



Assessment of cellulose acetate/manganese oxide thin film as adsorbent for selective extraction of flavone

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Abstract. The present study depicts the efficiency of cellulose acetate/manganese oxide thin films as adsorbents for selective extraction and detection of flavone in environmental waters. The selectivity of thin films (CA/Mn-1 and CA/Mn-2) was evaluated towards several organic compounds. Based on selectivity study results, CA/Mn-2 thin film was the most selective towards flavone among other compounds. In addition, the effect of other parameters such as contact time and initial concentration of flavone was investigated to optimize adsorption conditions. The adsorption capacity of flavone was experimentally obtained as 57.96 mg g⁻¹ and theoretically calculated from Langmuir equation as 58.48 mg g⁻¹, which indicates the high agreement of the results. Moreover, data obtained from kinetic study suggested that the adsorption of flavone onto CA/Mn-1 phase followed a pseudo-second-order kinetic model. Finally, validation of this method has attained reasonable results for determination of flavone in real water samples.

Keywords. Flavone; thin film; cellulose acetate/manganese oxide; uptake capacity; adsorption isotherm models; kinetic study.

1. Introduction

As a result of growth population and increasing human activities in agriculture and industry during the last few decades, large amounts of chemical compounds and contaminants were emerged into the environment [1]. The analysis of these compounds in the meager levels in numerous biological and environmental media, especially water samples, is necessary for the assessment of the efficiency of a product as well as knowledge of its impact on human health or environmental pollution [2,3]. There are several analytical techniques employed for the extraction of organic and inorganic compounds at trace levels from aquatic media. For instance, traditional liquid–liquid extraction (LLE) was used for sample preparation of target analyte prior to measurements. Nevertheless, LLE process is a time-consuming method and also consumes high volume of organic solvents, which are toxic and environmentally harmful [4,5]. Thus, most researchers tend to use other developed extraction techniques for target analyte separation, such as co-precipitation [6], cloud point extraction [7], ion exchange [8] and solid phase extraction (SPE) [9,10].

Among them, separation methods based on SPE technique play a critical role in modern analytical science and have become an alternative to LLE to avoid utilizing large volumes of toxic and harmful organic solvents. Moreover,

SPE offers several great advantages that involve simplicity, inexpensive, short equilibrium time, eco-friendly approach, widely applicable and the ability to use it alone or combined with other analytical techniques. In SPE procedure, selecting the adsorptive materials is a crucial part, because they have direct influence on the separation parameters such as selectivity, ability and capacity [4,11,12]. Various adsorbents were used as extractors, such as natural materials [13], activated carbon [14], zeolites [15], clays [16] and resins [17]. However, most of these adsorbents have fairly low surface area and insufficient functional groups, which lead to limited uptake capacities [18,19]. In other words, the perfect solid sorbent should have a large specific surface area, high selectivity to target analyte and good uptake capacity [2].

From this perspective, many efforts were made in the fabrication, improvement and development of advanced materials as adsorbents. More recently, nanomaterials become very important due to their special physical and chemical properties, hence, widely used as potential adsorbents. For instance, nanostructured materials have greater ratio of surface area to particle size compared with conventional materials [11,20]. In addition, nano-sized adsorbents have other physicochemical characteristics, such as the ability to external functionalization by varied functional groups to enhance the surface properties and increase the adsorption capacity [21]. There are various kinds of nano-sized adsorbents including metal

or metal oxide nanoparticles, carbon-based nanomaterials and polymer-based nanocomposites [11]. Recently, exploring the efficiency and ability of nanomaterials as potential adsorbents, especially polymer nanocomposites, for selective separation of organic and inorganic compounds in aqueous media have become an interesting research point [18,22–25]. Cellulose acetate (CA) is one of the most attractive polymers as it has significant properties, and several studies have examined the utility of CA in the adsorption and removal of various inorganic materials. However, nanocomposition is an efficient modification route for polymers, which enhances their characteristics and properties by adding inorganic nanomaterials. The better properties and performances of nanocomposites are usually due to the addition of nanofillers with large surface area which upshot the properties of the polymer [26–32].

Several studies on flavonoids separation from natural plants by resins and modified resins were reported, and the obtained adsorption capacities were as follows (9.55 mg g^{-1}) [33], ($11.72, 15.56, 19.25 \text{ mg g}^{-1}$) [34] and ($11.72, 32.90 \text{ mg g}^{-1}$) [35]. To the best of our knowledge, up to now, there are no reports on extraction of flavone itself, which is a basic structure of flavonoids, from aqueous media. In the present study, the selectivity of CA/Mn-1 and CA/Mn-2 thin films as solid-phase extractors towards adsorption of selected organic compounds was investigated. Other factors impacting the maximum uptake of flavone on CA/Mn-1 phase were also studied under batch technique, included initial flavone concentration and extraction time. Adsorption isotherm models, including Langmuir and Freundlich equations, were used to simulate the adsorption system of flavone onto CA/Mn-1 phase. To explain the kinetics behaviour of the adsorption process, both models of pseudo-first and second-orders were utilized. Further, efficiency of the recommended approach was supported by applying it to the detection of flavone concentration in environmental water specimens.

2. Experimental

2.1 Reagents and chemicals

Reagents used in this study (flavone, anthracene-9-carboxylic acid, isatin, coumarin, phenazine, phenanthrene-9-carboxaldehyde, 2-naphthaldehyde, phenazone and phenanthridine) were of analytical and spectral purity grades and were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Also, manganese nitrate and spectrophotometric grade ethanol were also procured from Sigma-Aldrich. Cellulose acetate was purchased from BDH. Doubly distilled-deionized water was used throughout experimental studies.

2.2 Preparation of the solid phase extractor

Aqueous solution of manganese nitrate was prepared, and then NaOH was added till pH of the solution turns into 10. The highly basic solution was kept on heating (60°C) for

10 h with continuous stirring. Then, the manganese oxide product was washed and dried. For preparation of CA/Mn nanocomposites, CA was first dissolved in acetone and then manganese oxide was added in different ratios and well dispersed by stirring. CA/Mn-1 and CA/Mn-2 contain 4 and 5 wt% of manganese oxide, respectively.

2.3 Instrumentation

CA/Mn-1 and CA/Mn-2 were characterized by transmission electron microscope (TEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Fourier transform (FTIR) spectroscopies. The crystal structure of the nanocomposite was studied using XRD, having PANalytical diffractometer with a $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) source. The diffractometer was operated at 20 mA and 20 kV and run at a scan rate of $1-2^\circ 2\theta \text{ min}^{-1}$. The morphology of the nanocomposite was investigated using TEM. EDS was used for the elemental analysis of the prepared nanocomposites. FTIR analysis was carried out using Thermo scientific FTIR spectrometer. UV-Vis spectrophotometer (MultiSpec 1501; Shimadzu) was used for spectrophotometric analysis of organic compound solutions.

2.4 Maximum absorbance and calibration curve

The concentrations of organic compounds before and after equilibrium were detected using a UV-Vis spectrophotometer. Selected wavelength detection for each compound was utilized in spectrophotometric measurements, as follows, 294 nm for flavone, 242 nm for anthracene-9-carboxylic acid, 243 nm for phenazine and isatin, 244 nm for phenanthridine, 246 nm for phenanthrene-9-carboxyaldehyde and 2-naphthaldehyde, 271 nm for phenazone and 275 nm for coumarin. Standard calibration curves of the compounds were linear ($R^2 > 0.997$) and in concentration series lies between $0-200 \text{ mg l}^{-1}$. However, maintaining the absorbance values to <1.0 was taken into account to ensure the accuracy and sensitivity of the detector.

2.5 Solid-phase extraction procedure

Stock solutions of organic compounds were prepared in ethanol and kept in a refrigerator at 4.0°C . To probe the selectivity of the synthesized adsorbents, batch adsorption experiments were performed by adding 10 mg of each thin film (CA/Mn-1 and CA/Mn-2) individually to 25 ml of 5 mg l^{-1} standard solutions of different organic compounds. All mixtures were shaken in a mechanical shaker at room temperature for 60 min. For investigation of flavone uptake capacity under batch conditions, desired concentrations of flavone (2, 5, 10, 15, 20, 30 and 50 mg l^{-1}) were prepared as above. Then, the impact of contact time on the uptake capacity of flavone was studied under the same batch conditions for selected intervals of time, including 2.5, 5, 10, 20, 30, 40, 50 and 60 min. After the equilibration time was

elapsed, flavone solution (or other compounds) was filtered through a filter paper to remove the adsorbent. Concentrations of organic compounds after filtration were determined using UV–Vis spectrophotometer.

3. Results and discussion

3.1 Structural characterization of CA/Mn-1 and CA/Mn-2

The morphology of CA/Mn-1 and CA/Mn-2 were evaluated by TEM analyses, as shown in figure 1a. In TEM images, manganese oxide can be observed in the form of aggregated particles, indicating that manganese oxide is successfully incorporated in the CA polymer matrix. Further, it can be noted that manganese oxide is more aggregated in CA/Mn-2, while in the case of CA/Mn-1, manganese oxide is less aggregated.

Energy dispersive spectroscopy (EDS) analyses were carried out to confirm the presence of manganese oxide in the CA polymer matrix. Results reveal a successful preparation of CA/Mn-1 and CA/Mn-2 (figure 1b). In both CA/Mn-1 and CA/Mn-2, elements of C, Mn and O can be observed. The element Mn can be observed in all the spectra, confirming the presence of manganese oxide in the CA polymer. Elements of carbon and oxygen, presented in CA polymer, can also be observed in all the EDS spectra.

In addition, XRD analysis was carried out, which shows an amorphous hump at around 20° without any crystalline

peaks (figure 2a). This amorphous halo comes from cellulose acetate, while lack of manganese oxide peaks might be due to low wt% of manganese oxide, which is used during the preparation of nanocomposites [36]. Moreover, the functional groups and chemical composition of CA/Mn-1 and CA/Mn-2 were evaluated by analysing FTIR spectra, which are presented in figure 2b. The FTIR spectra of both CA/Mn-1 and CA/Mn-2 have displayed peaks for both CA and Mn, which indicate the development of nanocomposites. The FTIR spectra of both CA/Mn-1 and CA/Mn-2 exhibit absorption bands for CA at 3460 (O–H stretching), 2800–2900 (C–H stretching), 1743 (C=O stretching), 1374, 1227, 1042 and 896 cm^{-1} (C–O and C–H stretching and bending), while Mn=O stretching appeared at almost 593 cm^{-1} [37].

3.2 Batch adsorption experiments

3.2a *Selectivity study*: Selectivity experiments were conducted for both CA/Mn-1 and CA/Mn-2 thin films to test their efficiency as extractors towards different organic compounds. The selectivity for each compound was evaluated on the basis of distribution coefficient values (K_d), and K_d was expressed as below [38]:

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

where C_o (mg l^{-1}) indicates to organic compound concentration before the adsorption process, and C_e (mg l^{-1}) refers to the organic compound concentration at equilibrium, V (ml)

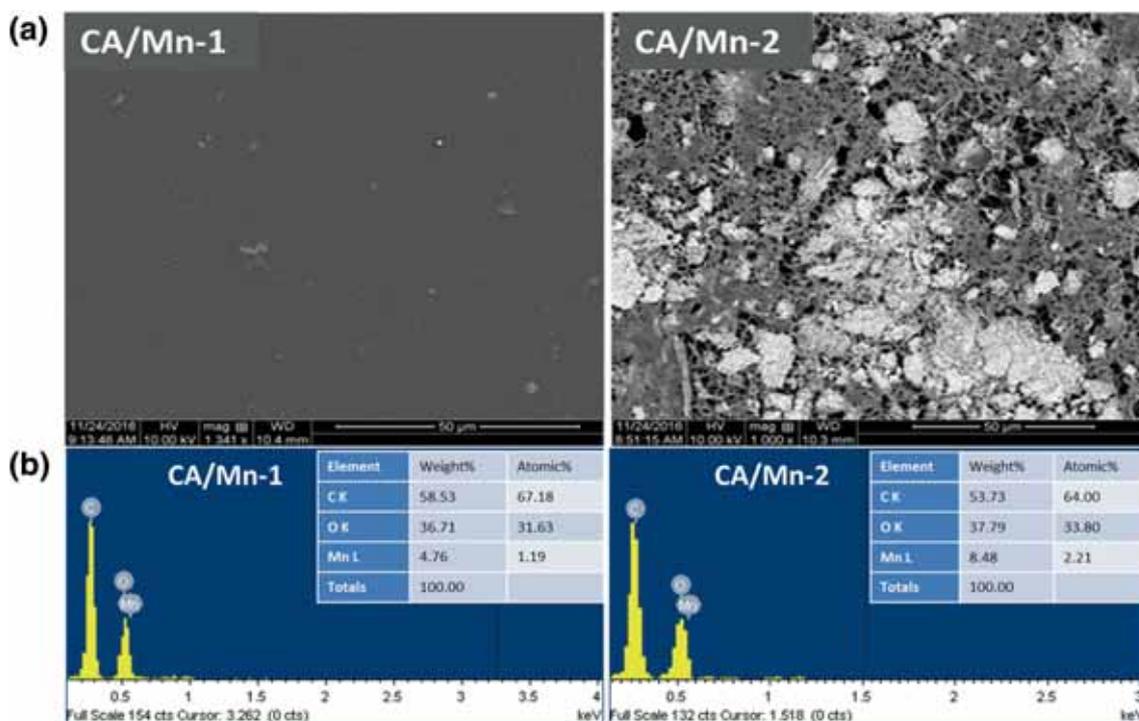


Figure 1. (a) TEM images and (b) EDS spectra of CA/Mn-1 and CA/Mn-2.

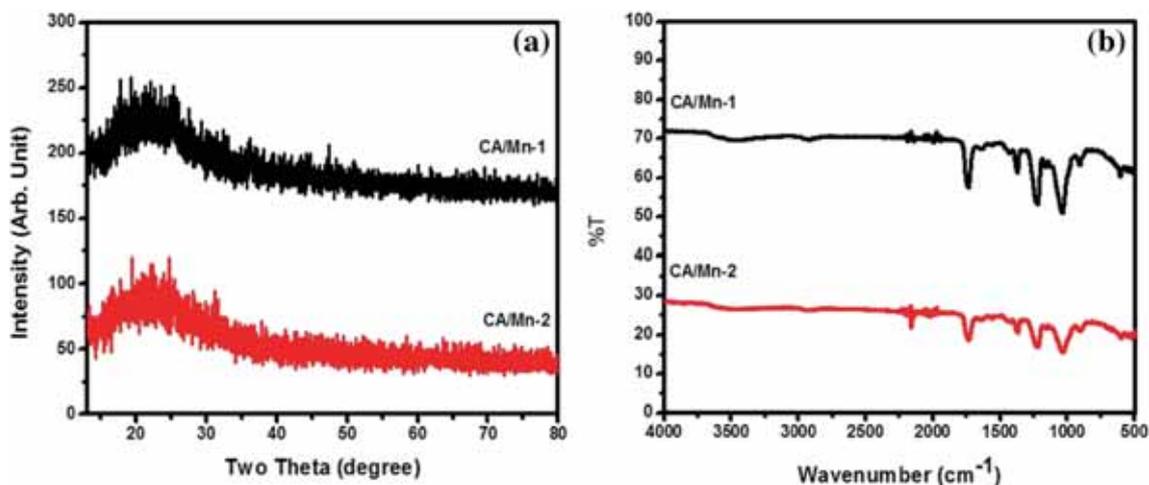


Figure 2. (a) XRD pattern and (b) FTIR spectra of CA/Mn-1 and CA/Mn-2.

Table 1. Selectivity study of CA/Mn thin films (10 mg) towards different organic compounds (5 mg l^{-1}).

Adsorbent	Compound	q_e (mg g^{-1})	K_d (ml g^{-1})
CA/Mn-2	Flavone	11.80	42135.54
CA/Mn-1	Flavone	12.41	334821.54
	Phenazine	5.17	1762.72
	Isatin	4.86	1588.21
	Phenazone	3.98	1165.69
	Coumarin	3.56	994.45
	Phenanthridine	3.05	806.88
	2-naphthaldehyde	2.88	746.75
	Phenanthrene-9-carboxyaldehyde	2.70	687.15
	Anthracene-9-carboxylic acid	2.62	662.07

and m (g) parameters correspond to the volume of sample and adsorbent mass, respectively. Table 1 summarizes the values of uptake capacities and distribution coefficients for all the examined compounds in this study. As can be clearly observed from table 1, CA/Mn-1 phase was more selective for flavone over other tested compounds, including anthracene-9-carboxylic acid, isatin, coumarin, phenazine, phenanthrene-9-carboxaldehyde, 2-naphthaldehyde, phenazone and phenanthridine. Besides, the uptake capacity of flavone on CA/Mn-2 was found to be lower than CA/Mn-1 thin film. Thus, the high ability of CA/Mn-1 phase to adsorb flavone on its surface perhaps referred to an electrostatic attraction, physical mechanism between solid thin film and liquid phase.

3.2b Determination of the uptake capacity of flavones:

For inspecting the influence of initial flavone concentration on the uptake capacity of CA/Mn-1 phase, different concentrations varied between 2 and 50 mg l^{-1} of flavone were separately prepared and mixed with 10 mg CA/Mn-1 phase under batch procedure. Figure 3a shows that flavone initial concentration affects the adsorption capacity greatly. As

observed from figure 3a, the adsorption capacity of flavone pointedly increased with raising the initial flavone concentration gradually until it reached 30 mg l^{-1} , and found to be 57.96 mg g^{-1} . However, increasing flavone initial concentration over 30 mg l^{-1} led to almost constant adsorption capacity. These findings are probably because of decrease of favourable active site numbers on the surface of CA/Mn-1 adsorbent.

3.2c Adsorption isotherm models: Adsorption isotherm models are essential for designing adsorption systems, which can be studied to describe the distribution of adsorbate on solid surface of adsorbent at equilibrium state [39]. In this study, data generated from equilibrium adsorption study of flavone on CA/Mn-1 phase were tested with classical adsorption isotherms, Langmuir and Freundlich models, to confirm which of these models accurately explains the adsorption process.

According to the theory of Langmuir model, each adsorption point on the solid surface is able to adsorb one molecule, which means that a homogeneous adsorbent surface covered by a monolayer of adsorbate molecules. The linear equation

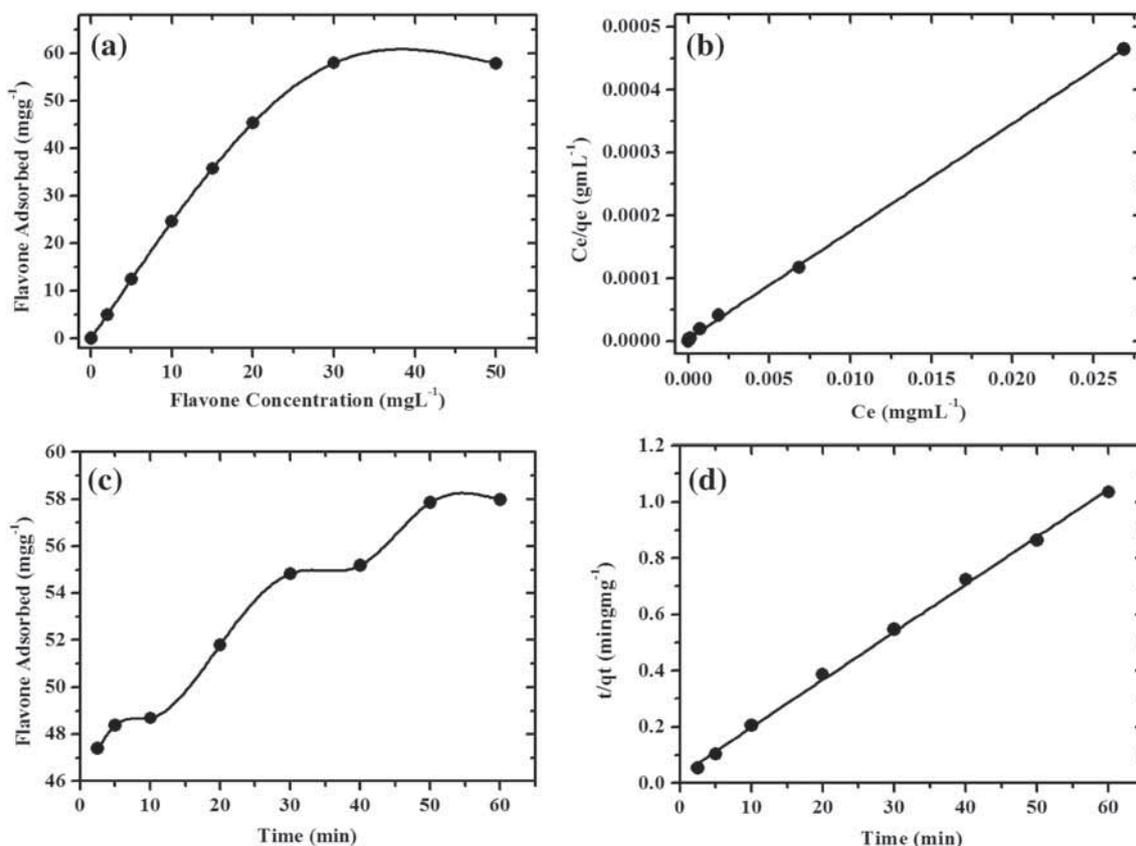


Figure 3. (a) Adsorption profile of flavone on CA/Mn-1 phase in relation to the concentration (2–50 mg l⁻¹). (b) Langmuir isotherm model of flavone uptake. (c) Effect of contact time on the adsorption of 30 mg l⁻¹ flavone on CA/Mn-1 phase. (d) Pseudo-second-order adsorption kinetic model of flavone adsorption (experimental conditions: CA/Mn-1 mass = 10 mg and temperature = 25°C).

form of Langmuir described as follows:

$$C_e/q_e = (C_e/Q_0) + 1/Q_0b, \tag{2}$$

where C_e (mg l⁻¹) corresponds to the equilibrium flavone concentration, q_e (mg g⁻¹) and Q_0 (mg g⁻¹) refer to the equilibrium and maximum amounts of flavone adsorbed, respectively. The b symbol indicates the Langmuir constant related to the adsorption rate [40].

A linear plot of C_e/q_e vs. C_e was obtained with an intercept of $1/Q_0b$ and slope of $1/Q_0$. Also, a dimensionless constant separation factor (R_L) can be classified if the adsorption process is favourable or unfavourable, and it is expressed by the following equation:

$$R_L = 1/(1 + bC_0). \tag{3}$$

The adsorption system is considered to be linear or irreversible, if the R_L value equal to 1 or 0, respectively, while favourable adsorption if $0 < R_L < 1$ and an unfavourable if $R_L > 1$ [41].

Otherwise, the Freundlich isotherm equation proposes a multilayer adsorption of a heterogeneous sorbent surface, and

it is commonly defined by the following equation [42]:

$$\log q_e = \log K_f + 1/n \log C_e, \tag{4}$$

where C_e corresponds to the concentration of flavones at equilibrium (mg l⁻¹), q_e indicates to the amount of flavone adsorbed (mg g⁻¹). Both n and K_f (mg g⁻¹) represent Freundlich constants, which can be estimated from an intercept and slope, respectively, of the linear plot of $\log q_e$ against $\log C_e$.

Herein, the parameters of Langmuir and Freundlich equations were calculated according to experimental adsorption data of flavone on CA/Mn-1 thin film. The equilibrium data were well-fitted with the Langmuir equation (figure 3b) according to the least square fit, supporting a validity of Langmuir equilibrium model for an adsorption process. In addition, values of Langmuir constants were obtained as $Q_0 = 58.48$ mg g⁻¹ and $b = 3.721$ mg⁻¹. The correlation coefficient acquired from the Langmuir equation was found to be $R^2 = 0.9997$ for flavone adsorption onto CA/Mn-1 phase. Furthermore, the theoretical adsorption capacity obtained from Langmuir model (58.48 mg g⁻¹) was consistent with the experimental data $q_{e(\text{exp})}$ (57.96 mg g⁻¹). In addition, the

Table 2. Constants and correlation coefficients of kinetic models for flavone adsorption onto CA/Mn-1 thin film.

C_0 (mg l ⁻¹)	$q_{e(\text{exp})}$ (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order		
		R^2	k_1 (min ⁻¹)	q_e (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)
30	57.96	0.765	0.0763	19.2	0.998	0.01	58.93

Table 3. Determination of flavone at different concentrations (1, 5 and 10 mg l⁻¹) in real water samples using 10 mg CA/Mn-1 at 25°C.

Samples	Added (mg l ⁻¹)	Unadsorbed (mg l ⁻¹)	Extraction (%)
Tap water	1	0.02	97.80
	5	0.18	96.36
	10	0.49	95.13
Lake water	1	0.03	97.11
	5	0.25	95.07
	10	0.63	93.72
Sea water	1	0.04	96.47
	5	0.25	95.04
	10	0.82	91.85
Drinking water	1	0.01	98.96
	5	0.11	97.80
	10	0.46	95.45

R_L value of flavone adsorption onto CA/Mn-1 phase was 0.01, confirming high and favourable adsorption process based on Langmuir model. Considering the results, it can be suggested that the adsorption of flavone takes place at homogeneous CA/Mn-1 surface through monolayer.

3.2d Influence of extraction time on adsorption: Contact time is an influential factor that determines the behaviour of the flavone extraction by CA/Mn-1. For kinetics study, several shaking times were chosen in the range of 2.5–60 min for investigating the contact time effect on the flavone adsorption onto CA/Mn-1 thin film at 25°C (figure 3c). Based on the results, the amount of flavone adsorbed onto CA/Mn-1 phase dramatically increased with an increase in the extraction time, indicating that CA/Mn-1 had rapid adsorption kinetics for flavone. As it is conspicuous from figure 3c, there is an increase in the equilibrium capacity of flavone from 48.69 to 57.96 mg g⁻¹ with increasing the shaking time from 10 to 60 min, respectively, in which the equilibrium time was reached to 50 min, while the maximum uptake capacity attained within 60 min.

3.2e Kinetic studies: To interpret the adsorption system nature, several kinetic models were used to construe the experimental data that accessed from adsorption experiments. Kinetic isotherms were analysed according to Pseudo-first and second-order kinetic models [43]. The equation of Pseudo-first-order is formulated as follows [44]:

$$\text{Log}(q_e - q_t) = \text{log } q_e - (k_1/2.303)t, \quad (5)$$

where k_1 (min⁻¹) denotes the first-order adsorption rate constant, q_t (mg g⁻¹) and q_e (mg g⁻¹) indicate the adsorbed amounts of flavone at time t (min) and at equilibrium, respectively. Log ($q_e - q_t$) against t was plotted and the values of uptake capacity (q_e) as well as adsorption rate constant (k_1) for CA/Mn-1 thin film were acquired from an intercept and slope.

On the other hand, a pseudo-second-order equation is given below [45]:

$$t/q_t = 1/v_o + (1/q_e)t, \quad (6)$$

where $v_o = k_2 q_e^2$ (mg g⁻¹ min⁻¹) corresponds to an initial rate of adsorption and k_2 (g mg⁻¹ min⁻¹) is the equilibrium rate constant. Amounts of flavone adsorbed on a surface of CA/Mn-1 phase at time t (min) and at equilibrium symbolize as q_t (mg g⁻¹) and q_e (mg g⁻¹), respectively. Based on equation (6), the values of q_e and v_o were defined through the intercept and slope of a linear plot of t/q_t vs. t , as displayed in figure 3d. Values of kinetic parameters obtained from pseudo-first and second-order equations and the corresponding correlation coefficients (R^2) were reported in table 2. It is obvious from table 2 that (R^2) value for pseudo-first-order model was very low and the experimentally obtained uptake capacity value did not agree with the calculated value from pseudo-first-order model, illustrating that flavone adsorption onto CA/Mn-1 phase could not be well characterized by pseudo-first-order model. Conversely, results of adsorption kinetic were well compatible with the pseudo-second-order model with a great value of R^2 (very close

to 1), as shown in figure 3d, suggesting the accuracy and authenticity of the pseudo-second-order adsorption model. Furthermore, the uptake capacity of flavone on CA/Mn-1 phase estimated from the pseudo-second-order equation (58.93 mg g^{-1}), was also compatible with experimentally acquired uptake capacity (57.96 mg g^{-1}) as well as Langmuir isotherm model (58.48 mg g^{-1}). The results indicated that pseudo-second-order was an optimal kinetic model that explained the adsorption processes for flavone onto CA/Mn-1 phase.

3.3 Analysis of real samples

The suggested methodology using CA/Mn-1 adsorbent was validated for extracting flavone from real water samples to evaluate the efficiency of the method in analytical applications. Water specimens were collected from different sources in Jeddah City, KSA; which includes tap water, red sea water, lake water and drinking water. The standard addition method was carried out by the overall SPE procedure to appraise the accuracy of flavone extraction. The percentage of extracted flavone for each sample was calculated, and the results are recorded in table 3. The extraction percentages of flavone from real samples by CA/Mn-1 thin film were in the range of 91.85–98.96%. These results reveal the suitability and reliability of CA/Mn-1 thin film for selective extraction and detection of flavone, at trace-level concentrations, from environmental samples.

4. Conclusions

The analytical potential of the developed cellulose acetate/manganese oxide thin film for selective separation and detection of flavone was evaluated and showed sensible static adsorption capacity. Adsorption isotherm data of flavone adsorption onto CA/Mn-1 were significantly consistent with the Langmuir equilibrium model, postulating that an adsorption process was occurred through a monolayer of adsorbate molecules on a homogeneous surface of the adsorbent. Results further indicated that flavone adsorption on CA/Mn-1 thin film kinetically well fit with the pseudo-second-order model. Thus, the proposed method achieved satisfactory results for selective extraction and detection of flavone in environmental water samples.

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