Nanomed. J., 2(4): 269-272, Autumn 2015
DOI: 10.7508/nmj. 2015.04.004

Synthesis of graphene oxide-TiO_2 nanocomposite as an adsorbent for the enrichment and determination of rutin

[1,3]M. R. Gaeeni; [2]M. Tohidian; [1]M. Sasani Ghamsari; [3]M.H. Majles Ara*

[1]*Laser and Optics Research School, Nuclear Science and Technology Research Institute, AEOI, North Karegar, Tehran, Iran*
[2]*Faculty of Medicine, Tehran University of Medical Sciences, Pour-Sina Ave, Tehran, Iran*
[3]*Photonic Laboratory, Physics Department, Kharazmi University,Tehran, Iran*

Received; 3 February 2015 Accepted; 21 March 2015

ABSTRACT:

Objective(s): In our study, graphene oxide-TiO_2 nanocomposite (GO/TiO_2) was prepared and used for the enrichment of rutin from real samples for the first time.

Materials and Methods: The synthesized GO/TiO_2 was characterized by X-ray diffraction, scanning electron microscopy, and FT-IR spectra. The enrichment process is fast and highly efficient. The factors including contact time, pH, and amount of GO/TiO_2 affecting the adsorption process were studied.

Results: The maximum adsorption capacity for ciprofloxacin was calculated to be 59.5 mg/g according to the Langmuir adsorption isotherm. The method yielded a linear calibration curve in the concentration ranges from 15 to 200 µg/L for the rutin with regression coefficients (r^2) of 0.9990. The limits of detection (LODs, S/N=3) and limits of quantification (LOQs, S/N=10) were found to be 8 µg/L and 28 µg/L , respectively. Both the intra-day and inter-day precisions (RSDs) were < 10% .

Conclusion: The developed approach offered wide linear range, and good reproducibility. Owing to the diverse structures and unique characteristic, GO/TiO_2 possesses great potential in the enrichment and analysis of trace rutin in real aqueous samples.

Keywords: *Enrichment, GO-TiO_2, Nanocomposite, Rutin*

INTRODUCTION

Flavonoids are polyphenolic compounds commonly found in vegetables and fruits and constitute a significant part of the human diet [1]. The antioxidant and anti-inflammatory capacities of these compounds are well reported [2] and many show cancer fighting potential. Flavonoids were reported to inhibit cancer cell proliferation and angiogenesis [3]. Rutin belong to the flavonoid family that is widely distributed in fruits and vegetables. The chemical structure of rutin contains several hydroxyl groups on the different aromatic rings. Rutin is commonly found in the human diet [4] and in plants such as (Flos Sophorae) buds and others species of plants [5, 6]. Several studies demonstrated that rutin has some hysiological properties such as anti-inflammatory [7], anti-tumor [8]and anti-bacterial activities [9]. In clinical chemistry, it has been used as therapeutic medicine [10].Graphene, which is consisted of extraordinarily hexagonal sp^2 carbon network with a two-dimensional honeycomb lattice structure, possesses many amazing characteristics such as high thermal conductivity, large surface area, remarkably optical, electrical and mechanical properties [11]. At present, graphene has been considered as a prospective material for various applications comprising super-capacitors, biotechnology, field effect transistors and Li ion batteries [12, 13]. Generally, graphene is easily exfoliated and oxidized by strong oxidants leading to the formation of graphene oxide (GO). The surface of GO can be decorated with biomolecules and organic molecules by van der Waals forces and p–p stacking interaction [14, 15]. The two dimensional plane structure and one-atom thickness provide GO with large specific surface and high aspect ratio. GO, one of the most significant derivatives of graphene, was obtained from the strong oxidation of graphite using Hummers method [16]. The functional groups such as carboxyl, hydroxyl and epoxy are formed because varieties of oxygen atoms are available on the surface of GO, which makes GO strongly hydrophilic [17]. As a wide band-gap

*Corresponding Author Email: *gaeeni@khu.ac.ir; mgaeeni@aeoi.gov.ir*. Tel: (+98) *21-82064132*
Note. This manuscript was submitted on February 3, 2015; approved on March 21, 2015

semiconductor, titanium dioxide (TiO_2) has been in the scientific limelight owning to its non-toxicity, low cost, chemical stability and higher photoactivity.

In this study, we successfully synthesized graphene oxide/TiO_2 nanocomposite for the determination of rutin. In literature, there is no report about determination of rutin performed by GO/TiO_2 nanocomposite. In addition, the developed method based on this nanocomposite shows high sensitivity for determination of rutin in real samples.

MATERIALS AND METHODS

Chemicals

Natural graphite powderÿ dopamine, H_2SO_4, $KMnO_4TiCl_3$, ammonia solution (28 wt %), $FeCl_3.6H_2O$, H_2O_2 (30 wt %) and all other chemicals were purchased from Sigma-Aldrich (USA) and were of analytical grade.

Synthesis of graphene oxide (GO)

The GO was pre-synthesized by modified Hummers method. In a typical synthesis, 10 g graphite powder was put into 230 mL H_2SO_4 in a big flask. While maintaining vigorous stirring, 30 g $KMnO_4$ was slowly added to the flask and the temperature was kept below 20 °C. The mixture was stirred at 35 °C for 40 min until it became pasty brownish, and then 460 mL distilled water was added into the reaction vessel keeping the temperature below 35 °C. After stirring for 90 min, 1.4 L distilled water and 100 mL 30% hydrogen peroxide were added into the above mixed solution and kept standing for 24 h. Finally, the GO was obtained by washing with a certain amount of distilled water and 5% HCl for several times until no SO_4 ion existed (tested by $BaCl_2$), and then dried at 50 °C for 6 h under vacuum.

Synthesis of graphene oxide-TiO_2 nanocomposite

Graphene oxide (60 mg) was dispersed in 30 ml of water by magnetic stirring for 1 h. $TiCl_3$ (10 mL) and ammonia solution (0.1 mL) were added, the mixture was sealed in a Teflon-lined stainless-steel autoclave and was heated at 180 °C for 12 h. The product was washed with deionized water and ethanol several times. Eventually, the GO/TiO_2 composites were dried in vacuum at 50 °C.

Structural characterizations

The SEM image of GO, GO/TiO_2 was obtained on a JEOL JSM-6330F. Fourier transform infrared (FTIR) spectra were acquired on a FTIR spectrometer (FTIR-S-8400) instrument using KBr disks in the 400–4000 cm^{-1} region. The X-ray diffraction (XRD) was recorded with a D/max-2500 diffractometer (Rigaku, Japan) using Cu_{Ka} radiati (λ=1.5418 Å).

Sample preparation

Human urine samples were collected from a healthy volunteer and stored below 0 °C and brought to room temperature before use.

Enrichment and determination procedure

The graphene oxide/TiO_2 nanocomposite was dried overnight at 50 °C before use. Then, 4 mg of GO/TiO2 was dispersed into sample solution (5 mL) in a 10 mL centrifuge tube. The mixture was vortexed for 60 min. The rutin captured by GO/TiO_2 nanocomposites were washed and eluted according to our method. Finally, the concentration of rutin was analyzed using an ultraviolet–visible spectrophotometer (Beijing Puxi UV-1900) at the wavelength of 361 nm.

RESULTS AND DISCUSSION

Characterization of the GO/TiO2

SEM analysis

The microstructures of the as-prepared products were characterized by SEM images. Figs 1a, and 1b are representative SEM images of the GO and GO/TiO_2, respectively. GO had a sheet-like structure with thick sheets, smooth surfaces, and wrinkled edges. It is clearly observed that TiO_2 spheres were supported on the surface of graphene oxide sheets.

FTIR analysis

The FT-IR spectra of GO and GO/TiO_2 are shown in Fig 2.the spectrum showed a strong adsorption peak at 3240 cm^{-1} which was assigned to O-H stretching vibrations. The peak at 1398 cm^{-1} corresponded to C=O, indicating that we successfully prepared GO.

Compared GO and GO/TiO_2, the strong IR band at 1650 cm^{-1} is attributed to the vibration of the Ti-O, confirming that we successfully prepared GO-TiO_2.

XRD analysis

The crystalline structure of the GO and GO/TiO_2 was rigorously investigated using powder X-ray diffraction (Fig 3). The XRD pattern of the GO-TiO_2 exhibited (101), (004), (200), (211), (204), and (105) diffraction peaks, which are characteristic peaks of the anatase phase (JCPDS, No. 21-1272). These results indicated that the GO/TiO_2 nanocomposite was prepared successfully. The crystallite size of the particles has been calculated from the Debye–Scherrer's formula using the x-ray line broadening by applying full width-half-maximum of highest intensity peak as follows (18).

$$s = \frac{k\lambda}{B\cos\theta} \quad (1)$$

where is the wavelength of the x-ray radiation (λ= 0.15406 nm), s is the crystallite size, k a constant taken as 0.94, θ the diffraction angle and B is the full width of diffraction peak at half maximum intensity. The average crystallite size of GO/TiO_2 nanocomposite was calculated to be about 53 nm, in good agreement with the SEM result. All of the above characterization clearly proved that the GO/TiO_2 was successfully synthesized with the synthesis method.

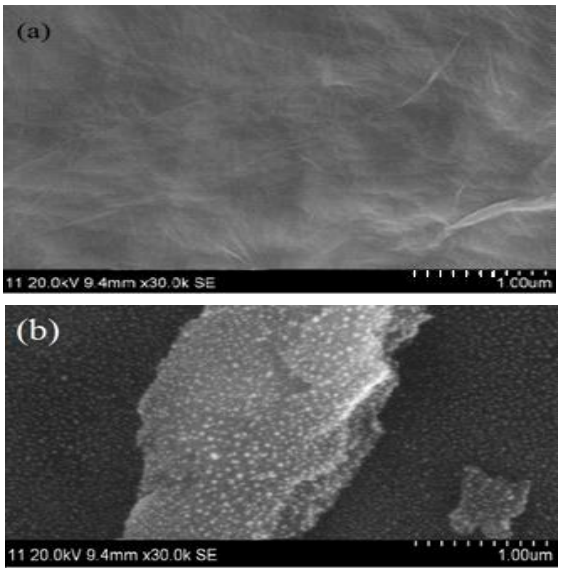

Fig. 1. SEM images of (a) GO and (b) GO/TiO2

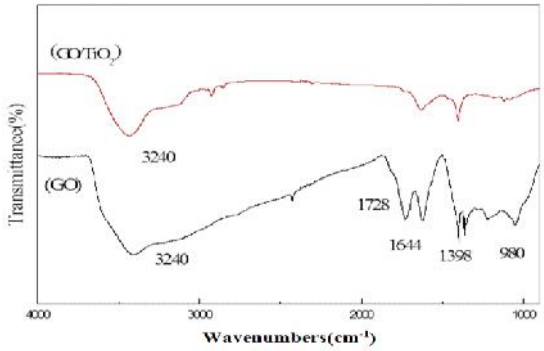

Fig. 2. FT-IR spectra of GO and GO/TiO2

Optimization of the enrichment conditions

Effect of pH

The sample pH is another important factor that affects the extraction of analytes. The sample pH not only influences on the molecular existing form of analytes but also closely affects the charge species and density on the sorbent surface. The effect of solution pH on the recoveries of rutin was investigated in a range of 3.0 to 7.0. The recoveries of analytes increased slightly when the solution pH increased from 3.0 to 5.5, then further increase of pH from 5.5 to 7.0 led to a decrease of the recoveries. Thus, pH 5.5 was chosen as the optimum sample pH.

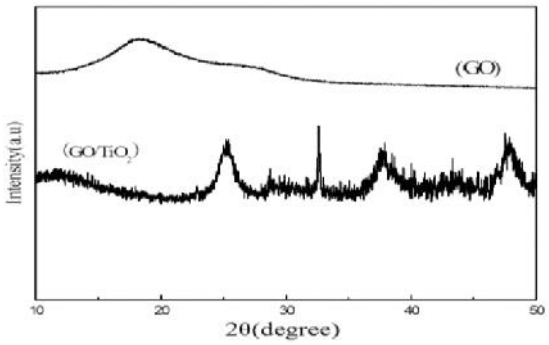

Fig. 3. X-ray diffraction patterns of GO and GO/TiO2

Effect of concentration of GO/TiO_2

In order to enhance extraction efficiency, the concentration of GO/TiO_2 must be high enough to extract the rutin as completely as possible. So, we optimized the amount of particles by testing concentration of 2, 3, 4, 5ÿ6, 7, and 8 mg. The results showed that more rutin could be extracted as the amount of GO/TiO_2 particles increased. When the amount reached to 6 mg, the curves turned out to be flat, and there was no distinct increase to extraction efficiency. So, we selected 6 mg GO/TiO_2 as the optimized amount.

Effect of extraction time

Extraction time is also an important parameter which affects the efficiency to a large extent. In this work, different extraction time (20, 30, 40, 50, 60, 70, and 80 min) was optimized. The results showed that the extraction efficiency increased when extraction time prolonged. For rutin, the efficiency increased intensely before 75 min, and the curve flattened out from 20 min to 60 min. It can be considered that extraction balance between water phases and sorbent was nearly reached after 60 min. Hence, we selected 75 min as the best extraction time in the following work.

Adsorption capacity

At pH 5.5, the adsorption capacities of GO/TiO_2 toward rutin were investigated as illustrated in the adsorption isotherms. For rutin, an increase of the adsorption amount of rutin is observed with the increase of rutin concentration. The results indicated that the adsorption behavior of rutin onto the GO/TiO_2 surface fited Langmuir adsorption model, the maximum adsorption capacity of GO/TiO_2 to rutin were deduced to be 59.5 mg/g.

Effect of desorption solvent

Different desorption solvents including HCl, NaOH, and sodium borate were tested. The experimental results showed that the 0.2 mol/L of NaOH as the eluent offered the higher recoveries of analytes. So, this data indicated that NaOH provided the best desorption efficiency due to its strongest dissolving ability toward analytes.

Analytical approach

Under the optimized conditions, the linearity of the calibration curves was in the range of 15.0–200 µg/L for rutin in samples. Satisfactory determination coefficients (r^2) (>0.9990) for rutin were obtained. The limits of detection (LODs, S/N=3) and limits of quantification (LOQs, S/N=10) were found to be 8.0 µg/L and 28.0 µg/L, respectively.

Real samples analysis

The development method was applied to the determination of rutin in human urine samples. The results showed that human urine samples were free of rutin. To validate the established method in real samples, the human urine samples were spiked rutin at three levels of 20, 50, and 100 µg/L, respectively. The recoveries were 93.1–107.6%. The intra- and inter-day reproducibilities (RSDs) were calculated with rutin spiked at 20, 50 and 100 µg/L. Five parallel extractions of a sample solution over a day gave the intra-day RSDs, and the inter-day RSDs were determined by extracting sample solutions that had been independently prepared for contiguous days. The intra- and inter-day RSDs were in the range of 5.3% and 9.2%, respectively, which indicated the acceptable reproducibility.

CONCLUSION

In this work, GO/TiO_2 composite was synthesized and successfully applied for the enrichment of rutin in human urine samples. The maximum adsorption capacity for rutin was calculated to be 59.5 mg/g according to the Langmuir adsorption isotherm, which makes GO/TiO_2 to be the potential adsorbents in the application of enrich rutin from real samples. The developed approach offered wide linear range, and good reproducibility. Owing to the diverse structures and unique characteristic, GO/TiO_2 possesses great potential in the enrichment and analysis of trace rutin in real aqueous samples.

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How to cite this article:
Gaeeni MR, Sasani Ghamsari M, Tohidian M, Majles Ara MH. Synthesis of graphene oxide-TiO_2 nanocomposite as an adsorbent for the enrichment and determination of Rutin. Nanomed. J., 2015; 2(4): 269-272.