

 **Journal of Food Science and Technology (Iran)**

**Homepage:www.fsct.modares.ir**

**Scientific Research**

#### **Application of multi-walled carbon nanotubes as sorbents for the extraction of flavonoids from Grapefruit peel**

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# **1-Introduction**

Citrus fruits, such as oranges, lemons, and grapefruits, are good sources of natural antioxidants and nutraceuticals, including ascorbic acid, flavonoids, and phenolic compounds [1,2]. Much waste is produced while producing citrus juice, such as grapefruit juice [3]. Consequently, there is interest in turning these waste products into valuable food ingredients to enhance economic viability, reduce environmental impacts, and ensure the food industry's sustainability. The peels of citrus fruits contain relatively high flavonoids, which are valuable as natural antioxidants and nutraceuticals [4]. Grapefruit has attracted considerable attention recently due to its beneficial biological activities [5]. Grapefruit peel contains relatively high bioactive flavanone glycosides, such as naringin and narirutin [6]. Naringin has exhibited antiulcer, anti-inflammatory, superoxide scavenging, and antioxidation properties [7, 8]. There is interest in using grapefruit peel flavonoids as nutraceutical ingredients to enhance human health and well-being [5].

Several approaches have been used to extract flavonoids from citrus fruit peels, including sonication [9], eutectic solvents [10], resins [11], supercritical fluids [12], and adsorption methods [13]. Adsorption methods are cost-effective and easy to implement because they do not require sophisticated equipment or processing operations commercially. Nanomaterials have been utilized as a sorbent in various branches for the qualitative and quantitative recognition of multiple complexes, such as for detecting flavonoids [14, 15], fungi [16], proteins and drugs [17], pesticides [18], toxic dyes [19], toxic metals [20], etc. Also, various nanomaterials such as siliconand carbon-based nanomaterials, metallic and metal oxides, and polymer-based nanocomposites have been used to extract and preconcentrate chemical species before determination by various analytical

techniques [17]. The potential applications of carbon nanomaterials as stationary phases can be found substantially in the field of chromatography, including gas<br>chromatography (GC), capillary  $chromatography$   $(GC)$ , electrochromatography (CEC), liquid chromatography (LC), and high-<br>performance liquid chromatography liquid chromatography (HPLC) [15]. Carbon nanotubes (CNTs) have been identified as effective adsorbent materials due to their high surface areas and strong preferential surface interactions, which lead to rapid, potent, and selective isolation of substances in complex mixtures [14]. The study's main objective was to determine the potential of using carboxylated multi-walled carbon nanotubes (MWCNT-COOH) to extract flavonoids from grapefruit peel.

# **2-Materials and methods**

# **2.1. Preparation of the Grapefruit peel extract**

Grapefruit peel extracts were prepared using the method used by Gholizadeh et al. (2019) [15]. Briefly, medium-weight pink grapefruits (Citrus Paradisi) were collected, washed with water, and manually skinned. The peels were then dehydrated in a vacuum oven at 40 °C for 48 h. The dried peels were milled using a hammer mill (Molinex) to form a grapefruit peel powder (GPP), packed, and stored in a sealed container at four °C.

At an ultrasonic (ROHS- Korea) bath, five grams of GPP were dispersed into 30 mL of the ethanol-water mixture  $(70:30, v/v)$  in an Erlenmeyer for 30 min at 25 °C. The suspension was filtered by vacuum filtration, and the remaining powder was extracted two times using 25 ml of the ethanol-water mixture (70:30, v/v). Subsequently, the filtrate was placed in a volumetric flask (100 mL), and the volume was adjusted to 100 mL using the ethanolwater mixture (70:30, v/v).

# **2.2. Effect of pH on the sorption process of the flavonoids**

Fifteen mg of purchased MWCNT-COOH was mixed with 10 mL of grapefruit peel extract by a magnetic stirrer. The pH was adjusted to a different value (3, 5, 7, or 9) using nitric acid or sodium hydroxide, depending on the treatment. After mixing the sample for an hour, MWCNT-COOHflavonoids were separated by centrifuge (2500 rpm) (Centric 220 CF, Domel). Experiments were carried out in triplicates. The percentage of flavonoids adsorbed to the carbon nanotubes was calculated by measuring the absorbance of the solution at wavelengths of 260 and 280 nm (lambda max of Rutin and Naringin respectively) using a UV-visible spectrometer (7310, Jenway, South Korea).

$$
\%A = \frac{A_I - A_F}{A_I} \times 100\tag{1}
$$

Where  $\%A$ ,  $A_I$  and  $A_F$  are the adsorption percentage of flavonoids, initial absorbance, and final absorbance, respectively.

#### **2.3. Desorption of MWCNT-COOHflavonoids**

The MWCNT-COOH-flavonoids complexes from the extract were dispersed in 10 mL of ethanol-water  $(70:30, v/v)$ solutions to maintain the equilibrium between the two phases and to avoid any changes in the chemical properties of the sorbent or the sorbate with pH values 3, 5, 7, or 9, depending on the treatment, and then stirred for an hour. The flavonoids were filtered by centrifuge and measured using high-performance liquid chromatography (HPLC). The HPLC instrument (Agilent Technologies 1200) was equipped with a quaternary solventdelivery system with an autosampler, a separating column (Agilent Zorbax SB-C18 column,  $100 \times 4.6$  mm, five μm particle size), and a UV detector. The mobile phase components were methanol (A) and 0.1% acetic acid (B). The separation protocol is described in Table 1. The re-equilibration time between runs was set to 10 min. Experiments were carried out at 30 °C (column oven temperature) at a flow rate of 0.6 mL.min−1 and an injection volume of 5 μL. Chromatography peaks were identified by comparing their retention times with known standard samples (Rutin, Naringin, and Catechin). Diode-array detection (DAD) was used to perform a spectral scan of the HPLC peaks from 254–360 nm. All chromatography operations were carried out at an ambient temperature and in triplicate. The linearity of the method was established using five naringin concentrations (from 10 to 50 mg/L) evaluated in triplicate. The calibration curve for naringin was modeled using a linear equation of Y =  $1.515X + 10.517$ , R<sup>2</sup>  $= 0.9958$ , where X is the naringin concentration, and Y is the peak height**.**

Time(min.)	Mobile Phase-A (methanol)	Mobile Phase-B $(0.1\% \text{ acetic acid})$
00:00		85
04:00	30	70
08:00	45	55
12:00	65	35
16:00		55
20:00	30	70
24:00		

Table1. HPLC gradient solvent program

# **2.4. Batch sorption experiments of naringin**

Naringin was one of the main flavonoids of Grapefruit peels. This substance has been employed as an indicator to achieve a more practical knowledge of the process of flavonoid absorption. A 10 mL ethanol/water solution series contained 100 mg/L of naringin and different pH values (3-9). Fifty mg of MWCNT-COOH was then added to each of these solutions. The fraction of naringin that adsorbed to the carbon nanotubes was then determined by measuring the concentration before and after adding them. In addition, adsorption isotherms were established by preparing 10 mL solutions containing a range of naringin concentrations (10-100 mg.L-1) but a constant MWCNT-COOH concentration (5000 mg.L-1) and then agitating for 90 minutes. The fraction of naringin removed from the solutions due to adsorption to the carbon nanotubes was then determined by measuring the absorbance of the keys using a UV-visible spectrometer at wavelengths of 260 and 280 nm [21].

Removal 
$$
\% = \frac{C_I - C_F}{C_0} \times 100\%
$$
 (2)

$$
q_S = \frac{(c_I - c_F) \times V}{m} \tag{3}
$$

Here, C*<sup>1</sup>* and C*<sup>F</sup>* are the initial and final concentrations (mg.L-1) of naringin in the aqueous solution determined by UV-visible spectroscopy. Respectively, *V* (L) is the volume of the naringin solution, *m*(g) is the weight of the sorbent, and qs is the sorption<br>ability (mg.g-1). Kinetic investigations  $(mg.g-1)$ .Kinetic investigations were also carried out by measuring the change in naringin adsorption over time. Kinetic studies were achieved by measuring the absorbance of the solutions after the MWCNT-COOH was separated. All experiments were carried out at ambient temperature  $(25\pm1$  °C).

# **2.5. FTIR analysis**

Fourier-transform infrared spectroscopy (FTIR) identifies the functional groups available on the adsorbent. This functional group analysis helps understand the adsorption mechanism that promotes flavonoids' adsorption process. The FTIR spectra of the MWCNT-COOH samples were characterized using an FTIR spectrometer (Thermo Nicolet Nexus 870, Triad Scientific, Waltham, Massachusetts) with KBr pellet technique in the

wavelength range of 4000 – 650 cm-1 with a resolution of 0.5 cm-1.

# **2.6. Thermal analysis**

Information about the presence of surface functional groups on the carbon nanotubes was obtained by measuring their change in mass when 5 mg of samples were heated up to 1000  $\mathrm{C}$  at a constant rate (10  $\mathrm{C}$ .min-1) by 0.1 micrograms resolution using a thermogravimetric analysis (TGA) instrument (Netzsch TG 209 F1 Iris1, Netzsch, Berlin, Selb, Germany) under a nitrogen gas atmosphere. This method is based on the fact that the surface groups are thermally degraded at a lower temperature than the carbon nanotubes.

# **2.7. FESEM analysis**

The morphology of the samples was investigated by Field-emission scanning electron microscopy (FESEM) (MIRA3\\TESCAN-XMU model, TESCAN, Czech Republic). This characterization method shows the size and shape of the nanoparticles. Before analysis, each sample was sputter-coated with gold, and the magnification was  $200 \times$  for images under an accelerating voltage of 5 kV.

## **2.8. Impact of pH on flavonoid adsorption**

The experimental protocol used to determine the impact of pH on flavonoid adsorption is shown schematically in Figure 2a. After separation from the carbon nanotubes, UV-visible spectrophotometry and gravimetric analysis measured the concentration of non-adsorbed flavonoids in the aqueous phase.

# **2.9. Adsorption isotherms**

The Dubinin-Radushkevich (D-R) isotherm assumes that the binding sites on the absorbent surfaces are heterogeneous and that binding occurs with Gaussian energy distribution [22, 23]. The following equations describe the D-R model:

$$
ln(q_e) = ln q_m - K_{DR} \varepsilon^2(4)
$$

$$
\varepsilon = RT\ln\left(1 + \frac{1}{c_e}\right) \tag{5}
$$

Here,  $q_e$  (mg. g-1) is the amount of naringin adsorbed, *q<sup>m</sup>* (mg.g-1) is the maximum amount of naringin absorbed, KDR (mol2. kJ2) is the D-R isotherm constant,  $\varepsilon$  is Polanyi potential,  $R$  is the gas constant  $(0.008314 \text{ kJ} \cdot \text{(mol. K)}-1)$ , and T (K) is the absolute temperature (K). The mean free energy,  $E$  (kJ.mol-1), of adsorption can be calculated using the following equation [24]:

$$
E = \frac{1}{\sqrt{2K_{DR}}} (6)
$$

#### **3- Result and discussion**

#### **3.1. Characterization of carbon nanotubes**

The FTIR spectrum of the MWCNT-COOH had peaked at 1722, 3427, 1626, and 1000-1450 cm-1 (Figure 1a), which can be attributed to C=O, OH, C=C, and C-O stretching vibrations, respectively. These functional groups are consistent with carboxyl groups on the carbon nanotubes.



**Figure 1a. FT-IR spectra (after baseline correction) of MWCNT–COOH.**

Thermal gravimetric analysis (TGA) and derivative thermogravimetry (DTG) provided information about whether or not the carbon nanotubes adsorbed flavonoids. As shown in Figure 1a, there was only a slight decrease in the mass of the MWCNT-COOH samples during heating from 30 to 680 °C, which indicated the solid thermal stability of the carbon nanotubes. In contrast, there was a substantial reduction in the MWCNT-COOH-flavonoid complexes during heating, with an 18.3%

mass loss from around 140 to 400 °C. This reduction was assigned to the thermal degradation of flavonoids adsorbed to the surfaces of the MWCNT. This hypothesis was based on the mass loss-temperature profile of the grapefruit peel powder (GPP), which showed a reduction in mass over a similar temperature range as the MWCNT-COOH-flavonoid complexes. The DTG plots provided insights into the temperature ranges where specific thermal evaporation or degradation events occurred in the samples (Figure 1b). Prominent peaks were observed around 203 and 343 °C in the DTG plots for the MWCNT-COOHflavonoid complexes, which were similar to those observed for the GPP samples, again suggesting that the mass loss from the complexes was due to the thermal decomposition of flavonoids. These results indicate that valuable information about the adsorption of flavonoids to MWCNT-COOH sorbents can be obtained from TGA and DTG data.

Scanning electron microscopy images of the microstructures of the carbon nanotubes before and after flavonoid absorption were acquired (Figure 1c). These images show that both samples comprised a network of entangled and agglomerated fiber-like structures. The diameter of the fibers in the MWCNT-COOH-flavonoid samples was greater than that in the MWCNT-COOH ones, which is consistent with the presence of a layer of adsorbed flavonoids on the surfaces of the carbon nanotubes.





**MWCNT-COOH** 

**MWCNT-flavonoids** 

## **Figure 1b-c. TGA and SEM (after baseline correction) of MWCNT–COOH.**

**3.2. Impact of pH on flavonoid adsorption**

Figure 2b shows UV-visible spectra of the non-adsorbed flavonoid solutions separated from the MWCNT-COOH-flavonoid complexes after incubation at various pH values. The absorbance increased with decreasing pH value, which indicates that more flavonoids were adsorbed to the surfaces of the MWCNT-COOH at lower pH values [25]. The percentage of adsorbed flavonoids at pH 3, 5, 7, and 9 were calculated to be 43%, 32%, 23%, and 20 %, respectively. These results suggest a stronger attraction between the flavonoids and carbon nanotubes under acidic conditions than basic ones, which may have been due to changes in the ionization of the charged groups. The carboxyl groups on the carbon nanotubes are negatively charged (- COO-) at high pH values but neutral (- COOH) at low pH values. At high pH values, the hydroxyl groups on the flavonoids may gain some negative charge, leading to electrostatic repulsion between them and the carbon nanotubes, thereby reducing their adsorption. Alternatively, the them and the carbon nanotube surfaces.

deprotonation of the carboxyl groups at high pH values may have disrupted hydrogen bond formation between the flavonoids and MWCNT-COOH. The water in the extract solutions was evaporated after the adsorption process to assess the impact of pH on the concentration of non-adsorbed flavonoids (Figure 2a). The remaining extract mass was measured (Figure 3a), and the percentage of the extract adsorbed to the carbon nanotubes was (Figure 3b). Consistent with the UV-visible measurements, the fraction of flavonoids that had adsorbed to the carbon nanotubes decreased with increasing pH. Overall, these results show that the best solution to remove the flavonoids from the keys is pH three, increasing the attraction between

**.**



**Figure 2a-b shows UV-visible spectra of the non-adsorbed flavonoid solutions separated from the MWCNT-COOH-flavonoid complexes after incubation at various pH values**



## **Figure 3 a-b. Percentage of the extract adsorbed to the carbon nanotubes in ph different**

## **3.3. Desorption efficiency of flavonoids from MWCNT-COOH-flavonoid complexes**

Once flavonoids have been adsorbed to the sorbent, it is shown that they can be successfully removed. Therefore, the impact of pH on the desorption of flavonoids from MWCNT-COOHflavonoid complexes was assessed (Figure 4). The desorption of the flavonoids increased with increasing pH, with the

highest value (around 91%) being obtained at pH 9 (Figure 4a). Moreover, the adsorption-desorption cycling efficiency of the carbon nanotubes was assessed. The MWCNT-COOH-flavonoids could be utilized multiple times since the adsorption of the flavonoids only dropped by around 8% after five cycles (Figure 4b). These experiments highlight the potential to utilize carbon nanotubes numerous times for separating flavonoids from solutions.



**Figure 4 a-b. Desorption efficiency of flavonoids from MWCNT-COOH**

## **-flavonoid complexes**

# **3.4. Impact of flavonoid type on adsorption**

HPLC analysis was used to determine the type of flavonoids extracted from the grapefruit extract solutions using carbon nanotubes (Figure 5). The chromatograms obtained indicated three main flavonoids within the initial grapefruit extract powder: naringin, quercetin, and rutin, with naringin being the dominant one (Figure 5a). These flavonoids were also observed in the chromatographs of the materials isolated from the dissolved grapefruit extract using carbon nanotubes (Figure 5b).

The identity of the different flavonoids was determined by running standards containing naringin, rutin, and quercetin (Figure 5c). The carbon nanotubes calculated the percentage of naringin,

quercetin, and rutin extracted from the grapefruit extract powder was about 49%, 90%, and 78%, respectively. Since naringin was the principal constituent in the grapefruit extract, further studies were conducted to provide more insights into the adsorption mechanism of this flavonoid.



**Figure 5. HPLC analysis was used to determine the type of flavonoids extracted from the grapefruit extract solutions using carbon nanotubes.**

# **3.5. Characterization of naringin adsorption**

#### **3.5.1. Impact of pH**

In this series of experiments, the influence of pH on the adsorption capacity of the carbon nanotubes (MWCNT-COOH) was measured (Figure 6a). As with the total flavonoids, there was a decrease in the fraction adsorbed as the pH increased, which can be attributed to the weakening of the attractive interactions between the naringin and the surfaces of the carbon nanotubes higher pH values. As mentioned earlier, there may have been an electrostatic repulsion between the anionic carboxyl groups on the carbon nanotubes and the flavonoids at higher pH values, which opposed adsorption. Previous studies have

also shown a decrease in the solubility of flavonoids with decreasing pH, which may also have contributed to this effect. We used pH 3 for the adsorption studies in the remainder of the experiments because the most substantial adsorption occurred.

#### **3.5.2. Impact of carbon nanotube dose**

In this series of experiments, we examined the impact of carbon nanotube mass on the efficiency of naringin extraction (Figure 6b). The adsorption percentage of naringin by the carbon nanotubes increased with increasing dose, from around 0.7% to 66%, when the MWCNT-COOH concentration increased from 0.01 to 0.10 g. This increase can be attributed to the more accessible surface sites on the carbon nanotubes at higher concentrations.



**Figure 6 a-b. Influence of pH and mass on the efficiency of naringin extraction on the adsorption capacity of the carbon nanotubes (MWCNT-COOH)**

#### **3.6. Proposed adsorption mechanism of naringin by carbon nanotubes**

A schematic diagram of the two main mechanisms responsible for naringin adsorption to the carbon nanotubes is shown in Figure 7. First, hydrogen bond formation is likely between the hydroxyl and carbonyl groups on the naringin and

MWCNT-COOH. Second, there are likely to be  $\pi$ - $\pi$  interactions between the double bonds in the naringin and MWCNT-COOH. The deprotonation of the carboxylic acid groups on the surfaces of the carbon nanotubes at high pH values may have disrupted these interactions, leading to the observed weaker adsorption under neutral and alkaline conditions.



**Figure 7. Schematic diagram of the two main mechanisms responsible for naringin adsorption to the carbon nanotubes**

#### **3.7. Adsorption isotherms**

Further insights into the mechanism of naringin adsorption were obtained by fitting three adsorption isotherm models to the experimental data: the Langmuir, Freundlich, and Dubinin-Radushkevich models (Table 2). The Langmuir adsorption isotherm assumes that each binding site has the same monolayer coverage of the adsorbent surface [20]. The Freundlich model accounts for heterogeneous surfaces and multilayer adsorption [21]. Based on the correlation coefficient, the Freundlich model was the best isotherm model for describing naringin adsorption to the carbon nanotubes (Table 2). This result suggests that the naringin may have adsorbed as multilayers. According to Table 2, the value of  $E$  was 0.219 kJ/mol, indicating that the adsorption of naringin to MWCNT-COOH was due to physical (rather than chemical) interactions since free energy below eight kJ/mol is considered to be physical adsorption [14].

Table 2. Parameters of pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models naringin sorption onto MWCNTs-COOH. Temperature, 298 K; initial naringin concentration, 50 mg L-1 ; mass of MWCNTs, 50 mg; volume of solution, 10 mL; and pH of the sample solution, 3.0.



#### **3.8. Adsorption efficiency of naringin from model solution and grapefruit peel extract**

In these experiments, we compared the adsorption efficiency of naringin onto the carbon nanotubes (MWCNT-COOH) from

a model solution (50 ppm naringin) and from a solution containing grapefruit peel extract (20.85 ppm naringin) under similar conditions (solution volume: 10 ml; carbon nanotube dosage: 50 mg; contact time: 90 min). In both cases, the adsorption efficiency was around 49%, suggesting that the results obtained for the model solutions should also apply to the grapefruit peel extract (Table  $\overline{5}$ ).





## **4- Conclusion**

Carboxylated carbon nanotubes (MWCNT-COOH) were suitable for separating flavonoids from grapefruit peel extracts. The adsorption of the flavonoids onto the carbon nanotubes was higher under acidic conditions, mainly attributed to an increase in hydrogen bonding and a decrease in electrostatic repulsion. Conversely, the

#### **Declaration Statements**

## **Ethical Approval**

This manuscript does not report the use of any animal or human data or tissue.

#### **Competing interests**

The authors have no relevant financial or non-financial interests to disclose.

#### **Funding**

No funding was received to assist with the preparation of this manuscript.

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desorption of the flavonoids from the carbon nanotubes was higher under alkaline conditions because of the weakening of attractive interactions. The carbon nanotubes were shown to have good reusability, with the adsorption/desorption efficiency were 83% after five cycles. Therefore, carbon nanotubes may be useful for constructing filters to separate valuable bioactive components from the food waste streams.

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استفاده از نانولوله های کربنی چند جداره به عنوان جاذب برای استخراج فلاونوئیدها از پوست گریپ فروت

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