

Silica Gel Supported Hydrophobic Ionic Liquid for Selective Extraction and Determination of Coumarin

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ABSTRACT

In this study, a modified silica gel surface with a hydrophobic ionic liquid (SG-1,10-PhenanNTf₂) was used as an adsorbent for a selective extraction of coumarin prior to its determination by use of high performance liquid chromatography. Results demonstrated that SG-1,10-PhenanNTf₂ phase had a good adsorption capacity up to 85.29 mg·g⁻¹, high selectivity, good site accessibility and fast binding kinetics toward coumarin. The adsorption capacity for coumarin was improved by 62.33% with the SG-1,10-PhenanNTf₂ phase as compared to activated silica gel. Adsorption isotherm data displayed that the adsorption process was mainly monolayer on a homogeneous adsorbent surface, confirming the validity of Langmuir adsorption isotherm model. The adsorption of coumarin on the SG-1,10-PhenanNTf₂ phase was accomplished after only 60 min contact time. Results of kinetic models showed that the adsorption of coumarin on the SG-1,10-PhenanNTf₂ phase obeyed a pseudo second-order kinetic model. Finally, the efficiency of this methodology was confirmed by applying it to real water samples.

Keywords: Coumarin; Silica Gel; Uptake Capacity; Ionic Liquid; Batch Method

1. Introduction

Most of organic compounds have a limited solubility in water and as a result they exist only at ultra concentrations level. Direct determination of these compounds in different kinds of environmental samples is often a challenging task for analysts. Also, it may cause serious interferences during measurement because of the lack of sensitivity and selectivity of analytical methods. In addition, a clean-up step is often required because of high levels of other components usually accompany the target compound. Therefore, an efficient extraction step is often necessary for accurate, sensitive and interference-free determination. There are several extraction techniques, including liquid-liquid extraction [1,2], ion exchange [3], accelerated solvent extraction [4], cloud point extraction [5], supercritical fluid extraction [6] and solid phase extraction (SPE) [7,8]. However, SPE is one of the most widely and commonly used techniques for pre-treatment of environmental samples. This is attributed to its advantages of higher enrichment factor, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of organic solvent, environment friendly, flexibility and easier incorporation into automated analytical techniques [9]. Moreover, several ad-

sorbents have been used as solid phase extractors, such as alumina [10], activated carbon [11], carbon nanotubes [8], cellulose [12], C18 [13], resins [14], molecular imprinted polymers [15] and silica gel [16-19]. Silica gel (SG) is one of the most widely used adsorbent due its simple handling, high surface area, fast kinetics, mechanical, thermal and chemical stability under various conditions [20]. It is also an efficient adsorbent for the extraction and separation of various types of compounds. However, adsorption of organic compounds at ultra-trace levels by SG alone cannot be directly achieved, and it is often necessary to modify the SG with chelating agents for enhancing its selectivity and capability for monitoring organic compounds in the environment.

Ionic liquids (ILs) have recently gained recognition as in different chemical fields due to their unique properties and their potential as greener solvent for many organic, inorganic, and polymeric substances as compared to the traditional organic solvents which are toxic and environmentally harmful [21,22]. Because of their unique properties, the applications of ILs have been expanded in various fields, such as solvent extractions [23], liquid-liquid extractions [24,25], enzymatic reactions [26], pharmaceutical studies [27], electrochemical studies [28], dye-sensitized solar cells and batteries [29,30], gas sensors for detection of polar and non-polar organic vapors

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[31], supported electrolytes in capillary electrophoresis, mobile phase additives in liquid chromatography and stationary phases in gas-liquid chromatography [32,33]. In addition, ILs can be physically adsorbed onto solid phase extractors surface by electrostatic interaction due to their high viscosities and negligible vapor pressure [34]. Several studies have described the efficiency of ionic liquid functionalized silica as an adsorbent for selective extraction of organic compounds [35,36].

However, finding a selective chelating agent capable to selectively bind to the target compound is one of the problems often encountered in applications of ILs for organic compounds extraction from various matrices using different extraction methods. In accordance, the present study was purposed to explore the analytical potential of SG-1,10-PhenanNTf₂ phase as an adsorbent on the selectivity and adsorption capacity of coumarin prior to its determination by high performance liquid chromatography (HPLC). The SG-1,10-PhenanNTf₂ phase has already been proven to be an effective adsorbent for selective extraction of Pb(II) prior to its determination by use of inductively coupled plasma-optical emission spectrometry in our previous study [37]. The preparation of the adsorbent was accomplished by combining a hybridization process of the hydrophobic ionic liquid characters with high adsorption efficiency and surface area of SG. The resulted SG-1,10-PhenanNTf₂ adsorbent was characterized by use of Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscope (SEM). The selectivity of SG-1,10-PhenanNTf₂ toward several organic compounds was investigated. In addition, the effect of different factors controlling the maximum uptake of coumarin on the SG-1,10-PhenanNTf₂ phase was studied under batch conditions. Langmuir classical adsorption isotherm model accurately represented the results of coumarin adsorption isotherm. Results of the kinetic analysis also demonstrated that the adsorption process obeyed a pseudo second-order adsorption model. Furthermore, the efficiency of this methodology was validated by applying it to real water samples.

2. Experimental

2.1. Chemicals and Reagents

1,10-Phenanthroline monohydrate hydrochloride (1,10-PhenanCl), bis(trifluoromethane)sulfonimide lithium (LiNTf₂), coumarin, 4-chloroaniline, flavone, 9-fluorenone, isatin, naphthalene, phenanthrene, phenazine, phenazone and HPLC grade acetonitrile (ACN) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). SG (SiO₂, particle size 10 - 20 nm) with purity of 99.5% was also obtained from Sigma-Aldrich. All reagents used were of analytical and spectral purity grade. Doubly dis-

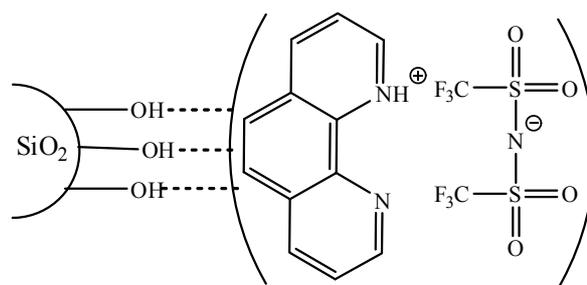
tilled deionized water was used throughout experimental studies.

2.2. Preparation of the SG-1,10-PhenanNTf₂ Adsorbent

SG-1,10-PhenanNTf₂, as shown in **Scheme 1**, was synthesized according to previously reported procedures by Marwani [37,38]. Specifically, the SG-1,10-PhenanNTf₂ phase was prepared based on the physical adsorption of hydrophobic ionic liquid (1,10-PhenanNTf₂) on the activated SG surface. An amount of 5 g activated SG was suspended in 100 mL toluene, and 1g 1,10-PhenanNTf₂ was completely dissolved by warming in 50 mL toluene and added to the activated SG suspension. The reaction mixture was heated and stirred at 60°C for 12 h. The modified SG-1,10-PhenanNTf₂ phase was filtered and washed with 50 mL toluene on three portions followed by ethanol and diethyl ether. Then, the SG-1,10-PhenanNTf₂ adsorbent was dried in an oven at 80°C for 5 h and kept in a desiccator for further use. The concentration of 1,10-PhenanNTf₂ ionic liquid on the surface of activated SG was determined to be 0.25 mmol g⁻¹ based on thermal desorption method [37].

2.3. Batch Method Procedure

All stock solutions were prepared in ACN (HPLC grade) and stored in the dark at 4°C. To examine the selectivity of SG-1,10-PhenanNTf₂ toward different organic compounds, 5 and 50 mg·L⁻¹ standard solutions of coumarin, 4-chloroaniline, flavone, 9-fluorenone, isatin, naphthalene, phenanthrene, phenazine and phenazone were prepared by adding appropriate amounts of each stock solution. All standard solutions were individually mixed with 20 mg SG-1, 10-PhenanNTf₂. For the study of coumarin adsorption capacity under batch conditions, standard solutions of 5, 10, 20, 30, 40, 50, 60, 80, 100, 125, 150 and 200 mg·L⁻¹ coumarin were prepared as above and individually mixed with 20 mg SG-1,10-PhenanNTf₂. In addition, the effect of shaking time on the coumarin adsorption capacity was investigated under the same batch



Scheme 1. Chemical structure of the SG-1,10-PhenanNTf₂ phase [37].

conditions but at different equilibrium periods, including 2.5, 5, 10, 20, 30, 40, 50 and 60 min. The concentration of each substrate solution was monitored by HPLC and calculated from the calibration plot of the peak area as a function of the concentration. For the study of the effect of matrix interferences on the extraction of coumarin by SG-1,10-PhenanNTf₂, a standard solution of 150 mg·L⁻¹ coumarin, flavone, naphthalene and phenanthrene was prepared and mixed with 20 mg SG-1,10-PhenanNTf₂. The mixture was then mechanically shaken for 1 h at room temperature.

2.4. Methods

SEM studies were performed before and after modification of the SG phase by use of a field emission-scanning electron microscope (FE-SEM, QUANT FEG 450, Amsterdam, Netherlands). The microscope was operated at an accelerating voltage of 15 kV. HPLC measurements were acquired by use of an Agilent Technologies 1200 Series, USA. The chromatographic system consisted of a model G1361A pump and G1315B DAD UV detector. All separations were achieved on an analytical reversed phase column (ZORBAX ODS, 4.6 × 150 nm) with a flow rate of 1 mL·min⁻¹, and the volume of sample injection was 20 µL. An isocratic elution was established with a mobile phase composition of 60% ACN and 40% water at room temperature. The UV detector was operated at wavelengths of 198 nm for 4-chloroaniline, 252 nm for 9-fluorenone, 215 nm for naphthalene, 251 nm for phenanthrene, 244 nm for phenazine, 243 nm for isatin and phenazone and 203 nm for coumarin and flavone.

3. Results and Discussion

3.1. Characterization of SG-1,10-PhenanNTf₂ Phase

FT-IR spectra confirmed the formation of the physically modified phase (SG-1,10-PhenanNTf₂) as previously reported elsewhere [37]. In addition, SEM images were taken for activated SG and SG-1,10-PhenanNTf₂ in order to further confirm the formation of the physically modified SG-1,10-PhenanNTf₂ adsorbent (**Figures 1(a)** and **(b)**). As shown in **Figure 1(b)**, the immobilization of hydrophobic ionic liquid (1,10-PhenanNTf₂) on the surface of activated SG resulted in a pronounced and characterized change of the surface morphology of activated SG. It can be noticed that 1,10-PhenanNTf₂ collected activated SG particles in aggregate forms that are completely covered with it. In addition, the SEM image given in **Figure 1(b)** of the modified SG-1,10-PhenanNTf₂ adsorbent clearly displays the particles as individually distributed in uniform and homogeneous shapes as compared with that of activated SG (**Figure 1(a)**).

3.2. Selectivity Study

For the study of the selectivity of the SG-1,10-PhenanNTf₂ phase toward different organic compounds, desired concentrations of 5 and 50 mg·L⁻¹ coumarin, 4-chloroaniline, flavone, 9-fluorenone, isatin, naphthalene, phenanthrene, phenazine and phenazone were chosen. All solutions were individually mixed with 20 mg SG-1,10-PhenanNTf₂. As can be observed in **Table 1**, the distribution coefficient value and amount of each compound adsorbed per unit mass of the SG-1,10-PhenanNTf₂ adsorbent at equilibrium (q_e , mg·g⁻¹) were calculated in these competitive experiments. The distribution coefficient (K_d , mL·g⁻¹) value corresponds to the character of a compound adsorbed by an adsorbent and can be calculated from the following equation [39]:

$$K_d = [(C_i - C_e)/C_e] \times (V/m) \quad (1)$$

where C_i and C_e are initial and final concentrations (mg·L⁻¹), respectively, V refers to the volume of solution (mL), and m is the mass of adsorbent (g). The final concentrations (C_e) were determined based on the calibration plot of the peak area as a function of the concentration. The results displayed that coumarin had the greatest K_d value up to 21476.27 and 4004.12 mL⁻¹ for 5 and 50 mg·L⁻¹, respectively, on the SG-1,10-PhenanNTf₂ adsorbent as compared with other compounds examined on SG-1,10-PhenanNTf₂. Therefore, the results of selectivity study indicated that SG-1,10-PhenanNTf₂ was most selective for coumarin over all other compounds, including 4-chloroaniline, flavone, 9-fluorenone, isatin, naphthalene, phenanthrene, phenazine and phenazone. The partial ionic charges produced on the surface of activated SG and incorporated donor atoms (O, N and S) presented in SG-1,10-PhenanNTf₂, as a result of immobilization of the 1,10-PhenanNTf₂ ionic liquid on the activated SG, strongly attained the selective adsorption of SG-1,10-PhenanNTf₂ toward coumarin. Thus, the highest selectivity of SG-1,10-PhenanNTf₂ toward coumarin may be attributed to an electrostatic attraction, physical, mechanism between SG-1,10-PhenanNTf₂ and coumarin (**Scheme 2**).

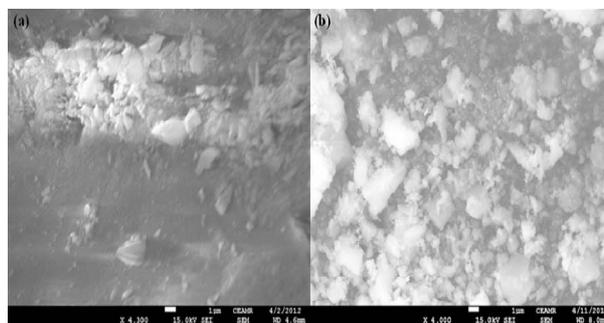
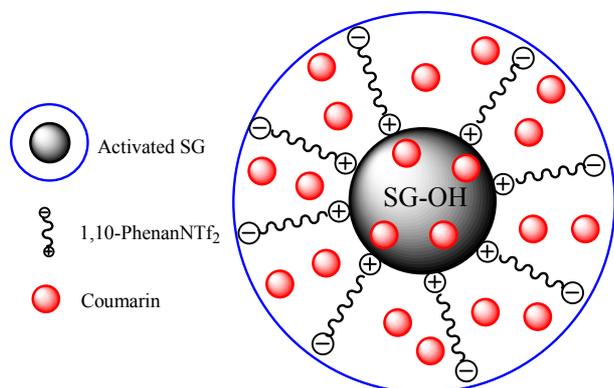


Figure 1. SEM images of (a) activated SG and (b) SG-1,10-PhenanNTf₂ phase.



Scheme 2. Interaction mechanism between SG-1,10-PhenanNTf₂ and coumarin.

Table 1. Selectivity study of 20 mg SG-1,10-PhenanNTf₂ toward different compounds.

| Compound | Concentration (mg·L ⁻¹) | q_e (mg·g ⁻¹) | K_d (mL·g ⁻¹) |
|-----------------|-------------------------------------|-----------------------------|-----------------------------|
| Coumarin | 5 | 5.91 | 21476.27 |
| | 50 | 47.63 | 4004.12 |
| Flavone | 5 | 0.57 | 124.63 |
| | 50 | 2.25 | 46.73 |
| Isatin | 5 | 0.01 | 2.51 |
| | 50 | 4.23 | 90.65 |
| Phenazone | 5 | 0.01 | 2.51 |
| | 50 | 1.38 | 28.27 |
| Phenazine | 5 | 0.79 | 181.11 |
| | 50 | 8.88 | 207.10 |
| Phenanthrene | 5 | 0.22 | 44.64 |
| | 50 | 7.61 | 173.32 |
| Naphthalene | 5 | 0.97 | 228.85 |
| | 50 | 9.22 | 216.27 |
| 4-Chloroaniline | 5 | 0.82 | 189.01 |
| | 50 | 7.44 | 169.00 |
| 9-Fluorenone | 5 | 0.77 | 174.76 |
| | 50 | 8.63 | 200.36 |

3.3. Adsorption Capacity

In order to evaluate the static uptake capacity of coumarin on the SG-1,10-PhenanNTf₂ phase, different desired concentrations of coumarin ranging from 0 to 200 mg·L⁻¹ in 25 mL sample solutions were mixed with 20 mg SG-1,10-PhenanNTf₂. All these mixtures were mechanically shaken for a period of 1 h at room temperature, and the amount of coumarin adsorbed at each concentration level was determined. The adsorption profile of coumarin on 20 mg SG-1,10-PhenanNTf₂ was obtained by plotting the coumarin concentration (mg·L⁻¹) versus milligrams of coumarin adsorbed per gram SG-1,10-PhenanNTf₂ (**Figure 2**). From adsorption isotherm study, the adsorption capacity of SG-1,10-PhenanNTf₂ for coumarin was determined to be 85.29 mg·g⁻¹ (**Figure 2**), which is the greatest adsorption capacity reached in com-

parison with adsorption capacity values previously reported for coumarin with other adsorbents (7.17, 10.56 and 10.64 mg·g⁻¹) [14]. For comparison with the coumarin adsorption capacity of SG-1,10-PhenanNTf₂, the coumarin uptake capacity on activated SG was also determined under the same batch conditions (**Figure 2**). As shown in **Figure 2**, the adsorption capacity of activated SG for coumarin was found to be 52.54 mg·g⁻¹. These results showed that the adsorption capacity for coumarin was improved by 62.33% with the modified SG-1,10-PhenanNTf₂ phase.

3.4. Adsorption Isotherm Models

The adsorption isotherms represent the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in the solution at equilibrium. Data collected from adsorption isotherm experiments of coumarin with the SG-1,10-PhenanNTf₂ phase were evaluated by different isotherms models in order to develop an equation, which accurately represents the results [40,41]. The Langmuir isotherm model assumes a monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface, and it is given by the following equation:

$$C_e/q_e = (C_e/Q_o) + 1/Q_o b \quad (2)$$

where C_e is the equilibrium concentration of coumarin (mg·L⁻¹), q_e and Q_o represent the equilibrium amount and maximum amount of coumarin adsorbed per unit mass of adsorbate (mg·g⁻¹), respectively, and b denotes the Langmuir constant related to the rate of adsorption. Based on the least square fit, adsorption isotherm data were well fit with the Langmuir model (**Figure 3**). As illustrated in **Figure 3**, a linear plot with correlation coefficient (R^2) value of 0.993 was obtained from Langmuir isotherm equation when plotting C_e/q_e against C_e with a slope and intercept equal to $1/Q_o$ and $1/Q_o b$, respectively. Consequently, adsorption isotherm data provided that the adsorption process was mainly monolayer on a homogeneous adsorbent surface. The Langmuir constants Q_o and b were found to be 88.77 mg·g⁻¹ and 0.13 L·mg⁻¹, respectively. It is also interesting to note that the coumarin adsorption capacity (88.77 mg·g⁻¹) calculated from Langmuir equation was closely associated with that (85.29 mg·g⁻¹) experimentally obtained from the isotherm study. The effect of the isotherm shape has been discussed with a view to predict whether an adsorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of a dimensionless constant separation factor or equilibrium parameter (R_L). R_L is calculated using the following equation:

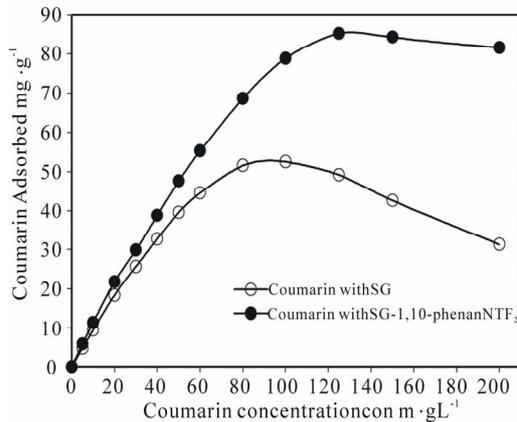


Figure 2. Adsorption isotherm of coumarin on 20 activated SG and SG-1,10-PhenanNTf₂ phase in relation to the concentration at 25°C.

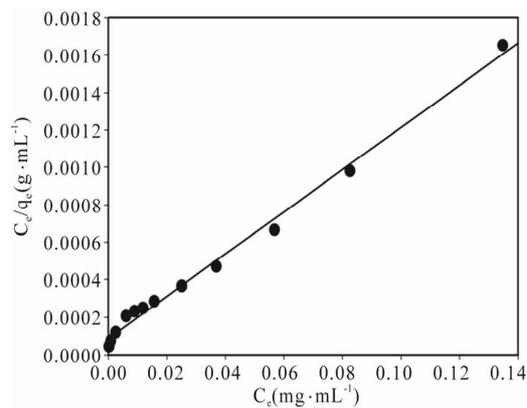


Figure 3. Langmuir adsorption isotherm model of coumarin adsorption on 20 mg SG-1,10-PhenanNTf₂ at 25°C. Adsorption experiments were obtained at different concentrations (0 - 200 mg·L⁻¹) of coumarin under batch conditions.

$$R_L = 1/(1 + bC_o) \quad (3)$$

where b is the Langmuir constant which indicates the nature of adsorption and the shape of the isotherm, and C_o refers to the initial coumarin concentration (mg·L⁻¹). The R_L value indicates the type of the isotherm, and R_L values lying between 0 and 1 provided that the conditions were favorable for adsorption [42]. The R_L value of coumarin adsorption on SG-1,10-PhenanNTf₂ was estimated to be 0.05, confirming that the adsorption is strongly favorable under conditions used in this study. Thus, adsorption data indicated the formation of monolayer on a homogeneous adsorbent surface with a highly favorable adsorption process based on the Langmuir adsorption isotherm model.

3.5. Effect of Shaking Time

The effect of shaking time is one of the most important factors when using the batch technique in processes of

the adsorption capacity determination for organic compounds. In this study, different shaking times were chosen, ranging from 2.5 to 60.0 min, in order to study the behavior of adsorption kinetics for coumarin on the SG-1,10-PhenanNTf₂ phase. Based on the results, it was observed that equilibrium kinetics were very fast. As displayed in **Figure 4**, an amount of 67.56 mg·g⁻¹ coumarin was adsorbed on SG-1,10-PhenanNTf₂ after only 20 min of the equilibrium period. Then, the amount of coumarin adsorbed was raised up to 76.53 mg·g⁻¹ after 40 min until the maximum adsorption of SG-1,10-PhenanNTf₂ for coumarin was reached to 85.29 mg·g⁻¹ after 60 min.

3.6. Kinetic Models

Different kinetic models were also investigated in order to find intrinsic kinetic adsorption parameters for explaining the nature of adsorption process. Kinetic models were used for goodness of fit for experimental data using the correlation coefficient (R^2) as a measure of convention between experimental data. The adsorption kinetic equation of a pseudo second-order adsorption is expressed as follows:

$$t/q_t = 1/v_o + (1/q_e)t \quad (4)$$

where $v_o = k_2 q_e^2$ is the initial adsorption rate (mg·g⁻¹·min⁻¹) and k_2 (g·mg⁻¹·min⁻¹) corresponds to the rate constant of adsorption, q_e (mg·g⁻¹) denotes the amount of compound adsorbed at equilibrium, and q_t (mg·g⁻¹) refers to the amount of compound on the adsorbent surface at any time t (min). The parameters q_e and v_o can be obtained from the slope and intercept, respectively, of a plot of t/q_t versus t [43]. The kinetic parameters q_e and v_o were calculated from the slope and intercept, respectively, of the linear plots of t/q_t versus t , as shown in **Figure 5**. The correlation coefficient (R^2) factor was found to be 0.997, providing that the pseudo second-order adsorption is more reliable and accurate. The parameters q_e , v_o and k_2 were determined to be 92.72 mg·g⁻¹, 11.61 mg·g⁻¹·min⁻¹ and 0.0013 g·mg⁻¹·min⁻¹, respectively. The coumarin adsorption capacity on SG-1,10-PhenanNTf₂ obtained from the pseudo second-order kinetic model (92.72 mg·g⁻¹) was also in good agreement with adsorption capacities obtained from adsorption isotherm experiments (85.29 mg·g⁻¹) and from the Langmuir isotherm model (88.77 mg·g⁻¹), supporting the highest applicability of the pseudo second-order nature of the adsorption of coumarin by SG-1,10-PhenanNTf₂.

3.7. Performance of Method in Analytical Applications

3.7.1. Effect of Matrix Interferences

In order to evaluate the possibility of analytical applications for the proposed procedure in analyzing real samples, the effect of several compounds was investigated

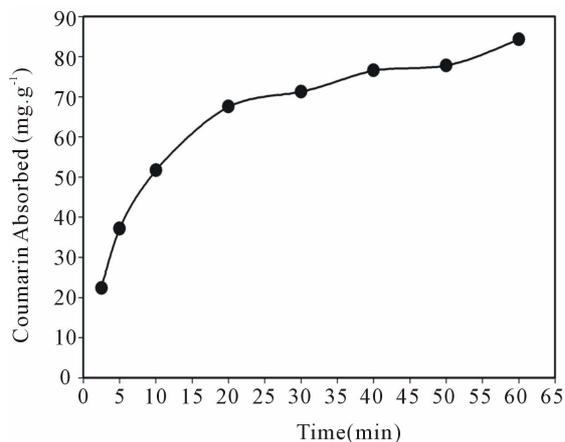


Figure 4. Effect of shaking time on coumarin uptake using 20 mg SG-1, 10-PhenanNTf₂ phase at 25°C.

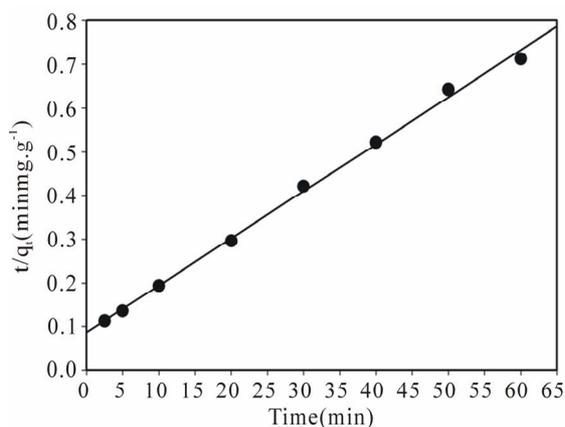


Figure 5. Pseudo second-order adsorption kinetic model of coumarin uptake on 20 mg SG-1,10-PhenanNTf₂ at 25°C.

under optimized conditions. A model standard solution containing fixed amount of 150 mg·L⁻¹ coumarin with mixed matrix compounds, including 150 mg·L⁻¹ flavone, naphthalene and phenanthrene, was treated according to the recommended procedure. As shown in **Figure 6**, it can be clearly observed that coumarin was retained more than other compounds, providing that the SG-1,10-PhenanNTf₂ adsorbent was most selective toward coumarin. Calculated uptake capacity and distribution coefficient values are reported in **Table 2** for each compound adsorbed on the SG-1,10-PhenanNTf₂ phase in this mixed matrix. As displayed in **Table 2**, coumarin had the largest static uptake capacity, q_e , (76.38 mg·g⁻¹) and distribution coefficient, K_d , value up to 859.11 mL·g⁻¹ on the SG-1, 10-PhenanNTf₂ adsorbent as compared with other compounds in the mixed matrix. The effect of medium composition containing mixed compounds has, therefore, no significant influence on the extraction of coumarin. Thus, the selectivity of the proposed method is high enough to be applied to the determination of coumarin in real samples.

3.7.2. Application of the Proposed Method

In order to establish the validity of the proposed procedure, the method was applied to the determination of coumarin in real water samples. A standard addition method was performed under the same batch conditions to estimate the accuracy of the extraction of coumarin. An amount of 5, 10 or 20 mg·L⁻¹ coumarin was spiked in three different types of water samples, including ground water, lake water and waste water, collected from Jeddah in Saudi Arabia. The % extraction of each amount of coumarin in real water samples was calculated, and the results are summarized in **Table 3**. As can be observed in **Table 3**, the % extraction of coumarin in real water samples was reasonable, in the range of 85.02% - 94.39%. In addition, it is interesting to note that the unadsorbed fraction of coumarin was largely decreased when the added fraction was increased to 20 mg·L⁻¹. In fact, this behavior can be ascribed to the low adsorption capacity or rate for interfering chemical species presented in real water samples toward the SG-1,10-PhenanNTf₂ phase. Thus, results suggested that the extraction of coumarin in spiked water samples was satisfactory for trace analysis and apparently demonstrated that the method is reliable, feasible and suitable for analyzing real samples.

4. Conclusion

It can be concluded from the results that SG-1,10-PhenanNTf₂ is an effective adsorbent for selective extraction and determination of trace levels of coumarin at short contact time. Adsorption isotherm data of coumarin adsorption on SG-1,10-PhenanNTf₂ were well fit with Langmuir adsorption isotherm model, providing that the adsorption process was mainly monolayer onto a homogeneous adsorbent surface. Results also demonstrated that the adsorption of coumarin on the SG-1,10-PhenanNTf₂ phase obeyed a pseudo second-order kinetic model. Moreover, the extraction of coumarin by the SG-1,10-PhenanNTf₂ was not affected by the medium composition containing mixed compounds. The proposed method ultimately afforded acceptable and reliable results for a selective adsorption and determination of coumarin in real

Table 2. Effect of matrix interferences on the extraction of 150 mg·L⁻¹ coumarin on 20 mg SG-1,10-PhenanNTf₂ (N = 3).

| Compound | Concentration (mg·L ⁻¹) | q_e (mg·g ⁻¹) | K_d (mL·g ⁻¹) |
|--------------|-------------------------------------|-----------------------------|-----------------------------|
| Coumarin | 150 | 76.38 | 859.11 |
| Flavone | 150 | 6.68 | 46.20 |
| Phenanthrene | 150 | 2.31 | 15.62 |
| Naphthalene | 150 | 7.91 | 55.08 |

Table 3. Determination of coumarin at different concentrations (5, 10 and 20 mg·L⁻¹) in real water samples using 20 mg SG-1,10-PhenanNTf₂ (N = 3).

| Samples | Added (mg·L ⁻¹) | Unadsorbed (mg·L ⁻¹) | Extraction (%) |
|--------------|-----------------------------|----------------------------------|----------------|
| Ground water | 5 | 0.33 | 93.38 |
| | 10 | 0.97 | 90.30 |
| | 20 | 2.70 | 86.50 |
| Lake water | 5 | 0.28 | 94.39 |
| | 10 | 0.88 | 91.21 |
| | 20 | 2.60 | 87.00 |
| Waste water | 5 | 0.35 | 92.96 |
| | 10 | 0.99 | 90.11 |
| | 20 | 3.00 | 85.02 |

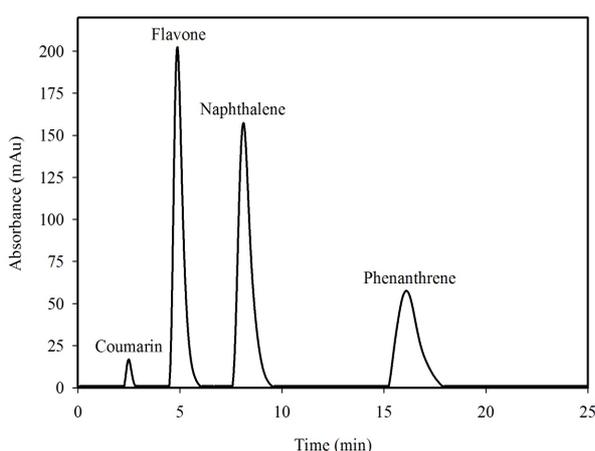


Figure 6. Effect of matrix interferences on the extraction of coumarin by 20 mg SG-1,10-PhenanNTf₂ at 25°C. Adsorption experiments were performed with 150 mg·L⁻¹ coumarin, flavone, naphthalene and phenanthrene mixture under batch conditions.

water samples with complicated and variable matrices.

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