



Assess the ability of detecting low concentration analyte with near-infrared spectroscopy based on dynamic enrichment

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ABSTRACT

The ability to detect low concentration analyte with near-infrared diffuse reflectance spectroscopy (NIRDRS) based on dynamic enrichment method has been assessed. A special design of fluidized bed enrichment device was used to enrich a large volume of analyte's dilute solution before spectrum detection, in order to improve the detection sensitivity of NIRDRS. A kinetic model, which considers the mass transfer with liquid film diffusion, has been used to characterize the adsorption process in this device. The developed model agreed with the experimental results very well in a wide range of the influent flow rate (F) and solution concentration (C_0). Based on this model, the lowest detectable concentration was estimated, at the same time the effects of liquid fluid rate and operation time on this value were also investigated. Meanwhile, a comparison between this model and the static adsorption model was made. Furthermore, a series of carbaryl aqueous solutions at different concentrations were treated with the enrichment device to verify the estimated lowest concentration. This study reveals that the specially designed fluidized bed device is able to enrich enough amount of analyte in a quite short time, and based on this dynamic adsorption model, it is possible to detect analyte in solution quantitatively at ppm-level by NIRDRS.

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1. Introduction

Near-infrared spectroscopy (NIRS) has proven to be a powerful analytical tool and has been widely applied in many fields, such as agriculture [1,2], food [3,4], pharmaceutical [5,6], routine chemical analysis [7–9] and the petroleum industry [10,11]. It has attracted growing attention due to its advantages of rapidness, non-destruction, simple-pretreatment, few-reagent and low cost. However, the low molar absorptivity of near infrared signals which considerably reduces its sensitivity, makes common NIR technique impossible for micro- and trace level analysis. Therefore, it is very meaningful to improve the sensitivity of NIRS for low concentration analysis.

In recent years, aiming to improve the sensitivity of NIR technique, some researchers have reported the ppm (mg/L) level detection [12–24]. Among these work, adsorption technique as an effective pre-concentration process was often introduced into NIR technique to improve the sensitivity. In this combination method, solid adsorbents are employed to enrich analytes selectively from dilute solutions, and then the solid materials with adsorbed analytes are directly measured by NIR without any elution process. The advantages of this method are obvious. It simplifies the enrichment process, reduces or even eliminates the interference of water, avoids the loss of analytes and abandons the use of toxic reagents that are commonly encountered during elution process. Meanwhile, the work using this combination method

usually show good results with very small values of root mean square error of cross validation (RMSECV) and/or root mean square error of prediction (RMSEP), which seem to be satisfactory for quantitative analysis. However, if we take a closer look at the RMSECV and RMSEP values, we will find that they are not small enough comparing with the concentrations of the analyte to build a satisfactory model. If we evaluate these work based on the value of relative error (RE), which is calculated by the RMSECVs or RMSEPs divided by the mean concentration of sample solutions, some work do not show a good performance with large relative errors (normally larger than 15%). More details about this conclusion has been discussed and reported in our previous work [25], it is unnecessary to go into a lot of details here.

As mentioned in our previous research [25], the reason of the large errors is the low content of the analyte adsorbed on the adsorbent, i.e. mass of adsorbed analyte per unit weight of adsorbent (q_t), which are directly related to the NIR spectra. In some work, several or tens of milliliter solutions were used, so it was hard to obtain a high q_t , e.g. 20 mL of 2 mg/L analyte solution only contains 0.04 mg analyte, and if it adsorbed on the 2 g adsorbent completely, q_t is only 0.02 mg/g. Thus, increasing the concentration of the adsorbed phase q_t (mg/g) is particularly important to improve the sensitivity of the method based on enrichment. There are two important factors influencing the value of q_t , which are mass of adsorbent and volume of sample solution denoted by m and V . Too small m will affect the spectral accuracy, therefore, larger V should be used to ensure that more amounts of analytes could be adsorbed on the adsorbent.

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For this reason, some studies were reported to solve this problem by employing a relatively large volume solution to enrich. For example, Shao et al. [20] used resin as an adsorbent to extract phenol and p-nitrophenol from a solution of 100 mL before NIRDRS. The results showed that the concentrations that can be quantitatively detected were as low as 39.02 and 39.01 mg/L, with relative errors of 9.36 and 9.04%, respectively. Recently they [23] prepared a high capacity adsorbent of amino-modified silica particle (AMSP) as the adsorbent to determine low concentration fish sperm deoxyribonucleic acid (fsDNA). With the solution volume of 100 mL, the mean relative error was about 7.8% in the concentration range of 3.00–29.38 mg/L.

In our group, a new enrichment device [26–28] was designed based on fluidized bed idea, which could supply a rapid, effective enrichment using a large volume (such as 500 or 1000 mL) of sample solution, and could be directly detected by NIRS without filtration. This novel dynamic on-line enrichment device has been successfully applied to determine trace Cu^{2+} [26], β -naphthalenesulfonic acid [27] and dimethyl fumarate [29] (DMF). The work of Cu^{2+} determination showed that the RMSECV was 0.2381 $\mu\text{g/mL}$ in the concentration range of 0.5–4.4 $\mu\text{g/mL}$ and the mean relative error of the independent test set was 2.51%. Meanwhile, the determination of β -naphthalenesulfonic acid and DMF could reach to the mean relative error of 10 independent test samples of 3.72 and 5.33%, respectively.

Despite its successful use, the mass transfer between the solid resin and liquid solution during the adsorption process should be considered in advance, as it is a crucial issue involving the sensitivity of NIR determination based on dynamic pre-concentration technique. Because higher sensitivity of an analytical method can detect lower concentration analytes in a sample, however, the NIR spectrum directly reflects the spectral absorbance of the adsorbent and analytes adsorbed on the adsorbent, but not the concentration of original sample solution, i.e., the spectrum directly relating to q_t , but not C_0 . So it is necessary to investigate the kinetic adsorption process and potential rate-controlling step for derivation of the adsorption model. Although there are many empirical models widely used and reported in the literature to describe the kinetic adsorption process, including the pseudo-first-order equation [30], pseudo-second-order equation [31,32], and the Elovich equation, building models with theoretical basis are better ways to design and study the system considering a wide range of operation conditions. In addition, they allow the correlation of the model parameters to the physical and chemical properties of the system, leading to a better understanding of the process.

The purpose of this work is to build a kinetic model for an accurate description of mass transfer process of carbaryl from an aqueous phase onto solid HZ818 resin in the fluidized bed device based on rational theoretical assumptions. Experiments under various conditions were carried out to verify the reliability of the model and investigate the influence of the parameters. Afterwards, the lowest detectable concentration of carbaryl in solution using the dynamic enrichment coupled with NIR technique was evaluated based on the constructed model. Meanwhile, it is interesting to make a comparison between the kinetic and static adsorption models [25]. Furthermore, an attempt was made to get a relatively exact value of the minimal detectable mass of carbaryl on resin and the lowest detectable concentration in solution under a fixed operation condition.

2. Experimental

2.1. Reagents and adsorbent

All chemical reagents used, including methanol (MeOH), ethanol (EtOH, $\geq 99.5\%$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were of analytical purity grade and used without further purification. Carbaryl (analytical standard grade) applied as the adsorbate in the present study was purchased from Dr. Ehrenstorfer GmbH. All glasswares were rinsed with ultra-pure water that was obtained from an

ultra-pure water purification system (SARTORIUS arium 611DI, Germany, $18.2 \text{ M}\Omega \cdot \text{cm}$) 3 times.

HZ818 macroporous adsorption resin used as the adsorbent was purchased from Shanghai Huazhen Science and Technology Co., Ltd. of East China University of Science and Technology. Prior to pretreatment, the resin was sieved and the fractions within the range of 0.30–0.35 mm were collected. Then, firstly, the resin was being swelled with ethanol for 24 h, and then washed by ultra-pure water repeatedly to remove excess solvent, oligomer and other impurities until there was no ethanol left. Secondly, it was infiltrated with 5% HCl solution for 4 h, and thoroughly washed with ultra-pure water to remove free acid. Finally, the resin was soaked in 2% NaOH solution for 4 h, and sequentially being rinsed with ultra-pure water to neutral. The pretreated resin was stored in ultra-pure water for future use.

2.2. Analytical methods

Quantification of the carbaryl concentration in aqueous solution was carried out by a Liquid Chromatograph (Agilent Technologies 1260 infinity, Germany) using a SinoChrom ODS-BP column, 250 mm \times 4.6 mm I.D., 5 μm , dp (Elite, Dalian, China). The injection volume was 20 μL throughout the study. The mobile phase was a mixture of MeOH and H_2O 65:35 (v/v), with a flow-rate of 1.0 mL/min under isocratic condition. The concentration of carbaryl was monitored by the ultraviolet detector at 280 nm and quantified using the corresponding calibration curve.

The diffuse reflectance spectra of the analyte adsorbed on resin were obtained by a Near-infrared Spectrometer (Thermo Fisher Scientific Inc., Antaris II, USA), equipped with an integrating sphere diffuse reflectance accessory and an InGaAs detector.

2.3. Experimental procedure

2.3.1. Preparation of samples

A 1000 mg/L carbaryl standard stock solution was prepared by dissolving the powder carbaryl standard with MeOH. All sample solutions were obtained by diluting the appropriate volumes of the stock solution with ultra-pure water into 1 L flask. 9 carbaryl solutions (as shown in Table 1) were prepared for adsorption kinetic experiment (Section 2.3.2), and another 45 sample solutions with the concentration range of 0.1–10.0 mg/L (as shown in Table 6) were prepared for dynamic enrichment and NIR spectral determination (Section 2.3.3).

2.3.2. Adsorption kinetics of fluidized bed system

An accurately weighed 2.0 g (the optimal adsorbent dosage that has been discussed in our previous research [25]) of activated HZ818 adsorption resin was introduced into the specially designed fluidized bed enrichment device in advance. Then 1 L sample solution was passed through the container with the aid of a peristaltic pump at an appropriate flow rate. At proper time intervals, effluents were taken from the exit to measure the residual concentrations of carbaryl C_t with HPLC

Table 1
Operation conditions of the fluidized bed system.

Experiment No.	C_0 (mg/L)	m (mg)	P^a (rpm)	F^b (mL/min)
1	2.444	2.0	25	41.38
2	4.764	2.0	25	41.38
3	11.52	2.0	25	41.38
4	2.427	2.0	10	16.68
5	2.381	2.0	50	83.12
6	2.419	2.0	75	125.0
7	2.373	2.0	100	165.7
8	2.432	2.0	125	210.5
9	2.435	2.0	150	251.9

^a Rotation speed of peristaltic pump.

^b From experimental measurement.

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