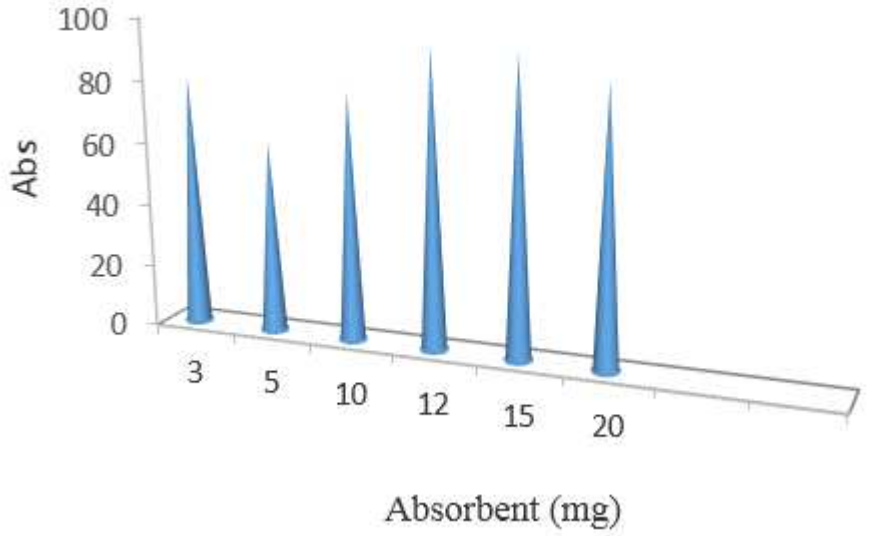

Figure 6. The curve of changes in the norfloxacin with Absorbent amount

Salt effect

This test shows that adding 0.20 g sodium chloride produces appropriate electrostatic charge on absorbent and drug sample for norfloxacin extraction and 2%W/V is the optimum salt concentration showing highest drug absorption [19].

Effect of elusion solvent type

According to this chart, basic solvents show best conditions in the equilibrium between absorbent and elusion solvent. Consequently, basic methanol was selected as optimum solvent for the highest absorption [20].

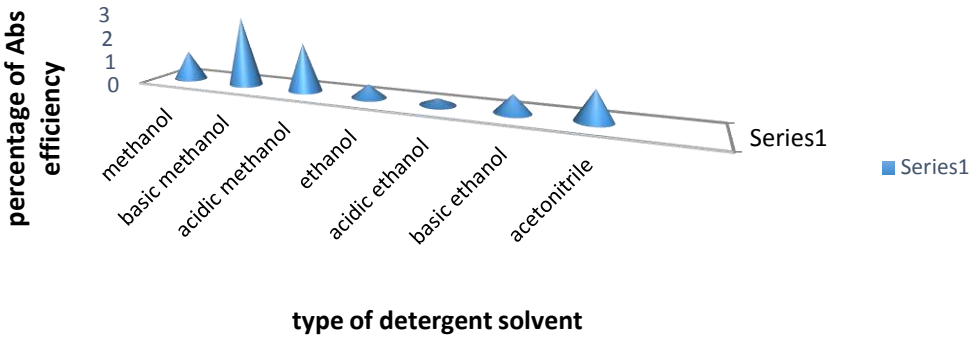

Figure 7. Effect of the Type of Desorption Solvent

Effect of elusion solvent volume

According to this chart, for volumes above 10 ml, all the medication enters the elusion solvent and the equilibrium goes to the side of elusion solvent and complete resorption takes place. Thus, 10 ml was selected as optimum volume for norfloxacin [21].

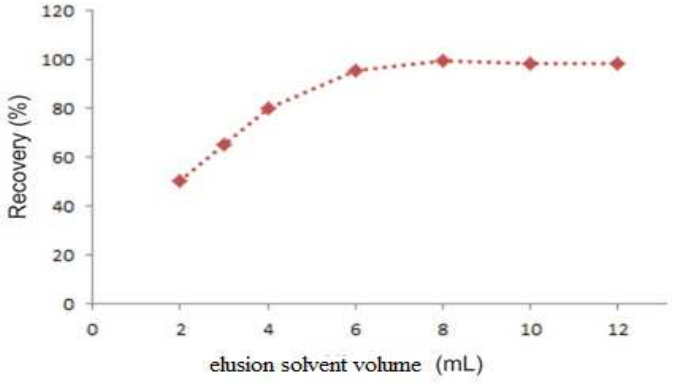

Figure 8. The curve of changes in the norfloxacin with elusion solvent volume

Determining limit volume and break through volume

According to this chart, as the medication is diluted, the possibility of complete absorption on the absorbent decreases. Thus, 100 ml was selected as limit volume for norfloxacin.

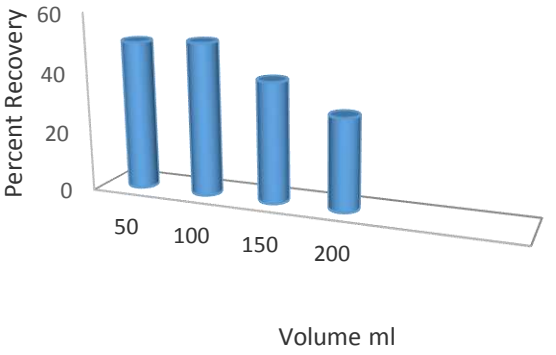

Figure 9. The curve of changes in the norfloxacin with break through volume

Numerator V = limit volume
Denominator V = elusion solvent volume
F = condensation factor

$$F = \frac{V}{V}$$

$$F = \frac{100}{6} = 16.7$$

Condensation factor for norfloxacin

Calibration curve for norfloxacin medication method

According to the obtained results in optimum conditions, there is a linear relationship between absorption intensity and the concentration of the drug [22].

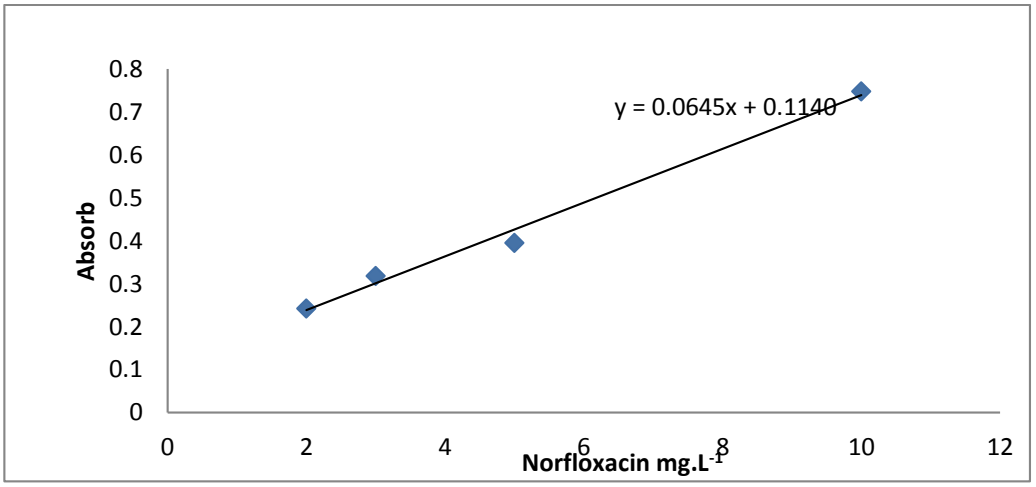

Figure 10. Calibration Curve of norfloxacin

Fluoxetine is the disturbing specie and more disturbance is observed in higher concentrations. The absolute amount of disturbing specie is decreased by dilution. In this step we reassure that the amount of added drug and the amount of found drug in plasma and urine are the same which shows that accuracy of this method is acceptable [23].

Table 1
Recovery of norfloxacin added to 1000mL of different water samples (pH= 10.0)

Sample	Norfloxacin added (µg)	Norfloxacin determined (ng.mL^{-1})	
urine	0.0	3.342 (2.3)[a]	ND
	10.0	13.42 (2.5)	13.3
plasma	0.0	4.33 (2.5)	ND
	10.0	14.44 (2.3)	14.4

[a] Values in parentheses are %RSDs based on five individual replicate analysis
[b] Not detected

Conclusion

In the research method and the results presented in the previous chapters, solid phase extraction method and UV-vis spectrophotometer, extraction and measurement of small amount of norfloxacin in biological samples have been used. The aim of this study was to increase the efficiency, selective, inexpensive and simple method for evaluating the amount of norfloxacin in biological samples. The development of solid phase extraction methods in recent years has shown the need for an effective adsorbent. Therefore, in this study2-aminopyridine/graphene oxide nano-plates were used to increase the extraction performance of norfloxacin. Parameters including effect including pH, type of buffer and concentration, amount of adsorbent, type and volume of solvent, time of reaction

and effect of salt were investigated. This method has good reproducibility and a wide linear range (1-11 ppm) and a suitable density coefficient for the determination of norfloxacin. Also as a good linear range, 5.9 ppb detection limit and high reproducibility are other properties of this method. According to the results, the advantage of this method compared to other methods is that the adsorbent used in high profile surfaces, which is a key factor in choosing this material to be used as) adsorbent used in the method. The proposal can be retrieved, many can be tested. Another advantage of the proposed method compared to other methods, the detection limit is lower than most of the proposed methods and has a better concentration factor than many other methods and easy technique and high accuracy.

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