ГІДРОХІМІЯ

УДК 546.27:547.914

Х.Х. КУЄН,
Університет Науки і Технологій,
Да Нанг 550000, В'єтнам
e-mail: hhquyen@dut.udn.vn
Х.М. НГУЄН,
Університет Науки і Технологій,
Да Нанг 550000, В'єтнам
e-mail: hhquyen@dut.udn.vn
В.Ч.М. ТРАН,
Університет Науки і Технологій,
Да Нанг 550000, В'єтнам
Ф.Ц. ЛЕ,
Університет Науки і Технологій,
Да Нанг 550000, В'єтнам
Л. НГУЄН-ДІН,
Університет Науки і Технологій,
Да Нанг 550000, В'єтнам
Л.Т. НГУЄН,
Інститут Науки і Технологій з Енергетики та Навколишнього Середовища,
Академія Наук і Технологій В'єтнама,
Ханой 11300, В'єтнам

ПЕРЕТВОРЕННЯ МОРСЬКИХ ВІДХОДІВ НА АДСОРБЕНТИ: ВИДАЛЕННЯ БОРУ З ВОДИ ЗА ДОПОМОГОЮ КАЛЬЦИНОВАНИХ ПАНЦИРІВ КРАБІВ ТА РАКОВИН МОЛЮСКІВ[1]

Надмірна кількість бору у водних екосистемах становить потенційну загрозу для здоров'я людини. Тому метою дослідження було вивчення ефективності використання кальцинованих панцирів крабів та раковин кров'яних молюсків (Tegillarca granosa (Linnaeus, 1758)) як адсорбентів для видалення бору з водних розчинів. Для оцінки ефективності адсорбентів за різних умов, таких як температура кальцинації, початкове значення pH розчину, початкова концентрація, час контакту, температура адсорбції та іонна сила, було проведено комплекс експериментів. Здатність до адсорбції бору підвищується з підвищенням температури кальци-

[1] This research is funded by the Ministry of Education and Training of Vietnam (Project N B2023.DNA.09).

Ц и т у в а н н я: Куєн Х.Х., Нгуєн Х.М., Тран В.Ч.М., Ле Ф.Ц., Нгуєн-Дін Л., Нгуєн Л.Т. Перетворення морських відходів на адсорбенти: видалення бору з води за допомогою кальцинованих панцирів крабів та раковин молюсків. *Гідробіол. журн.* 2026. Т. 62, № 4. С. 110—125.

нації, pH розчину, температурою та присутністю $CaCl_2$ і $MgCl_2$. Крім того ізотерми адсорбції бору добре описуються моделлю Ленгмюра, тоді як кінетика адсорбції відповідає моделі псевдо-другого порядку. Максимальна здатність кальцинованих панцирів крабів та раковин кров'яних молюсків до адсорбції бору становила 23,9 та 34,1 мг/дм^3, відповідно. Стан адсорбційної рівноваги обох адсорбентів було отримано через дев'ять годин. Термодинамічні параметри ($\Delta S°$, $\Delta G°$, $\Delta H°$) досліджували під час процесу адсорбції бору. Кальциновані панцирі крабів та раковини кров'яних молюсків також демонструють високоефективне видалення бору зі стічних вод локальної системи вологої десульфуризації димових газів на рівні 98,1 та 99,6 %, відповідно. Проведені дослідження свідчать про економічну ефективність кальцинованих панцирів крабів та раковин кров'яних молюсків як ефективних адсорбентів, підкреслюючи їхній потенціал для сталого видалення бору під час очищення стічних вод.

Ключові слова: *видалення бору, панцирі крабів, раковини кров'яних молюсків, адсорбція, стічні води локальної системи вологої десульфуризації димових газів.*

Introduction

Boron represents a geochemically significant trace element that is ubiquitously distributed across terrestrial and aquatic compartments of the Earth system. Originating from both lithogenic weathering and anthropogenic mobilization, it migrates through rocks, soils, sediments, and natural waters, ultimately integrating into biological tissues across trophic levels [5]. Boron's dynamic environmental cycling reflects a combination of geological processes, such as volcanic emissions and crustal leaching, and human-driven activities, including industrial discharge, fertilizer application, and wastewater effluent.

Due to its versatile physicochemical characteristics, boron plays an indispensable role in a wide spectrum of industrial and technological domains. It serves as a critical additive in glass and ceramic fabrication, semiconductor and electronic manufacturing, detergent and cosmetic formulations, and agricultural fertilizers [21]. Within aqueous environments, boron predominantly exists as boric acid (H_3BO_3) and borate ions $[B(OH)_4]^-$, while under alkaline or concentrated conditions, it forms more complex polyborate anions such as $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$, and $[B_5O_6(OH)_4]^-$ [20].

Although boron is essential in trace quantities for metabolic and physiological functions in plants and microorganisms, its narrow margin between nutritional necessity and toxicity presents a major environmental management challenge. In irrigated agriculture, minor fluctuations above the tolerance threshold can suppress photosynthesis, disrupt nutrient uptake, and diminish crop yields. In humans and animals, chronic exposure through contaminated water or food has been correlated with cardiovascular, gastrointestinal, and neurotoxic disturbances [23]. This dualistic nature-biological indispensability, juxtaposed with toxic potential, demands precise monitoring and control of boron concentrations in environmental and engineered water systems.

Recognizing these risks, international regulatory agencies have imposed increasingly stringent quality standards. The World Health Organization recommends a maximum boron concentration of 2.4 mg L^{-1} in potable water, while the European Union, Singapore, South Korea, and Japan enforce more conservative thresholds of 1.0 mg/L [9]. These limits have intensified the se-

arch for reliable, scalable, and cost-effective remediation technologies capable of selectively removing boron from both natural and industrial water matrices.

A variety of physicochemical treatment methods, such as reverse osmosis, ion exchange, electrocoagulation, electrodialysis, and adsorption, have been explored for boron mitigation [22]. Among them, adsorption stands out as an operationally simple, energy-efficient, and environmentally sustainable approach. Its effectiveness depends largely on the structural and surface chemical properties of the adsorbent, prompting extensive research into both synthetic and naturally derived materials. Conventional adsorbents include activated carbon [11], alumina [13], graphene oxide [7], hydroxides [18], layered double hydroxides (LDHs) [8], selective resins [12], and metal-organic frameworks (MOFs) [21]. However, to reduce operational costs and environmental burden, contemporary studies have increasingly shifted toward valorizing biomass-derived sorbents and agricultural or food wastes transformed into functional materials capable of high boron uptake.

Numerous examples demonstrate the promise of such bio-based adsorbents. Powdered banana peels (1.0—3.0 mm) exhibited a maximum sorption capacity (q_{max}) of 3.40 mg/g due to abundant hydroxyl, amine, alkane, and carboxylic groups contributing to boron complexation [6]. Additionally, modified jering seed peels treated with NaOH or $FeCl_3$ displayed q_{max} values between 0.72 and 0.75 mg/g [1], while pomegranate peel powders modified by HCl or NaOH achieved slightly higher efficiencies of 0.91—0.97 mg/g [2]. Advanced biosorbents such as amine-functionalized tannin gels (q_{max} = 24.3 mg/g [14]), date seed ash (q_{max} = 31.7 mg/g [4]), and calcined eggshells (q_{max} = 32.26 mg/g [3]) have demonstrated that low-cost waste resources can rival or even outperform engineered adsorbents.

This work explores calcined crab shells and calcined blood cockle shells as novel calcium-based biosorbents for boron removal. Upon calcination, the natural $CaCO_3$ matrix transforms into CaO, generating reactive hydroxyl sites in aqueous solution that promote boron uptake through surface complexation. The study systematically examines the effects of calcination temperature, initial pH of the solution, initial concentration, contact time, adsorption temperature, and ionic strength on boron adsorption performance. Langmuir and pseudo-second-order models describe the process well, indicating monolayer chemisorption governed by active $Ca(OH)_2$ sites. Thermodynamic analyses confirm that boron adsorption is spontaneous and endothermic. Notably, calcined crab shells and calcined blood cockle shells achieved boron removal efficiencies of 98.1 % and 99.6 % from real wet flue gas desulfurization wastewater, demonstrating their strong potential for practical deployment. This research highlights a sustainable, low-cost pathway for boron remediation using biogenic calcium materials and advances understanding of $Ca(OH)_2$ and boron binding mechanisms.

Material and Methods

Two types of marine shells, including crab shells (CS) and blood cockle shells (BS), were collected from a local seafood market in Da Nang City, Viet-

nam. Analytical-grade boron standard solution (1000 mg/L) and boric acid (H_3BO_3), used for the preparation of boron stock solutions, were obtained from Kanto Chemical Industry Co., Ltd. (Japan). Hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) were also procured from the same supplier. All reagents were of analytical grade and used without further purification.

The preparation of adsorbents is illustrated in Figure 1. CS and BS were brushed and thoroughly washed several times with deionized water to remove impurities. Subsequently, shell samples were dried in an oven at 100 °C for 24 h. The dried shells were then crushed and screened through a sieve with a size less than 1.19 mm (16 mesh) to collect the fine particles, which were utilized as adsorbents. Furthermore, the raw CS powder and BS powder were subjected to the furnace to be calcined at 600 °C for 3 h (CS 600 and BS 600), 700 °C for 2 h (CS 700 and BS 700), 800 °C for 1 h (CS 800 and BS 800), and 900 °C for 45 min (CS 900 and BS 900). The calcination conditions were carried out in accordance with the results of our previous study, with some adjustments [16].

Batch adsorption tests (Fig. 1) were conducted to evaluate the boron removal performance of both raw and calcined shell adsorbents. In each experiment, 0.1 g of adsorbent was added to 100 mL of boric acid solution containing 100 mg/L of boron. The suspensions were agitated in a thermostatic shaker at 25 °C for 24 h under an initial pH of 5.5. Following adsorption, the mixtures were filtered through 0.45 μm membrane filters, and blank controls were prepared under identical conditions. Boron concentrations in the filtrates were quantified using a UV-VIS-NIR spectrophotometer (λ = 415 nm) via the Azomethine-H method. The boron removal efficiency (H, %) and adsorption capacity (q_e, mg/g) were calculated using the following equations:

$$H = \frac{C_0 - C_e}{C_0} \times 100, \tag{1}$$

$$q_e = \frac{C_0 - C_e}{M} \times V, \tag{2}$$

where q_e is the amount of boron on the surface of the adsorbent (mg/g). C_o and C_e (mg/L) are initial and equilibrium concentrations of boron (mg/L), respectively. M and V are the adsorbent mass (g) and solution volume (L).

The influence of key operational variables on boron adsorption was systematically evaluated. The initial pH was adjusted across a wide range (2.2—12.3) to determine its effect on adsorption performance. Boron adsorption isotherms were obtained at initial concentrations of 5, 10, 20, 50, 70, and 100 mg/L, while kinetic studies were performed at contact times of 0.25, 0.5, 1, 2, 3, 9, 12, and 24 h. Thermodynamic behavior was examined at temperatures

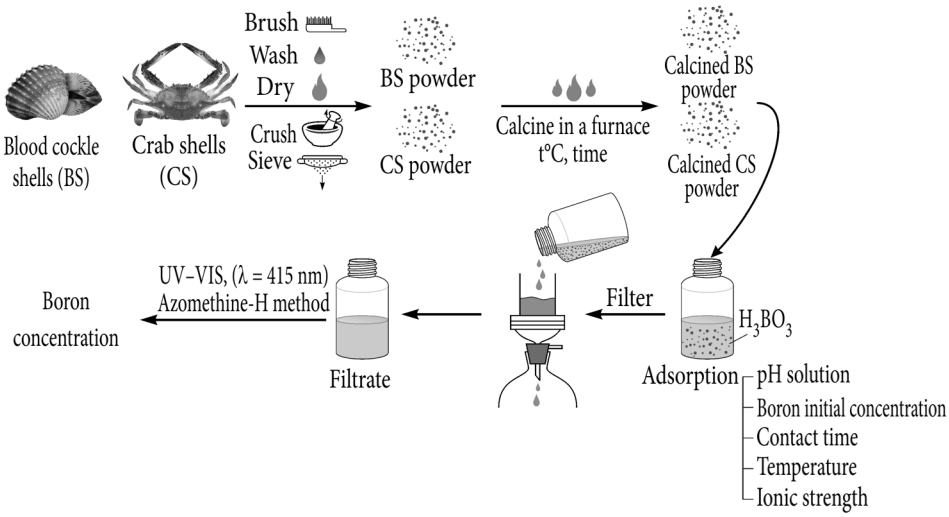

Fig. 1. Schematic diagram of adsorbent preparations and adsorption test

of 25, 35, 45, and 55°C. To investigate the effect of ionic strength, different electrolytes (NaCl, KCl, $CaCl_2$, and $MgCl_2$) were introduced at varying concentrations: 1.0—4.0 mol/L for Na^+, K^+, and Ca^{2+}, and 0.5—2.0 mol/L for Mg^{2+}. All experiments were conducted in duplicate to ensure reproducibility.

Results and Discussion

The calcination of crab shells (CS) and blood cockle shells (BS) was performed at 600 °C for 3 h, 700 °C for 2 h, 800 °C for 1 h, and 900 °C for 45 min to investigate the influence of temperature on boron adsorption capacity. As shown in Figure 2, boron uptake increased progressively with calcination temperature, indicating that thermal activation enhances the surface reactivity of the materials. The calcined BS consistently exhibited higher adsorption capacity than CS across all conditions. Specifically, the boron adsorption capacity of the raw CS and BS was 8.3 mg/g and 10.6 mg/g, respectively, which increased to 24.5 mg/g for CS 900 and 34.4 mg/g for BS 900 after calcination at 900 °C for 45 min. The improvement in performance can be attributed to the thermal decomposition of calcium carbonate ($CaCO_3$), the dominant mineral phase in seashells, into calcium oxide (CaO) [19]. This transformation increases porosity and generates reactive -OH surface sites that promote the boron complexation mechanism.

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2, \quad (3)$$

$$CaO + H_2O \rightarrow Ca(OH)_2. \quad (4)$$

Moreover, increasing the calcination temperature enhances the formation of calcium oxide (CaO), which subsequently hydrates to calcium hydroxide

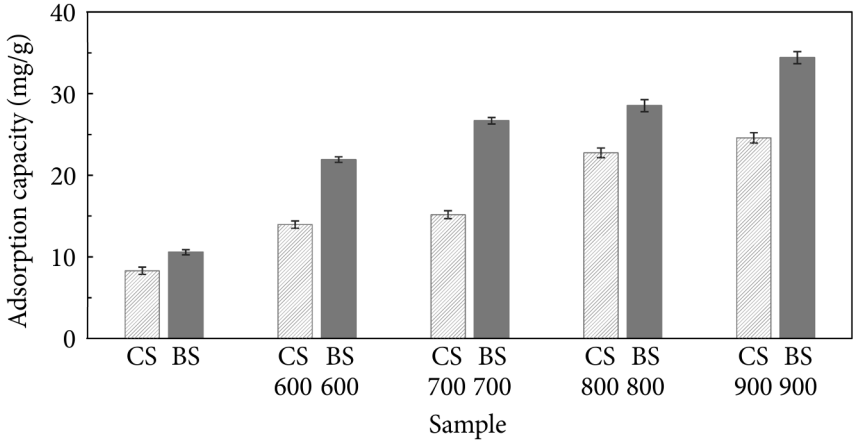

Fig. 2. Effect of calcination temperature on boron adsorption. (Initial concentration of boron: 100 mg/L, mass of adsorbent: 0.1 g, initial pH solution: 5.5, solution volume: 100 mL, contact time: 24 h, and temperature: 25 °C)

($Ca(OH)_2$) upon contact with water [15]. The presence of calcium oxide contributes to the formation of calcium hydroxide ($Ca(OH)_2$) in aqueous solution. The hydroxyl groups provided by $Ca(OH)_2$ act as active sites for boron binding, as adjacent -OH groups can coordinate with borate species to form stable borate complexes [10]. This synergistic transformation from $CaCO_3$ to CaO and then to $Ca(OH)_2$ significantly contributes to the improved adsorption performance of calcined shells. Based on these observations, the samples calcined at 900°C for 45 min, designated as CS 900 and BS 900, exhibited the highest boron adsorption capacities and were therefore selected for subsequent experiments.

The effect of initial pH on boron removal was examined for CS 900 and BS 900 under identical experimental conditions. As shown in Figure 3, the adsorption capacity of both materials increased markedly as the pH rose from 2.2 to 12.3, confirming the strong dependence of boron uptake on solution chemistry. The pH governs not only the surface charge of the adsorbent but also the speciation of boron in solution. At pH<6, boron predominantly exists as molecular boric acid $[B(OH)_3]^0$. Between pH 6 and 10, polyborate species such as $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$, and $[B_5O_6(OH)_4]^-$ become dominant, while at pH>10, the monovalent borate ion $[B(OH)_4]^-$ is the prevailing form [10]. Among these species, $[B(OH)_4]^-$ exhibits the strongest affinity for surface hydroxyl groups, leading to the formation of stable borate complexes. Consequently, higher pH levels favor boron adsorption by enhancing electrostatic attraction and complexation between borate ions and reactive $Ca(OH)_2$ sites on the calcined shell surfaces.

The Langmuir, Freundlich, and Temkin isotherm models were applied in this study. The Langmuir model assumes that the energies of adsorption on the surface are homogeneous, and there is no movement of adsorbates across the

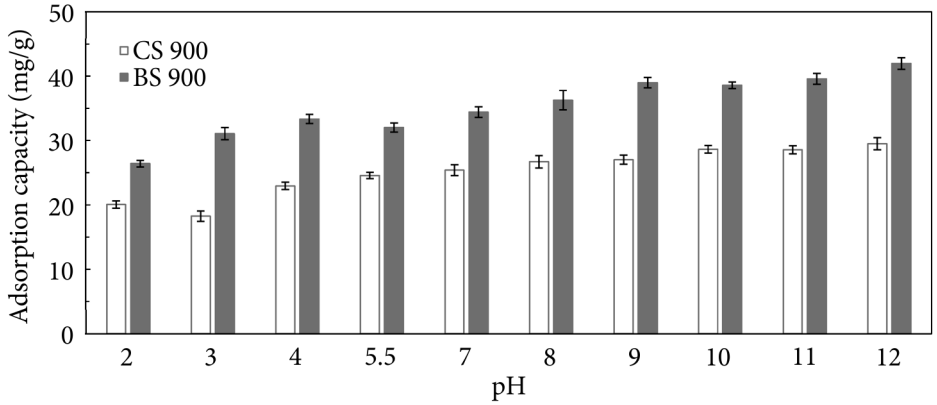

Fig. 3. Effect of pH on boron adsorption by CS 900 and BS 900. (Initial concentration of boron: 100 mg/L, mass of adsorbent: 0.1 g, initial pH solution: 2.2—12.3, solution volume: 100 mL, contact time: 24 h, and temperature: 25 °C)

surface. The Langmuir isotherm model can be expressed mathematically as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{1}{q_{\max}} C_e, \tag{5}$$

where q_e represents the quantity of adsorbed boron per unit weight of adsorbent at equilibrium (mg/g). q_{max} is the maximum adsorption capacity of the adsorbent (mg/g), C_e is the equilibrium boron concentration (mg/L), and b is the Langmuir adsorption constant (L/mg adsorbent).

The Freundlich isotherm model is an empirical equation for describing multilayer adsorption on an irregular surface. This model is provided below by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \tag{6}$$

where K_F and n are Freundlich adsorption constants involved in relative capacity and the intensity of adsorption, respectively.

The Temkin isotherm model suggests that the heat of adsorption from molecules demonstrates a linear decline as the surface coverage rises. The Temkin isotherm equation can be described as follows:

$$q_e = \frac{RT}{b_T} \ln(A_T) + \frac{RT}{b_T} \ln(C_e), \tag{7}$$

where b_T is the Temkin isotherm constant (kJ g/mol^2), R is the ideal gas constant (8.3145 J/mol K), T is thermodynamic temperature (K), and A_T is the equilibrium binding constant (L/g).

The corresponding models are given in Figure 4. The calculated parameters and the results obtained from the fitting of three isotherm models are summarized in Table. The plots of C_e/q_e versus C_e, $\log(q_e)$ versus $\log(C_e)$, and q_e versus $\ln(C_e)$ for the boron adsorption onto CS 900 and BS 900, derived from the linear forms of the Langmuir, Freundlich, and Temkin isotherms, are displayed in Figure 1. According to Table, R^2 value for Langmuir adsorption isotherm of BS 900 was recorded at 0.9989. In contrast, this value was obtained at 0.9920 and 0.9116 for Freundlich and Temkin models, respectively. A similar finding was also discovered for CS 900. These results recommend the conclusion that the Langmuir model is particularly effective in characterization of boron adsorption onto CS 900 and BS 900, indicating that the homogeneity of the adsorbent's surface characteristics plays a crucial role in the adsorption process.

Evaluating adsorption kinetics is essential for understanding the effectiveness of the adsorption process. The adsorption kinetics of boron onto CS 900 and BS 900 were carried out by pseudo-first order, pseudo-second order, and intra-particle diffusion models. These models are expressed as follows:

$$\log(q_e - q_t) = \log\left(q_e - \frac{k_1 t}{2.303}\right), \tag{8}$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}, \tag{9}$$

$$q_t = K_{\text{diff}} t^{1/2} + C, \tag{10}$$

where q_t is the amount of boron adsorbed at a given time (mg/g), q_e is the amount of boron adsorbed at equilibrium (mg/g adsorbent), k_1 (min^{-1}) is the rate constant of pseudo-first order model, k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order model, K_{diff} is the constant of diffusion rate (mg g^{-1} min$^{-1/2}$), and C is intra-particle diffusion constant (mg/g).

The corresponding plots are shown in Figures 2 and 5. Among the tested models, the pseudo-second-order model exhibited the best fit, with correlation coefficients of $R^2 = 0.9990$ for CS 900 and $R^2 = 0.9951$ for BS 900. In comparison, the pseudo-first-order model yielded R^2 values of 0.9930 and 0.9901, while the intra-particle diffusion model showed lower correlations ($R^2 = 0.9516$ and $R^2 = 0.8639$). These results indicate that boron adsorption on both calcined shell adsorbents follows pseudo-second-order model, suggesting a chemisorption-dominated mechanism involving valence forces or electron sharing between boron species and active surface sites. As illustrated in Figure 5, equilibrium was achieved after approximately 9 h for both CS 900 and BS 900.

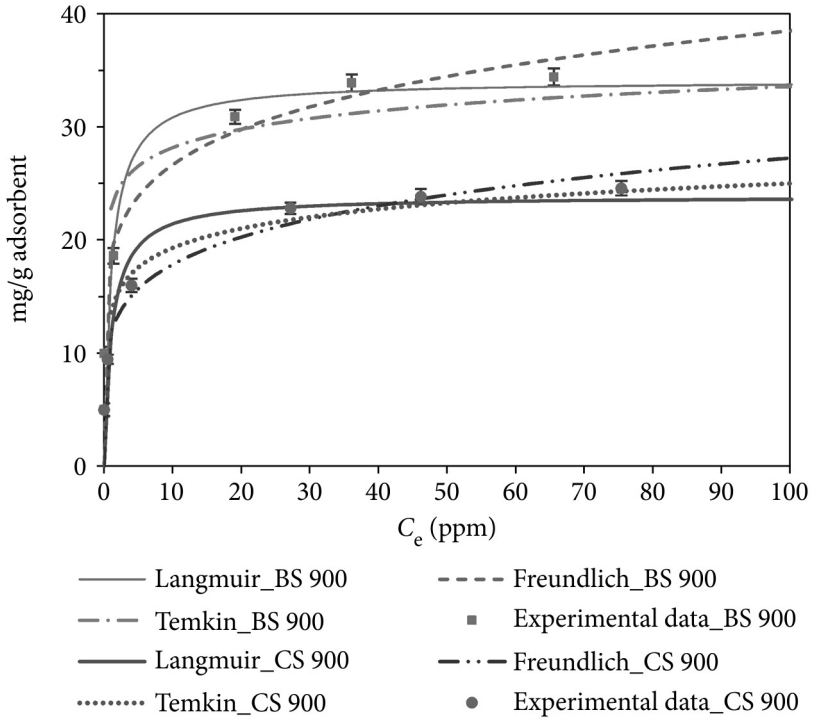

Fig. 4. Isotherm adsorption models of boron removal using CS 900 and BS 900. (Initial concentration of boron: 5 — 100 mg/L, mass of adsorbent: 0.1 g, initial pH solution: 5.5, solution volume: 100 mL, contact time: 24 h, and temperature: 25 °C)

To comprehend the influence of temperature on the boron adsorption by CS 900 and BS 900, an investigation into the adsorption thermodynamics was conducted. A series of parameters, such as temperature T (K), the gas constant R (8.314 J mol^{-1} K^{-1}), the distribution coefficient (K_a), Gibbs free energy change ΔG° (kJ mol^{-1}), enthalpy change ΔH° (kJ mol^{-1}), and entropy change ΔS° (J mol^{-1} K^{-1}) could be determined as follows:

$$\Delta G^0 = -RT \ln K_a \tag{11}$$

$$\ln K_a = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}. \tag{12}$$

The values of ΔH° and ΔS° can be determined by the slope and intercept of the linear fitting of ($\ln K_a$) against (1/T). The thermodynamic parameters calculated from the linear equation are presented in Table and Figure 3. The values of ΔG° are negative and decline as the temperature rises at various temperatures, suggesting that CS 900 and BS 900 adsorb boron spontaneously, with

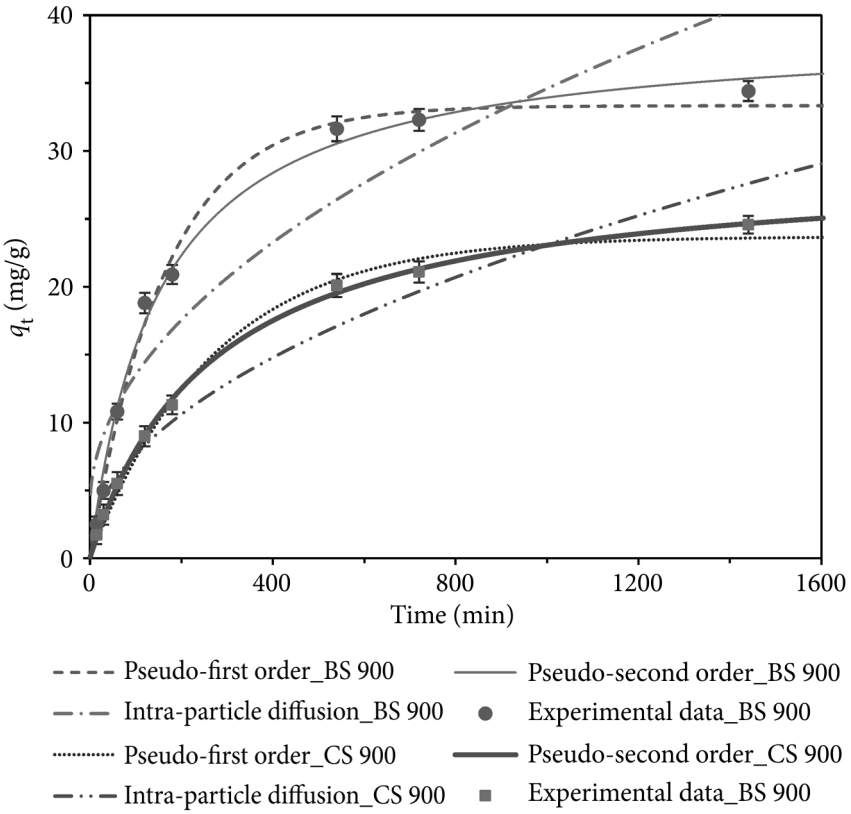

Fig. 5. Kinetic adsorption models of boron removal using CS 900 and BS 900. (Initial concentration of boron: 100 mg/L, mass of adsorbent: 0.1 g, initial pH solution: 5.5, solution volume: 100 mL, contact time: 0—24 h, and temperature: 25 °C)

Table

Thermodynamic parameters of the boron adsorption by CS 900 and BS 900

Adsorbent	T (K)	K_L	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	R^2
CS 900	298	32.58	-80.71	12.28	70.44	0.9342
	308	42.87	-109.77			
	328	52.24	-142.47			
BS 900	298	52.46	-129.98	17.51	91.48	0.9893
	308	61.91	-158.54			
	328	99.02	-270.04			

higher temperatures enhancing the adsorption process. The $\Delta H°$ values of CS 900 and BS 900 are positive, indicating that the adsorption is an endothermic process. Additionally, $\Delta S°>0$ implies that the surface disorder of CS 900 and BS 900 will increase throughout the adsorption process.

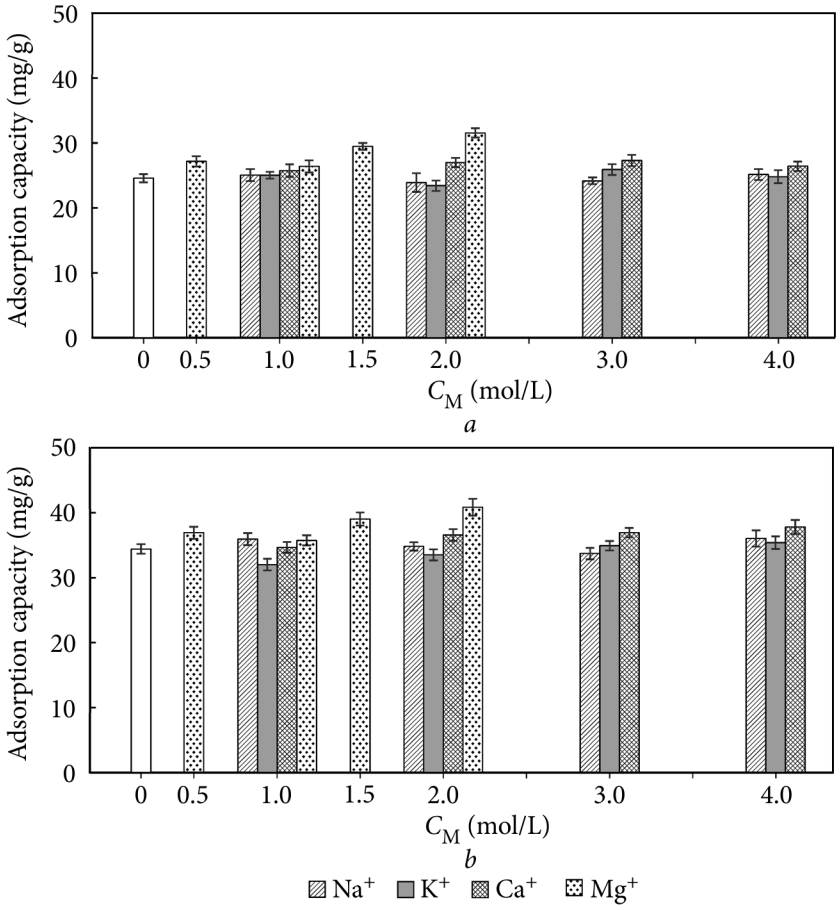

Fig. 6. Impact of Na^+, K^+, Ca^{2+} and Mg^{2+} on boron adsorption capacity using CS 900 (*a*) and BS 900 (*b*). (Initial concentration of boron: 100 mg/L, mass of adsorbent: 0.1 g, initial pH solution: 5.5, solution volume: 100 mL, contact time: 24 h, and temperature: 25 °C)

The influence of common ions on boron adsorption was investigated in the presence of Na^+, K^+, Ca^{2+} and Mg^{2+}, representative cations found in seawater and natural waters. As illustrated in Figure 6, the addition of Na^+ and K^+ produced only a slight reduction in boron uptake, likely due to minor electrostatic shielding effects. In contrast, the presence of divalent cations (Ca^{2+} and Mg^{2+}) markedly enhanced the adsorption capacity of both CS 900 and BS 900. This enhancement can be attributed to the «*salting-out*» phenomenon and the generation of surface hydroxyl complexes ($Ca(OH)_2$ and $Mg(OH)_2$), which serve as active coordination sites for borate binding [17]. The formation of stable borate complexes strengthens chemisorption interactions, thereby improving boron removal efficiency. These results confirm that CS 900 and BS 900 are highly effective adsorbents for boron removal even in saline or mineral-rich wastewaters containing Ca^{2+} and Mg^{2+} ions.

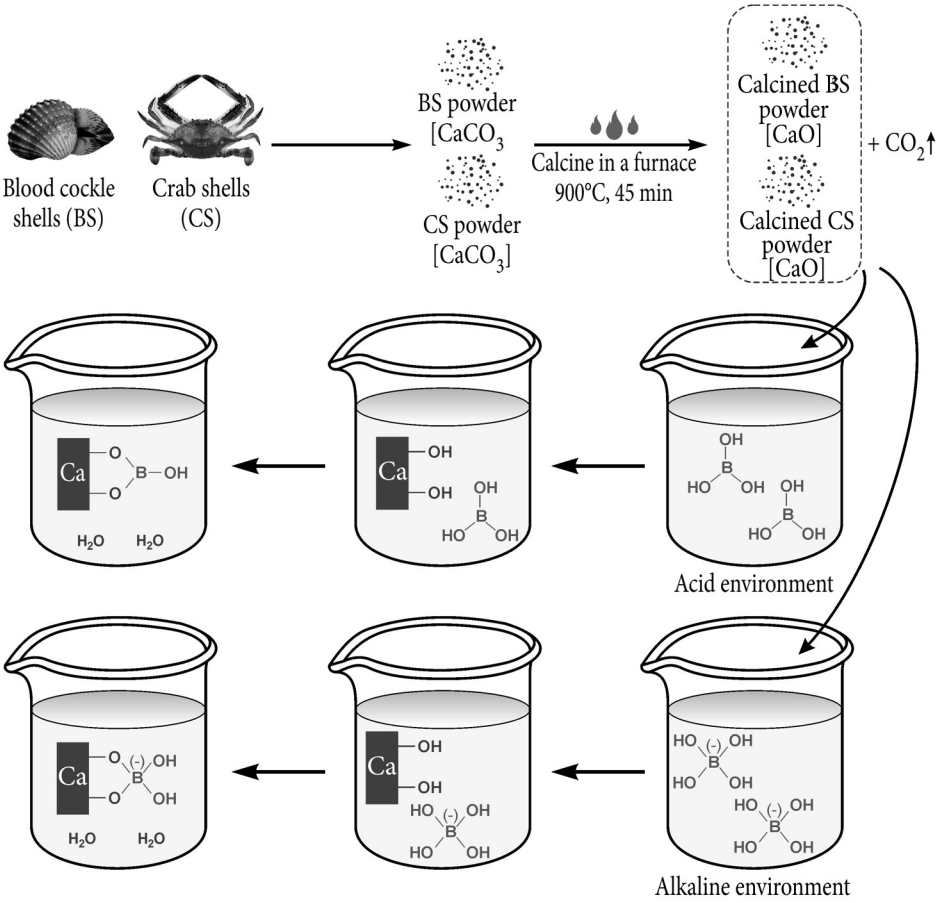

Fig. 7. The possible boron adsorption mechanism of CS 900 and BS 900

According to the above results, the possible boron adsorption mechanism is illustrated in Figure 7. The enhanced boron adsorption capacity of CS 900 and BS 900 can be attributed to surface transformations induced by thermal activation and subsequent hydration. The conversion of $CaCO_3$ to CaO during calcination and its partial hydration to $Ca(OH)_2$ in aqueous solution introduce abundant surface hydroxyl (-OH) that serves as active sites for boron uptake.

The pH-dependent adsorption behavior, where boron removal increases from acidic to alkaline conditions, indicates that boron species interact strongly with these surface hydroxyl groups. At low pH, boron mainly exists as neutral boric acid $[B(OH)_3]^0$, which can weakly associate with surface -OH groups through hydrogen bonding or ligand exchange. As the pH increases, $[B(OH)_4]^-$ becomes the dominant species, leading to stronger electrostatic attraction and the formation of stable borate complexes between borate ions and hydroxyl groups on the calcined shell surfaces.

This interpretation is consistent with kinetic data, which show pseudo-second-order behavior, and with thermodynamic results indicating an endother-

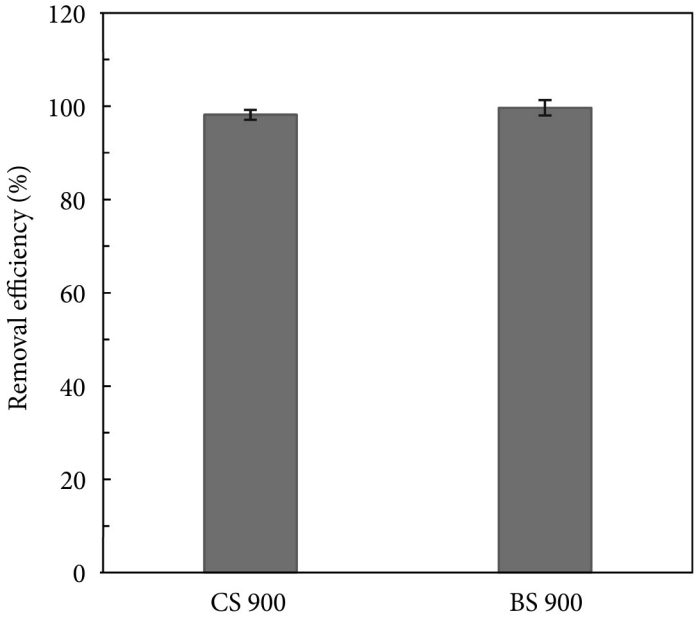

Fig. 8. Boron removal efficiency from the FGD wastewater of coal-fired power plants by CS 900 or BS 900

mic and spontaneous reaction. Moreover, the observed enhancement of adsorption in the presence of Ca^{2+} and Mg^{2+} supports the involvement of divalent cations in stabilizing borate-surface complexes. The combined evidence from kinetic fitting, pH-dependent behavior, thermodynamic parameters, and ionic strength effects supports a chemisorption-controlled boron adsorption process.

A real wastewater sample was collected from the flue gas desulfurization (FGD) system of a local coal-fired power plant in Vietnam and used to evaluate the practical applicability of the proposed adsorbents. The sample was first filtered through 0.45 μm filter paper to remove total suspended solids (TSS). Subsequently, 0.1 g of CS 900 or BS 900 was added to 100 mL of the pretreated wastewater, and the suspensions were agitated at 25 °C for 24 h to attain equilibrium.

As presented in Figure 8, the boron removal efficiencies of CS 900 and BS 900 reached 98.1 % and 99.6 %, respectively, demonstrating excellent adsorption performance under realistic conditions. These high efficiencies confirm that the calcined shell materials maintain strong boron affinity even in complex industrial wastewater matrices containing multiple ions and potential competing species.

The findings highlight the substantial potential of these biogenic calcium-based adsorbents for cost-effective boron removal from industrial effluents, particularly in developing countries such as Vietnam, where large volumes of shell waste and the FGD wastewater are generated. The use of locally

available shell byproducts not only minimizes treatment costs but also promotes circular resource utilization and environmental sustainability. This approach offers a practical and scalable solution for integrating low-cost substitutes into existing wastewater treatment systems in emerging economies.

Conclusion

This study demonstrated that calcined crab shells (CS 900) and calcined blood cockle shells (BS 900) are highly effective biosorbents for boron removal from aqueous solutions and real industrial wastewater. The conversion of $CaCO_3$ to CaO through thermal activation was identified as a key factor enhancing surface reactivity and boron affinity. Boron uptake increased with higher calcination temperature, alkaline pH, and the presence of Ca^{2+} and Mg^{2+} ions, reflecting the strong contribution of hydroxyl group sites to borate complexation. The adsorption behavior followed the Langmuir isotherm and pseudo-second-order kinetics, while thermodynamic analyses confirmed a spontaneous and endothermic process. Remarkably, CS 900 and BS 900 achieved boron removal efficiencies of 98.1% and 99.6%, respectively, when applied to real FGD wastewater. These findings not only validate the mechanistic basis of CaO-mediated boron adsorption but also underscore the feasibility of converting abundant shell waste into functional, low-cost materials for industrial wastewater treatment. The approach offers a sustainable and circular solution, particularly suited to developing countries, where resource recovery and cost-effective technologies are essential for achieving cleaner production and environmental protection goals. In addition, the possible regeneration or reuse of boron-loaded adsorbents would be investigated in the future to strengthen the practical relevance of the study.

Literature Cited

1. Al-Badaii, F., R.A. Hassan, N.A.A. Jalil & A.A. Halim. 2023. Adsorptive removal of boron from aqueous solutions using peels of jering seeds (*Archidendron pauciflorum*): isotherm, kinetic and thermodynamic studies. *Desalin. Water Treat*. **312**: 139–157. https://doi.org/10.5004/dwt.2023.30074

2. Al-Badaii, F., K.M. Jansar, N.A.A. Jalil & A.A. Halim. 2024. Sustainable boron removal from aqueous solutions using pomegranate peel adsorbents: A comprehensive study on isotherms, kinetics, and thermodynamics. *Desalin. Water Treat*. **317**: 100045. https://doi.org/https://doi.org/10.1016/j.dwt.2024.100045.

3. Al-Ghouti, M.A. & N.R. Salih. 2018. Application of eggshell wastes for boron remediation from water. *J. Mol. Liq.* **256**: 599–610. https://doi.org/10.1016/j.molliq.2018.02.074

4. Al.Haddabi, M., M. Ahmed, Z. Al.Zebri et al. 2016. Boron removal from seawater using date palm (Phoenix dactylifera) seed ash. *Desalin. Water Treat.* **57**(11): 5130–5137. https://doi.org/10.1080/19443994.2014.1000385

5. Akdağ, S., R. Keyikoğlu, A. Karagunduz et al. 2023. Recent advances in boron species removal and recovery using layered double hydroxides. *Appl. Clay Sci.* **233**: 106814. https://doi.org/https://doi.org/10.1016/j.clay.2023.106814.

6. Çelebi, H., I. Şimşek, Ş. Tulun & T. Bahadir. 2023. Use of banana peel for the removal of boron from aqueous solutions in the batch adsorption system. *Int. J. Environ. Sci. Technol.* **20**(1): 161–176. https://doi.org/10.1007/s13762-022-04566-1

7. de Lucena, I.O., J.S. de Gois & R.J. Cassella. 2024. Graphene oxide functionalized with N-methyl-D-glucamine as a novel sorbent for boron removal from produced and formation waters. *RSC Advances*. **14**(8): 5319–5330. https://doi.org/10.1039/d4ra00037d

8. Eljamal, O., I. Maamoum, S. Alkhudnayri et al. 2022. Insights into boron removal from water using Mg-Al-LDH: Reaction parameters optimization & 3D-RSM modeling. *J. Water Process Eng.* **46**: 102608. https://doi.org/10.1016/j.jwpe.2022.102608

9. Guan, Z., J. Lv, P. Bai & X. Guo. 2016. Boron removal from aqueous solutions by adsorption. A review. *Desalination* **383**: 29–37. https://doi.org/10.1016/j.desal.2015.12.026

10. Ho, H.Q. 2019. Synthesis of eco-friendly adsorbents for the removal of contaminants in wastewater. Doctor Thesis. Tokushima.

11. Kluczka, J., W. Pudło & K. Krukiewicz. 2019. Boron adsorption removal by commercial and modified activated carbons. *Chem. Eng. Res. Des.* **147**: 30–42. https://doi.org/10.1016/j.cherd.2019.04.021

12. Lee, C.-H., P.-H. Chen & W.-S. Chen. 2022. Recovery of boron from desalination brine through Amberlite IRA 743 resin. *DWT* **264**: 133—140. https://doi.org/10.5004/dwt.2022.28569

13. Lou, X.-Y., R. Boada, L.Y. del Cerro & M. Valiente. 2023. Outstanding performance of hierarchical alumina microspheres for boron removal in the presence of competing ions. *J. Water Process Eng.* **55**: 104218. https://doi.org/10.1016/j.jwpe.2023.104218

14. Morisada, S., T. Rin, T. Ogata et al. 2011. Adsorption removal of boron in aqueous solutions by amine-modified tannin gel. *Water Research* **45**(13): 4028–4034. https://doi.org/10.1016/j.watres.2011.05.010

15. Panagiotou, E., N. Kafa, L. Koutsokeras et al. 2018. Turning calcined waste egg shells and wastewater to Brushite: Phosphorus adsorption from aqua media and anaerobic sludge leach water. *J. Clean. Prod.* **178**: 419–428. https://doi.org/10.1016/j.jclepro.2018.01.014

16. Quyen, H.H., M. Kurashina & M. Yasuzawa. 2022. Removal of phosphate from aqueous solution by using thermally modified clamshell. *Mod Phys. Lett. B* **36**(16): 2242011. https://doi.org/10.1142/S0217984922420118

17. Quyen, H.H., H.M. Nguyen, V.C.M. Tran et al. 2025. Hydroxyl-modified chitosan nanofiber beads for sustainable boron removal and environmental applications. *RSC Adv.* **15**(9): 7090—7102. https://doi.org/10.1039/D5RA00077G

18. Song, T., Q. Luo, F. Gao et al. 2023. Adsorption and electro-assisted method removal of boron in aqueous solution by nickel hydroxide. *J. Ind. Eng. Chem.* **118**: 372–382. https://doi.org/10.1016/j.jiec.2022.11.022

19. Tsai, H.-C., S.-L. Lo & J. Kuo. 2011. Using pretreated waste oyster and clam shells and microwave hydrothermal treatment to recover boron from concentrated wastewater. *Bioresour. Technol.* **102**(17): 7802–7806. https://doi.org/10.1016/j.biortech.2011.06.036

20. Türker, O.C., C. Türe, A. Yakar & Ç. Sar. 2017. Engineered wetland reactors with different media types to treat drinking water contaminated by boron (B). *J. Clean. Prod.* **168**: 823–832. https://doi.org/10.1016/j.jclepro.2017.09.067

21. Wang, T., J. Fu, W. Zhang & D. Liu. 2024. Construction of defective hydroxyl-rich metal–organic framework for effective capture of borate ion. *Chem. Eng. J.* **483**(10): 149023. https://doi.org/10.1016/j.cej.2024.149023

22. Wang, X., H. Shao, Z. Chen et al. 2024. PEI grafted defective MOF-808 for enhanced boron removal. *Sep. Purif. Technol.* **336**: 126293. https://doi.org/10.1016/j.seppur.2024.126293

23. Wu, M.-C., Y.-H. Kao & C.-H. Hou. 2024. Evaluating boron removal from aqueous solutions using membrane capacitive deionization (MCDI): Efficacy and limitations. *J. Environ. Chem. Eng.* **12**: 113104. https://doi.org/10.1016/j.jece.2024.113104

Надійшла 29.09.2025

H.H. Quyen,
University of Da Nang, University of Science and Technology,
Da Nang 550000, Vietnam
e-mail: hhquyen@dut.udn.vn
H.M. Nguyen,
University of Da Nang, University of Science and Technology,
Da Nang 550000, Vietnam
e-mail: hnguye28@nd.edu
V.C.M. Tran,
University of Da Nang, University of Science and Technology,
Da Nang 550000, Vietnam
P.-C. Le,
University of Da Nang, University of Science and Technology,
Da Nang 550000, Vietnam
L. Nguyen-Dinh,
University of Da Nang, University of Science and Technology,
Da Nang 550000, Vietnam
L.T. Nguyen,
Institute of Science and Technology for Energy and Environment, Vietnam Academy of Science and Technology,
Hanoi 11300, Vietnam

TRANSFORMING MARINE WASTE INTO ADSORBENTS: BORON REMOVAL FROM WATER VIA CALCINED CRAB AND BLOOD COCKLE SHELLS

The excessive presence of boron in aquatic ecosystems poses potential risks to human health. Hence, this research aimed to investigate the efficiency of calcined crab shells and blood cockle shells (*Tegillarca granosa* (Linnaeus, 1758)) as adsorbents for boron removal from aqueous solutions. A batch experiment was employed to evaluate the performance of adsorbents under various conditions, such as calcination temperature, initial pH of the solution, initial concentration, contact time, adsorption temperature and ionic strength. Boron adsorption capacity is enhanced with higher calcination temperature, pH solution, adsorption temperature, and the presence of $CaCl_2$ and $MgCl_2$. In addition, the boron adsorption isotherms were described well by the Langmuir model, while adsorption kinetics followed the pseudo-second-order model. The maximum boron adsorption capacity of calcined crab shells and calcined blood cockle shells was 23.9 and 34.1 mg/L, respectively. The adsorption equilibrium state of both adsorbents was obtained after 9 h. Thermodynamic parameters (ΔS°, ΔG°, ΔH°) were investigated during the boron adsorption process. Calcined crab shells and calcined blood cockle shells also exhibit the high-efficiency removal of boron from wastewater of a local wet flue gas desulfurization system at 98.1 % and 99.6 %, respectively. This work highlights the cost-effective aspect of calcined crab shells and calcined blood cockle shells as effective adsorbents, stressing their potential for sustainable approaches in boron removal in wastewater treatment.

Keywords: *boron removal, crab shell, blood cockle shell, adsorption, wet flue gas desulfurization wastewater.*