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Graphene oxide enhances SBA-15 ability towards preconcentration as well as determination of barbiturate drug in real samples

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Abstract

In this study, a simple, sensitive, and high-performance method was employed to extract and preconcentrate ofI a trace amount of sodium barbiturate drug by using mesoporous silica (SBA-15) modified by graphene oxide (GO). TEM, BET, TGA, FE-SEM, EDS, and elemental analysis CHN were used to characterize mesoporous SBA-15 and nanocomposite. Effective parameters in barbiturate extraction such as pH, amount of nanocomposite, eluent type, contacting time, the ionic power of solution, and sample volume were optimized for quantitative determination of the barbiturate. Analytical figures of merit such as accuracy, limit of detection, preconcentration, and enrichment factors were calculated and proved the suitability of our proposed method. The calibration curve shows a linear correlation in the concentration range of 50-2000 ng mL^{-1} with the detection limit of 17 ng mL^{-1}. The relative standard deviation (n=10) was calculated to be 1.39% and the preconcentration factor was achieved 50 using 100 mL of sample.

Keywords: Drug deliver; graphene oxide; preconcentration; SBA-15 nanocomposite; sodium barbiturate.

1. Introduction

Barbiturates are central nervous system depressants (Milhorn, 1990). Sodium barbiturate, as a derivative of barbituric acid, is a drug that can result in a wide series of effects (Garrett *et al.*, 2006). If it is used in high dosages, it may be poisonous, and there is no therapeutic antidote (Jufe *et al.*, 2007). Therefore, the measuring of barbiturates in clinical and medical applications is of great value. Different analytical techniques such as spectrophotometric (Zarei, 2011), reversed-phase high performance liquid chromatographic (Shabir *et al.,* 2010), ultra-fast liquid chromatography-tandem mass spectrometry (Lee *et al*., 2013), capillary electrophoresis (Jiang *et al.*, 2007) and gas chromatography-mass spectrometry (Zhao *et al*., 2006; Iwai *et al.*, 2004) have been used for barbiturate measuring. Without its preconcentration and by using only conventional analytical devices such as a spectrophotometer, the direct measuring of abarbiturate at trace levels is not possible. Different methods for the extraction and preconcentration of sodium barbiturate have been reported in the literature (i.e solid phase extraction (Fritch *et al.*, 2011), cloud point extraction (Madej, 2009), stir bar sorptive extraction (Tienpont *et al.*, 2003), hollow fiber–liquid phase microextraction (Menck *et al*., 2012), solid-phase microextraction (Ouyanga & Pawliszyn, 2006), liquid-phase microextraction (Dadfarnia & Shabani, 2010), single drop microextraction (Jeannot *et al*., 2010), and solvent microextraction (Zanjani *et al.*, 2006)). Among the reported methods, application of the earlier (SPE) is in growing (Marsh & Rodriguez-Reinoso, 2006) because this method is rapid and simple to automate. It gives high performance results with no need for organic solvents (Mirabi & Dalirandeh, 2015; Mirabi & Siadati, 2016). In SPE, a high surface area is needed, hence different types of sorbents (with different applications) can be extended towards extraction and preconcentration (Mirabi & Jamali, 2017; Mirabi & Khodadad, 2015). Nanostructured materials have been used for different applications owing to their excellent surface area (Rad, 2016a,b,c,d,e,f,g; Rad, 2017a,b,c,d); Rad, 2018). Researchers have found that nanostructures are excellent adsorbents for preconcentration purposes (Mirabi & Alavi-Tabari, 2016; Mirabi & Abdollahi, 2017; Mirabi & Divsalar, 2017).

In this study, mesoporous SBA-15 was used for the preconcentration of a barbiturate drug. It is characterized by a large surface area and has excellent adsorption on its inside surface (Zareyee *et al.*, 2011; Zareyee *et al*., 2012; Zareyee *et al.*, 2016). To increase the exterior surface of SBA-15, we used graphene oxide (GO) as the surface modifier. We found that the addition of GO onto SBA-15 enhances its sorbent property towards drug adsorption. In our recent publication (Mirabi & Khanjari, 2017), the adsorbent capability of SBA-15/GO nanocomposite was investigated regarding trace amounts of rutoside drug. We found that the adsorbent ability of SBA-15 will significantly increase upon composite formation with GO. Since the suitability of this modified adsorbent was proved by us for drug adsorption application, here we decide to continue this study by focusing on the potential of this synthetic nanocomposite as a carrier for

the barbiturate. For this reason, in this study, the potential of GO functionalized SBA-15 as a nanocomposite sorbent was examined for simple and fast preconcentration of sodium barbiturate in blood serum and real urine samples.

2. Experimental

2.1. Materials and reagents

All materials and solvents were purchased from Merck Co. (Germany). Urine and human blood serum were purchased from the research center of Rohani Hospital (Babol, Iran) under the trade name of U1010 and HB1018, respectively, and were used without any purification. The sodium barbiturate drug with a purity of 95% and the pluronic P-123 were purchased from Sigma Aldrich Co. A pH meter model Metrohm 744 from Switzerland was used to measuring the pH of the solutions. A centrifuge set (Kokusan, model H-11n) was used to precipitation the nanocomposite. Measuring the concentration of barbiturate was carried out by spectrophotometry (Jenway 6550 model) at λ_{max}= 245 nm. The transmission electron microscope (TEM model HF2000) was used for measuring the porous size. The surface area was measured using the Brunauer-Emmett-Teller technique (BET, model Chem BET 300 TPR/TPD). To examine the stabilization of GO on the surface of the sorbent, the elemental CHN analysis (model Costech ECS4010), thermogravimetric analysis (TGA, model Bahr thermo analyze) and a field emission scanningelectron microscope (FE-SEM, Zeiss model) were used.

2.2. Preparation of mesoporous SBA-15

To prepare SBA-15 we followed a well-established method (Mirabi & Khanjari, 2017; Yu *et al.*, 2002) firstly, 375.6 mL distilled water and 74.4 concentrated HCl and 12.5 g P-123 were mixed in a round-bottom balloon equipped with magnetic stirrer using water bath at 42 ˚C for 2 hours. Then, 31.5 g tetraethyl orthosilicate (TEOS) was added to the primary solution and stirred for 8 minutes to be completely solved. Then the solution was kept in a water bath for 24 hours for the formation of micelles. Then the solution was filtered by sinter glass (mesh= 4) and washed several times to reach neutral pH. Then the precipitation was calcined in an electrical furnace at 500 ˚C for 5 hours.

2.3. Modification of nanocomposites

For this study, 0.1 g SBA-15 and 25 mL NaHCO3 0.16 M were mixed and refluxed at 80˚C for 24 hours. This is necessary for proton catching, which results in the conversion of hydroxyl (–OH) to oxide (-O-) groups. Then 0.1 g GO was added to 25 mL toluene and was then moved to the primary solution and refluxed at 110˚C for 24 hours. Finally, the precipitation was dried in an oven at 60˚C (see Figure 1).

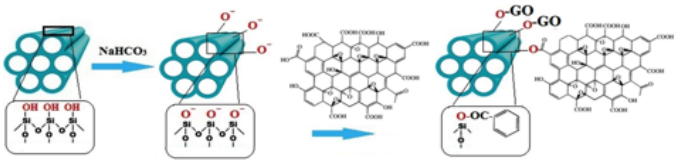

Fig. 1. Preparation of GO functionalized SBA-15

2.4. The general procedure of extraction

For extraction, 0.01 g of the nanocomposite was added to the 100 mL of a solution containing 100 ng mL^{-1} sodium barbiturate. At that time, 2 mL of a buffer (pH=4) were added to this mixture. The whole mixture was mixed in a shaker for 5 min in order to aim the drug adsorption on the nanocomposite. Then the solution was centrifuged at 4000 rpm for 5 min for phase separation. The upper solution was overflowed, but the precipitation was used to the addition of 2 mL methanol. After the addition of methanol, the mixture was mixed for 10 minutes, and the solution was centrifuged again. Finally, the absorbance of the solution was measured by spectrophotometer adjusted at λ=245 nm.

3. Results and discussion

3.1. Characterization of SBA-15 and nanocomposite

Mesoporous SBA-15 contains 2D-hexagonal pores with uniform distribution. According to Figure 2(a), the TEM image of SBA-15 shows uniformly structural arrangement, and its diameter is about 8-10 nm (Figure 2.b).

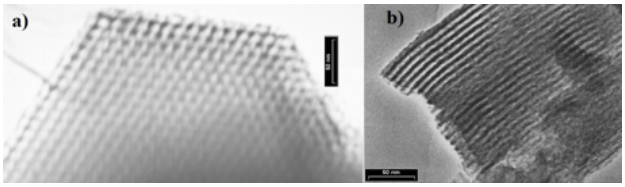

Fig. 2. The TEM images of SBA-15

BET analysis for SBA-15 was performed before and after surface modification (see Table 1). Pore size of the nanocomposite is about 8.8 nm with the surface area of 276.8 m^2 g^{-1} that increases to 324.5 m^2 g^{-1} after coating with GO. This confirms that the sorbent potential of SBA-15 increases upon modification with GO.

Table 1. Analyzer placement.

BET Surface area before coating (m^2/g)	**276.8**
BET Surface area after coating (m^2/g)	**324.5**
Adsorption average pore width (nm)	**8.846**

TGA was employed to the characterization of the thermal stability of the SBA-15/GO nanocomposite. Figure 3 shows that a mass loss at around 126˚C is related to the water. In the temperature range of 399-606˚C, it corresponds to the evaporation of GO. This result

confirms GO existence within the nanocomposite backbone. Moreover, we can conclude that SBA-15 has good thermal stability because there is very little mass loss when temperatures are increased up to 800˚C.

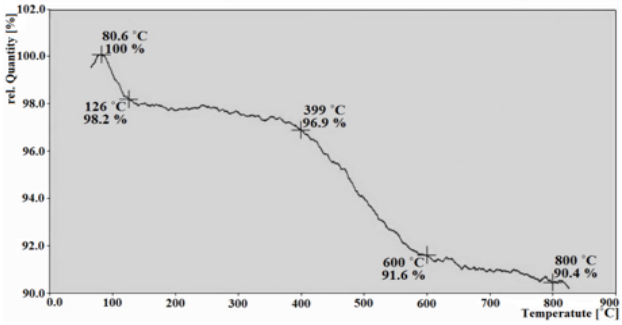

Fig. 3. Thermogravimetric analysis (TGA) curve of nanocomposites

Figure 4(a) shows an FE-SEM image of GO sheets. The main surface of the GO is flat and partly transparent, but the accumulation of the GO sheets can also be observed in some places. After nanocomposite formation, it can be seen that SBA-15 particles with well-ordered mesoporous structures were inserted into GO layers (Figure 4.b).

Elemental CHN analysis (that shows the percent

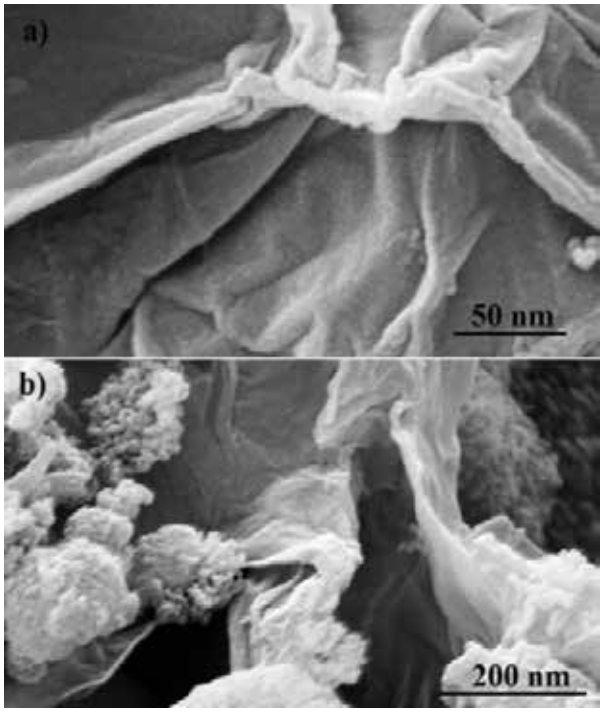

Fig. 4. The FE-SEM images of GO (a) and SBA-15/GO (b)

of C, H, and N atoms) was used for the characterization of GO absorption. Table 2 confirms that the carbon resource attributes to the GO in the nanocomposite. As we know, mesoporous SBA-15 contains Si, O, and H atoms. The data show that GO is stabilized on the surface of mesoporous SBA-15 (Table 2).

These results are in accordance with the result of the energy dispersive spectroscopy (EDS) analysis.

Table 2. Elemental analysis of the nanocomposites

Retention Time (min)	Response	Weight (mg)	Weight (%)	Element Name	Carbon Response Ration
1.120	0.007	0.004	0.06	Nitrogen	0.000
2.156	8219.416	1.167	40.85	Carbon	1.000
7.634	4128.659	0.328	18.84	Hydrogen	0.398

Figure 5 shows EDS analysis of nanocomposites. The existence of O, C and Si atoms shows the good purity of the sample. The result shows a presence of 40.4% O, 39.3% C and 20.3% Si for the nanocomposites.

3.2. Optimization of the preconcentration system

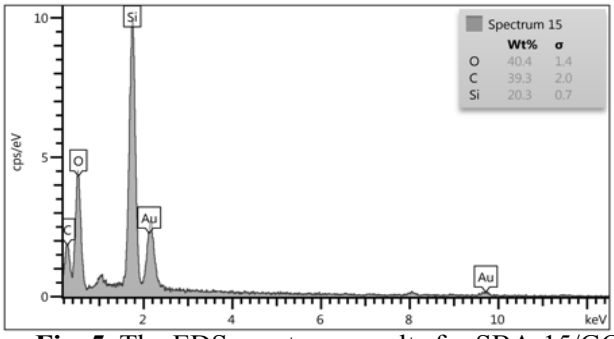

Fig. 5. The EDS spectrum results for SBA-15/GO nanocomposites

For this part, the impact of each effective parameter on the extraction and preconcentration of sodium barbiturate was investigated. In all the optimization steps, the concentration of sodium barbiturate was adjusted to 100 ng mL^{-1}.

3.2.1 The effect of pH

To find the best pH for the maximum extraction of sodium barbiturate, different pH values from 2 to 11 were analyzed. As shown in Figure 6, maximum extraction resulted at pH=4. At low pH values, owing to the electrostatic attraction between the positive charge of the nanocomposite surface and the negative charge of sodium barbiturate, the adsorption of the drug will increase. On the other hand, at high pH values, the charge of the nanocomposite surface is negative owing to existing hydroxide ions. Therefore, a decrease in the adsorption of the drug due to the electrostatic repulsion between them can be assumed.

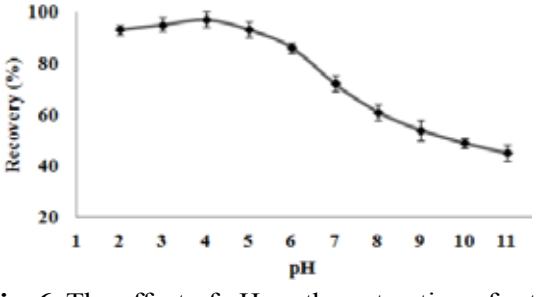

Fig. 6. The effect of pH on the extraction of rutoside

3.2.2 The value of nanocomposite

Figure 7 shows the effects of different amounts of SBA-15/GO and SBA-15 in the extraction of the sodium barbiturate drug (100 ml solvent). As can be seen in Figure 7, for each concentration of nanosorbents, the recovery of the SBA-15/GO nanocomposite is much higher compared to SBA-15, thus confirming the good performance of the nanocomposite in regards to drug extraction. However, we can conclude that by increasing the amount of adsorbent up to 0.01 g, the extraction of the drug increases because there is an increase in the surface of interaction (Figure 7). The amount of 0.0.1 g of the nanocomposite gives the highest recovery percent, and there is no significant increase in drug extraction by increasing the amount of adsorbent to 0.02 g. Thus, 0.01 g of SBA-15/GO was selected for further studies.

3.2.3 The effect of contacting time

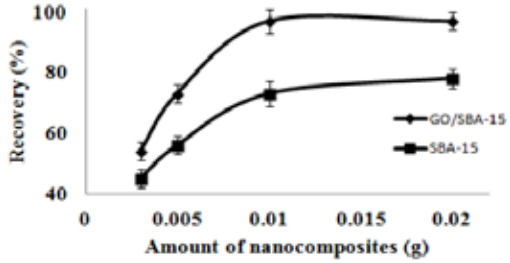

Fig. 7. The effect of different doses of GO/SBA-15 and SBA-15 for extraction of sodium barbiturate

The contacting time is an important factor when seeking to achieve the maximum potential of extraction. This is because it attributes to the mass transfer limitations. In identical situations, we considered different contacting times ranging from 3 to 20 minutes. Figure 8 shows that at 3 min, the sodium barbiturate adsorption is not completed, but at 5 min, adsorption potential reaches the maximum value. Higher contacting times do not greatly effect the recovery percent of the drug. Note that sodium the barbiturate extraction process is fast. As a result, the contacting time of 5 min was selected for the next studies.

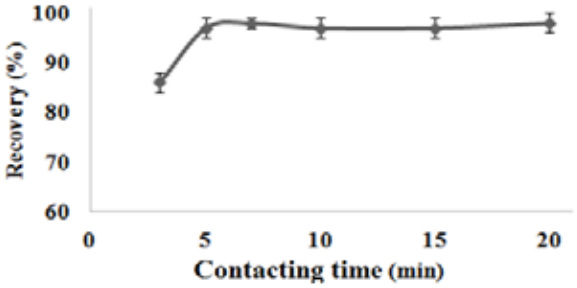

Fig. 8. The effect of contacting time on the extraction of sodium barbiturate

3.2.4 The effect of eluent type

Selection of a good solvent is important since different solvents have different impacts on recovery percent of a drug. We searched for different solvents (acetic acid, acetone, acetonitrile, methanol, ethanol, and n-hexane) for the investigation of the recovery percent of sodium barbiturate drug during elution. Results are depicted in Figure 9. Typically, eluent selection is based on its selectivity for analyte, time and performance of desorption. An ideal eluent includes maximum recovery. As can be seen in Fig. ure 9, methanol has the maximum performance in elution, so it was selected as the best recovery solvent. This result may be due to the organic structure of sodium barbiturate; it can be eluted more efficiently by an organic solvent.

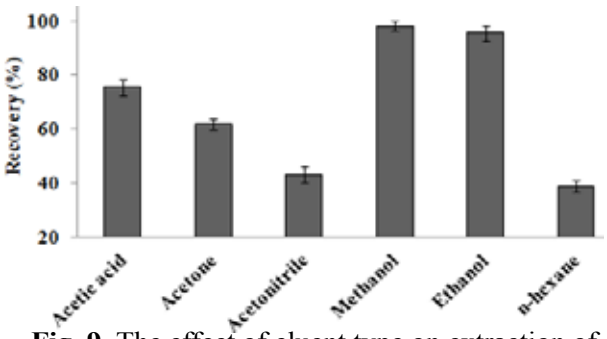

Fig. 9. The effect of eluent type on extraction of sodium barbiturate

3.2.5 The effect of salinity

To analyze the salinity effect on the extraction of the barbiturate drug, different NaCl concentrations (in the range of 0.1-1.0 mol L^{-1}) of were separately added for each analysis. The results showed no significant effect on drug adsorption. It can be concluded that the existence of salt has no major effect on the electrostatic force between the positive charge of the nanocomposite surface and the negative charge of sodium barbiturate. As a result, this method is applicable for drug extraction in saline solutions up to the concentration of 1 mol L^{-1}.

3.2.6 The effects of sample volume and preconcentration factor

To use a low concentration of sodium barbiturate in the spectrophotometer, a high preconcentration factor is needed. The goal of studying different volumes of the extraction solution is to find the maximum volume of solution for the determination of the preconcentration factor.For this purpose, a series of 10-150 mL of sample solutions (see Figure 10) containing 100 ng/ml sodium barbiturate were prepared and used at the above-mentioned optimum conditions. The results showed that 100 mL is the suitable solvent volume. A higher volume of solvent causes a decrease in extraction. Considering 100 mL as the volume solvent and 2 mL as the volume of the recovery solvent, the preconcentration factor is calculated to be 50.

Reuse capability of nanocomposite

The ability of nanocomposite for reuse was analyzed. The results showed that nanocomposite could be reused up to 6 times after refreshing (washing by eluent). However, the adsorption level slightly

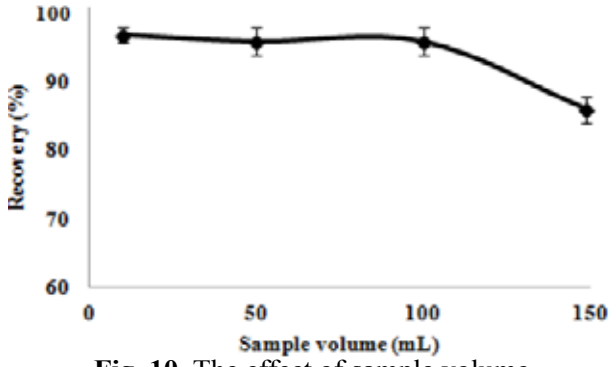

Fig. 10. The effect of sample volume

decreased after 6 washes because of the successive decomposition of the nanocomposite during washing by eluent.

3.4. Interferences studies

One of the most influencial factors on the recovery percent of an analyte is the coexistence of interfering species. The interferences can affect the preconcentration factor. In fact, an ideal sorbent should be able to adsorb analyte in the presence of other species with different concentrations. For this purpose, by spiking appropriate amounts of potentially interfering species from 20-100 µg mL^{-1} in 100.0 mL of a solution containing 100 ng mL-1 of sodium barbiturate, the effect of different interferences was investigated. Interfering species are those that result in ±5% changes in the extraction of sodium barbiturate. According to the results in Table 3, it can be confirmed that none of the added species results in important interference towards the determination of sodium barbiturate.

Table 3. Effect of the interfering species on the determination of sodium barbiturate.

Interfering species	Tolerance limit (µg L^{-1})	Recovery (%)
Sucrose	**100**	**97 ± 1.4**
Fructose	**100**	**96 ± 1.6**
Lactose	**50**	**95 ± 2.1**
Galactose	**50**	**101 ± 1.7**
Ascorbic acid	**30**	**98 ± 2.5**
Cysteine	**20**	**102 ± 1.8**

3.5. Validation of the proposed method

Figures of merit for each analytical method provide a comparison with other methods. Table 4 shows analytical features for the suggested method. The linear range of the calibration curve is 50-2000 g mL^{-1}, with a detecting limit of 17 ng mL^{-1} and a relative standard deviation (RSD) of 1.39% for 100 ng mL^{-1} (n=10). The preconcentration factor (PF=50) was calculated from the ratio of sample volume (100 mL) to eluent volume (recovery solvent) (2 mL). Enrichment factor (EF=50) was calculated from the ratio of the sodium barbiturate concentration before and after extraction.

Table 4. Analytical characteristics of proposed method.

Parameter	Analytical Feature
Linear range (ng mL^{-1})	**50-2000**
Limit of detection (ng mL^{-1})	**17**
Repeatability (RSD %) (n =10)	**1.39**
Preconcentration factor	**50**
Enrichment factor	**50**
Correlation coefficient (r^2)	**0.9963**

In this study, the extraction percentage is nearly 100%.

3.6. Application of method

For surveying the ability of suggested method in real samples, urine, and human blood serum were used for detection of sodium barbiturate using standard addition method. The results are given in Table 5. As it can be seen in Table 5, the complex matrix has no important effect on the extraction performance. Table 5 shows the amount of sodium barbiturate in 100 ng mL-1 of solution sample.

Table 5. Determination of sodium barbiturate in real and spiked samples.

Sample	Barbiturate spiked (ng mL^{-1})	Barbiturate detected (ng mL^{-1})	Recovery (%)
Urine	**-**	**BDL[1]**	**-**
Urine	**100.0**	**98.1**	**98.1 (±2.8)**
Blood serum	**-**	**BDL**	**-**
Blood serum	**100.0**	**102.5**	**102.5 (±3.1)**

[1]Below the detection limit

3.7. Comparison with other methods

The suggested method was compared with other methods, which are used for preconcentration and the measurement of sodium barbiturate. The comparison of parameters of the suggested method with other methods is shown in Table 6. The table shows that the use of SBA-15/GO provides considerable LOD (17 ng/ml barbiturate) compared to the most of the other methods. Despite the LOD value of 10 for reference (Garrett *et al.*, 2006) is comparable value, However, we should consider that the spectrophotometry method that is used in our method is more economical technique compared to GC-MS used in the above-mentioned reference. Furthermore, the result of this study are in total agreement with the result of our recently paper

Table 6. Comparison of the proposed method with other methods

Matrices	Extraction	Detection	LOD (ng mL^{-1})	Reference
Oral fluid, plasma,urine	SPE	LC-MS	100	(Fritch *et al.*, 2011)
Dried blood	SPE	LC-MS-MS	34	(Marca *et al.*, 2009)
Serum	SPE	GC-MS	100	(Saka *et al.*, 2008)
Serum, plasma, urine	LLE	GC-MS	5000	(Johnson & Garg, 2010)
Urine	SPE	GC-MS	20	(Pocci *et al.*, 1992)
Whole blood and urine	SPME	GC-MS	200	(Iwai *et al.*, 2004)
Urine	SPME	GC-MS	10	(Hall & Brodbelt, 1997)
Serum, urine	SPE	spectro-photometry	17	This work

(Mirabi *et al.*, 2017) in which the same nanocomposite was used for the preconcentration and measurement of rutoside

in blood plasma and urine with an LOD of 4.2 ng mL^{-1} .

4. Conclusion

In this research, a mesoporous SBA-15/GO nanocomposite was used as a nanosorbent for sodium barbiturate using the SPE method. By using this nanocomposite, we found that the drug adsorption capacity increased compared to the pristine SBA-15. This is attributed to its high surface area and low resistance to mass transfer. In this research, we used the spectrophotometry technique to analyze the drug samples. The results showed that the nanocomposite is very sensitive to detecting low concentrations of sodium barbiturate in urine and blood serum media at ng mL^{-1} levels. The proposed method has a low RSD, suitable linear range and limit of detection, and high values of preconcentration and enrichment factor.

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أكسيد الجرافين يعمل على تحسين قدرة السيليكا المسامية SBA-15 نحو فصل واستخلاص وتحديد العقاقير الباربيتورية في العينات الحقيقية

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الملخص

في هذه الدراسة، تم استخدام طريقة بسيطة وحساسة وعالية الأداء لفصل واستخلاص كمية ضئيلة من عقار باربيتورات الصوديوم باستخدام السيليكا المسامية (SBA-15) المُعدلة بواسطة أكسيد الجرافين (GO). تم استخدام EDS ، FE-SEM ، TGA ، BET ، TEM، وتحليل العناصر CHN لتوصيف SBA-15 والمركبات متناهية الصغر. تم تحسين المعلمات الفعالة في استخراج الباربيتورات مثل الرقم الهيدروجيني (pH)، وكمية المركبات متناهية الصغر، ونوع الشاطف، وأوقات الاتصال، والقوة الأيونية للمحلول، وحجم العينة لتحديد كمية الباربيتورات. تم حساب المعطيات التحليلية مثل الدقة، وحد الكشف، والفصل والاستخلاص، ومعامل التركيز وقد أثبتت ملاءمة طريقتنا المقترحة. وأظهر منحنى المعايرة ارتباط خطي في نطاق التركيز من 50-2000 $ng\ mL^{-1}$ مع حد الكشف البالغ 17 $ng\ mL^{-1}$. وتم حساب الانحراف المعياري النسبي (n=10) ليكون 1.39٪ وقد حقق معامل الفصل والاستخلاص 50 باستخدام عينة 100 مل.