Research Article

Adsorption Ability for Toxic Chromium (VI) Ions in Aqueous Solution of Some Modified Oyster Shell Types

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In this paper, the chromium, Cr (VI), ion adsorption ability of oyster shell samples collected from two sea regions in Vietnam (Phu Yen province and Quang Ninh province) was investigated and compared. The oyster shell samples were calcined at different temperatures and denatured by using ethylenediaminetetraacetic acid (EDTA). The Cr (VI) ion adsorption ability of the prismatic (PP) and nacreous (NP) shell layers of oysters was also evaluated. The characteristics of oyster shell samples before and after treatment were determined by using analysis methods including XRD, IR, BET, UV-Vis, and FESEM. The Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models and fit statistic equations were used to study the adsorption isotherms of Cr (VI) ion adsorption by oyster shells. The Cr (VI) ions adsorption kinetic has been set up using four reaction models consisting of first-order, pseudo-first-order, second-order, and pseudo-second-order reaction models. Effects of experimental factors on the Cr (VI) ion adsorption process using oyster shells were also investigated and discussed in this work.

1. Introduction

Nowadays, the strong development of industry, agriculture, and services is leading to the pollution of water by various sources and directly affecting the environment and human health. Heavy metals pollution is one of the urgent issues, causing great impacts on people's life, health, and living. Pollution sources are commonly found in water basins near industrial parks, large cities, and mining areas. Water polluted by heavy metals has a negative impact on the living environment of organisms and humans because heavy metals can bioaccumulate in the food chain and penetrate into the human body.

Chromium, Cr, a very common and toxic heavy metal pollutant, is released into natural waters mainly from a variety of industrial wastewater sources. Hexavalent chromium, mainly found in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), with its high ability to solute can accumulate in kidneys, stomach, and liver. Besides, it can cause gastrointestinal and dermatological problems as well as abnormal hematological functions [1]. The concentration of chromium in drinking water must be under 0.02 ppm. Therefore, it is important to treat the waterbodies to reduce or remove the pollutants. Recently, adsorption technology using common and abundant waste sources, for example,

oyster shells [2], is becoming a popular solution in reducing and removing the pollutant from waterbodies thanks to its high efficiency and cost-effectiveness. Oysters are mollusks species of bivalve mollusks like mussels, scallops, and clams. They live on the coast or in coastal cliffs or estuaries and feed on plankton and creatures in mud, sand, sea water, etc. Being one of the most popular seafood dishes today, the amount of oyster shells released from seafood processing factories, seafood shops, and restaurants can be up to several tons/day. This creates a burden on the environment due to space taken for discarded shells and the odor from the remaining flesh. In the world, oyster shell was recycled for making new oyster reefs or returning these shells to the waterto restore native oysters. The oyster shell is primarily composed of calcium carbonate, but it also contains polysaccharides and minerals such as magnesium, calcium, sodium, iron, copper, nickel, and some other trace elements. Several studies have shown that oyster shells in different regions have different content of calcium carbonate and chemical composition [3–6]. Chemical and microstructure analysis showed that oyster shells account for about 90% of the total oyster weight and contain about 50% of calcium carbonate, so it is an appropriate material for manufacturing industries, lime, cement, and manure fertilizers, and other industries. For each material from different geographical location, the process of modification of materials will also be different [7–9]. Furthermore, oyster shells have been applied in the treatment of waste water [10], immobilization of arsenic in highly contaminated soils [11], immobilization of phosphorus in constructed wetlands [12], and adsorbing some metal ions such as Cu^{2+} and Ni^{2+} [13]. Most of the researches indicate promising results which can resolve some environmental issues and the disposal of oyster shells. However, application of oyster shells as an absorbent of Cr (VI) ion in aqueous solution has been not focused on in study. The use of oyster shells as absorbents for the removal of heavy metal ions in aqueous solution can be considered as one of the safe disposal ways because the chemicals used in treatment process of oyster shells can be reused many times and they were neutralized before being discharged into the environment without precipitates.

Although Vietnam has tropical climate, the north and south of Vietnam exhibit a different climate. Herein, there are four seasons in the north of Vietnam but there are only two seasons in the south of Vietnam. Unlikely natural conditions can lead to the variation of some characteristics of animals and vegetation in which they live. Biodiversity and life's environment have an important influence on the characterizations and adsorption ability of oyster shells. Quang Ninh province has a typical tropical climate for the north of Vietnam and Phu Yen province characterized for a typical tropical climate for the south of Vietnam. Therefore, in this work, two oyster shells collected at Quang Ninh province and Phu Yen province were selected to compare their adsorption ability for removal of Cr (VI) ion in aqueous solution. From the results, the geographical position and climatic influence on the characteristics of oyster shells were evaluated and compared. The IR, XRD, BET, and FESEM as

well as Cr (VI) ion adsorption ability of the above oyster shells were investigated and discussed.

2. Experimental

2.1. Materials. Oyster shell (OS) samples were collected at Quang Ninh province sea, North Vietnam (coordinates in $20^{\circ}54'N$ $107^{\circ}12'E$) (designed as QNOS), and Phu Yen province sea, South Vietnam (coordinates in $12^{\circ}09'N$ $109^{\circ}11'E$) (designed as PYOS) (Figure 1). Both of these sea regions are in the East Sea.

Some other chemicals (NaClO , NaOH , $\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , 1,5-diphenylcarbazide (DCP), and ethylenediaminetetraacetic acid (EDTA)) were analytical chemicals and used as received.

2.2. Treatment of Oyster Shell Samples. Both QNOS and PYOS samples were treated as follows: The shells were washed with clean water and dried in a natural air convection oven until reaching the stable weight (OS-raw). The oyster shell contains prismatic (PP) and nacreous (NP) shell layers, and the PP shell layer has proved to have better Cu (II) ion adsorption ability than NP shell layer [9]. Based on some preliminary surveys about the Cr (VI) ions adsorption ability of the mixture of PP and NP shell layers of QNOS sample and compared to that of PP shell layer of QNOS sample, we recognized that the PP shell layers of QNOS sample have better Cr (VI) ions adsorption ability than the mixture of PP and NP shell layers. Therefore, in this work, PP shell layers were chosen for further study of the Cr (VI) ions adsorption ability.

Next, these shells were immersed in NaClO solution for 24 hours to remove sand and organic substances on the surface of OS before washing and drying at 100°C for 5 hours. Then, the shells were milled in NaOH/NaClO solution (the ratio of OS/solution is 1/20 w/v; the ratio of NaOH/NaClO is 5/1, v/v) by a ball mill machine for 24 hours. After milling, the oyster shell particles were washed by distilled water and dried in a natural air convection oven until reaching the stable weight (OS-Na). The OS raw and OS-Na particles then were calcined at 750°C , 800°C , and 900°C for 2 hours (OS-Na-calcined) on the Nabertherm furnace (Germany).

After that, these OS particles were applied for the removal of Cr (VI) ion in aqueous solution. Based on the best highest Cr (VI) ion absorption ability, the OS particles will be chosen for modification surface by EDTA in 50 mL of distilled water with the OS/EDTA ratio of 10/1 (w/w) at 60°C for 2 hours. The abbreviation of OS samples is shown in Table 1. The suggested scheme and reaction for synthesis OS samples are shown in Figure 2.

2.3. Chromium (VI) Ion Absorption Ability in Aqueous Solution by Oyster Shell Particles. Preparation of 0.5% solution of 1,5-diphenylcarbazide (DCP): 0.5 grams of DCP was dissolved in 100 mL acetone (solvent) and stored in a dark bottle at 4°C .

FIGURE 1: Positions for collecting oyster shells.

Preparation of Cr (VI) ion solution 1000 ppm: 2.829 grams of $K_2Cr_2O_7$ was dissolved in 1 L of distilled water and stored in dark bottle at low temperature.

Cr (VI) ion adsorption process by OS samples as follows: 0.5 grams of OS particles was added into 100 mL of Cr (VI) ion solution. This mixture was stirred continuously on the magnetic stirrer for 2 hours. Then, it was filtered by a filter paper and 25 mL of filtered solution was withdrawn into a 50 mL glass flask. Next, 1 mL of H_2SO_4 1 M solution and 1 mL of DCP solution were introduced into the filtered solution and this solution was kept stable for 10 minutes to obtain a red purple solution caused by reaction of Cr (VI) ions and DCP. Finally, this red purple solution was taken on an Ultraviolet-Visible (UV-Vis) Spectrophotometer (CINTRA 40, GBC, USA) at maximum wavelength (λ_{max}) of 540 nm to determine the absorbance of Cr (VI) ions solution.

2.3.1. Adsorption of Cr (VI) Ion by OS Samples. The amount of Cr (VI) ions adsorbed per gram of adsorbent was calculated using the following equation:

$$Q = \frac{(C_0 - C_e) \cdot V}{W}, \quad (1)$$

where Q is the amount of Cr (VI) ions absorbed per amount of adsorbent at equilibrium condition (mg/g), C_0 and C_e are the initial and equilibrium concentration of metal ion in solution (mg L^{-1}), V is the volume of solution (L), and W is the sorbent mass (g).

The removal of metal ion was calculated using the following equation:

$$H = \frac{(C_0 - C_e) \cdot 100}{C_0}, \quad (2)$$

where H is the percentage of removed metal ion, %.

The equilibrium concentration of Cr (VI) ions in solution (C_e) was calculated based on the calibration equation of Cr (VI) ions in aqueous solution at λ_{max} of 540 nm as follows:

$$y = 0.4609x + 0.0378, \quad (3)$$

where y is the absorbance of Cr (VI) ions in aqueous solution and x is the concentration of Cr (VI) ions in aqueous solution (the linear regression coefficient, $R^2 = 0.9991$).

Some factors which can influence Cr (VI) ions adsorption ability by OS samples were investigated, including the pH of solution (by varying the volume of H_2SO_4 1 M solution to change pH of solution from 2 to 7), OS weight (changed from 0.1 to 1.0 gram), adsorption time (changed from 20 to 180 minutes), and Cr (VI) ions concentration (changed from 3 to 15 ppm).

Although 20 samples of oyster shells were treated as listed in Table 1, there are only 4 samples (QNOS-PP-800, QNOS-PP-800-EDTA, PYOS-PP-Na-800, and PYOS-PP-Na-800-EDTA) exhibiting a good Cr (VI) ions adsorption ability. Therefore, 4 OS samples were focused on characterization and compared to initial samples (QNOS-PP and PYOS-PP).

2.3.2. Study on Adsorption Isotherms. In this work, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms have been selected for study of Cr (VI) ions adsorption behavior in solid–liquid system.

The Langmuir isotherm equation for ion adsorption can be written as follows:

$$Q_e = \frac{Q_0 k_L C_e}{1 + k_L C_e}, \quad (4)$$

where Q_e is the amount of Cr (VI) ions absorbed per amount of adsorbent at equilibrium (mol/g) and C_e is the equilibrium concentration of the solute (mol/L). The Q_0 and k_L are the Langmuir constants, where Q_0 represents the maximum monolayer adsorption capacity and k_L represents binding energy or affinity parameter of the adsorption system.

The Freundlich isotherm is expressed as

$$Q_e = k_F C_e^{(1/n_F)}, \quad (5)$$

where k_F is Freundlich isotherm constant ($L^{1/n} mg^{(1-1/n)} g^{-1}$) and $1/n_F$ is the Freundlich exponent.

The Temkin isotherm equation is described as follows:

$$Q_e = B \ln A_T + B \ln C_e, \quad (6)$$

with $B = R_T/b_T$, where A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant, R is universal gas constant ($R = 8.314 J/mol \cdot K$), and $T = 298 K$.

The Dubinin–Radushkevich (DR) isotherm equation is

$$\ln Q_e = \ln Q_S - K^{ad\epsilon^2}, \quad (7)$$

TABLE 1: Signature of oyster shell samples.

No.	Sample	Abbreviation of sample
1	Prismatic shell layer of Quang Ninh oyster shells	QNOS-PP
2	QNOS-PP calcined at 800°C	QNOS-PP-800
3	QNOS-PP-800 modified with EDTA	QNOS-PP-800-EDTA
4	Prismatic shell layer of Phu Yen oyster shells	PYOS-PP
5	PYOS-PP treated with NaClO and ball milled in NaOH/NaClO solution	PYOS-PP-Na
6	PYOS-PP-Na calcined at 750°C	PYOS-PP-Na-750
7	PYOS-PP-Na calcined at 800°C	PYOS-PP-Na-800
8	PYOS-PP-Na calcined at 900°C	PYOS-PP-Na-900
9	PYOS-PP-Na-800 modified with EDTA	PYOS-PP-Na-800-EDTA

FIGURE 2: The suggested scheme and reaction for the synthesis of the OS samples.

with $\varepsilon = RT \ln(1 + 1/C_e)$, where Q_s is the theoretical isotherm saturation capacity (mg/g) and K^{ad} is Dubinin–Radushkevich isotherm constant (mol²/kJ²).

2.3.3. Study on Adsorption Kinetics. In this work, first-order, pseudo-first-order, second-order, and pseudo-second-order reaction model have been selected for study on ion adsorption kinetics.

First-order reaction model is as follows:

$$\ln C_t = \ln C_0 - k_1 t. \quad (8)$$

Pseudo-first-order reaction model is as follows:

$$\ln(Q_0 - Q_t) = \ln Q_0 - k_{s1} t. \quad (9)$$

Second-order reaction model is as follows:

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t. \quad (10)$$

Pseudo-second-order reaction model is as follows:

$$\frac{1}{(Q_e - Q_t)} = \frac{1}{Q_e} + kt \Rightarrow \frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_e} t, \quad (11)$$

with $h = kQ_e^2$, where C_0 and C_t are the concentration of the solute at the initial time and the testing time t (mg/L); Q_0 is

the maximum monolayer coverage capacity (mg/g); Q_t and Q_e are the amount of metal ions adsorbed per gram of adsorbent at testing time t and at equilibrium (mg/g); k_1 , k_{s1} , k_2 , and k are first-order reaction model, pseudo-first-order reaction model, second-order reaction model, and pseudo-second-order reaction model constant, respectively.

2.4. Characterizations. Infrared (IR) spectroscopy: IR spectra of samples were recorded using a Nicolet iS10 spectrometer (Thermo Scientific, USA) at room temperature in 400 to 4000 cm^{-1} wavenumber range by 32 scans averaging with 8 cm^{-1} resolution.

Field emission scanning electron microscopy (FESEM): FESEM images of samples in solid state were taken by using a S-4800 FESEM machine (Hitachi, Japan).

X-ray diffraction (XRD) analysis: XRD patterns of samples were performed on a Siemens D5000 X-ray Diffractometer (XRD) with CuK_α radiation source ($\lambda = 0.154 \text{ nm}$) at 40 kV generator voltage with 0.03° step and 30 mA current by $0.043^\circ/\text{s}$ scan speed in the range of 2θ from 2° to 70° .

Brunauer–Emmett–Teller (BET) isotherm equation: specific surface area of samples was calculated from data by nitrogen adsorption-desorption method on a Tristar 3000 V 6.07 A device (Micromeritics Instrument Corporation).

The pH zero point charge (pH_{ZPC}) of OS samples has been measured by the electrochemical method [14]. 50 mL of a 0.01 M NaCl solution was placed in 100 mL glass flasks. Next, the pH of NaCl solution was firstly adjusted to successive initial values between 2 and 12 by using either 0.1 M HCl or 0.1 M NaOH solutions and 0.15 grams of OS samples was added to the solutions. The final pH was measured after a 48-hour testing period. The final pH values were plotted against the initial pH and pH_{ZPC} was taken at which the curve crosses the line $\text{pH}(\text{final}) = \text{pH}(\text{initial})$. The measures of pH have been made using a pH-meter (Hanna Instruments).

2.5. Error Analyzation. In this paper, apart from using the R-square method (square of the correlation between the response values and the predicted response values), we also apply other loss functions such as sum of squared error (SSE); mean squared error (MSE); and root mean squared error (RMSE) to determine the most suitable isotherms/kinetics model which can represent the adsorption process of Cr (VI) ions using oyster shells:

Sum of squared error (SSE): this statistic is the total deviation of the response values from the fit to the response values:

$$\text{SSE} = \text{Sum}_{(i=1 \text{ to } n)} \{ (y_i - f_i)^2 \}. \quad (12)$$

Mean squared error (MSE): mean of total error is given by

$$\text{MSE} = \frac{\text{SSE}}{n}. \quad (13)$$

Root mean squared error (RMSE): root of mean squared error of fit standard error is given as

$$\text{RMSE} = (\text{MSE})^{1/2}, \quad (14)$$

where y_i is the response value; f_i is the predicted response value, and n is the number of obtained values.

3. Results and Discussion

3.1. Characterization of Some Oyster Shell Samples

3.1.1. IR Spectra of Some Oyster Shell Samples. Figure 3 and Table 1S present IR spectra and characteristic wavenumbers for vibrations of functional groups of the surveyed OS samples. The position of characteristic peaks of all OS samples in the IR spectra is similar. For example, the peaks at wavenumbers about 3400 cm^{-1} and 1630 cm^{-1} are characterized for the valence oscillation and deformation fluctuations of OH groups in hydrogen bonds. The weak peak at 2512 cm^{-1} is specific to the valence oscillation of CO_3^{2-} group. The characteristic peaks for oscillation of C–O (875 cm^{-1}) and C = O (1798 cm^{-1}) groups are also shown in IR spectra of the surveyed OS samples. Some weak peaks specific to oscillation of group CH (at $2872\text{--}2985 \text{ cm}^{-1}$) may be due to the existence of organic impurities in the OS or CH group in EDTA grafted onto the OS surface after modification process.

From IR spectra of the QNOS and PYOS samples, it can be seen that the treatment process with NaClO/NaOH solution or calcination has negligible effect on the functional groups in OS samples. Comparing the IR spectra of the OS samples collected in Quang Ninh and Phu Yen province sea regions, a difference for the band at 3640 cm^{-1} with strong intensity in the IR spectra of Quang Ninh OS samples (QNOS-PP, QNOS-PP-800, and QNOS-PP-800-EDTA) can be observed. It is assigned to fluctuation of valence of OH group which is not involved in hydrogen bonding. Thus, the IR spectra of investigated OS samples also show that biodiversity and geographical position have an influence on their functional groups.

3.1.2. Crystal Structure of Some Oyster Shell Particles. XRD pattern of QNOS-PP particles indicates the calcite rhomboid crystal structure of CaCO_3 and hexagonal portlandite crystal of $\text{Ca}(\text{OH})_2$ (Figure 4(a)). In the QNOS-PP sample, there are two crystal phases; among them, the calcite crystals appeared at d-spacing of $3.037 \text{ \AA}$, while the portlandite crystals were found at d-spacing of $4.94 \text{ \AA}$. The intensity for diffraction peak of portlandite crystals is significantly stronger than that of the calcite crystals; the resulting portlandite crystals account for most of the crystalline structure of QNOS-PP sample.

FIGURE 3: IR spectra of PYOS and QNOS samples.

After treatment of QNOS-PP sample by NaClO/NaOH solution and calcination at 800°C, the crystal structure of QNOS-PP sample was changed significantly (Figure 4(b)). Besides the existence of calcite and portlandite crystals, the appearance of cubic calcium oxide crystals with $d = 2.405$ nm displays that CaO was formed as a new phase after the calcination process at high temperature. CaCO_3 and Ca(OH)_2 were pyrolysed and CaO was formed. The change in the phase structure of this OS sample after calcination has a significant influence on Cr (VI) ion adsorption ability as discussed above.

After modification of QNOS-PP-Na-800 sample by EDTA, the position and intensity of the characteristic diffraction peaks for CaCO_3 and Ca(OH)_2 are almost unchanged but the peaks for CaO are absent and the intensity of peaks characterized for Ca(OH)_2 was decreased (Figure 4(c)). The diffraction peak of Ca(OH)_2 in XRD pattern of QNOS-PP-Na-800 sample at position $d = 4.916$ nm was slightly shifted to position $d = 4.943$ nm in the XRD pattern of QNOS-PP-Na-800-EDTA sample. This indicates that EDTA reacted with CaO and Ca(OH)_2 in QNOS-PP-Na-800 particles through the reaction between the -COOH groups of EDTA and Ca(OH)_2 or CaO as the following equations:

In the XRD pattern of PYOS-PP sample, only the occurrence of rhombocalcite crystals is observed (Figure 5(a)). Compared to the crystal structure of QNOS-PP sample in Figure 4(a), it can be seen that two samples of OS collected in Quang Ninh and Phu Yen province sea areas have distinctly

different crystal structures. This explains the difference in the Cr (VI) ion adsorption capacity of the investigated OS samples. Herein, biodiversity and geographical position are important factors and should be investigated for the same material collected at different geographical regions and aquaculture conditions of oysters.

After treatment of PYOS-PP sample with NaClO/NaOH solution, the position of diffraction peaks for calcite in the XRD pattern of PYOS-PP-Na (Figure 5(b)) is similar to that of PYOS-PP. However, the intensity of these peaks was slightly decreased. When calcinating at 800°C, additional diffraction peaks with strong intensity were characterized for the hexagonal portlandite crystal of Ca(OH)_2 in the PYOS-PP-Na-800 sample (Figure 5(c)).

At different temperatures of calcination, the crystal structure of PYOS is affected significantly. For instance, at 750 C and 800 C, the portlandite crystals appeared with stronger intensity than calcite crystals, while at 900 C, the calcite crystals are occupied (Figures 5(c), 5(d), and 5(e)). The change in crystal structure of calcinated PYOS causes the difference in Cr (VI) ions adsorption ability of these samples.

Observing the XRD pattern of the PYOS-PP-Na-800-EDTA sample, only diffraction peaks of calcite crystals appeared (Figure 5(f)). This may be due to portlandite crystals formed after the calcination process has been rinsed in the denaturing process with EDTA.

The data of crystal size for the OS samples which were calculated according to Scherer equation based on the data of diffraction peaks on XRD diagram demonstrated that the crystal sizes of calcite, portlandite, and calcium oxide crystals are varied significantly (Table 2). Thus, the treatment process of OS samples not only influences the crystal phases but also affects the crystal size of these OS samples.

3.1.3. Special Surface Area of Some Oyster Shell Samples.

Table 3 and Figures 6 and 7 display nitrogen adsorption isotherm-desorption isotherm and parameters such as specific surface area (BET), capillary volume, and capillary diameter of the investigated OS samples. Compared to the IUPAC classification of adsorption isotherms, nitrogen adsorption lines and desorption lines of OS samples follow type III. Based on De Boer analysis, the OS samples have capillaries in the inclined slit pore form and almost no microcapillaries (the value of microcapillary area and volume in Table 3 are very small).

Comparing the data in Table 3, it can be seen that the samples of QNOS-PP and PYOS-PP have significant differences in specific surface area as well as pore volume and pore diameter. For OS samples collected in Quang Ninh sea region, after heat treatment, the crystal structure variation is an important reason leading to the change in the specific surface area of the QNOS-PP-800 sample. The pore diameter of this material was increased significantly, and this increase can result in an improvement in Cr (VI) ions absorption ability.

After modification of QNOS-PP-800 sample with EDTA, the specific surface area, capillary volume, and capillary

(a)

(b)

(c)

FIGURE 4: XRD patterns of QNOS-PP (a), QNOS-PP-Na-800 (b), and QNOS-PP-800-EDTA (c) samples.

(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 5: XRD patterns of PYOS-PP (a), PYOS-PP-Na (b), PYOS-PP-Na-800 (c), PYOS-PP-Na-750 (d), PYOS-PP-Na-900 (e), and PYOS-PP-Na-800-EDTA (f) samples.

TABLE 2: List of crystal parameters of OS samples obtained from XRD patterns.

Sample	Type of crystal	2θ (degree)	d-spacing (Å)	Crystallite size (Å)
QNOS-PP	CaCO ₃	29.4	3.037	2.87
	Ca(OH) ₂	34.0	2.630	1.79
	CaCO ₃	29.4	3.037	3.58
QNOS-PP-800	CaO	37.2	2.405	3.66
	Ca(OH) ₂	34.0	2.624	1.43
	CaCO ₃	29.4	3.039	4.78
QNOS-PP-800-EDTA	CaO	37.4	2.426	2.44
	Ca(OH) ₂	34.0	2.628	1.79
PYOS-PP	CaCO ₃	29.4	3.039	4.78
PYOS-PP-Na	CaCO ₃	29.4	3.039	7.17
	CaCO ₃	29.4	3.042	2.87
PYOS-PP-Na-800	Ca(OH) ₂	34.0	2.629	1.79
	CaCO ₃	29.4	3.040	14.33
PYOS-PP-Na-750	Ca(OH) ₂	34.0	2.629	2.87
	CaCO ₃	29.4	3.031	14.3
PYOS-PP-Na-900	Ca(OH) ₂	34.1	2.622	2.07
PYOS-PP-Na-800-EDTA	CaCO ₃	29.4	3.040	7.17

TABLE 3: Specific surface area, pore volume, and pore diameter of OS samples.

Sample	BET surface area (m ² /g)	t-plot micropore area (m ² /g)	t-plot external surface area (m ² /g)	t-plot micropore volume (cm ³ /g)	BJH adsorption cumulative volume of pores* (cm ³ /g)	BJH adsorption average pore width (nm)
QNOS-PP	10.2962	0.7658	9.5304	0.000170	0.043458	19.1191
QNOS-PP-800	0.9719	0.0319	0.9399	0.000003	0.006084	27.5392
QNOS-PP-800-EDTA	4.7673	—	—	—	0.034279	29.7813
PYOS-PP	1.3476	0.1504	1.1972	0.000039	0.008170	28.5818
PYOS-PP-Na-800	1.8008	0.2097	1.5911	0.000096	0.009444	24.0858
PYOS-PP-Na-800-EDTA	1.1372	0.2245	0.9127	0.000073	0.007769	31.9977

* Between 1.7000 nm and 300.0000 nm width.

diameter of this material were augmented; however, the microcapillaries in the sample cannot be observed. The change in the surface area of QNOS-PP-800-EDTA sample may be due to some crystalline phases such as CaO and Ca(OH)₂ being washed partially in the modification process. The increase in capillary diameter of QNOS-PP-800-EDTA sample also explains the increase in the Cr (VI) ions absorption ability of this material.

For OS samples collected in Phu Yen sea region, the presence of microcapillaries as well as larger capillary diameters has proved that Cr (VI) ions absorption ability of the OS samples in Phu Yen sea region was better than that of the OS samples in Quang Ninh sea region at the same treatment condition as discussed in the following.

3.1.4. pH of Zero Point Charge of Some Oyster Shell Samples.

The pH of the zero point charge (pH_{zpc}) for some OS samples is calculated from graphs of the dependence of final pH on the initial pH as shown in Figure 8 and listed in Table 4. The pH_{zpc} indicates surface charge of material (positively or negatively); for example, at the pH < pH_{zpc},

hydrogen ions (protons, H⁺) would be adsorbed more than other cations so that the other cations would be less adsorbed in the case of the negatively charged particle. On the other hand, if the surface is positively charged and pH is increased (pH > pH_{zpc}), anions will be less adsorbed as hydroxide ions are increased [14]. The pH_{zpc} is basic for choosing the suitable pH for ions adsorption study of the materials. The data in Table 4 display that initial OS samples (PYOS-PP and QNOS-PP) have a quite high pH_{zpc} value (9.68 and 9.15, respectively). After calcination, the pH_{zpc} value of these samples was reduced maybe due to the partial decomposition of CaCO₃ and Ca(OH)₂ as discussed in XRD patterns (Section 3.1.2).

3.2. Morphology of Some Oyster Shell Samples. Figure 9 and Figure 1S are FESEM images of the OS samples at different magnifications. It is clear that there are few pores on the surface of the original OS samples (QNOS-PP and PYOS-PP). These samples are in sheet shape. After treatment with NaClO/NaOH solution (PYOS-PP-Na), the shape of PYOS-PP samples was changed due to the impact of milling. The

FIGURE 6: Nitrogen adsorption-desorption isothermal linear plots of QNOS-PP, QNOS-PP-800, and QNOS-PP-800-EDTA samples.

FIGURE 7: Nitrogen adsorption-desorption isothermal linear plots of PYOS-PP, PYOS-PP-Na-800, and PYOS-PP-Na-800-EDTA samples.

calcination process at 750, 800, and 900°C made the shape of PYOS-PP-Na become the cubic shape. There are more holes on the surface of PYOS-PP-Na-800 sample than PYOS-PP-Na-750 and PYOS-PP-Na-900 samples. The OS samples calcined at 800°C (QN-PP-800 and PYOS-PP-Na-800) have more holes and porous structure than the original OS samples but after their modification by EDTA, the porous

FIGURE 8: Graphs of dependence of final pH on initial pH of OS sample.

TABLE 4: pH_{zpc} of some oyster shell samples.

Sample	pH_{zpc}
QNOS- PP	9.15
QNOS-PP-800	8.95
QNOS-PP-800-EDTA	7.04
PYOS-PP	9.68
PYOS-PP-Na-800	8.27
PYOS-PP-Na-800-EDTA	9.05

microstructure of QNOS-PP-800-EDTA and PYOS-PP-Na-800-EDTA samples is clearly observed. This is why the Cr (VI) ion adsorption efficiency of modified OS samples is higher than that of original and calcined OS samples. Comparing two OS samples taken from two different geographical positions (Phu Yen and Quang Ninh sea regions), it can be seen that Phu Yen OS samples have a porous surface and a higher number of holes than Quang Ninh OS samples; hence the Cr (VI) ions adsorption efficiency of PY-OS samples is higher than that of QNOS samples.

Combining the results of IR, XRD, FESEM, and BET analysis, it can be suggested that EDTA molecules can be absorbed into the microholes onto the surface of OS samples or reacted with $Ca(OH)_2$ and CaO in OS samples as described in Figure 2.

3.3. Evaluation of Cr (VI) Ions Adsorption Ability of Some Oyster Shell Types. Table 5 demonstrates removal percentage of Cr (VI) ions (H) and the amount of Cr (VI) ion adsorbed per gram of adsorbent (Q) for different investigated OS samples using 0.1 gram of OS adsorbent, the initial Cr (VI) ion concentration of 50 ppm, and the adsorption time of 2 hours.

As observed from Table 5, the Cr (VI) ions adsorption ability of PYOS particles treated with NaOH/NaClO solution (sample no. 5) is higher than that of pretreated PYOS

FIGURE 9: FESEM images of OS samples at the magnification of 50,000 times.

TABLE 5: Cr (VI) ions adsorption ability of oyster shell samples.

No.	Sample	Q (mg/g)	H (%)
1	QNOS-PP	14.90	29.80
2	QNOS-PP-800	19.50	39.00
3	QNOS-PP-800-EDTA	28.80	57.60
4	PYOS-PP	11.40	22.80
5	PYOS-PP-Na	25.70	51.40
6	PYOS-PP-Na-750	11.77	23.60
7	PYOS-PP-Na-800	25.88	51.56
8	PYOS-PP-Na-900	19.02	38.04
9	PYOS-PP-Na-800-EDTA	32.00	64.00

particles (sample no. 4). This confirms that treatment process is necessary to improve adsorption ability of the OS samples because sand, organic compounds, and impurities on the surface of OS particles were removed in the treatment process, leading to exposing the adsorption sites.

For further treatment, the initial OS and OS-Na samples were calcined at 750, 800, and 900°C to make a variation in their phase structure. At different temperatures, the Cr (VI) ions adsorption ability of PYOS samples was also varied significantly. This may be explained by the modification in structure of OS samples as impacted by calcination process at high temperature. According to XRD analysis results, the

main composition in OS samples is CaCO_3 ; under the impact of temperature, CaCO_3 was degraded and converted to CaO [15, 16]. The release of carbon dioxide and existence of CaO phase in calcined OS samples can lead to the increase in porosity of these samples, resulting in the enhancement of metal ions adsorption ability. The temperature of 800°C is the most suitable for calcination process of PYOS samples to give a better Cr (VI) ions adsorption ability (samples no. 5, no. 6, no. 7, and no. 8).

Considering the effect of biodiversity on Cr (VI) ions adsorption ability by OS particles, the results in Table 5 also show that the OS samples in Phu Yen sea region have adsorption ability better than the OS samples in Quang Ninh sea region (samples no.1 and no. 4). This proves that the differences in geographical position of two sea regions and aquaculture conditions of oysters can result in the formation and characteristics of OS samples as shown by their BET parameters and FESEM images (Sections 3.2.2 and 3.2.3 before).

EDTA also has a positive effect on the Cr (VI) ions adsorption ability by OS samples thanks to the formation of the complex between EDTA and Cr (VI) ions. The H and Q of samples no. 3 and no. 9 are 1.24–1.48 times larger than those of the samples no. 2 and no. 7. The effect of EDTA on the heavy metal adsorption ability was also proved by Min et al. [16].

From the obtained results, the PYOS-PP-Na-800-EDTA sample with the highest Cr (VI) ions adsorption ability is selected for further studies.

3.4. Effect of Some Experiment Conditions on Cr (VI) Ions Adsorption Ability of Oyster Shell Samples. Effect of some experiment conditions on the Cr (VI) ions adsorption ability of OS samples was carried out on PYOS-PP-Na-800-EDTA sample. The changes of pH solution, time adsorption, adsorbent weight, and initial concentration of Cr (VI) ions solution are investigated. The results of removal percent of Cr (VI) ions (H) and amount of Cr (VI) ions adsorbed per gram of adsorbent (Q) are listed in Table 6.

3.4.1. Effect of pH of Solution. The results in Table 6 show that when changing the pH of solutions and fixing other factors (the initial Cr (VI) ions concentration of 10 ppm, the adsorption time of 120 min, and the adsorbent weight of 0.2 grams), the Cr (VI) ions adsorption ability of the PYOS-PP-Na-800-EDTA sample was also affected significantly and reached the highest H and Q value in solution pH of 6 (2.36 mg/g and 47.10%, respectively). In solution pH range from 2 to 6, the Cr (VI) ions are in form of acid chromate ions (HCr_2O_7^- and HCrO_4^-). When the pH of solutions increases from 6 to 7, the Cr (VI) ions will be changed into $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} . In pH 7 solution, Cr (VI) ions are only in CrO_4^{2-} form and in solution pH higher 7, Cr (VI) ions will be in the form of $\text{Cr}(\text{OH})_6$. In case of $\text{pH} < \text{pH}_{\text{pzc}}$ (9.05), the PYOS-PP-Na-800-EDTA sample is positively charged; therefore, the anions adsorption ability by this sample was increased significantly [14]. Specifically, the CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions can be absorbed onto the surface of PYOS-PP-Na-800-EDTA sample better than HCr_2O_7^- and HCrO_4^- ions; thus, pH 6 is the most suitable pH for the Cr (VI) ions adsorption study by PYOS-PP-Na-800-EDTA sample. The same results were reported by Nagashanmugam et al. [17].

3.4.2. Effect of Adsorption Time. Adsorption time influences strongly the Cr (VI) ions adsorption ability of the PYOS-PP-Na-800-EDTA sample as fixing other adsorption factors (the initial Cr (VI) ions concentration of 10 ppm, the pH of 6, and the adsorbent weight of 0.2 grams). It can be seen that the H and Q of Cr (VI) ions are increased as rising adsorption time. This result indicates that the adsorption of Cr (VI) ions onto PYOS-PP-Na-800-EDTA sample requires a long stirring time. However, the H and Q were augmented extremely at the adsorption time of 120 min, and they were then varied slowly. The adsorbent with many active sites adsorbed a large part of Cr (VI) ions in the solution for first 120 min. While adsorption time is over 120 min, the occupation of these adsorption sites by Cr (VI) ions causes the reduction of the availability of active sites in the PYOS-PP-Na-800-EDTA sample. On the other hand, there is a possibility of release back of Cr (VI) ions from the surface of PYOS-PP-Na-800-EDTA sample to the solution due to the weak interaction between the adsorbent and the ion target. Therefore, the

period of 120 min was considered to reach adsorption equilibrium or equilibrium time.

3.4.3. Effect of Absorbent Weight. The results in Table 6 also prove that when changing the weight of the adsorbent and fixing other factors (the initial Cr (VI) ions concentration of 10 ppm, the pH of 6, and the time contact of 120 min), the Cr (VI) ions adsorption ability of PYOS-PP-Na-800-EDTA sample was increased because the higher volume of materials, the more voids to increase the adsorption ability of Cr (VI) ions into the adsorption material.

3.4.4. Effect of Initial Cr (VI) Ions Concentration. The effect of initial concentration on the Cr (VI) ions adsorption ability of PYOS-PP-Na-800-EDTA sample is carried out at condition of pH 6 with adsorption time of 120 min and the adsorbent weight of 0.2 grams. The obtained results described in Table 6 show that the Q value of sample was increased as rising initial Cr (VI) ions concentration.

3.5. Adsorption Isotherms of Cr (VI) Ions Adsorption Process Using Oyster Shell Samples and Error Analysis. Figure 10 and Table 7 display the parameters for plotting Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich adsorption isotherms of Cr (VI) ions using the PYOS-PP-Na-800-EDTA sample. The process of Cr (VI) ions adsorption by PYOS-PP-Na-800-EDTA sample is followed to the Langmuir isotherm model with the highest correlation coefficient, $R^2 = 0.9943$ (Table 8), which means that on the outer surface of OS samples formed a monolayer of adsorbed molecules and no further adsorption took place after that. The separation factor (also called equilibrium parameter), $R_L = 0.4988 < 1$, indicates that the equilibrium adsorption was favorable. The maximum adsorption capacity (Q_0) of adsorbent for the removal of Cr (VI) ions is 769.231 mg/g. The Freundlich isotherm model also shows a relatively high correlation coefficient of 0.9767 but the adsorption intensity $n = 0.971 < 1$; hence the sorption process is unfavorable (Table 8). The two other models indicate a lower value of R^2 and constants such as $B = 4.0698 \text{ J/mol}$ and $E = 0.80 \text{ kJ/mol}$ expressing physical adsorption process of PYOS-PP-Na-800 sample for Cr (VI) ions (Table 8). The Langmuir isotherm model was shown to be the best fitting for adsorption of Cr (VI) ions and Cu (II) [9].

The good Cr (VI) ions adsorption ability of oyster shell is a sign for the effectiveness regeneration of oyster shell waste as adsorbent. The oyster shell sample after calcination and modification with EDTA is a promising adsorbent material for the removal of heavy metal ions in aqueous solution, especially the anions in aqueous solutions.

Table 9 demonstrates the result of error analysis of the Cr (VI) ions adsorption isotherms models using various methods: R^2 (correlation coefficient), SSE (sum of square errors), MSE (mean square error), and RMSE (root mean square error). As can be seen, the Langmuir isotherms model has the highest correlation coefficient and smallest errors, which again confirms that this model fits to the adsorption

TABLE 6: Effect of some experiment conditions on Cr (VI) ions adsorption ability of PYOS-PP-Na-800-EDTA sample.

pH of solution			Adsorption time			Adsorbent weight			Initial Cr (VI) ions concentration		
pH	Q (mg/g)	H (%)	Time (min)	Q (mg/g)	H (%)	m _{os} (g)	Q (mg/g)	H (%)	C ₀ (ppm)	Q (mg/g)	H (%)
2	0.80	16.00	20	0.68	13.61	0.1	1.65	29.30	3	1.65	55.00
3	1.30	26.00	30	0.87	17.30	0.2	1.73	34.50	7	3.88	55.43
4	1.65	33.00	45	1.10	21.90	0.5	2.12	42.30	8	4.35	54.48
5	2.14	42.70	60	1.54	30.80	0.6	2.27	45.30	10	5.20	52.00
6	2.36	47.10	90	1.65	33.00	0.8	2.49	49.70	15	8.77	58.47
7	0.28	5.60	120	2.66	53.10	1.0	2.92	58.30			
			150	2.81	56.20						
			180	2.84	56.80

FIGURE 10: Different isotherm models with their equations and correlation coefficient values. (a) Langmuir adsorption isotherm. (b) Freundlich adsorption isotherm. (c) Temkin adsorption isotherm. (d) Dubinin–Radushkevich (D-R) adsorption isotherm.

TABLE 7: Parameters for plotting Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich adsorption isotherms of Cr (VI) ions using oyster shell samples.

No.	C ₀ (mg/L)	C _e (mg/L)	1/C _e	Log C _e	Ln C _e	Q _e (mg/g)	1/Q _e	Log Q _e	Ln Q _e	ε ²
1	3	1.35	0.74	0.13	0.30	1.65	0.61	0.22	0.50	1.89
2	7	3.12	0.32	0.49	1.14	3.88	0.26	0.59	1.36	0.47
3	8	3.65	0.27	0.56	1.29	4.35	0.23	0.64	1.47	0.36
4	10	4.8	0.21	0.68	1.57	5.20	0.19	0.72	1.65	0.22
5	15	6.23	0.16	0.79	1.83	8.77	0.11	0.94	2.17	0.14

mechanism of ion Cr (VI) ions into the selected oyster shell samples. The Freundlich model also shows relatively high R^2 and small errors. On the other hand, the Temkin model

exhibits the lowest correlation coefficient and highest error, which means the isotherms ion Cr (VI) ions adsorption using oyster shell samples does not follow this model.

TABLE 8: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm constants for the adsorption of Cr (VI) ions using oyster shell.

Langmuir constant				Freundlich constant			
Q_0 (mg/g)	K_L (L/mg)	R_L	R^2	$1/n$	n	k_f (mg/g)	R^2
769.231	0.0016	0.4988	0.9943	1.030	0.971	1.181	0.9767
Temkin constant				Dubinin–Radushkevich constant			
A_T (L/mg)	b_T	B (J/mol)	R^2	Q_s (mg/g)	K_{ad} (mol ² /kJ ²)	E (kJ/mol)	R^2
0.9474	608.770	4.0698	0.8324	6.739	0.778	0.80	0.8596

 TABLE 9: Error analysis of R^2 , SSE, MSE, and RMSE for Cr (VI) ions adsorption according to various isotherms models.

Adsorption isotherm equation	R^2	SSE	MSE	RMSE
Langmuir	0.994	0.00082	0.00016	0.01283
Freundlich	0.977	0.00645	0.00129	0.03592
Temkin	0.832	4.50704	0.90141	0.94943
D-R	0.860	0.20611	0.04122	0.20303

FIGURE 11: Different linear kinetic models of Cr (VI) ions adsorption according to their equations and correlation coefficient values. (a) First-order reaction model. (b) Pseudo-first-order reaction model. (c) Second-order reaction model. (d) Pseudo-second-order reaction model.

3.6. Adsorption Kinetics of Cr (VI) Ions Adsorption Process Using Oyster Shell Samples. The adsorption kinetics of Cr (VI) ions adsorption process are studied and four linear kinetic models are used in this work as presented in Figure 11. As can be seen in Figure 11, the first-order reaction model fitting the adsorption kinetic of Cr (VI) ions adsorption process is more suitable with the correlation coefficient R^2 of 0.9434. The pseudo-first-order reaction and second-order reaction models also indicate relatively high values of R^2 , approximately 0.94. The pseudo-second-order

 TABLE 10: Error analysis of R^2 , SSE, MSE, and RMSE for Cr (VI) ions adsorption according to various kinetic models.

Model	R^2	SSE	MSE	RMSE
First-order	0.9434	0.03367718	0.00420965	0.06488180
Pseudo-first-order	0.9396	0.00000059	0.00000007	0.00027147
Second-order	0.9393	0.00107378	0.00013422	0.01158544
Pseudo-second-order	0.8307	152.38357709	19.04794714	4.36439539

FIGURE 12: Proposed mechanism of the adsorption of Cr (VI) ions on the PYOS-PP-Na-800-EDTA adsorbent.

reaction model, on the other hand, shows a lower correlation coefficient, R^2 of 0.8307. For the regression coefficient evaluation using the square errors (as listed in Table 10), it can be seen that the pseudo-first-order kinetic model exhibits the smallest error. The errors of first-order model and second-order model are also relatively small. Based on the square errors, it is confirmed that pseudo-first-order kinetic model is complied with the Cr (VI) ions adsorption process by using oyster shell sample.

Based on the results of adsorption isotherms and kinetics, an adsorption mechanism of Cr (VI) ions by oyster shell can be recommended as presented in Figure 12.

4. Conclusion

From the results in this study, we can conclude that the characteristics and Cr (VI) ions adsorption ability of two kinds of oyster shell (OS) samples collected at two unlike sea regions in Vietnam are clearly different. The Phu Yen OS samples have a porous surface and holes more than the Quang Ninh OS samples; hence the Cr (VI) ions adsorption ability of PY-OS samples is higher than that of QNOS samples. This shows that biodiversity can influence the structure of the materials collected at the different geographical positions. The calcination and modification of OS samples with EDTA are necessary for enhancement of Cr (VI) ions adsorption ability of OS samples. The factors such as pH solution, adsorption time, adsorbent weight, and initial Cr (VI) ions concentration obviously affect Cr (VI) ions adsorption efficiency of treated OS sample. The solution pH of 6 is the most suitable to remove Cr (VI) ions by using treated OS samples and the Cr (VI) ions adsorption efficiency is increased with rising adsorption time, adsorbent weight, and initial Cr (VI) ions concentration. The Langmuir isotherm model with the highest correlation coefficient (R^2 of 0.9943) and the

lowest SSE, MSE, and RMSE is the most suitable for fitting the Cr (VI) ions adsorption by treated OS samples in aqueous solution. The maximum adsorption capacity of oyster shell adsorbent for the removal of Cr (VI) ions is 769.231 mg/g. The first-order reaction model is the best for studying the adsorption kinetic of Cr (VI) ions adsorption process. The treated OS samples are promising adsorbents for removal of heavy metal ions in aqueous solution.

Abbreviations

BET:	Brunauer–Emmett–Teller
DCP:	1,5-Diphenylcarbazine
EDTA:	Ethylenediaminetetraacetic acid
FESEM:	Field emission scanning electron microscopy
IR:	Infrared
NP:	Nacreous
OS:	Oyster shell
PP:	Prismatic
PYOS:	Oyster shell samples collected at Phu Yen province sea
QNOS:	Oyster shell samples collected at Quang Ninh province sea
XRD:	X-ray diffraction
UV-Vis:	Ultraviolet-visible.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Supplementary Materials

Table 1S: position of main peaks in FTIR spectra of OS samples. Figure 1S: FESEM images of OS samples at the magnification of 200000 times. (*Supplementary Materials*)

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