

Research Article

Determination of Cobalt in Seawater Using Neutron Activation Analysis after Preconcentration by Adsorption onto γ -MnO₂ Nanomaterial

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Received 14 September 2017; Revised 4 January 2018; Accepted 28 January 2018; Published 22 February 2018

Academic Editor: Jean-Marie Nedelec

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The γ -MnO₂ nanomaterial has been used to adsorb cobalt in the seawater at Phan Thiet City, Binh Thuan Province, Vietnam. Its concentration is determined by using the neutron activation analysis (NAA) method at the Dalat nuclear research reactor. Factors affecting the uptake of cobalt on the γ -MnO₂ material such as the pH, adsorption time, and initial cobalt(II) concentration are investigated. The irradiated experiment data are calculated using the K0-Dalat program. The results obtained show that the trace dissolved cobalt in Phan Thiet seawater is found equal to $0.25 \pm 0.04 \mu\text{g/L}$ ($n = 5$, $P = 95\%$) with the adsorption efficiency being higher than 95% ($n = 4$, $P = 95\%$).

1. Introduction

Cobalt is an essential micronutrient and the central metal cofactor in the Vitamin B₁₂ [1]. It can be found in the biological and environmental samples, such as fish, egg, milk, green vegetable, and seawater. In seawater, dissolved cobalt (DCo) exists mainly as a cobalt(II) ion in chloro-carbonate complexes [2] and bound to organic ligands [3]. Although the concentration of DCo in seawater is rather low, it can affect the growth rate of coccolithophorids and cyanobacteria, some metabolic processes, the phytoplankton community structure, and the carbon flux at the atmosphere-ocean interface [4]. In addition, the concentration of DCo in seawater, which can vary differently depending on the human activities at different ocean regions such as dust, mineral

activity, and industry, can lead to the unpredictable effects on environment and food resources. Therefore, determination of the DCo concentration in seawater has recently become an important topic for interdisciplinary researches including physics, chemistry, and environment. However, it is difficult to determine directly the total DCo in seawater by the most commonly used instrumental analytical methods due to their limited sensitivity and/or matrix effects. Therefore, the separation of cobalt from the sample matrices as well as the preconcentration of cobalt is crucial for the accurate and efficient determinations of cobalt at the ultratrace levels in seawater. Various methods in addition to the modern instrumental methods have been used to enrich the level of cobalt in seawater, such as the coprecipitation [2], liquid-liquid phase extraction [5], and solid phase extraction [6, 7].

Neutron activation analysis (NAA) is a sensitive and special method for determining simultaneously a large number of elements [8]. One of the advantages of the NAA method over the common spectrometric methods is that it allows us to directly analyze the samples in original forms without the use of dissolution steps that may cause the sample dilution and contamination. Within the NAA, the preconcentration of the trace elements from the aqueous samples such as seawater absorbed on solid materials is usually preferred among the other methods. However, a drawback of this method is that it is not able to analyze the water samples since the radiolysis of water itself may cause a release of radiogas or even an explosion out of the container [9]. Hence, the adsorption used to preconcentrate the elements from the water onto the solid phase is a promising method for the detection of trace elements in seawater as well as in other solutions. Some adsorbents have been used for these preconcentration steps such as the magnesium oxide [9], charcoal [10–14], and aluminium and iron(III) oxides [15]. However, the use of nanooxide as an adsorbent material for the retention of trace elements from seawater before being determined by the NAA method has still been limited so far.

In fact, the nanomaterials, which have their own physicochemical properties and therefore differ from the nonnanomaterials, have been applied to a variety of areas. Among the nanomaterials, the manganese oxides with various types of crystalline structures, such as α -, β -, γ - MnO_2 , have been extensively studied owing to their structural varieties and excellent chemical characteristics. As a result, they have been applied to different areas such as batteries, molecular sieves, catalysts, and adsorbents [16, 17]. However, the use of γ - MnO_2 nanomaterial as a solid phase for the preconcentration of cobalt from seawater has still been rarely studied.

In the present work, the γ - MnO_2 nanomaterial is used as a preconcentration agent to extract cobalt from the seawater collected at Hon Rom Beach, Phan Thiet City, Binh Thuan Province, Vietnam, before applying the NAA method to determine its concentration. Furthermore, factors affecting the adsorption capacity of this nanomaterial such as the pH, adsorption time, and initial cobalt concentration are also investigated within the present work.

2. Experimental Method

2.1. Reagents and Materials. The cobalt(II) ion is used as an adsorbate. A 1000 mg/L standard stock solution containing each set of cobalt(II) ions is prepared by dissolving the $\text{Co}(\text{NO}_3)_2$ (Merck, pa) in the double-distilled water. The HNO_3 (Merck, pa) and NaOH (Merck, pa) are then used to adjust the pH of the solution. The γ - MnO_2 nanomaterial is synthesized via the reaction between the potassium permanganate (KMnO_4) (Merck, pa) solution and the ethanol ($\text{C}_2\text{H}_5\text{OH}$) (Merck, pa) at the room temperature as reported previously in [17, 18]. A 300 ml potassium permanganate (KMnO_4) saturated solution is gradually placed into a 300 ml of the mixture between the ethanol ($\text{C}_2\text{H}_5\text{OH}$) and the distilled water, which is then strongly agitated during 8 h. The obtained solid precipitate is dried at 100°C in 12 h. After that

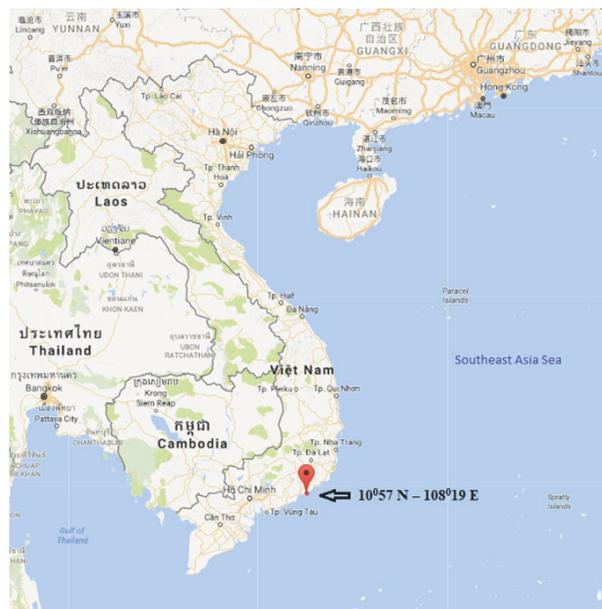


FIGURE 1: Hon Rom Beach, Phan Thiet City, Binh Thuan Province, Vietnam, where the seawater samples are collected.

it is cleaned several times by using the distilled water in order to get the γ - MnO_2 products.

Seawater, collected from the Hon Rom Beach, Phan Thiet City, Binh Thuan Province, Vietnam, at the position of $10^\circ 57' \text{N} - 108^\circ 19' \text{W}$ (see Figure 1), is filtered through 0.2 μm Sartobran 300 cartridges (Sartorius), which are later used for the DCo analyses. The samples are collected in the acid cleaned 250 mL LDPE Nalgene® bottles, which are rinsed 5 times together with the samples before the collection. After that, the processes are similar to those presented in Section 2 of [19], except that HNO_3 at 0.01 M (Merck) has been used to acidify the samples within an hour instead of using ultrapure® HCl as in [19].

2.2. Instruments. The phase of the crystalline structure is determined by using the X-ray diffractometer (XRD) D5000 made by Siemens (Germany) with the X-ray radiation of $\text{CuK}\alpha$ and wavelength $\lambda = 1,5406 \text{ \AA}$. The ultrahigh resolution scanning electron microscopy (SEM) S-4800 made by Hitachi (Japan) and the transmission electron microscope (TEM) JEM 1010 made by JEOL (Japan) are used to investigate the morphology of the materials. The surface area of the materials is calculated within the Brunauer–Emmett–Teller (BET) theory [26]. The concentration of the samples before and after the adsorption is determined by using the atomic absorption spectrophotometer (AA–7000) made by Shimadzu (Japan). In addition, the pH measurements are performed using a pH-meter Mi-150 (MARTINI Instruments made in Romania). The latter is standardized using the HANNA instrumental buffer solutions with different values of pH, namely, 4.01 ± 0.01 , 7.01 ± 0.01 , and 10.01 ± 0.01 . A temperature-controlled shaker (Model IKA R5) is used for the studies of the equilibrium states.

TABLE 1: Isotherm equilibrium parameters calculated from different models.

Models	Equations	Parameters	RMSE	χ^2		
Langmuir	$q_e = \frac{Q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$	Q_{\max} (mg/g): 90.91	K_L (L/mg): 0.5430	1.999	0.2918	
Freundlich	$q_e = K_F \cdot C_e^{1/n}$	K_F (Log/g): 63.82	$1/n$: 0.0769	2.233	0.3418	
Sips	$q_e = \frac{Q_s \cdot C_e^{\beta_s}}{1 + \alpha_s \cdot C_e^{\beta_s}}$	Q_s (mg/g): 95.00	α_s (L/mg): 0.9810	β_s : 0.5694	1.593	0.1751

Notations. q_e : adsorption capacity at equilibrium (mg/g); C_e : equilibrium concentration (mg/L); Q_{\max} : monolayer maximum adsorption capacity (mg/g); K_L : Langmuir constant; K_F : Freundlich constant; n : adsorption intensity; Q_s : the maximum adsorption capacity (mg/g); α_s : Sips isotherm model constant (L/mg); β_s : Sips isotherm model exponent; RMSE: root-mean-square error (RMSE = $\sqrt{(1/(n-1)) \sum_{n=1}^n (q_{e,meas} - q_{e,calc})^2}$); χ^2 : nonlinear chi-square test ($\chi^2 = \sum_{n=1}^n (q_{e,meas} - q_{e,calc})^2 / q_{e,calc}$).

2.3. Adsorption Study. A 0.1 gram of the nanomaterials is placed into a 100 mL conical flask containing 50 mL of the cobalt(II) ions. The influences of pH (2–5.5), adsorption time (10–240 min), and metal ion concentrations (40–400 mg/L) on the nanomaterials are also studied. The concentrations of cobalt(II) ions before and after the adsorption process are determined by using the atomic absorption spectroscopy method. The adsorption ability of the γ -MnO₂ nanomaterial is calculated as [27]

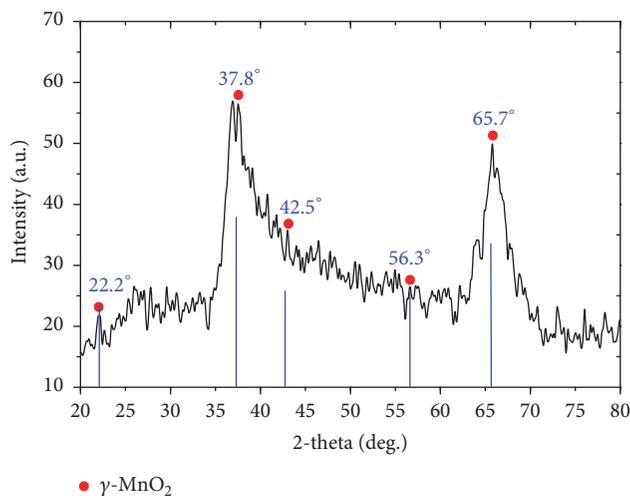
$$\% \text{ Removal} = \frac{(C_o - C_e) \times 100\%}{C_o}, \quad (1)$$

whereas the adsorption capacity can be obtained from the mass balance equation for the adsorbent as [27]

$$q = \frac{(C_o - C_e) \times V}{m}, \quad (2)$$

where q is the adsorption capacity (mg/g) at the equilibrium and C_o and C_e are the initial and equilibrium concentrations (mg/L), respectively. V is the volume (L) of the solution and m is the mass (g) of the adsorbent used. In fact, several adsorption isotherm equations [28] have been applied in the present work in order to assess the adsorption ability of the γ -MnO₂ materials as well as the nature of the uptake as presented in Table 1.

2.4. Neutron Activation Analysis. A 1-gram γ -MnO₂ is added to 1.5 liters of seawater and they are mixed by magnetically stirring at the speed of 240 rpm in 120 mins. The solid is collected via the filtration process and dried at 80°C in 24 hours. An accurate weight of the dried γ -MnO₂ is packed and sealed in the polyethylene containers and then irradiated in the core of the Dalat nuclear research reactor with the neutron flux of 3.10^{12} n/cm²·s in 002010 hours. After 30 days of radioactive decay, the samples are measured during 18000 sec in order to determine the cobalt concentration. To control our experimental method, the standard-addition technique has been used by placing 1.0 gram of γ -MnO₂ with 1.5 liters of seawater, which contain 10, 15, and 20 μ g of cobalt standard solution. The time for the added cobalt being equilibrated in seawater is 10 mins at the room temperature. The preparation, irradiation, and decaying and measuring times are kept to be the same as for the above samples.

FIGURE 2: The XRD spectrum of the γ -MnO₂ nanomaterial.

2.5. Gamma Activity Measurement. In order to measure the activated samples, we employ the calibrated gamma-ray spectrometers based on the HPGe detectors (ORTEC, GMX-30190 model) with the acquisition software provided by CANBERRA Genie-2K. The K0-Dalat program [29, 30] is applied to calculate the elemental concentrations, the uncertainties, and the detection limits.

3. Results and Discussion

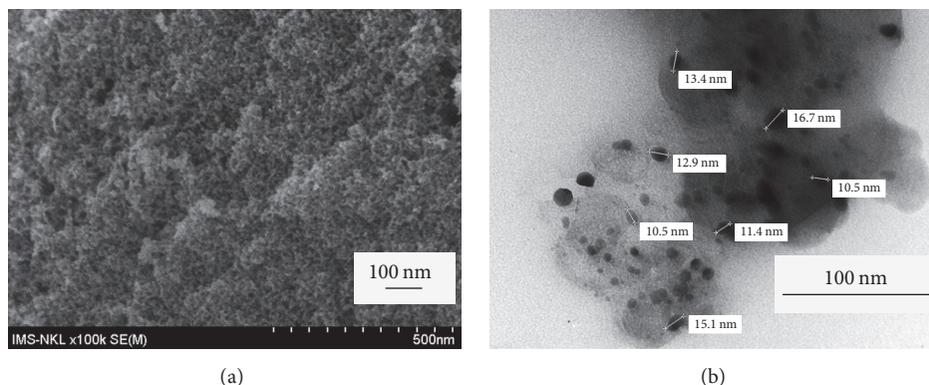
3.1. Characterization of the γ -MnO₂ Nanomaterial. Shown in Figure 2 are the XRD patterns of the γ -MnO₂ nanostructure. As can be seen in this Figure 2, some specific peaks are developed at the different angles 2θ equal to 22.2°, 37.8°, 42.5°, 56.3°, and 65.7°. These peaks are certainly associated with the orthorhombic structure of the γ -MnO₂ material (JCPDS card number 82-2169).

Figure 3 presents the SEM (a) and TEM (b) images of γ -MnO₂. These figures clearly show a porous surface, which includes many nanospheres with diameters from 10 nm to 80 nm. These results indicate that the γ -MnO₂ nanomaterial might offer more adsorption sites for the adsorbates.

The surface area and pore size of γ -MnO₂ are investigated within the BET and Barrett-Joyner-Halenda (BJH) [31] methods. The results obtained are presented in Table 2. It is

TABLE 2: The BET and BJH analytical results.

	BJH Adsorption average pore width	BJH desorption average pore width	BET surface area
γ -MnO ₂	417.8 Å	340.2 Å	65.0 m ² ·g ⁻¹

FIGURE 3: SEM (a) and TEM (b) images of the γ -MnO₂ nanomaterial.

seen that the surface area of γ -MnO₂ is about 65 m²/g with a pore size smaller than 500 Å and larger than 20 Å, which corresponds to the size of the mesoporous materials [32].

3.2. Factors Affecting the Adsorption of Cobalt. The pH is one of the essential factors, which affects the adsorption of the cobalt(II) ion onto the γ -MnO₂ nanomaterials. As can be seen in Figure 4(a), at the low pH values, the uptake of cobalt(II) ion on the material surfaces decreases because of two main reasons. The first reason is due to the charge of the material surface, which is positive and is not favorable for the uptake of Co(II) cation [33–38]. The second reason is that there is a competition between the H⁺ and Co²⁺ ions [37, 38]. At the high pH values, the adsorption of cobalt(II) ion reaches a plateau due to the formation of different types of cobalt(II) such as Co(OH)⁺ and Co(OH)₂, which inhibit the adsorption of Co²⁺ ions on γ -MnO₂ [39]. Therefore, a range of pH values has been chosen from 2.0 to 5.5 in order to achieve the optimum adsorption of cobalt. As a result, the maximum adsorption is obtained at pH \geq 4.0 with an approximate removal of 98.8% at the initial cobalt concentration of 150 mg/L.

The effects of pH and contact time on the adsorption of Co(II) onto the γ -MnO₂ nanomaterial are shown in Figures 4(a) and 4(b), respectively. These figures show that the adsorption increases with increasing both the pH and the contact time and reaches the equilibrium after 120 mins at the pH value of 4 despite different initial cobalt concentrations. Hence, 120 mins of adsorption time has been chosen for adsorbing cobalt from the seawater samples. Moreover, it can be seen also from these figures that the higher the initial concentration of Co(II) is, the lower the adsorption rate of Co(II) onto the γ -MnO₂ nanomaterial is achieved. This result can be explained by the saturation of the binding-sites of the nanomaterial when the concentration is increasing.

3.3. Adsorption Isotherm Studies. Figure 5 shows the plots of the Langmuir, Freundlich, and Sips nonlinear isotherm

models, whose parameters are given in Table 1. It is known that the Langmuir model assumes the uptake of cobalt(II) on the γ -MnO₂ nanomaterial to be monolayer adsorption. On the other hand, the Freundlich model is based on the assumption that the adsorption of cobalt(II) ions should be with multilayers and there is an interaction between the adsorbate and adsorbent. However, both of models above are restricted by the solute concentrations. Therefore, the Sips equation, which combines the Langmuir and Freundlich models, has been proposed in order to describe well the uptake of cobalt(II) onto the γ -MnO₂ nanomaterial. By comparing the results obtained from the root-mean-square error (RMSE) with the corresponding χ^2 values, it is found that the Sips model offers the best fit to experimental data as this model has the smallest RMSE and χ^2 values among the other two Langmuir and Freundlich models. The monolayer adsorption and adsorption capacities calculated from the Langmuir and Sips models are 90.91 mg/g and 95.00 mg/g, respectively. These results indicate that the γ -MnO₂ nanomaterial can be used as an adsorbent to extract and concentrate the cobalt ions from the water samples.

3.4. Determination of Cobalt in Seawater. Figures 6 and 7 depict the gamma-ray spectra of the γ -MnO₂ nanomaterial before and after the adsorption of elements in seawater. The results obtained from the analysis of some elements in the surface seawater at Hon Rom Beach, Phan Thiet City (10°57' North-108°19' East), using the NAA method after the preconcentration by adsorption onto the γ -MnO₂ nanomaterial are presented in Table 3. These results show that the content of cobalt in the surface seawater at the location above is found to be $0.25 \pm 0.04 \mu\text{g/L}$ ($n = 5$, $P = 0.95$) with the recovery of about 96.9%–104% ($n = 4$, $P = 0.95$). These results are also in good agreement with the original concentrations found in the seawater samples as well as the added analyte concentrations. Furthermore, some other elements are newly detected as shown in Table 4. It is worthwhile mentioning here that in principle the added cobalt can be bound to

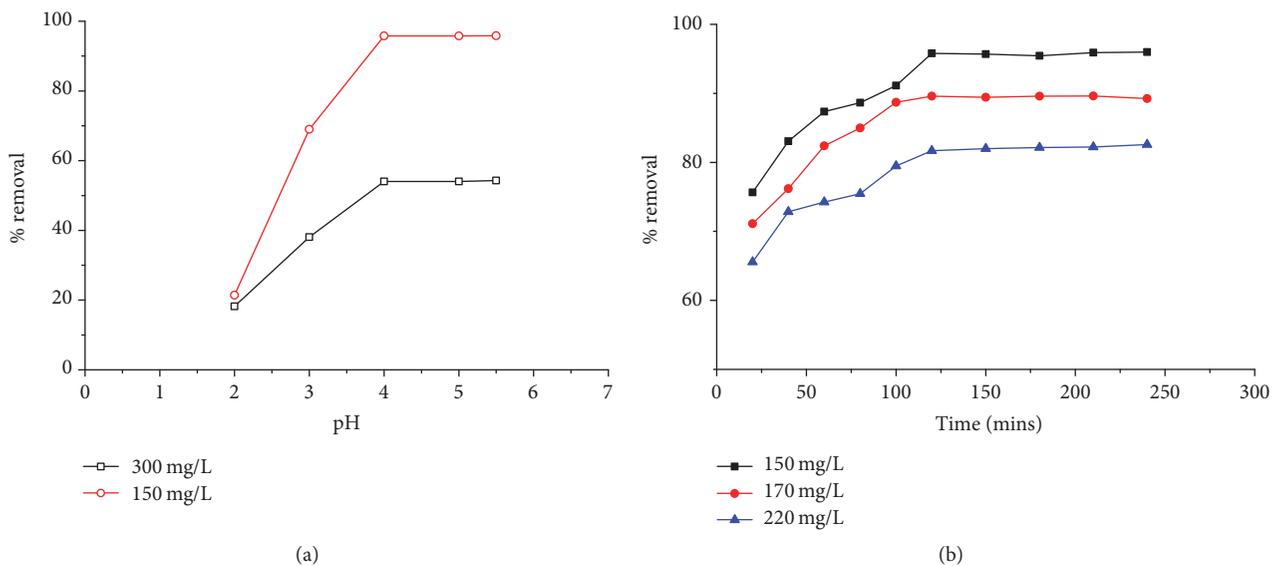


FIGURE 4: Effects of pH (a) and contact time (b) on the adsorption of Co(II) onto the γ -MnO₂ nanomaterial at different initial concentrations of cobalt.

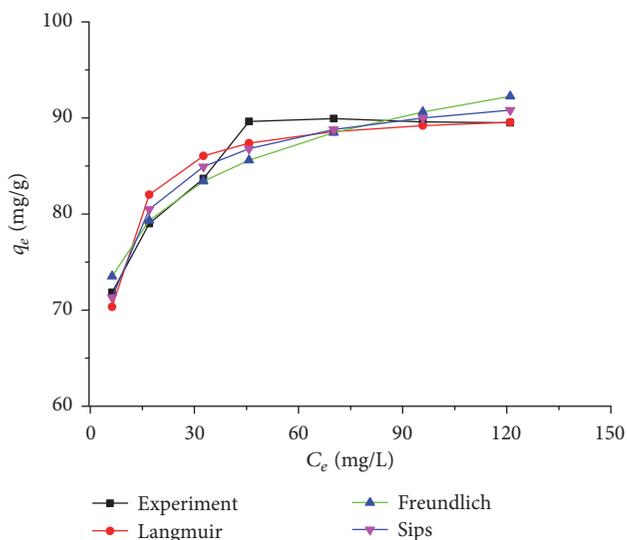


FIGURE 5: Plots of the adsorption capacity at the equilibrium q_e versus the equilibrium concentration C_e obtained within the Langmuir, Freundlich, and Sips nonlinear isotherm models.

make some particulate materials and/or dissolved organic ligands depending on the complexation kinetics and time for which the added cobalt can be exposed to the seawater. However, this effect, which might cause the change of the analytical results, is considered to be relatively small since the solubility of the solution used in the present study (10–20 μ g/L) is rather high and the seawater samples before being analyzed are carefully filtered and acidified as described in Section 2.1.

3.5. Comparison with Other Studies. Table 5 presents the content of cobalt in seawater at some areas in the world determined by the same and/or different methods. It is found that the concentration of DCo in the surface seawater at

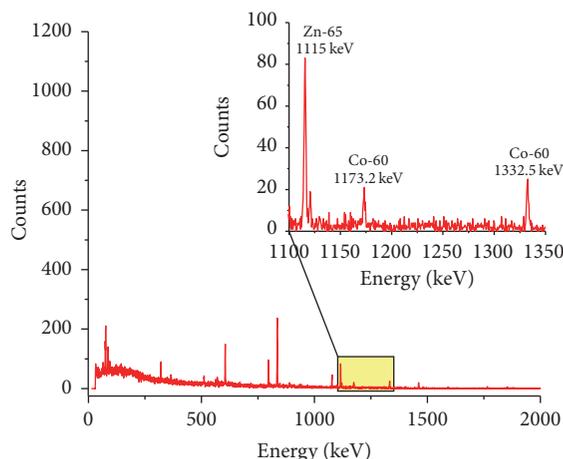


FIGURE 6: Gamma-ray spectrum of the γ -MnO₂ nanomaterial before the adsorption of elements in the seawater.

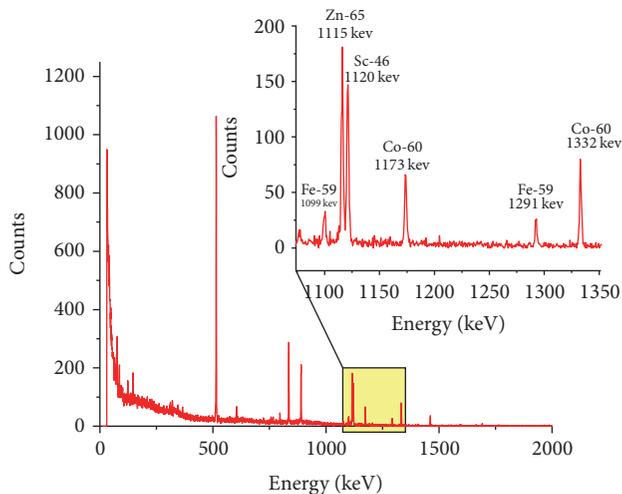


FIGURE 7: Same as Figure 6 but after the adsorption of elements in the seawater.

TABLE 3: Analytical results for cobalt in seawater.

Element	Co(II) added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)	SD	Recovery (%)
Cobalt	0	0.25 ± 0.05 ($n = 5, P = 0.95$)	0.04	
	10	10.1 ± 1.16 ($n = 4, P = 0.95$)	0.73	98.80
	15	14.8 ± 1.08 ($n = 4, P = 0.95$)	0.68	96.93
	20	21.1 ± 2.77 ($n = 4, P = 0.95$)	1.74	104.00

SD: standard deviation.

TABLE 4: Elements found in seawater by using the NAA method.

Elements	Found ($\mu\text{g/L}$) ($n = 5, P = 0.95$)	SD
Fe	213 ± 18.9	15.2
Zn	7.01 ± 1.72	1.38
Ce	1.92 ± 0.23	0.19
Sc	0.07 ± 0.01	0.008

SD: standard deviation.

TABLE 5: Content of cobalt in the seawater at some areas in the world obtained within the same and/or different analytical methods. Here GFAAS and SF-ICP-MS stand for graphite furnace atomic absorption and sector field inductively coupled plasma mass spectrometers, respectively.

Area	DCo ($\mu\text{g/L}$)	Analytical methods	Ref.
Mediterranean Sea	0.02	SF-ICP-MS	[19]
Bosphorus	4.28	GFAAS	[20]
South East Atlantic	$0.30 \cdot 10^{-3} - 3.48 \cdot 10^{-3}$	Flow-Injection Analysis (FIA) and chemiluminescence	[21]
Crozet Islands, Southern Ocean	$1.42 \cdot 10^{-3} - 2.89 \cdot 10^{-3}$	ICP-MS	[22]
Western Atlantic Ocean	$0.83 \cdot 10^{-3} - 5.85 \cdot 10^{-3}$	Chemiluminescence	[23]
North Atlantic gyre, Atlantic Ocean	$1.38 \cdot 10^{-3}$	FIA with chemiluminescence	[24]
South Atlantic gyre, Atlantic Ocean	$3.25 \cdot 10^{-3}$	FIA with chemiluminescence	[24]
Angola Gyre, Atlantic Ocean	$0.71 \cdot 10^{-3} - 9.74 \cdot 10^{-3}$	Ultrahigh resolution mass spectrometry	[25]
Binh Thuan, Vietnam	0.25	NAA	This study

Binh Thuan coast, Vietnam, obtained within the present work is $0.25 \mu\text{g/L}$. This amount is higher than the results obtained from some different locations in the world such as Mediterranean Sea [19], South East Atlantic [21], Crozet Islands, Southern Ocean [22], Western Atlantic Ocean [23], North and South Atlantic gyre of Atlantic Ocean [24], and Angola Gyre of Atlantic Ocean [25], except the Bosphorus area [21] (see Table 5). The reason is that the seawater samples used in the present analysis are collected from the beach, which is located near the residential area that might cause the increase in the level of cobalt.

4. Conclusions

The neutron activation analysis method at the Dalat nuclear reactor (Vietnam) has been used to determine the concentration of dissolved cobalt in the seawater at Phan Thiet City, Binh Thuan Province, Vietnam, after the preconcentration by adsorption onto the $\gamma\text{-MnO}_2$ nanomaterial. The concentration of dissolved cobalt in the surface seawater is found to be $0.25 \pm 0.04 \mu\text{g/L}$ ($n = 5, P = 0.95$) with the

approximate recovery of 96.93%–104% ($n = 4, P = 0.95$). In addition, some elements and their concentrations have been newly determined, namely, Fe ($212 \mu\text{g/L}$), Zn ($7.01 \mu\text{g/L}$), Ce ($1.92 \mu\text{g/L}$), and Sc ($0.07 \mu\text{g/L}$). All the results obtained show that the $\gamma\text{-MnO}_2$ nanomaterial can indeed be used as an adsorbent to preconcentrate the trace elements from the water samples before being determined by the neutron activation analysis method.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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