

Article

# Application of Sodium Dodecyl Sulfate/Activated Carbon onto the Preconcentration of Cadmium Ions in Solid-Phase Extraction Flow System

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**Abstract:** In the present study, activated carbon (AC) surface modified with sodium dodecyl sulfate (SDS), written as SDS/AC, was applied as an adsorbent for preconcentration and determination of trace amount of cadmium ions in environmental sample waters. The SDS modification on AC was performed at the same time, while cadmium ions were concentrated in the flow system as solid-phase extraction. After the separation and preconcentration steps, cadmium retained on SDS/AC was eluted with HNO<sub>3</sub> and was subsequently determined by flame atomic absorption spectrometry (FAAS). The analytical parameters that influence the quantitative determination of trace cadmium, such as SDS concentration, pH and volume of sample solution, eluent conditions, and interference, were optimized. At the optimum conditions, the general matrix elements had little interference on the proposed procedure. The detection limits was 17 ng·L<sup>-1</sup>, and the relative standard deviation (RSD) for 12 experiments at 10 µg·L<sup>-1</sup> cadmium solutions was 2.8%. The developed method was applied into the analysis of environmental samples spiked cadmium.

**Keywords:** cadmium; activated carbon; sodium dodecyl sulfate; solid-phase extraction; flame atomic absorption spectrometry; preconcentration

## 1. Introduction

Now, the environmental pollution with the heavy metals is one of the important problems. Cadmium (Cd) exists in the natural environment and is known to be a toxic environmental pollutant. Although Cd has been applied into the industrial materials, it causes many health problems in organs such as kidney, lung, and liver for the human body [1,2]. World Health Organization (WHO) and Environmental Protection Agency (EPA) have limited Cd concentration in drinking water to 3 µg·L<sup>-1</sup> and 5 µg·L<sup>-1</sup>, respectively [3,4]. In Japan, Ministry of the Environment established 30 µg·L<sup>-1</sup> for effluent standard [5] and 3 µg·L<sup>-1</sup> for environmental quality standards [6] for human health. Thus, it is necessary to control the exposure even at trace levels and monitor Cd concentration with sensitive analytical techniques.

Currently, the analytical methods for trace determination include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) [7], inductively coupled plasma-optical emission spectrometry (ICP-OES) [8] and inductively coupled plasma mass spectrometry (ICP-MS) [9]. Among them, FAAS has been widely employed in the determination of heavy metals because of inexpensive instrument, easy operation, good selectivity, and high sample throughput [10,11]. On the other hand, this method often suffers from worse detection limits [12]. The overcome of this limitation needs the preconcentration and separation of analytes from matrices in analytical procedure [13].

Preconcentration techniques have contained liquid–liquid extraction (LLE) [14], coprecipitation [15], cloud point extraction (CPE) [16], and solid phase extract (SPE). In particular, the SPE procedure has been used for the separation and preconcentration techniques of trace metal ions because of high recovery and enrichment factor, short extraction time, variation of adsorbent, and unnecessary of organic solvents [17–19]. In the SPE technique for metal ions in aqueous solution, activated carbon (AC) has been applied as the efficient adsorbent due to high adsorption capacity and low cost [20–22]. Moreover, the modification of functional groups onto AC surface can improve the selectivity and adsorption behavior of heavy metal ions. It has been reported that the metal complexes more effectively adsorbed onto activated carbon. For example, sodium diethyl dithiocarbamate [23], tetrabutylammonium hydroxide [24], ammonium pyrrolidinedithiocarbamate [25], and xylenol orange [26] were modified on activated carbon surfaces and were applied for separation/preconcentration. These techniques required the preparation of the adsorbent prior to preconcentration.

Sodium dodecyl sulfate (SDS), an anionic surfactant, is used as cleaning and hygiene products [27]. Recently, the modification that is based on SDS adsorption at the solid–fluid interface has been applied for the determination of various analytes [28–30]. Ahn et al. reported the removal of Cd from aqueous solution by AC impregnated with SDS [31]. Hon et al. investigated the AC modified with SDS as a solid phase sorbent for the separation and preconcentration of trace Cd in water samples [32]. It was necessary, in the study, to fabricate SDS/AC before the preconcentration. Therefore, we have developed the preconcentration technique that Cd was concentrated to AC at the same time while SDS, which was added in a sample solution, was modified to AC by batch method [33]. However, there is little information on the preconcentration flow system that Cd is concentrated to AC in aid of simultaneous modification of SDS.

In the present work, the novel preconcentration method was developed for the preconcentration of Cd in environmental water samples based on solid-phase extraction using sodium dodecyl sulfate/activated carbon with the flow system. In the flow system, SDS was adsorbed onto AC during the preconcentration of Cd.

## 2. Materials and Methods

### 2.1. Reagents and Materials

Cadmium standard stock solution ( $1000 \text{ mg L}^{-1}$  of  $\text{Cd}^{2+}$  in  $0.1 \text{ mol}\cdot\text{L}^{-1}$  nitric acid) was purchased from NACALAI TESQUE, INC. (Tokyo, Japan). Working solutions were carefully diluted from the stock solution with nitric acid solution. Activated carbon (DarcoKB-G) was purchased from SIGMA-ALDRICH® (St. Louis, MO, USA). Sodium dodecyl sulfate (SDS) from Kanto Chemical Co. (Tokyo, Japan) was employed without further purification. Other surfactants—cetyl trimethyl ammonium bromide (CTAB), and octyl phenol ethoxylate (OPE)—were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Matrix solutions of  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  were prepared by dissolution of nitrates and hydrochlorides. All reagents were in analytical grade. Ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}$ ) was obtained from the Advantec ultrapure water system CPW-102 (Tokyo, Japan). The pH of the sample solutions was adjusted with  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $\text{HNO}_3$  and/or  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $\text{NaOH}$ .

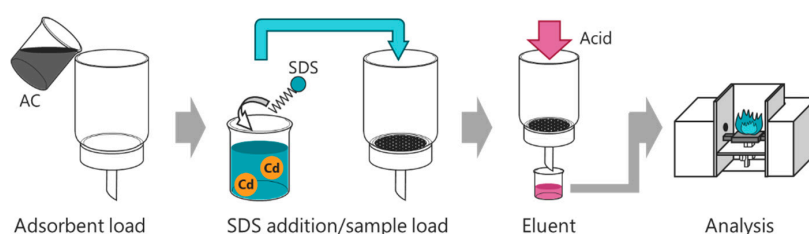
### 2.2. Apparatus

The determination of cadmium ions was carried out with Thermo Solaar S2 (Thermo Fisher Scientific K.K., Tokyo, Japan) flame atomic absorption spectrometer (FAAS) equipped with deuterium background corrector. Cadmium hollow cathode lamp (Hamamatsu Photonics K.K., Shizuoka, Japan) was used as the radiation source with wavelength of 228.8 nm. An air/acetylene flame was employed in all measurements, and the slit length of the burner was 5 cm. The instrumental parameters recommended by the manufacturer were used for FAAS measurements.

A pH/DO METER D-55 (HORIBA, Ltd., Kyoto, Japan) pH meter was used to monitor the pH of the solutions.

### 2.3. Preconcentration Procedure

Fifty mg activated carbon was added and stirred into 50 mL pure water. For the adsorption, the suspended solution was poured into the column ( $\phi 40 \times 100$  mm) and AC was put on the membrane filter. After pH adjustment, the sample solution containing  $10 \mu\text{g}\cdot\text{L}^{-1}$  Cd and  $100 \text{mg}\cdot\text{L}^{-1}$  SDS was passed through AC-loaded filter with the flow rate of  $1 \text{mL}\cdot\text{s}^{-1}$ . Subsequently, the eluent of 3 mL was poured with the flow rate of  $0.5 \text{mL}\cdot\text{s}^{-1}$  to desorb the adsorbed Cd ion from AC adsorbent. The collected eluent was determined by flame atomic absorption spectrometry. This preconcentration procedure is shown in Figure 1.



**Figure 1.** Experimental procedure for the preconcentration of cadmium using sodium dodecyl sulfate/activated carbon (SDS/AC).

Analytical techniques employed in the preconcentration provide analyte isolation and enrichment factor. Enrichment factor is one of important parameters to compare the analyte concentration before and after the preconcentration method and is obtained by the following Equation (1).

$$\text{Enrichment factor (EF)} = C_{\text{eluent}}/C_{\text{sample}} \quad (1)$$

Additionally, since some analytes may be lost during the preconcentration, recovery is calculated by the following Equation (2) in order to evaluate the analyte amount in sample solution before and after the preconcentration.

$$\text{Recovery} = \text{EF} \times (V_{\text{eluent}}/V_{\text{sample}}) \times 100 \quad (2)$$

Here,  $C_{\text{eluent}}$ ,  $C_{\text{sample}}$ ,  $V_{\text{eluent}}$ , and  $V_{\text{sample}}$  are the concentration in the eluent, the concentration in sample solution, the eluent volume, and the sample volume, respectively.

The analytical parameters, such as surfactant type and concentration, pH of sample, eluent conditions, interfering elements, sample volume, and reusability were evaluated and optimized for the recovery of Cd ion in the preconcentration.

### 3. Results

The preconcentration cadmium on SDS/AC while modifying SDS to AC surface was attempted by passing the sample solution containing relatively low concentration ( $100 \text{mg}\cdot\text{L}^{-1}$ ) of SDS through AC-loaded filter.

Sigma-Aldrich activated carbon Darco<sup>®</sup> KB-G was applied as the adsorbent. The characterization of DarcoKB-G was reported in the previous work [33].

It was reported from the nitrogen adsorption/desorption isotherm analysis that the curve shape of the activated carbon belonged to type IV isotherm with hysteresis loops characteristic of mesoporous structure. BET specific surface, total pore volume and average pore diameter were  $1414 \text{m}^2\cdot\text{g}^{-1}$ ,  $1.2 \text{cm}^3\cdot\text{g}^{-1}$ , and  $3.3 \text{nm}$ , respectively. The peak of pore diameter distribution was  $\sim 9 \text{nm}$ , according to pore distribution calculation.

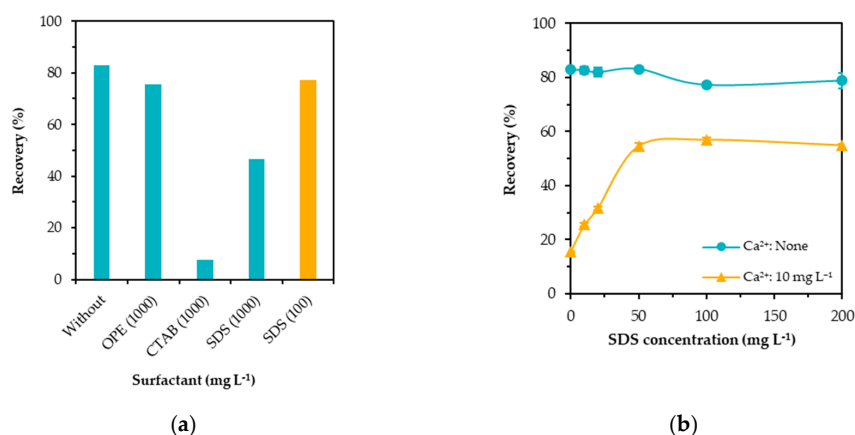
In the present work, normal sodium dodecyl sulfate (n-SDS) was applied for improvement of recovery. As the result of previous work, FT-IR spectra for AC and AC/SDS showed it that AC could be modified with SDS. SEM and TEM images of the samples indicated the surface morphology and conditions of activated carbon could hardly be changed due to the SDS modification.

### 3.1. Effect of Surfactants

In the preconcentration with the catch system, the addition of SDS was effective for the improvement of recovery of Cd. Therefore, the effect of surfactant on the preconcentration of Cd by the flow system was investigated.

As shown in Figure 2a, in the case of cetyl trimethyl ammonium bromide (CTAB, cationic surfactant), the recovery became worse compared with those obtained with only Cd solution. The reason may be due to electrostatic repulsion between positively charged hydrophilic groups and cadmium ions. The presence of nonionic surfactant (octyl phenol ethoxylate (OPE)) gave the slightly decrease in recovery. Although the addition of SDS in Cd solution deteriorated the recovery with high concentrations ( $1000 \text{ mg}\cdot\text{L}^{-1}$ ), in the Cd sample with low concentration SDS ( $100 \text{ mg}\cdot\text{L}^{-1}$ ), the factor was almost the same as that without the surfactants.

Next, in Figure 2b, the influence of SDS concentration on the recovery in the presence of interfering element (Ca) was investigated. In the condition without SDS, calcium ions severely affected the recovery of Cd. On the other hand, with the addition of SDS, the recovery of Cd was improved in the flow system. The recovery of Cd in the presence of SDS was not so bad with the Ca matrix (for instance; 16% and 58% in the absence and presence of SDS, respectively); however, the effect of matrix Ca element in the flow system was negligible, which is very advantageous. Therefore,  $100 \text{ mg}\cdot\text{L}^{-1}$  of SDS was selected as co-existing surfactant in the Cd solution with the flow system.



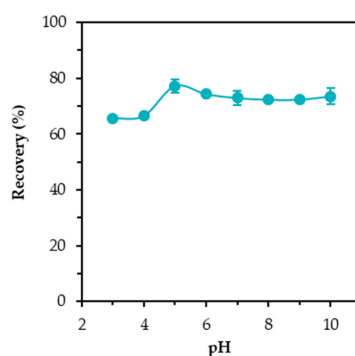
**Figure 2.** Effect of (a) various surfactants ( $1000 \text{ mg}\cdot\text{L}^{-1}$ ) and (b) SDS concentrations on recovery of cadmium ions. Experimental conditions: Cd  $10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ ; AC 50 mg; pH 5; sample volume 200 mL; flow rate  $1 \text{ mL}\cdot\text{s}^{-1}$ ; eluent  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$  3 mL.

### 3.2. Effect of Initial PH

The pH of the sample solutions is an important analytical factor in the solid-phase extraction for Cd element. Also, the chemical species for Cd in the solution can depend on the solution pH. Hence, solution pH can regulate the release of free Cd species through the forms that are chemically bound to mineral, organic and colloidal components in environmental samples. At  $\text{pH} < 3.5$ , all metals are generally released, except for the most strongly bound fractions of the mineral, organic, and colloidal components [34]. Hot acid digestion is the only reliable technique for charging the total amount of metal to a simple ionic form. Finally, the solution pH can be adjusted to the desired value.

Therefore, the effect of sample pH on the recovery of Cd was investigated in the range of 3 to 10. The results show it that the recovery of Cd became a maximum at pH around 5, as illustrated in Figure 3.

The tendency may result from the charges of AC surface condition and chemical species for Cd. The distribution of cadmium species at various pHs has been already reported by Ahn et al. [35,36]. The zero point charge (ZPC)  $pH_{ZPC}$  of AC Darco KB-G is  $\sim 2.2$  [37]. The AC surface is positively charged in strong acidic media ( $pH < 2.2$ ), whereas it is negatively charged under neutral and alkaline conditions ( $pH > 2.2$ ). At pH 5, the hydrophobic tail in SDS can connect with the negatively charged surface of AC, because the hydrophilic sulfonate head with negative charge can repulse the AC surface with negative charge. The main species for cadmium is  $Cd^{2+}$  in the pH range of 0 to 8. Below pH 5, the recoveries of Cd decreased with the decrease in pH, owing to the electrostatic repulsion of the protonated sites in SDS/AC with the positively charged cadmium species. At pH of more 5, the fraction of another species ( $CdOH^+$  and  $Cd_2OH^{2+}$ ) may increase with pH. Consequently, pH 5 was selected as the optimum pH for subsequent works.



**Figure 3.** Effect of initial pH in sample solution on Cd recovery. Experimental conditions: Cd  $10 \mu\text{g}\cdot\text{L}^{-1}$ ; AC  $50 \text{ mg}$ ; SDS  $100 \text{ mg}\cdot\text{L}^{-1}$ ; sample volume  $200 \text{ mL}$ ; flow rate  $1 \text{ mL}\cdot\text{s}^{-1}$ ; eluent  $0.1 \text{ mol/L HNO}_3$   $3 \text{ mL}$ .

### 3.3. Optimization of Elution Conditions

The effect of eluent on the recovery of Cd ions was also studied. The elution (acid) conditions can affect the stripping of analytes from SDS/AC, and sometimes acid elution may give impart damage to the atomizer for AAS. The stripping power depends on the type, concentration and volume of acid eluent. Therefore, the different eluents including  $\text{HNO}_3$ ,  $\text{HCl}$  and their mixed acid ( $\text{HNO}_3:\text{HCl} = 1:1$ ) were used in order to acquire the most suitable eluent. The results are shown in Table 1.

**Table 1.** Effect of type, concentration, and volume of eluent on enrichment factor (EF) and recovery. Experimental conditions: Cd  $10 \mu\text{g}\cdot\text{L}^{-1}$ ; AC  $50 \text{ mg}$ ; SDS  $100 \text{ mg}\cdot\text{L}^{-1}$ ; sample volume  $200 \text{ mL}$ ; flow rate  $1 \text{ mL}\cdot\text{s}^{-1}$ .

Type	Concentration ( $\text{mol}\cdot\text{L}^{-1}$ )	Vol. (mL)	EF	Rec. (%)	RSD%
$\text{HNO}_3$	0.1	6	26.5	79.5	5.4
	0.1	5	35.3	88.3	2.9
	0.1	3	47.3	77.3	4.9
	0.1	2 + 1	58.9	88.4	1.8
	1	3	62.5	93.8	1.3
$\text{HCl}$	0.1	3	51.6	77.5	3.9
	1	3	52.1	78.1	3.9
$\text{HCl}:\text{HNO}_3$	0.1:0.1	3	58.2	87.3	5.5

According to the comparison between the recovery with various acid types, better result were obtained with nitric acid, while lower recovery was observed with hydrochloric acid and mixed acid ( $\text{HNO}_3:\text{HCl} = 1:1$ ). In the case of eluent volume, 2 + 1 mL, It is considered that it takes slightly long time for the desorption process and the moving action has occurred. The adsorbent becomes wet and further desorption process proceeds after first elution of 2 mL  $\text{HNO}_3$ . Furthermore, the adsorbent

is washed away by addition 1 mL eluent. Considering the atomizer exhibits low tolerance to the introduction of strong acid, the optimum elution conditions were  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$  (2 + 1) mL for all further experiments.

### 3.4. Interferences

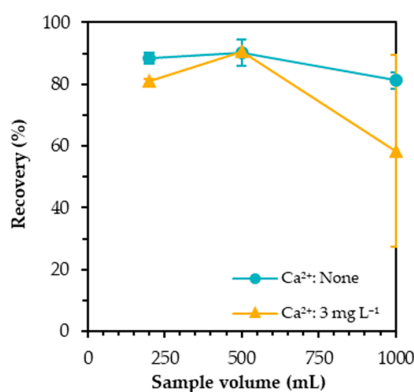
The one of main problems is interference by matrix elements for the determination of heavy metals in real samples with atomic absorption spectrometry. Therefore, the interference of coexisting elements on the preconcentration and determination must be conducted, because it links directly to the performance of the proposed analytical method. For the interference study on cadmium, the element contained in environmental sample such as Al, Ca, Cu, Fe, K, Mg, and Zn were selected. In these experiments, the interfering element was added into 200 mL of sample solution ( $10 \mu\text{g}\cdot\text{L}^{-1}$  of cadmium ion). As shown in Table 2, because the cadmium recovery was almost quantitative in the presence of excessive amount of the interfering cations, there was insignificant variation of difference value calculated by comparing EF with and without interference ions. As a consequence, the proposed preconcentration technique was independent on matrix interferences.

**Table 2.** Effect of interfering ions on  $\text{EF}_{\text{in the matrix}}/\text{EF}$  of  $\text{Cd}^{2+}$  ions. Experimental conditions: Cd  $10 \mu\text{g}\cdot\text{L}^{-1}$ ; AC 50 mg; SDS  $100 \text{ mg}\cdot\text{L}^{-1}$ ; sample volume 200 mL; flow rate  $1 \text{ mL}\cdot\text{s}^{-1}$ ; eluent  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$  2 + 1 mL.

Interference	Concentration ( $\text{mg}\cdot\text{L}^{-1}$ )	$\text{EF}_{\text{in the matrix}}/\text{EF} \times 100$ (%)	RSD (%)
$\text{K}^+$	5	94.0	1.4
$\text{Mg}^{2+}$	3	81.2	1.4
$\text{Ca}^{2+}$	3	91.4	0.8
$\text{Al}^{3+}$	2	101.9	1.5
$\text{Fe}^{3+}$	1	102.7	5.7
$\text{Ni}^{2+}$	5	90.0	4.7
$\text{Cu}^{2+}$	5	95.8	1.5
$\text{Zn}^{2+}$	5	98.2	0.4

### 3.5. Effect of Sample Volume

In the case of preconcentration and determination for trace concentration of analytes, the volume of sample solution as an analytical parameter has an important role because the enrichment factor becomes large by increasing the sample volume and/or decreasing the eluent volume as shown in Equation (1). In order to investigate the effect of the volume of sample solution, three different volumes of 200, 500, and 1000 mL containing  $10 \mu\text{g}\cdot\text{L}^{-1}$  were examined, as shown in Figure 4.



**Figure 4.** Effect of sample volume on recovery of cadmium ions. Experimental conditions: Cd  $10 \mu\text{g}\cdot\text{L}^{-1}$ ; AC 50 mg; SDS  $100 \text{ mg}\cdot\text{L}^{-1}$ ; sample volume 200 mL; flow rate  $1 \text{ mL}\cdot\text{s}^{-1}$ ; eluent  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$  3 mL.

Without the addition of an interfering element (Ca), the recovery would not be affected by the sample volume. On the other hand, when the Ca matrix element was added, a slight decrease in recovery was observed. Taking into account that determination of trace Cd requires relative large sample volume, 500 mL of sample volume was chosen for the subsequent experiment.

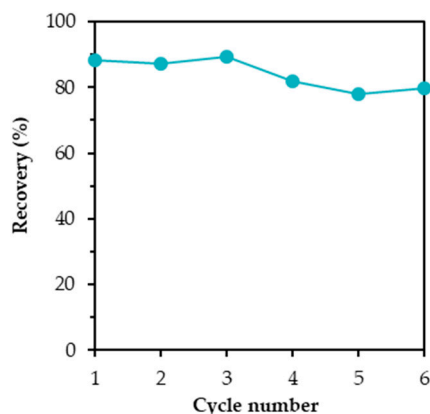
### 3.6. Analytical Performance

Under the optimized conditions, the enrichment factor (EF), recovery, dynamic range (linear range), detection limit, and reproducibility were investigated. When the sample solution and eluent volumes were 500 and 3 mL, respectively, the calibration curves was linear in the dynamic range of 0.1–15  $\mu\text{g}\cdot\text{L}^{-1}$  and the regression equation was  $A$  (absorbance) =  $0.0762C$  (concentration of  $\text{Cd}^{2+}$  in  $\mu\text{g}\cdot\text{L}^{-1}$ ) + 0.058 ( $R^2 = 0.9982$ ). The enrichment factor was 150 with the recovery of 90.2%. The detection limit ( $3S/N$ ) was  $17\text{ ng}\cdot\text{L}^{-1}$ , which was calculated by dividing the Cd concentration, which was obtained from 3 times the standard deviation of the blank by the enrichment factor. The value was better than the detection limit ( $8\text{ }\mu\text{g}\cdot\text{L}^{-1}$ ) obtained with graphite atomizer [38]. Since FAAS is in much more general use throughout the world, the proposed preconcentration is very advantageous. The reproducibility (variability of the preconcentration effect with each system) was studied by FAAS and preconcentration by adsorption. The relative standard deviation (RSD) for  $10\text{ }\mu\text{g}\cdot\text{L}^{-1}$  of Cd was 2.8% for 12 measurements.

### 3.7. Reusability

The reusability of adsorbent is one of the significant factors in assessing the performance of adsorbent materials. In order to examine the reusability of activated carbon on the filter, the preconcentration experiments, that is, adsorption–desorption cycles, were repeatedly performed by using the same AC adsorbent. After each preconcentration operation, 5 mL of  $0.1\text{ mol}\cdot\text{L}^{-1}$   $\text{HNO}_3$  and pure water were added into the AC filter for the perfect removal of cadmium ions onto AC.

The recoveries of Cd until 3 cycles became almost the same, and after 4 cycles, the values decreased slightly because of the remaining and accumulation of SDS into AC, as shown in Figure 5. Consequently, AC could be reused for 3 cycles without losing the significant adsorption.

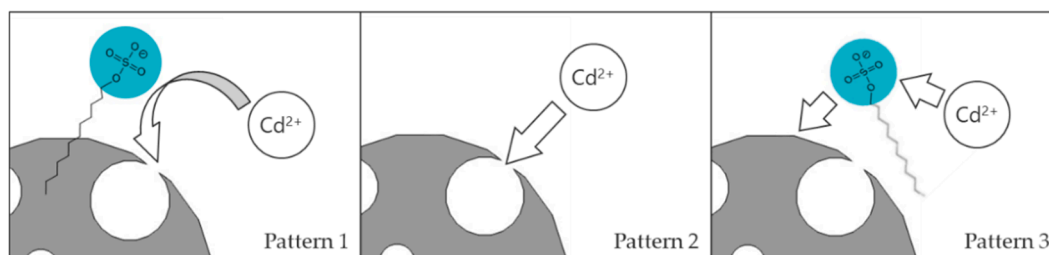


**Figure 5.** Effect of the adsorbent reuse on preconcentration and determination of cadmium. Experimental conditions: Cd  $10\text{ }\mu\text{g}\cdot\text{L}^{-1}$ ; AC 50 mg; SDS  $100\text{ mg}\cdot\text{L}^{-1}$ ; sample volume 200 mL; flow rate  $1\text{ mL}\cdot\text{s}^{-1}$ ; eluent  $0.1\text{ mol}\cdot\text{L}^{-1}$   $\text{HNO}_3$  2 + 1 mL.

### 3.8. Reaction Mechanism

A mechanism for the adsorption of cadmium on the SDS/AC is proposed in Figure 6 as well. Because the zero point charge (ZPC)  $\text{pH}_{\text{ZPC}}$  is 2.2 [37], the AC surface may become negatively in the pH range of 3 to 10. Hence, the hydrophobic tail as alkyl group ( $-\text{C}_{12}\text{H}_{25}$ ) can be linked to the AC surface, and a negatively charged hydrophilic head, such as a sulfonate group, is oriented to bulk solution. The cadmium ion with positively charge can be related to the adsorption site of AC surface or

hydrophilic head. Furthermore, it can be considered that the adsorption of SDS associated with Cd ion might also occur as the preconcentration mechanism. According to the effect of SDS, the interaction process between the hydrophilic head and  $\text{Cd}^{2+}$  will become predominant for the preconcentration.



**Figure 6.** Reaction mechanism that cadmium ions are attracted/absorbed by SDS and AC.

### 3.9. Analysis of Environmental Samples

In order to confirm the validity of the proposed method, the present procedure was applied into the preconcentration and determination of Cd in different environmental samples such as rain and mineral waters.

Since the concentration of Cd in the environmental samples was less than the detection limit, the spiked recoveries were evaluated for spiked samples. The equation of spike recovery is given as

$$\text{Spike recovery} = (C_{\text{found}} - C_{\text{original}})/C_{\text{spiked}} \times 100 \quad (3)$$

where  $C_{\text{found}}$ ,  $C_{\text{original}}$ , and  $C_{\text{spiked}}$  are the concentration obtained by determination using the established preconcentration procedure, the concentration in initial sample solution, and spiked concentration, respectively.

The recovery for the spiked Cd was in the range of 92 to 116% as seen in Table 3. The relative standard deviations for 3 experiments for samples spiked with Cd were better than 1.9%. Hence, the results obtained that the present flow system could be employed for the preconcentration of cadmium in environmental samples.

**Table 3.** Determination of cadmium ions in different real samples using the proposed method ( $n = 3$ ).

Sample	Added ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Found ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Spike/Recovery (%)
Rain water 1 (Tsu, Mie)	- 5.0	N.D. $5.80 \pm 0.02$	116
Rain water 2 (Tsu, Mie)	- 5.0	N.D. $5.32 \pm 0.10$	106
Mineral water	- 5.0 10.0	N.D. $5.21 \pm 0.09$ $9.17 \pm 0.01$	104 92

N.D.: Not detected.

### 3.10. Comparative Analysis

The comparison of this proposed procedure with other SPE procedures is shown in Table 4 [39–42]. The proposed preconcentration has good or comparable enrichment factor, linear range, detection limit (LOD) in comparison with other preconcentration techniques combined with SPE, and atomic absorption spectrometry.



**Table 4.** Comparison of analytical performances of the present work with those reported in the literatures for SPE methods combined with atomic absorption spectrometry for cadmium determination.

Adsorbent	EF	Linear Range ( $\mu\text{g}\cdot\text{L}^{-1}$ )	LOD ( $\text{ng}\cdot\text{L}^{-1}$ )	Detection	Ref.
$\text{Fe}_3\text{O}_4@\text{FePO}_4$	10	0.05–0.5	21	ETAAS	[39]
Tween 80 coated alumina	9.5	1.0–400.0	200	FAAS	[40]
Dowex Marathon C	250	1–10	130	FAAS	[41]
Cd(II)-II-MMS	50	0.01–0.2	6.1	GFAAS	[42]
SDS/AC	150	0.1–15	17	FAAS	This work

#### 4. Conclusions

Sodium dodecyl sulfate-modified activated carbon (SDS/AC) was used as a sorbent for efficient preconcentration and determination of trace cadmium ions in the flow system. As a result of optimizing the conditions, the proposed procedure gave quantitative and reproducible results. This method is simple and rapid, and serves high enrichment factor. Furthermore, it is very advantageous that the organic solvent is unnecessary for the present method.

**Author Contributions:** M.F. and S.K. conceived and designed the experiments. M.F. performed the experiments and wrote the paper. I.T. and H.K. analyzed the results and advised the project.

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**Notes:** All experiments were conducted at Mie University. Any opinions, findings, conclusions, or recommendations expressed in this paper are those of the authors and do not necessarily reflect the view of the supporting organizations.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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