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Elaboration of impregnated guava seed by Cu(II) for fixing glimepiride using Square-wave Adsorptive Stripping Voltammetry

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Abstract

A simple and novel adsorbent has been developed for the determination of glimepiride (Glim) drug in aqueous media. This adsorbent is prepared by impregnation of guava seed with Cu(II) (GS-Cu). The effect of different parameters such as effect of pH, amount of adsorbent and drug concentrations on the adsorption process is studied. Point zero charges for this adsorbent (GS-Cu) is determined and found to be 4.1. The adsorption percent of Glim using GS-Cu reach to 99.8 % at pH = 4.0. Limit of detection (LOD) and limit of quantitation (LOQ) were found to be 3.4 and 7.7 µg mL^{-1}, respectively for Glim using GS-Cu. The proposed method was used successfully for Glim determination in environmental water samples with high recovery values.

1. Introduction

The increasing worldwide consumption of pharmaceuticals and their occurrence in the environment has become an important issue in recent years [1]. Typical water treatment facilities are not designed to remove pharmaceuticals (drugs) from drinking water. These drugs, both prescription and over-the-counter, can end up in water supplies. There are many concerns to remove these drugs, but many of these drugs are not completely metabolized by the body, and enter the environment after passing through wastewater treatment facilities [2]. The effluents from such treatment facilities are discharged into bodies of water that can end up in water supplies, from which drinking water is taken. Therefore, the development of simple, sensitive, rapid and reliable method for the determination and removal of drugs in environment is of great importance. Different processing methods including solid phase extraction (SPE) being used for removal of drug contributes in water pollutiondue to its advantages [3]. The cost effectiveness of the whole process and the ease of production of the composite adsorbent material in required bulk quantities are also important for drug removal applications [4]. Recently, cheaper and effective adsorbents can be formed from numerous natural materials or certain waste materials from industrial and agricultural activities. These adsorbents are economic and environment friendly, available, renewable nature and low cost which helpful for water and wastewater treatment [5]. Guava seeds (GS) are considered as a solid waste produced at great quantities by agricultural and industrial activities. They have structural properties, like high content of cellulose, lignin and protein that make them suitable for their use as a biosorbent[6]. It was used for removal of some pollutants [7 – 9] but there are no previous studies on using it for removal or determination of any drug. Moreover, for increasing the selectivity and loading capacity of adsorbent surface, modification processes have been developed with complicated procedures [10]. For this reason, simple and few steps modification through impregnation technique was used to increase surface adsorption and removal capacity of adsorbent [5, 11].

On the other hand, some drugs such as glimepiride drug (Glim) can form coordination complexes with metal ions, especially copper(II), cobalt(II), and manganese(II) [12]. Glim is a third generation sulfonylurea type oral hypoglycemic agent, which is widely used in treatment of type 2 diabetes [13]. Chemically, it is 1-[[4-[2-(3-ethyl-4-methyl-2-oxo-3-pyrroline-1-carboxamido)-ethyl] phenyl] sulfonyl]-3-trans-(4- methyl cyclo hexyl) urea, Fig. 1.

So, the main objective of this paper is to develop a new and simple method for modification of GS surface through impregnated with Cu(II) which has the ability to bind with Glim drug. This new adsorbent was used successfully for the determination of Glim from different environmental water samples.

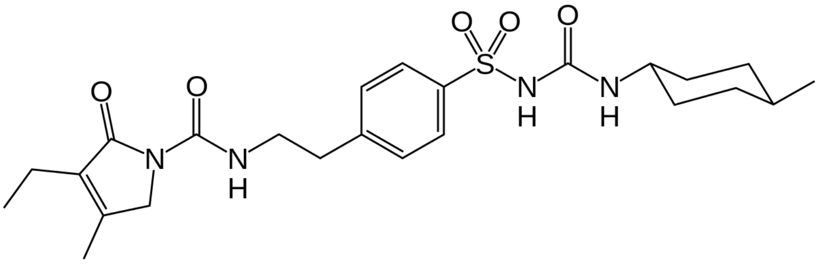

Figure 1: structure of glimepiride drug

2. Material and Methods

2.1. Materials

Fresh guavas were obtained from a local market in Minia, Egypt. Cupric chloride ($CuCl_2.2H_2O$), methanol were analytical grade from Merck, Germany. Glimepiride was obtained from Sigma Company for pharmaceuticals, Cairo, Egypt. ACS reagent grade of sodium hydroxide were obtained from Aldrich, USA. Acetic, hydrochloric, O-phosphoric and boric acids were obtained from Merck, Germany. Doubly distilled water (DDW)was used throughout all experiments.

2.2. Apparatus

Square-wave adsorptive cathodic stripping voltammetric (SWAdCSV) determination of Glim was carried out using AMEL Model 433 TRACE ANALYSER involving three–electrode system consisted of a hanging mercury dropping electrode (HMDE) as a working electrode, an Ag/AgCl with saturated KCl as a reference electrode and a platinum wire as a counter electrode. A magnetic stirrer and stirring bar provided the convective transport during the pre-concentration. The peak heights were automatically or manually measured using the 'tangent fit' capability of the instrument. The pH measurements were made with Accumet® Model 825 pH meter (Germany). The infrared spectra of the adsorbents were obtained using Fourier transform infrared (FT-IR) spectroscopy (410 JASCO, Japan). The crystal structure of the adsorbents was studied using X-ray diffractometer (JSX-60 PA JEOL, Japan). Wrist Action mechanical shaker Model 75 (manufactured by Burrell Corporation Pittsburgh. PA. U.S.A.).

2.3. Adsorbent preparation

2.3.1. Preparation of guava seed

Guava seeds were collected from the fruit. They were washed with excess DDW to remove adhering materials then air dried and finely ground. The ground materials were sieved to obtain a powdery form which was washed with DDW and dried well in an oven at 60 ^oC for 1h. Then, it was kept in a closed dark glass bottles and stored until utilization.

2.3.2. Modification of guava seed

500.0 g of GS was transferred into100-mL measuring flasks and soaked for two days in 0.5M $CuCl_2.2H_2O$. This mixture was filtrated and the modified adsorbent was washed with DDW to remove the excess of Cu(II). The product material was left to dry in an oven at 60 ^oC for 1h then stored in glass bottles for utilization.

2.4. Preparation of Glimepiride solution

A stock standard solution (100.0 μg mL^{-1}) of Glim was prepared by dissolving in methanol. The standard solution was kept at 4 °C to be stable and the drug concentration did not change with time. Aliquots of this standard solution were transferred into100-mL volumetric flasks and made up to volume with DDW to get the final desired concentrations.

2.5. Studies on point zero charge (PH_{zpc}) of adsorbent

In pH_{zpc} determination, 200.0 mg of each adsorbent (GS and GS-Cu) was added to 50.0 mL of 0.01 M NaCl and its pH was adjusted in the range of 2.0 – 12.0 by adding appropriate volumes of 1.0 M HCl or 1.0 M NaOH [11]. These solutions were kept for 48 hrs. Graphs were then plotted for pH_{final} versus $pH_{initial}$.

2.6. Batch adsorption method

The effect of pH, shaking time, amount of adsorbent and concentration of drug were tested and evaluated by batch method. In the proposed procedure, to achieve maximum adsorption efficiency, various parameters affecting the removal of Glim were studied and optimized. Known weight for each adsorbent (GS and GS-Cu) was added to 50.0 mL of 10.0 μg mL^{-1} of Glim solution and the pH of the solution was adjusted with 0.1M HCl and 1.0M NaOH solutions and controlled from 1.0 to 10.0. The suspension was then shaken at room temperature for 30 min. Subsequently, the suspension was filtrated and the concentration of Glim was determined using square-wave adsorptive cathodic voltammetric (SWAdCSV) technique through standard additions method at $E_{acc.} = -1.16$ V and $t_{acc.} = 60$ in 10.0 mL of 0.04 M B.R. buffer at pH= 9.0 [14].Moreover, the effect of contact time, drug concentration and amount of adsorbent on drug uptake were determined using the same procedure at the optimum pH value of adsorption.

2.7. Removal and determination of Glimepiride in water samples

Samples of Nile River water (NRW), drinking tap-water (DTW) and ground water (GW) were collected from Minia. Sea water (SW) was collected from Alexandria City, Egypt. The new adsorbent (GS-Cu) was applied for the removal of Glim spiked natural water samples (DTW, SW, NRW and GW). 50.0 mL of each water sample spiked with 3.4 μg L^{-1} of Glim was shaken with 50.0 mg of adsorbent for 30 min at pH 4.0 then filtrated. The concentration of Glim in the filtrate was determined using SWAdCSV by standard additions method. An aliquot (5.0 μL) of the filtrate was spiked in 10.0 mL of 0.04 M B.R. buffer at pH= 9.0 including different standard additions of 10.0 μg L^{-1} of Glim at $E_{acc.} = -1.16$ V and $t_{acc.} = 60$ s.

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. FT-IR

Fig. 2 shows the FT-IR spectra for both GS and GS-Cu adsorbents. The GS spectrum is complex and contains different bands due to the functional groups of proteins, sugars, and complex carbohydrates (dietary fiber components) [7].

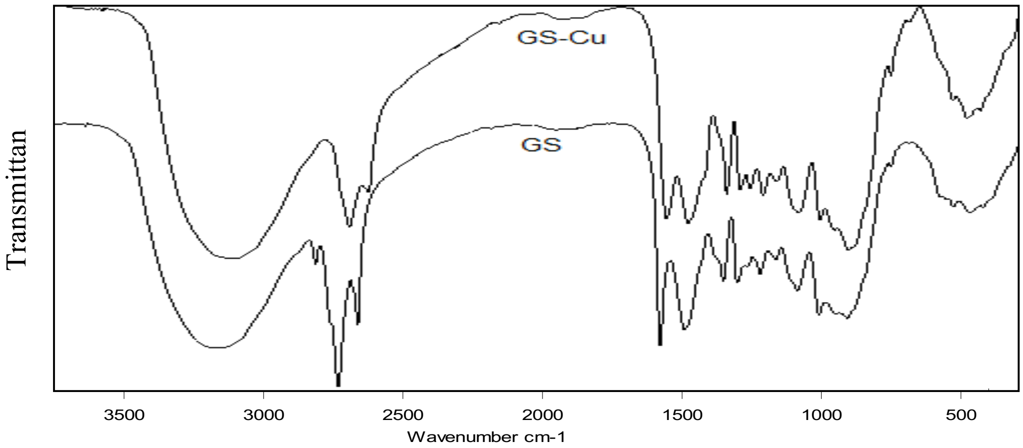

Figure 2: FT-IR spectra of GS and GS-Cu adsorbents

The broad overlapping band at 3358 cm^{-1} can be attributed to υ(O−H) groups and υ(N–H) stretching alkyl or aryl amine which may be present in the amino acids of protein found in guava seeds. This band increased in the intensity in GS-Cu due to the binding between Cu(II) and (N–H) or (O−H) groups. The aromatic =C–H stretch observed at 2800 cm^{-1} in GS adsorbent, disappeared in GS-Cu. Two strong bands observed at2700 cm^{-1} and 2600 cm^{-1} are assigned to asymmetric and symmetric υ(C–H) bands, respectively, decreased in the intensity in GS-Cu adsorbent. The two strong absorption bands at 1650 and 1500cm^{-1} were assigned to carbonyl υ(C=O) stretching (present in esters, aldehydes, ketones groups and acetyl derivatives) and υ(C=C), respectively decreased also in GS-Cu adsorbent and shifted to 1550 and 1480cm^{-1}. The region of 1300 – 1000 cm^{-1} is a superposition of number of broad overlapping bands. The assignment in this region is a complex nature, so they cannot be described in terms of the simple motion of specific functional groups or chemical bonds [9]. This region of bands increased in intensity in the case of GS-Cu. The changes intensity and shifts in the transmittance bands in the FT-IR spectra were directly related to changes in the molecules of GS-Cu adsorbent after the modification.

3.1.2. X-ray

The x-ray diffraction patterns for these adsorbents were shown in Fig. 3. The band of GS was broad band which indicates that it has amorphous surface [11]. After impregnation process with Cu(II) for the adsorbent, the intensity of the bands decreased.

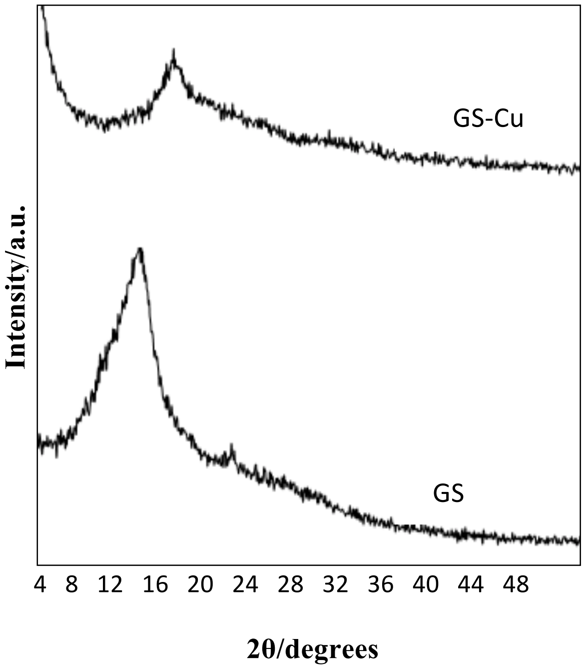

Figure 3: X-ray diffraction patterns of GSand GS-Cu adsorbents

3.2. Determination of point zero charge (pH_{zpc})

Point zero charges (pH_{zpc}) were determined for the adsorbent, i.e., GS and GS-Cu. The value of pH_{zpc} is an important property and indicates the electrical neutrality of the adsorbent and surface at a particular value of pH. The graph of pH_{intial} vs. pH_{final} was plotted inFig. 4. The intersections of the curves with the straight line are known as the end points of the $pH_{zpc,}$ and these values are 6.5 and 4.1for GS and GS-Cu, respectively.

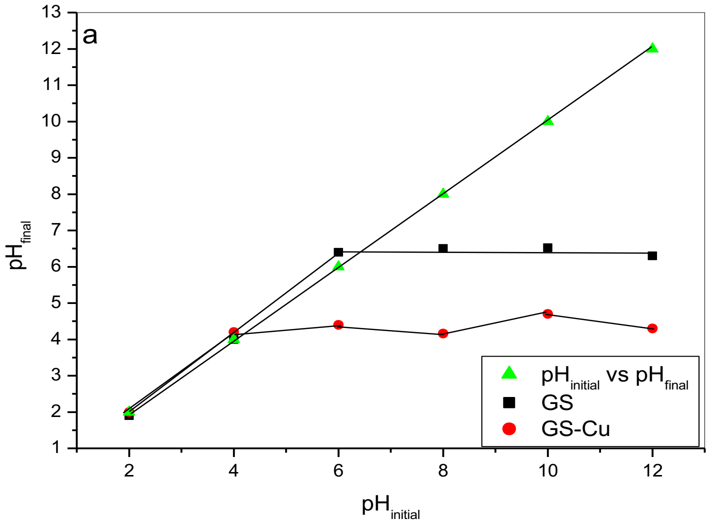

Figure 4: Plot for determination of point zero charge of GS and GS-Cu adsorbents

3.3. Effect of pH

It is known that pH value has a critical role in solid phase extraction. In order to determine the optimal pH, the effect of pH on the adsorption of Glim was investigated over a pH range of 1.0 to 10.0. As shown in (Fig. 5), it could be observed that when the initial pH of Glim aqueous solution increased from 1.0 to 4.0, there was a sharp increase of the amount of Glim adsorbed on the GS and GS-Cu adsorbents. In the case of GS, the adsorption percentages at pH 4.0 were 60.0 % which lower than that of their modified adsorbents. Due to the impregnation process with Cu, the adsorbent (GS-Cu) has higher opportunities to bind with Glim than GS. By increasing the pH from 5.0 up to 10.0, the adsorption percent decrease for the two adsorbents.

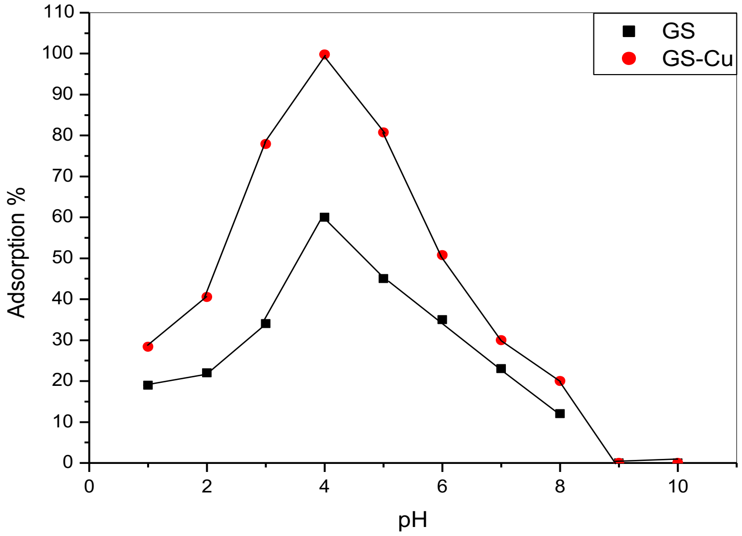

Figure 5: Effect of pH on adsorption percent values of GS and GS-Cu adsorbents

3.4. Effect of the amount of adsorbent

The amount of adsorbent is an important factor in a SPE method, because it influences on the analyte recovery, directly. Fewer amounts of the adsorbents may achieve acceptable results because of their greater surface areas. The amounts of each GS and GS-Cu at the ranges of 10.0–150.0 mg were investigated and respective results presented in Fig. 6. The results showed that the adsorption percent of Glim were increased with the increase of adsorbent up to 50.0 mg of each adsorbent, but then, the adsorption percent decreased. This can be due to the preventive effect of excess amounts of adsorbent on the elution of the retained analyte [15]. The adsorption percent for GS and GS-Cu were found to be 60.0 and 99.8, respectively.

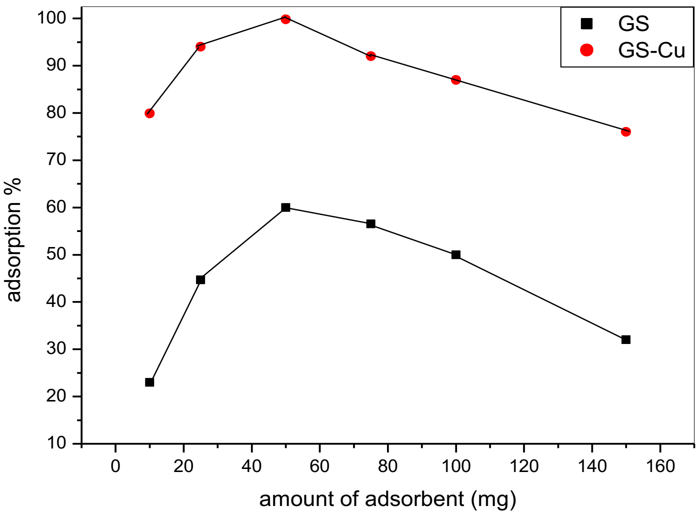

Figure 6: Effect of amount of adsorbent on adsorption percent values of GS and GS-Cu adsorbents

3.5. Method validation

Quantitative parameters of SPE, such as linear range, correlative coefficients, limits of detection (LOD), limits of quantitation (LOQ), and precision were evaluated and summarized in Table 1. Calibration curves for Glim were attempted under the optimized procedure conditions at −1.16 V with correlative coefficient 0.9996. The regression equation associated with the calibration curves, exhibited a good linearity thatsupported the proposed procedure. The Results showed good precision of the method with SD in the range of Glim. Limit of detection (LOD) and limit of quantitation (LOQ) were estimated from the following equations [16]:

$$\mathrm{LOD} = 3.3\frac{\mathrm{SD_a}}{\mathrm{b}}\,(1)\mathrm{LOQ} = 10\frac{\mathrm{SD_a}}{\mathrm{b}}\,(2)$$

where SD_a is the standard deviation of the intercept, and b is the slope. Both LOD and LOQ values confirmed the sensitivity of the proposed method.

Table 1: Characteristic of the calibration plots of Glimat $E_{acc.}$ = − 1.16 V, $t_{acc.}$ = 60 s, rest time = 5 s, wave amplitude E_{sw} = 120 mV, wave increment ΔE = 12 mV, wave period = 100 ms & sampling time = 8 ms

Parameter	$t_{acc.}$ = 60 s
Linearity range (μg mL^{-1})	1.0 – 10.0
Regression equation	i_p= 6.17 + 0.13 c
Correlation coefficient (r)	0.9996
Determination coefficient (r^2)	0.9992
LOD (μg mL^{-1})	2.4
LOQ (μg mL^{-1})	7.7

* Average of three determinations

3.6. Determination of Glimepiride in water samples

To evaluate the practical performance of the developed method, the concentration of Glim in environmental water samples were measured using GS-Cu. Initial analysis confirmed that the water samples (DTW, SW, NRW and GW) were free of target analyte. The recoveries were in the range of 98.97–99.79 % for all water samples with RSDs less than 1.0% (Table 2), which indicated good method utility.

Table 2: Results obtained for Glim drug determination in various water samples after adsorption by GS-Cu adsorbent

Water sample	Spiked Glim drug (μg mL^{-1})	Mass of the phase (mg)	Recovery^a (%)
NRW	3.4	50.0	99.00 ± 0.1
DTW	3.4	50.0	99.3 ± 0.05
GW	3.4	50.0	98.99 ± 0.03
SW	3.4	50.0	99.79 ± 0.01

Conclusion

A simple, fast and selective solid phase extraction procedure, based on modification of GS with Cu(II) for the determination of Glim has been developed. It was found that GS-Cu has higher capacity factor and low limit of detection than GS. The proposed method has been applied to determine Glim in environmental water samples using SWAdCSV technique.

References

1. M.R. Payán, M.A.B. López, R. Fernández-Torres, M.C. Mochón, G.L., Gómez Ariza, *Talanta* 82 (2010) 854−858.2 & A. Mani, V. Thawani, The persisting environmental problem of disposal of expired and unused medicines. *J Mahatma Gandhi Inst Med Sci* 24(2019)13-6
3. S.A. Ahmed, A.A. Abdel Gaber, A.M. Abdel Rahim, *Applied Water Science* 7(2015) 677–688.
4. X. Luo, Y. Zhan, X. Tu, Y. Huang, S. Luo, L. Yan, *Journal of Chromatography A,* 1218 (2011) 1115–1121.
5. A.M. Abdel Rahim, *J. Mater. Environ. Sci.,* 9 (2018) 444-451.
6. A. Bhatnagar, M.,Sillanpää, Chemical Engineering Journal, 157 (2010) 277–296.
7. H.A. Sánchez-Sáncheza, R. Cortés-Martínezb, R. Alfaro-Cuevas-Villanueva, *International Journal of Sciences: Basic and Applied Research*, 11 (2013) 159−172.
8. N. Amri, R.Alrozi, M.S. Osman, N. Nasuha, *Journal of Materials and Chemical Engineering*, 1(2013)32-43.
9. C.G. Joseph, A. Bono, D. Krishnaiah, K.O. Soon, *Materials Science*, 13 (2007).
10. C. Namasivayam, D. Sangeetha, *J. Hazard. Mater.,* B 135 (2006) 449–452.
11. S.A. Ahmed, A.A. Abdel Gaber, A.M. Abdel Rahim, *International Journal of Advanced Research*, 3 (2015) 621-632
12. M.G. Abd El-Wahed, M.Y. El-Sayed, S.M. El-Megharbel, Y.M. Zahran, M.S. Refat, *J Infect. Dis. Ther.,* 2 (2014) 1-9.
13. M.R. Rezk, S.M. Riad, G.Y. Mahmoud, A.E. Abdel Aleem, *Der Pharma Chemica,* 3 (2011) 176–184.
14. I., Suslu, S. Altinoz, *Current Analytical Chemistry* 7 (2011) 333.
15. M. Rajabi, B. Mohammadi, A. Asghari, B. Barfi, M. Behzad, *Journal of Industrial and Engineering* Chemistry 20 (2014), 3737−3743.
16. A.A. Abdel Gaber, S.A. Ahmed, A.M. Abdel Rahim, *Arabian Journal of Chemistry* 10(2017)S2175–S2181.

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