18th National and 3rd International Conference of Iranian Biophysical chemistry
هجدهمین همایش ملی و سومین همایش بین المللی بیوشیمی فیزیک ایران
25-26 Des, 2024, University of Hormozgan
۶-۵ دی ماه ۱۴۰۳، دانشگاه هرمزگان

UIO66-NH_2@PANI nanocomposite for the adsorption of antiradical biomolecule quercetin: A kinetic and thermodynamic insight

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Abstract

In this study, the UIO66-NH_2@PANI nanocomposite was synthesized using a straightforward step-by-step self-assembly method and tested for its selective adsorption of the biomolecule quercetin. The synthesized nanocomposite underwent comprehensive analysis using FTIR and TGA techniques. The adsorption kinetics and thermodynamics of the magnetic nanocomposite for quercetin were rigorously investigated. The results indicated that the experimental data for adsorption kinetics was well-described by the pseudo-second-order kinetic model. Additionally, the effect of temperature analysis revealed that the adsorption of quercetin onto UIO66-NH_2@PANI is a spontaneous process ($\Delta G^\circ < 0$) and exothermic ($\Delta H^\circ < 0$).

Key words: Biomolecule quercetin, kinetics, nanocomposite, Thermodynamics, Adsorption

1. Introduction

Flavonoids are one of the most important polyphenolic compounds [1]. This group of plants due to their antioxidant, anti-tumor, antiviral, anti-bacterial activities and immune-modulatory properties and also, low toxicity and environmentally friendly characteristics have been used in the treatment of numerous diseases [2].

Quercetin (Figure 1) is a polyphenolic bioflavonoid and is knowned an anti-allergic, anti-inflammatory, antiviral, anti-obesity, and anti-carcinogenic compound [3]. The antioxidant quercetin, with the scientific name 3,5,7,3',4'-pentahydroxyflavone is structurally composed of 15 carbon skeleton consisting of two benzene rings, a heterocyclic pyrane and five hydroxyl groups [4]. Flowers, many fruits and vegetables are rich in quercetin. Tere are many routine methods for extraction of active compounds from plants. However, these methods have limitations due to their complexity, time-consuming, high costs, and low efficiency [5]. For example, solid phase extraction (SPE) is the most popular extraction method used to separation flavonoids [2] but, its disadvantages, it can be mentioned that it is time-consuming and the possibility of not dissolving small amounts of analyte and as a result of its inefficient extraction. Therefore, a new effective extraction method can be designed as adsorbents that absorb antioxidant molecules of medicinal plants. [6]. Recently, the use of nanotechnology has solved the problems and limitations. Nanomaterials have a high absorption capacity due to the large surface area and functional groups to create activity sites [7]. So, nanocomposites can be introduced as new absorbents. Recently, metal-organic framework (MOF) materials have attracted much attention. Metal-organic frameworks (MOFs) are a novel class of inorganic-organic hybrid porous materials, created by linking metal ions or inorganic cluster nodes with organic linkers through strong coordination bonds [8]. In recent years, the use of MOFs has garnered significant attention. This interest is due to their unique characteristics, including large surface area, exceptional thermal and chemical stability, tunable pore size, and ease of functionalization [9]. On the other hand, utilizing polymers and their functional groups can create additional active sites for interaction with the target molecule, thereby enhancing the surface area of the adsorbent. Integrating metal-organic frameworks (MOFs) into polymers has the potential to further improve the efficiency of the adsorbent.

This study examined the preparation and identification of a metal-organic framework nanocomposite composed of polyaniline and UIO66-NH_2 using an in situ method. The produced nanocomposite was utilized for the selective adsorption of the quercetin from non-aqueous solutions. Subsequent batch adsorption experiments were conducted to investigate the kinetics and thermodynamics of the quercetin adsorption process.

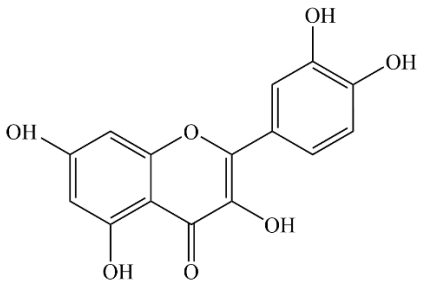

Figure 1 : Molecular structure of quercetin

2. Experimental

2.1. Adsorption experiments

The adsorption efficiency of UIO66-NH_2@PANI nanocomposite for quercetin from organic/aqueous solution was investigated through batch adsorption experiments. 20 mg of UIO66-NH_2@PANI was added to a 30 mL vial containing 10 mL of quercetin solution (20 mg/L). The obtained mixture was stirred for 100 minutes, and after separating the nanoabsorbents from the reaction medium, the remaining concentration of quercetin was analyzed with a UV-Vis spectrophotometer. A calibration curve for quercetin was generated by measuring its absorbance maximum at 373 nm (Figure 2). Results from three separate experiments were averaged and reported accordingly.

Specifically, the adsorption efficiency (R%) of UIO66-NH_2@PANI for quercetin was calculated using a designated equation, while another equation was utilized to determine the equilibrium adsorption capacity (q_e, mg/g) [10]:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100$$

$$q_e = \frac{(C_0 - C_e)}{W} \times V$$

where C_0 (mg/L) and C_e (mg/L) represent the initial and equilibrium concentrations of quercetin, respectively, and V (mL) and m (mg) denote the volume of the quercetin solution used and the amount of UIO66-NH_2@PANI, respectively.

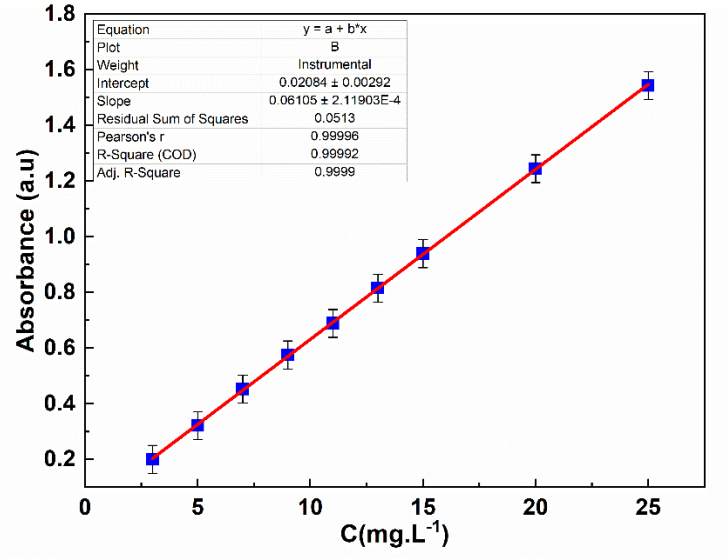

Figure 2 : Calibration Quercetin (3-25 mg/L)

3. Results and discussion

3.1. Characterization of UIO66-NH_2@PANI nanocomposite

3.1.1. FT-IR

A broad absorption peak seen above 3400 cm^{-1} in all samples consistently indicates the vibration of the O-H group associated with either the samples or water. The FT-IR spectrum of PANI shows peaks at 1574 cm^{-1} and 1499 cm^{-1}, corresponding to the stretching vibrations of the quinoid ring (Q) and benzenoid (B), respectively. Additionally, there is a low-intensity band at 1339 cm^{-1}, which is attributed to the stretching of C-N bonds adjacent to the quinoid ring (C-N=Q=N-C). The band at 1303 cm^{-1} is associated with the stretching of C-N bonds in secondary aromatic amines [11], and/or the displacement of π electrons caused by the acid doping of the polymer.

In the FT-IR spectrum of UIO66-NH_2, the most prominent peak at 1579 cm^{-1} relates to the reaction between -COOH groups and Zr^{4+} ions. Furthermore, the peak at 3430 cm^{-1} corresponds to the NH_2 group present in the organic linker (2-aminoterephthalic acid) [12].

The presence of all the peaks associated with materials UIO66-NH_2 and PANI in the nanocomposite spectrum indicates that the synthesis of the nanocomposite was successful.

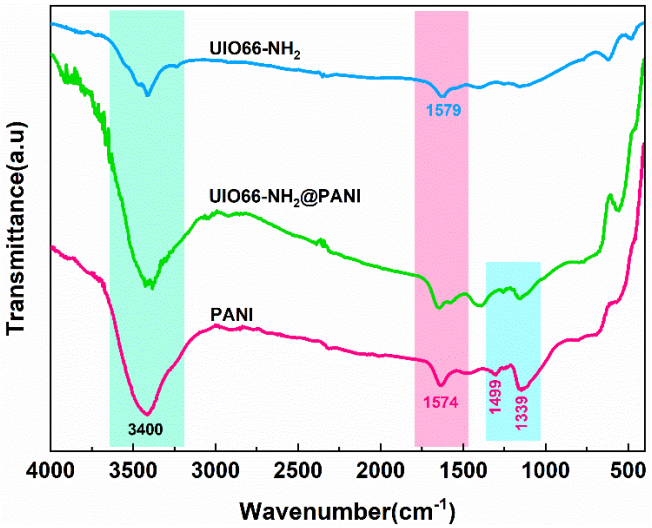

Figure 3 : FT-IR spectra of the UIO66-NH_2, PANI and UIO66-NH_2@PANI

3.1.2. TGA

The thermal degradation of UIO66-NH_2 occurs in three stages. The first stage, which takes place at temperatures below 200 °C, results in a 2.719% weight loss attributed to the evaporation and removal of water from the MOF. The second stage, occurring between 200 and 400 °C, shows a weight loss of 20.397%, likely due to the breakdown of amino groups in UIO66-NH_2. In the third stage, at temperatures ranging from 400 to 800 °C, the weight of UIO66-NH_2 decreases by approximately 12.893% as a result of the decomposition of the 2-aminoterephthalic acid ligands within the MOFs.

In the TGA curves of the PANI (Figure 4) observeed a three-step weight loss. The initial weight loss occurs at 100 °C, which is attributed to the evaporation of water that has been absorbed. The second weight loss, occurring between 100 and 350 °C, is probably due to the decomposition of the dopant. The third weight loss, beginning at approximately 350 °C, is associated with the degradation and breakdown of PANI's backbone units, leading to the generation of substituted aromatic fragments. The thermogram of the UIO66-NH_2@PANI sample shows a three-stage weight loss pattern that is similar to that of PANI and UIO66-NH_2.

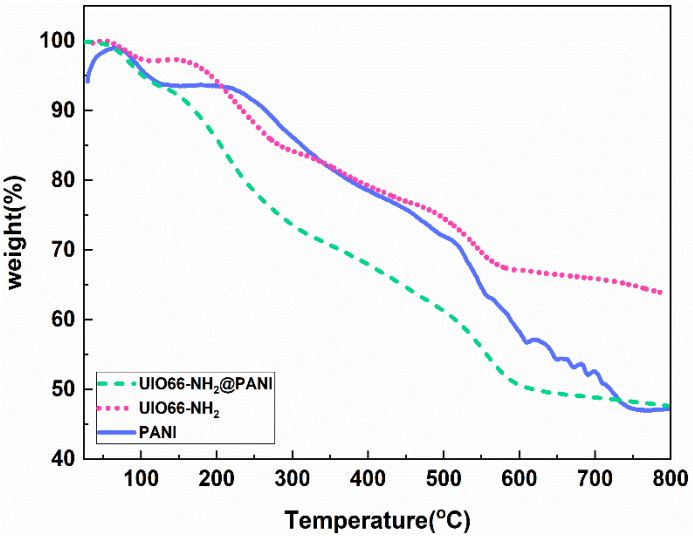

Figure 4 : TGA thermogram of the UIO66-NH_2, PANI and UIO66-NH_2@PANI

3.2. Adsorption kinetics

In the context of adsorption, reaction kinetics refers to the temporal changes in the process of adsorbing substances onto the surfaces of adsorbents. By analyzing adsorption kinetics, researchers can identify the limiting phases, rate mechanisms, and the time required to reach equilibrium. The adsorption efficiency of UIO66-NH_2@PANI gradually increased with longer adsorption times, as illustrated in Figure 5, reaching equilibrium at around 100 minutes. This analysis aids scientists in exploring various kinetic models to select the most suitable one for describing the adsorption process.

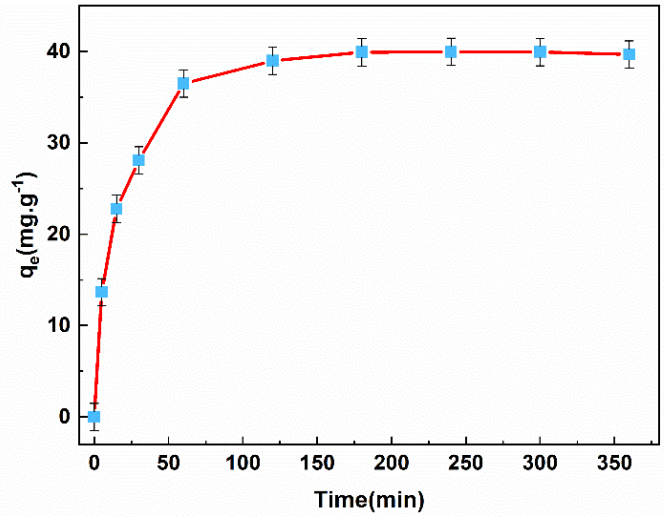

Figure 5 : Adsorption kinetic profile of UIO66-NH_2@PANI nanocomposite

The Pseudo-First-Order (P.F.O) model is a commonly used kinetic model to describe the rate of adsorption processes. It assumes that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. This model is often used when the initial concentration of the adsorbate is low and the adsorption process occurs primarily on the outer surface of the adsorbent. The P.F.O model helps in understanding the kinetics of adsorption and in determining the rate at which adsorption occurs [13].

The Pseudo-Second-Order (P.S.O) Model is a kinetic model used to describe the adsorption process where the rate of adsorption is dependent on the square of the amount of adsorbate adsorbed. This model is applicable when the adsorption process is not limited to the initial phase. In this model, the rate of adsorption is assumed to be proportional to the square of the difference between the equilibrium adsorption capacity and the amount adsorbed at any given time. The P.S.O model is useful for characterizing adsorption processes that involve chemisorption, where adsorption sites are limited and each site can accommodate only one molecule [14]. As shown in Figure 6, the comparative analysis of the coefficient of determination (R^2) values reveals that the pseudo-second-order model provides an excellent fit, with the highest R^2 value of 0.9994. This strong correlation between the experimental data and the model indicates that chemisorption predominantly controls the adsorption process.

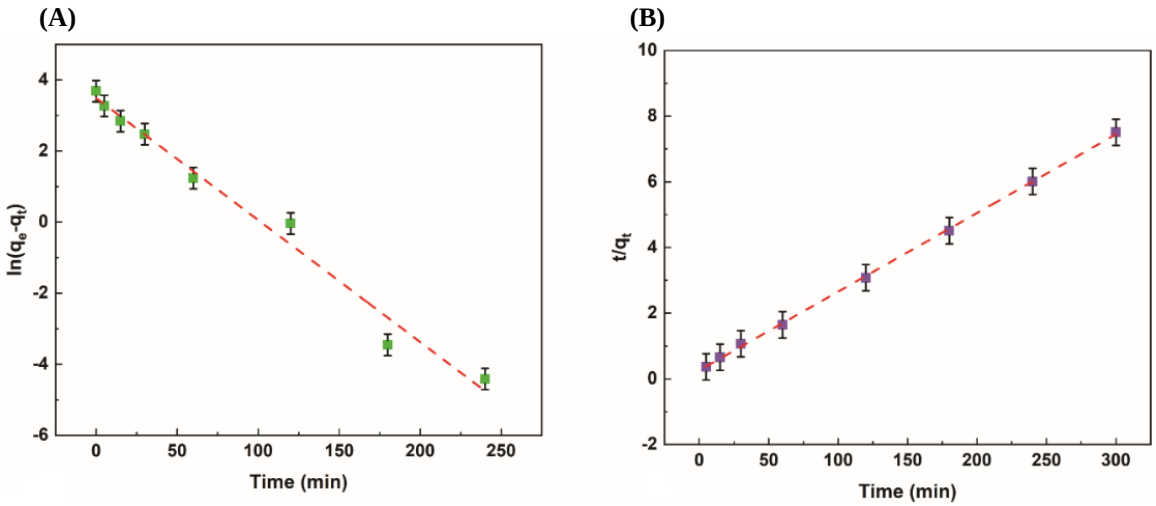

Figure 6 : Plots of kinetics model P.F.O (A), P.S.O (B)

Table 1: Adsorption kinetics parameter

Kinetic model	equation	Parameters		
P.F.O	$\ln(q_e-q_t)=\ln q_e-k_1 t$	q_e (mg.g^{-1})	k_1 (min^{-1})	R^2
		32.7836	3.432×10^{-2}	0.9803
P.S.O	$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{1}{q_e}t$	q_e (mg.g^{-1})	k_2 (g.mg^{-1}.min^{-1})	R^2
		41.7536	2.202×10^{-3}	0.9994

3.4. Adsorption thermodynamics

The research investigated the variation in biomolecule quercetin adsorption on the UIO66-NH_2@PANI nanocomposite under different equilibrium conditions at temperatures of 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15 K. The aim was to investigate the temperature dependence of the adsorption process and calculate thermodynamic parameters such as the standard Gibbs free energy change (kJ/mol), enthalpy change (kJ/mol), and entropy change (kJ/mol.K). The values for ΔG°, ΔH°, and ΔS° and K_c were determined using specific equations:

$$K_c=\frac{q_e}{C_e}$$

$$\Delta G^\circ=-RT\ln K_c$$

$$\ln K_c=-\left(\frac{\Delta H^\circ}{R}\right)\frac{1}{T}+\left(\frac{\Delta S^\circ}{R}\right)$$

T (K) represents the absolute temperature, R (J/mol.K) signifies the universal gas constant, and K_c stands for the thermodynamic equilibrium constant [15].

Table 3 reveals that all ΔG◦ values are negative (ΔG◦ < 0) at different temperatures, indicating that the adsorption of quercetin is favorable, spontaneous, and feasible. Moreover, the decline in ΔG◦ values with increasing temperature suggests that quercetin adsorption onto UIO66-NH_2@PANI becomes more favorable at higher temperatures. The negative ΔH◦ and ΔS◦ values imply that the process is endothermic. The negative entropy change (ΔS◦) suggests a reduction in disorder, likely due to a more organized arrangement of quercetin molecules at the adsorbent surface, which can result from specific interactions between the nanocomposite and the quercetin molecules.

Figure 7 shows the thermodynamic graph related to the adsorption of quercetin onto the nanocomposite. Also the thermodynamic parameters of adsorption are presented in Table 2. According to this table, the negative ΔG° values indicate that the adsorption of quercetin onto the nanosorbent is a spontaneous process. Furthermore, the negative change in entropy during the adsorption of quercetin on the UIO66-NH_2@PANI surface implies a decrease in randomness and a more ordered arrangement of quercetin molecules on the adsorbent surface. Similarly, the negative change in enthalpy indicates that the adsorption of quercetin is an exothermic process.

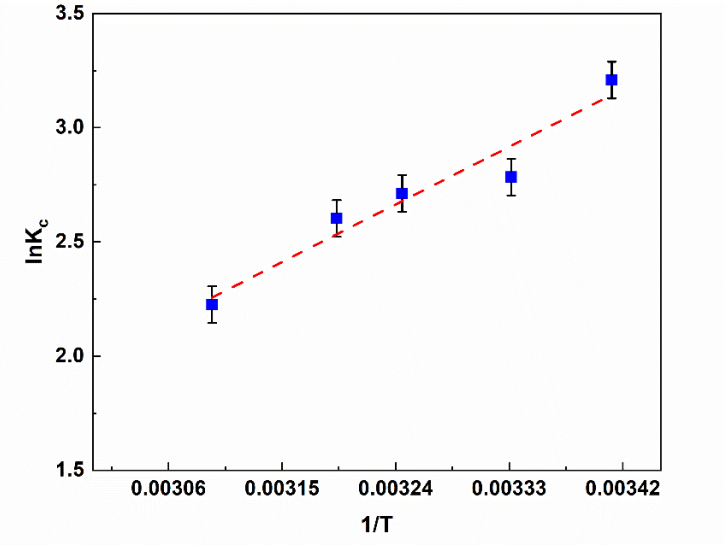

Figure 7: Plots of thermodynamic

Table 2: Adsorption thermodynamic parameter

T (K)	293.15	300.15	308.15	313.15	323.15
ΔG°(kJ.mol^{-1})	-7.6610	-7.2885	-6.8621	-6.5955	-6.0624
ΔH°(kJ.mol^{-1})	-23.2887				
ΔS°(J.K.mol^{-1})	-53.3072				

4. Conclusion

The synthesized UIO66-NH_2@PANI nanocomposite for use as an efficient nanosorbent successfully adsorbs the biomolecule quercetin from aqueous and organic solutions. The kinetic analysis of the adsorption data showed a pseudo-second-order linear behavior (R^2 = 0.9994), indicating that chemisorption predominantly controlled the adsorption process. The thermodynamic evaluation confirmed the spontaneity of the adsorption process, as indicated by the negative ΔG° value of -7.661 kJ.mol^{-1} at 293.15 K. A negative Gibbs free energy (ΔG°) suggests that the adsorption occurs naturally and is energetically favorable under the given conditions. Additionally, both enthalpy change (ΔH°) and entropy change (ΔS°) are negative, offering further insight into the adsorption mechanism. A negative ΔH° indicates that the process is exothermic, meaning heat is released during adsorption, which often suggests strong interactions between the adsorbent and the adsorbate. The negative ΔS° implies a decrease in randomness at the solid-liquid interface, likely due to the ordered arrangement of quercetin molecules on the nanocomposite surface, reducing the system's overall entropy.

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