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Removal of bismuth ion from aqueous solution by pulverized eggshells

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ABSTRACT

Due to the considerable calcium carbonate content, eggshell can serve as an effective, cheap, and efficient adsorbent in treating contaminated water. The removal of bismuth (Bi) ion by 0.45 µm pulverized chicken eggshells was investigated and the effects of various factors including contact time, initial pH, adsorbent dosage, initial Bi ion concentration, and temperature were studied. The optimal removal efficiency of Bi ions (50 mg/L) was 891.29 mg/g by treating with 6.25 g/L eggshells at pH 8 for 45 min at 40°C. Results obtained by scanning electron micrograph, energy dispersive spectrum and Fourier transform infrared spectroscopy analysis yielded the adsorption capacity based on the interaction of the alcohol hydroxyl group, methyl group and carbonyl functional groups present on the pulverized eggshell with Bi ion. The adsorption kinetics were better described by the pseudo-second-order kinetic model (R^2 = 0.9999) compared with the pseudo-first-order model (R^2 = 0.7633). The adsorption was endothermic. The equilibrium data fitted better with the Langmuir model than the Freundlich and Temkin isotherm models. Based on proposed mechanism, the adsorption of Bi ions onto the eggshell followed the electrostatic interaction and cation exchange principle. Moreover, the Bi ion removal efficiency decreased by the presence of coexisting ions (Mg^{2+} and Zn^{2+}), and the highest decrease of 326.58 and 379.22 mg/g was determined with the presence of 100 mg/L Mg^{2+} and 100 mg/L Zn^{2+}, respectively. Overall, the pulverized eggshell is a potentially low-cost adsorbent for treatment of Bi wastewater.

Keywords: Eggshell; Bismuth; Adsorption; Water pollution; Kinetics; Isotherm

1. Introduction

A large amount of excessive heavy metal waste and sewage are discharged into the water system with the rapid development of industry [1,2]. Water pollution by toxic metal is one of the major threats not only to human being but also to all aquatic creatures [3,4]. To date, many heavy metal pollutants including cadmium, chromium, lead, and zinc in industrial wastewater have been widely reported [5,6]. Nevertheless, bismuth (Bi), a widely used heavy metal in industry, is rarely concerned by researchers. In addition to the natural occurrence, Bi is mainly introduced from the chemical industry and pharmaceutical industry, which resulted in increased Bi levels in water and soil systems [7]. High levels of Bi and its compounds can cause hypotension, insanity, and renal failure [8]. Meanwhile, the concentration of Bi in seawater systems is 20 ng/L, which is two orders of magnitude lower than that of arsenic [9]. Although limited information is available for Bi concentration in sewage, some researches showed that the concentration of Bi had a fairly high value (5 mg/kg) in the industrial sewage sludge, which is even higher than the concentration of arsenic [9,10]. Therefore, wastewaters containing excessive Bi must be treated before being discharged into the natural water system.

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Currently, various methodologies have been developed for the removal of heavy metals from polluted waters such as adsorption, chemical precipitation, ion exchange, electrocoagulation, membrane filtration, phytoremediation, etc. [11–15]. However, most of these methods are low efficient and high cost in many cases. In contrast, adsorption has been proposed as an efficient, cost-effective, and flexible technology for heavy metal–contaminated water [16–18]. Moreover, the application of low-cost and easily available adsorbents has been concerned by researchers. In particular, biomaterials which are usually considered as waste such as hydrolyzed bamboo [19], sugarcane bagasse [20], mung bean waste [21], peanut shell [22], longleaf pine [23], and eggshell wastes [24] have been investigated as potential bioadsorbents for the removal of heavy metals from aqueous solution. The application of these biomaterials for removal of toxic metals from wastewater is a promising and inexpensive method, which has two potential advantages: (1) recovery of useful materials to remove heavy metals and (2) minimization of biomass waste, for instance, eggshell wastes.

In 2018, egg production was about 120 million tons around the world [25]. The weight of eggshell is approximately 11% of the total egg weight, and around 13 million tons of eggshell waste are produced per year [26,27]. Eggshell can be used as an additive of traditional Chinese medicine, fertilizer or animal feed, whereas most of the eggshell is sent to the landfill with a high management cost [28]. Eggshell is constituted of 94% calcium carbonate, 1% calcium phosphate, 1% magnesium carbonate, and 4% organic matter [24]. In recent years, many studies have been conducted for the assessment of utilization of eggshell as green and efficient adsorbent for removal of toxic metals from wastewaters [26,29]. For instance, Elabbas et al. [30] reported that eggshell was a very efficient adsorbent for chromium removal from tanning effluent and the removal rate reached a maximum value (100%) at 20 g/L eggshells. Furthermore, Zhang et al. [31] also found that chicken eggshells as alkaline sorbent can effectively remove multiple heavy metals (Cd^{2+}, Pb^{2+}, and Cu^{2+}) from acid mine drainage. Although numerous investigations have been performed to remove toxic metals using eggshells; to date, there is still no work reported the use of eggshell for the removal of Bi ions from wastewater.

In this study, we investigated the removal of Bi ion from contaminated water by pulverized eggshells. The objectives of this study were: (1) to evaluate the Bi ion removal efficiency of eggshell; (2) to explore the effects of solution pH, contact time, temperature, adsorbent dosage, initial Bi ion concentration, and coexisting ions on the adsorption performance; (3) to analyze the mechanisms of Bi ion adsorption by the pulverized eggshells.

2. Materials and methods

2.1. Preparation of stock solutions

Bismuth subnitrate [$4BiNO_5H_2{\cdot}BiO(OH)$] was used for the preparation of stock standard solutions of Bi ion (Cologne Chemicals Co. Ltd., Chengdu, China). The stock solution of Bi ion was prepared by adding 1 mL HNO_3 (65%) to 1.4 g bismuth subnitrate and then the mixture was diluted to 1,000 mg/L with deionized water. To adjust solution pH throughout the experiment, 0.1 M HCl and 0.1 M NaOH were used. Chemical reagents used in the present study except bismuth subnitrate were purchased from Shanghai Aladdin Biochemical Technology Company, China. Dithizone reagent (diphenyl thiocarbazone) was used for the determination of Bi ion. The dithizone reagent was prepared by dissolving 0.02 g of dithizone in 100 mL of ethanol [32,33].

2.2. Preparation of adsorbent

Approximately 150 g eggshells were used as the adsorbent. The eggshells were collected from daily kitchen waste and washed with deionized water for three times to remove the dirt. The excess water on the eggshells was adsorbed with filter paper (Qualitative filter paper, Liaoning, China) and the eggshells were dried at 40°C for 10 h. The eggshells were then pulverized and sieved to obtain a homogenous size (0.45 μm) [34].

2.3. Preparation of ions for coexistence

To study the effect of Mg^{2+} and Zn^{2+} on the removal capacity of Bi ion by the eggshells, solutions containing different concentrations of Mg^{2+} and Zn^{2+} (0, 20, 40, 60, 80, 100 mg/L) were prepared by dissolving $MgCl_2{\cdot}6H_2O$ and $ZnSO_4{\cdot}7H_2O$ into deionized water, respectively [35]. The initial concentration of Bi ion was 50 mg/L.

2.4. Batch experiments

Batch adsorption tests were conducted to determine the effect of adsorbent dosage, contact time, initial Bi ion concentration, pH, and operating temperature on the adsorption performance of the eggshells. To determine the effect of adsorbent dosage, 1.25, 2.50, 3.75, 5.00, and 6.25 g/L of eggshells were separately introduced into tubes filled with 40 mL of Bi solution. Samples were shaken for 5, 10, 15, 30, 45, 60, 75, 90, 120, and 180 min and then filtrated. The batch adsorption process was studied at different initial Bi ion concentrations (5, 10, 15, 20, 30, 40, and 50 mg/L) to study the impact of initial Bi ion contaminant level.

Solution pH was adjusted to 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0 to determine the effect of initial pH on adsorption of Bi ion (50 mg/L). Effects of various operating temperatures (20°C, 30°C, 40°C, and 50°C) were also investigated in the batch studies at Bi ion concentration of 50 mg/L. Temperature adjustments were conducted in the same orbital shaker (THZ-82, Changzhou Guohua Electric Appliance Company, China). Bismuth concentrations in the samples were analyzed with spectrometer at 398 nm (UV 1100, Shanghai Mapada Instruments Co., Ltd., Shanghai, China) [39]. The efficiency of adsorption (%) was calculated as follows [35]:

$$R = \left[\frac{\left(C_{\text{ini}} - C_{\text{fin}}\right)}{C_{\text{ini}}}\right] \times 100\% \quad (1)$$

where C_{ini} is the initial Bi ion concentration; C_{fin} is the final Bi ion concentration in solution; and R is the removal efficiency (%).

2.5. Adsorption isotherm and kinetic studies

Three isotherm equations have been employed in the present study, namely, Langmuir, Freundlich, and Temkin models, in order to describe the equilibrium characteristics of Bi ion adsorption on the eggshell [36,37].

The Langmuir equation can be written as follows:

$$q_e = \frac{abC_e}{1 + bC_e} \quad (2)$$

where q_e represents the adsorption capacity of the adsorbent at equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate (mg/L); a (mg/g) and b mean the maximum adsorption capacity and equilibrium adsorption constant [38].

Freundlich isotherm model can be written as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

where q_e represents the adsorption capacity of the adsorbent at equilibrium (mg/g); C_e is the equilibrium concentration of the sorbate remaining in the solution (mg/L); and $1/n$ is the heterogeneity factor of the adsorbent, which indicates the relative distribution of energy sites. $1/n$ ranges between 0 and 1 indicating more heterogeneity as it gets closer to zero, while $1/n > 1$ indicates chemisorption, reflecting the high affinity between the sorbate and the biosorbent. The K_f is the Freundlich empirical constant concerned with the adsorption ability of biosorbent [39].

The Temkin isotherm is generally given by:

$$q_e = B_T \ln A_T + B_t \ln C_e \quad (4)$$

where B_T is Temkin constant related to the heat of adsorption (J/mol); A_T is the Temkin isotherm binding constant (L/mg); q_e represents the adsorption capacity of the adsorbent at equilibrium (mg/g); C_e is the equilibrium concentration (mg/L); and T is the temperature in Kelvin [40].

Two kinetic equations have been employed in the present study, namely, pseudo-first-order and pseudo-second-order models. The linear form of the models was expressed by Eqs. (5) and (6):

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_e (mg g^{-1}) is the theoretical adsorption capacity at predominate time; q_t (mg g^{-1}) is the adsorption capacity at different times (t). k_1 (min^{-1}) is the rate constant for first-order model and k_2 (g mg^{-1} min^{-1}) is rate constant for second-order model [41,42].

2.6. Thermodynamic functions

The thermodynamic study was undertaken for the determination of the parameters that include change in Gibbs free energy (ΔG), entropy change (ΔS), and enthalpy change (ΔH). These parameters were calculated using the following equations:

$$\Delta G = -RT\ln K_c \quad (7)$$

$$K_c = \frac{Q_e}{C_t} \quad (8)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

where K_c is the equilibrium partition constant; Q_e is the adsorption capacity; C_t is the concentration at time t; R is the gas constant (R = 8.314 J/mol K); and T is the temperature in Kelvin (K) [43].

2.7. Characterization of biosorbent

The surface of the studied eggshell before and after biosorption process was analyzed and photographed by a scanning electron microscope (JEOL-JSM-5300, California, USA) coupled with an energy dispersive X-ray spectroscopy (EDS). The studied eggshell was mounted on copper stubs with double sided adhesive tape and then analyzed for relative metal contents by the EDS. Samples were then coated with 30 nm layer of gold using Polaron E 5000 Sputter Coater (JSM-7500F JOEL, Japan), examined, and photographed at 100×; 500×; 1,000×; and 5,000× scanning electron micrography (SEM). Fourier transform infrared (FTIR) spectroscopy (Thermtest company, Canada) was carried out to investigate adsorbent before and after the adsorption to test if any changes had taken place on metal binding sites on the biomaterial. FTIR spectroscopy gives information on what functional groups are present in the biosorbent. The spectra were collected using PerkinElmer spectrum BX FTIR system equipped with diffuse reflectance accessory within the range of 500–4,000 cm^{-1}.

2.8. Statistical analysis

The experimental tests were conducted in triplicate with standard deviation. Analysis of variance (ANOVA) was used for the statistical analysis.

3. Results and discussions

3.1. Effect of contact time and kinetic model studies

The adsorption of Bi ions by the eggshells increased with contact time and reached equilibrium with a considerable removal efficiency of 741.98 mg/g at 45 min (Fig. 1). The Bi ion removal efficiency by the eggshells remained unchanged after 45 min. Faridi and Arabhosseini [44] also reported that with an increase in the adsorbate dose, rate of adsorption increased up to a certain level, and then it became constant. The higher adsorption rates at the initial periods of reaction were due to the larger surface area of the adsorbent, and as time proceeds, the surface adsorption sites became exhausted, leading to a decrease of adsorption rate [45,46].

Kinetic models showed the rate limiting on the adsorbent surface followed by chemisorption, physisorption,

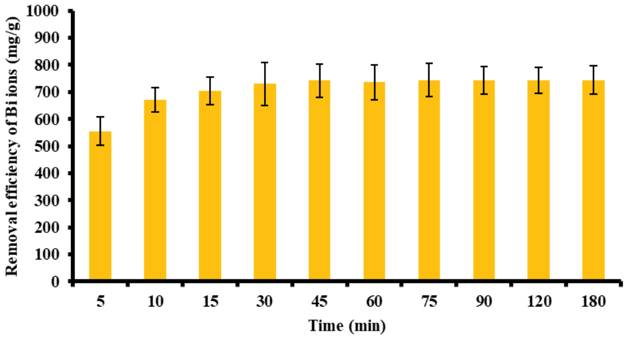


Fig. 1. Effect of contact time on the removal efficiency of Bi ion by the eggshell. Agitation speed, 150 rpm; initial Bi concentration, 30 mg/L; dose of eggshell, 5.00 g/L; and pH, 6.

or physicochemical sorption [47]. Compared with calculated q_e values (121.32 mg/g) by pseudo-first-order kinetic model, the calculated q_e values (149.25 mg/g) by the pseudo-second-order kinetic model were closer to the experimental values of q_e (149 mg/g). Meanwhile, the pseudo-second-order kinetic model had higher correlation coefficient ($R^2 = 0.9999$) than the pseudo-first-order kinetic model ($R^2 = 0.7633$). The rate constant for the pseudo-first-order model (k_1) and the pseudo-second-order model (k_2) was 0.027 and 0.0068, respectively. These results indicate that Bi ions adsorption by the pulverized eggshells can be more favorably described by the pseudo-second-order kinetic model than the pseudo-first-order kinetic model and that the adsorption process was mainly regulated by chemisorption process [48]. This may be due to that the exchange of electrons between the functional group on the eggshells and Bi ion [41,48].

Table 1 compares the results of the present study with some of the results in previous literatures. The eggshell has a strong adsorption capacity for various metals ions. The adsorption capacity of eggshell to Bi ion was higher than that of other adsorbents including coconut shell activated carbon, bayberry tannin, and polyurethane foam. This result implies that the pulverized eggshell could be used effectively for treatment of wastewater containing Bi ion.

3.2. Effect of pH on adsorption

The solution pH is one of the most important factors influencing the adsorption processes, not only due to its influence on the dissociation of active functional groups on the surface of adsorbent but also because it can alter the speciation and availability of heavy metals in solution [52,53]. The removal rate of Bi ion by the eggshells was pH dependent (Fig. 2a and b). The maximum adsorption was obtained at pH 8 with the removal efficiency of 834.24 mg/g. This can be attributed to the fact that Bi ions could precipitate by forming Bi hydroxides with hydroxide anions in alkaline solution. Nevertheless, Asgari and Dayari [54] tested the effect of pH on cyanide adsorption using acid-treated eggshells and found maximum removal at solution pH of 9–11. The reason is possible due to the difference of surface activity between the pulverized eggshells and the acid-treated eggshells. At pH ≤ 6.0, H^+ compete with Bi ion for the surface of the adsorbent, which would hinder metal

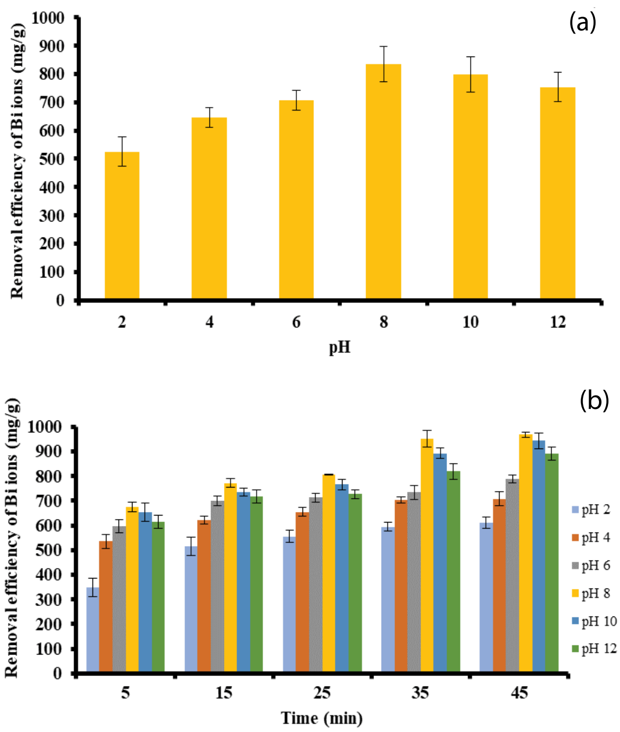


Fig. 2. Effect of pH on the removal efficiency of Bi ion by the eggshell. (a) removal efficiency of Bi ion at different pH at 45 min and (b) removal efficiency of Bi ion through 45 min. Initial Bi ion concentration, 30 mg/L; dose of eggshell, 5.00 g/L; and agitation speed, 150 rpm.

Table 1
Comparison of the present study with some of the results in previous literatures

Metal ion	Adsorbent	q_e (mg/g)	Reference
Bismuth	Eggshell	149.00	The present study
Nickel	Eggshell	109.00	[24]
Chromium	Eggshell	200.25	[30]
Bismuth	Coconut shell activated carbon	54.35	[49]
Bismuth	Bayberry tannin	83.81	[50]
Bismuth	Polyurethane foam	12.54	[51]

ions from reaching the binding sites of the sorbate caused by the repulsive forces.

3.3. Effect of eggshell dose

Adsorbent dosage is one of the most important parameters studied when conducting batch adsorption study [55]. In this study, Bi ion removal rates increased as adsorbent dose increased gradually from 1.25 to 6.25 g/L (Fig. 3a and b). The removal efficiency was associated with the adsorbent dose due to the availability of more adsorbing sites at higher doses [56]. Such a trend is mostly attributed to the increase of the sorptive surface area and the availability of more active adsorption sites.

3.4. Effect of initial Bi ion concentration on removal rate

The adsorption of heavy metals by adsorbent depends strongly on the initial concentration of the heavy metals [3]. The removal rate of Bi ion decreased from 920.72 to 628.47 mg/g with increasing initial Bi ion concentrations from 5 to 50 mg/L with 6.25 g/L eggshell (Fig. 4a and b), suggesting that the amount of these contaminants adsorbed per unit mass of adsorbent decreased with the increase in initial Bi ion concentration. This represents the saturation of the active sites available on the eggshell samples for interaction with contaminants, indicating that less favorable sites became involved in the process with increasing initial Bi ion concentration [57]. This is consistent with the conclusion of Soares et al. [58] that removal rate of Pb ion by the eggshell biosorbent decreased with increase in initial Pb ion concentration.

3.5. Effect of temperature on Bi ion adsorption and thermodynamic studies

It is well established that temperature is an additional factor that greatly influences any adsorption process [59]. The raise of temperature between 40°C and 50°C resulted in an increase of the removal efficiency of Bi ions (Fig. 5a and b). The removal efficiency was 891.29 mg/g at 40°C. The thickness of the boundary layer tends to decrease due to the increasing tendency of the molecules to escape from the adsorbent surface to the solution phase [35], which results in a decrease of the adsorption capacity. According to Park et al. [59], the adsorption was the existence functional groups which are alkynes or alkenes bonds after adsorption on the eggshell surface due to the additional reactions formed by the process of thermal cracking.

The thermodynamic parameters of the adsorption of Bi ions on the surface of the eggshells were studied at different temperatures (Fig. 5; Table 2). The adsorption process of Bi ions on the surface of the eggshells was a spontaneous and favorable process at 40°C or 50°C due to that ΔG values

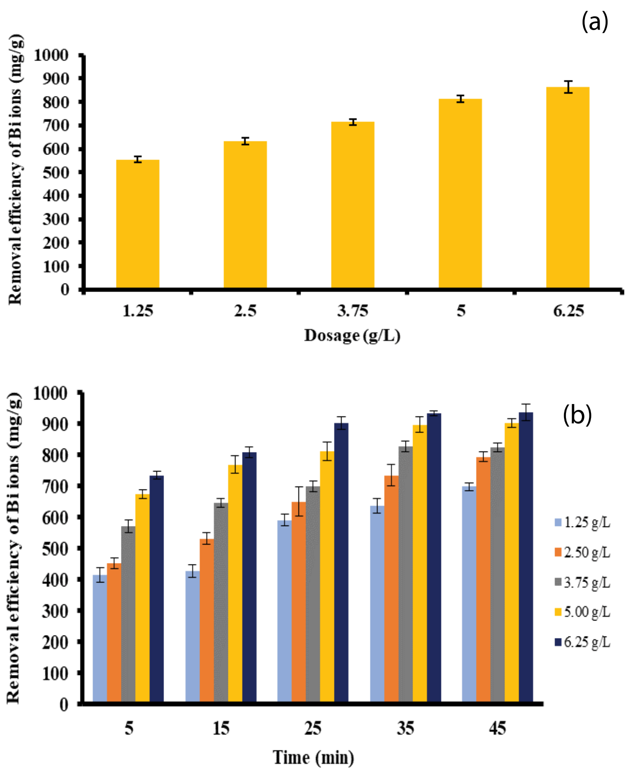


Fig. 3. Effect of the eggshell dosage on the removal efficiency of Bi ion. (a) removal efficiency of Bi ion with different dosage at 45 min and (b) removal efficiency of Bi ion through 45 min. Initial Bi ion concentration, 30 mg/L; pH, 8; agitation speed, 150 rpm; and temperature, 20°C.

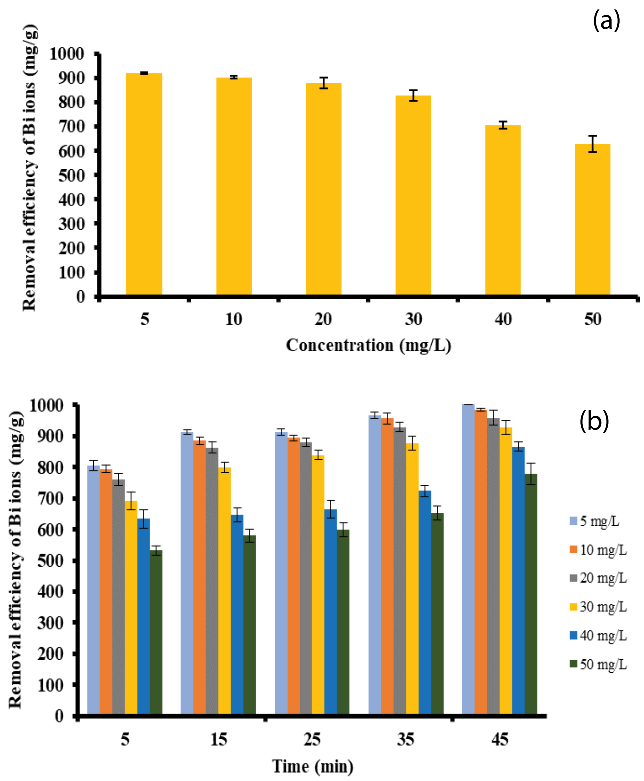


Fig. 4. Effect of initial Bi ion concentration on the removal efficiency. (a) removal efficiency of Bi ion with different concentration at 45 min and (b) removal efficiency of Bi ion through 45 min. Adsorbent dose, 6.25 g/L; pH, 8; agitation speed, 150 rpm; and temperature, 20°C.

were negative. Meanwhile, the positive values of ΔH confirmed that chemical adsorption played an important role in the adsorption of Bi ion by the eggshells. Higher temperature offered the energy for the adsorption, which promoted the complexation of Bi ions and the functional groups on the pulverized eggshells [24]. At 50°C, polymerization among the carboxyl groups or phenolic hydroxyl on pulverized eggshells might occur, thus reducing the number of adsorption sites [24]. The positive value of ΔS might be attributed to an increased randomness at the solid–solution interface during the fixation of Bi ions on the active sites of the pulverized eggshells [43]. Similar results were also observed by Yari et al. [60], studying the adsorption of cadmium and lead on organic adsorbents modified with citric acid and Fe_3O_4.

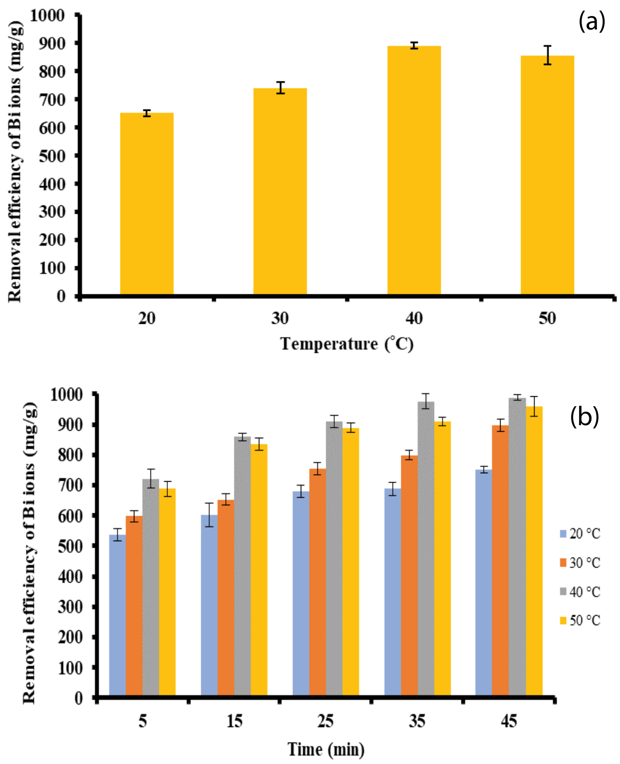


Fig. 5. Effect of temperature on the removal efficiency of Bi ions by eggshell. (a) removal efficiency of Bi ions at 45 min and (b) removal efficiency of Bi ions through 45 min. Adsorbent dose, 6.25 g/L; pH, 8; initial Bi ion concentration, 50 mg/L; and agitation speed, 150 rpm.

3.6. Isotherm study

The isotherm studies are important to describe how the adsorbate interacts with the adsorbent, and Langmuir, Freundlich and Temkin models have been used (Table 3) [61–63]. The adsorption process of Bi ion by the eggshell was better described by Langmuir model compared with Freundlich and Temkin models, indicating homogeneous and monolayer coverage of Bi ions at the surface of the pulverized eggshells [16]. The Freundlich constant n between 1 and 10 tends to imply a favorable adsorption ability [18], and thus the value of 2.439 in the present study manifested a beneficial adsorption of Bi ion by the eggshells.

3.7. Effect of coexisting ions

Actually, the naturally contaminated water contains a range of inorganic and organic materials, and these materials may impact the removal rate of Bi ion by any adsorbent. The removal efficiency of eggshells was prohibited by the co-existing Mg^{2+} and Zn^{2+} ions. Under the conditions of this study (the initial Bi ion concentration 50 mg/L), the removal efficiency decreased with higher Mg^{2+} concentrations (20, 40, 60, 80, and 100 mg/L), and the removal efficiency was 826.29; 686.72; 619.13; 517.70; and 499.71 mg/g, respectively. With co-existence of Zn^{2+} ions, the Bi ion removal efficiency was 765.52, 754.23, 558.31, 411.91, and 386.3 mg/g, respectively. The adsorption of Bi ion was not only dependent on the surface area and porosity of the adsorbent but essentially dependent on surface

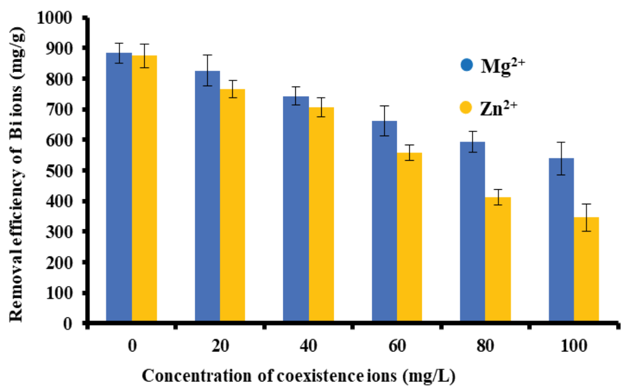


Fig. 6. Effect of co-existing ions (Mg^{2+} and Zn^{2+}) on Bi ion removal efficiency. Initial Bi ion concentration, 50 mg/L; pH, 8; contact time, 45 min; temperature, 40°C; and adsorbent dose, 6.25 g/L).

Table 2
Thermodynamics parameters for adsorption of Bi ions by eggshell

Temperature (°C)	C_t (mg/L)	Q_e (mg/g)	lnK_c	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
20	9.981	3.203	–1.1	2.7687	43.85	0.14
30	6.887	3.938	–0.3	0.7892		
40	5.440	4.456	0.7	–1.9043		
50	5.497	4.312	0.3	–0.9348		

K_c is the equilibrium partition constant; Q_e is the adsorption capacity; and C_t is the concentration at the time t. ΔG represents Gibbs free energy; ΔS represents entropy change. ΔH represents enthalpy change.

Table 3
Langmuir, Freundlich and Temkin for Bi ion adsorbed onto eggshells. Contact time, 45 min; initial concentration, 50 mg/L; dose, 6.25 g/L; pH, 8; and temperature, 313 K

Models	Langmuir model			Freundlich model				Temkin model		
Parameters	*a* (mg/g)	*b* (mg/L)	R^2	R_L	K_f	*n*	R^2	B_T	A_T	R^2
Values	5.5991	0.2723	0.9529	0.0684	1.4226	2.439	0.9508	0.8985	7.0272	0.8483

charged properties. Since the surface of the adsorbent carried a large quantity of positive and negative charges, they could attract Mg^{2+} and Zn^{2+}, which decreased the removal efficiency for Bi ion. Ahmad et al. [64] also reported that sulfate sorption from $ZnSO_4·7H_2O$ solution onto the eggshell powder decreased with the increase of co-existence of chloride ions from $MgCl_2·6H_2O$ solution.

3.8. SEM, EDS, and FTIR analysis of the eggshells

The eggshells have a highly porous structure revealing the substantial ability of adsorption due to large surface area. In addition, the presence of more negatively charged binding sites on the eggshell made it a potential adsorbent for the removal of Bi ion from aqueous solution. After adsorption, the surface appeared to be crammed with tiny granules in the cavities, indicating the ability to adsorb the Bi ions from the solution (Fig. 7). These SEM images revealed the combination of small and large particles size, heterogeneous rough and porous surfaces similar to the bronchioles structure.

EDS spectra for eggshell before and after Bi ion adsorption are shown in Fig. 8. Before adsorption, the spectrum exhibits peaks for C, N, O, and Ca (Fig. 8a). After reaction

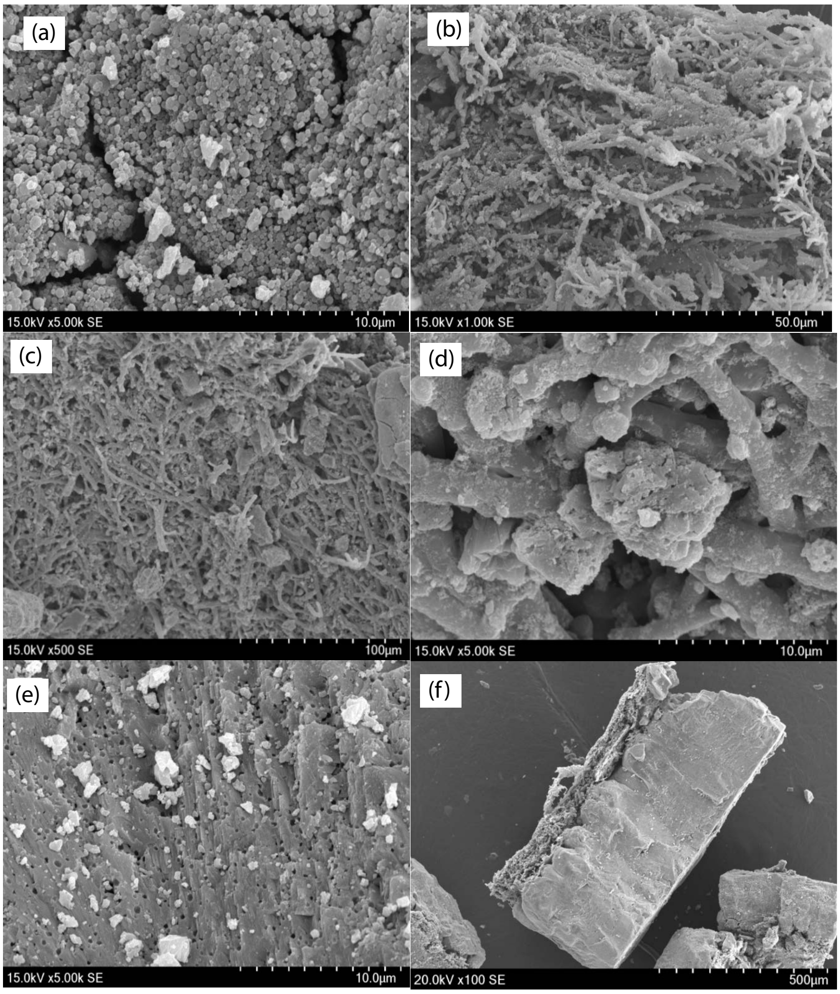
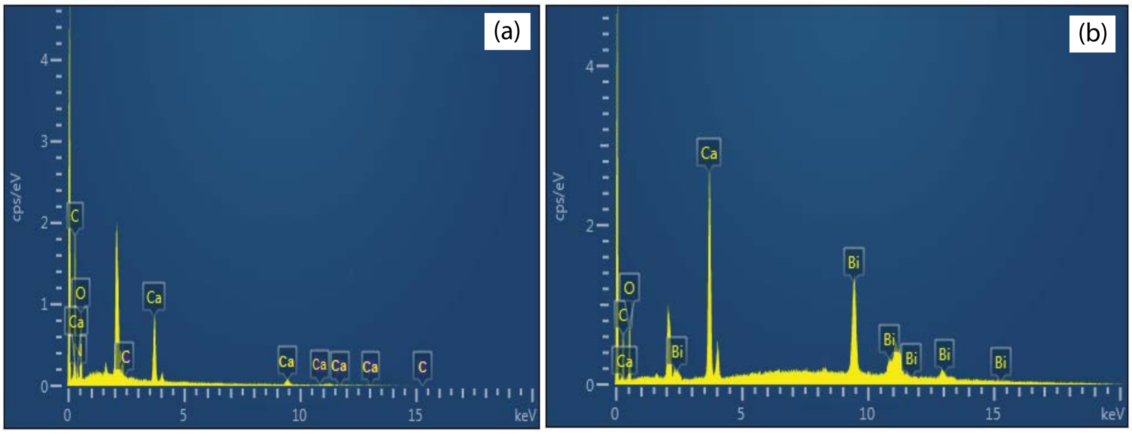


Fig. 7. SEM images (a and b) of the original eggshells, and (c–f) of the eggshells after adsorption (initial Bi ion concentration, 50 mg/L; pH, 8; contact time, 45 min; temperature, 40°C; and adsorbent dose, 6.25 g/L).



Element	Before adsorption		After adsorption	
	Weight %	Atom %	Weight %	Atom %
C	27.71	28.38	25.26	24.87
N	12.11	11.83	10.67	09.82
O	28.07	28.00	24.94	29.64
Ca	32.11	31.79	29.87	26.69
Bi	0.00	0.00	9.26	8.98
Total	100.00	100.00	100.00	100.00

Fig. 8. EDS spectra and elemental analysis of the eggshells. (a) Before and (b) after adsorption (initial Bi ion concentration, 50 mg/L; pH, 8; contact time, 45 min; temperature, 40°C; and adsorbent dose, 6.25 g/L).

with Bi ions containing solution, new peaks appeared in the spectrum, which were attributed to Bi ions (9.26%). The appearance of strong Bi peaks in the spectrum is accompanied by the decrease in the intensity of C, N, O, and Ca peaks, and the O peaks exhibited the most decrease (Fig. 8b). This phenomenon suggests the substitution of C, N, O, and Ca by Bi in the eggshell grains.

In general, from the SEM and EDS results, a real interaction between the eggshells and Bi ion can be seen. Basically, the sorption of metals onto sorbent material is attributable to the active groups and bonds present on the material. FTIR can provide the molecular and structural information about adsorbent materials [65,66]. The FTIR spectrum (Fig. 9) of the eggshell powder was recorded to obtain the information regarding the stretching and bending vibrations of these functional groups shift from 3,435 to 3,403 cm^{-1}. These peak stretching vibrations indicate the mixed stretching vibration bands of –OH group in hydrogen bonding and chemisorbed water. The characteristic peak was found between the surfaces of the eggshell but adsorption at 2,140.32 cm^{-1} refers to the –C≡C bond. This bond means the occurrence of alkyne or alkene bonds by the undergoing reactions formed by the process of thermal cracking, and this result agrees with Shafiq et al. [67] who studied the removal of several heavy metals by date palm biosorbent. Generally, for the eggshell after adsorption, the peaks at 3,435; 2,978; 2,876; 2,518; 1,418; 774; 515; and 425 cm^{-1} shifted to 3,403; 2,936 2,831; 2,515; 1,409; 791; 588; and 468 cm^{-1}, respectively, indicating that carboxyl, phenolic hydroxyl, aromatic ring, amino and aliphatic hydrocarbons were involved in the adsorption process.

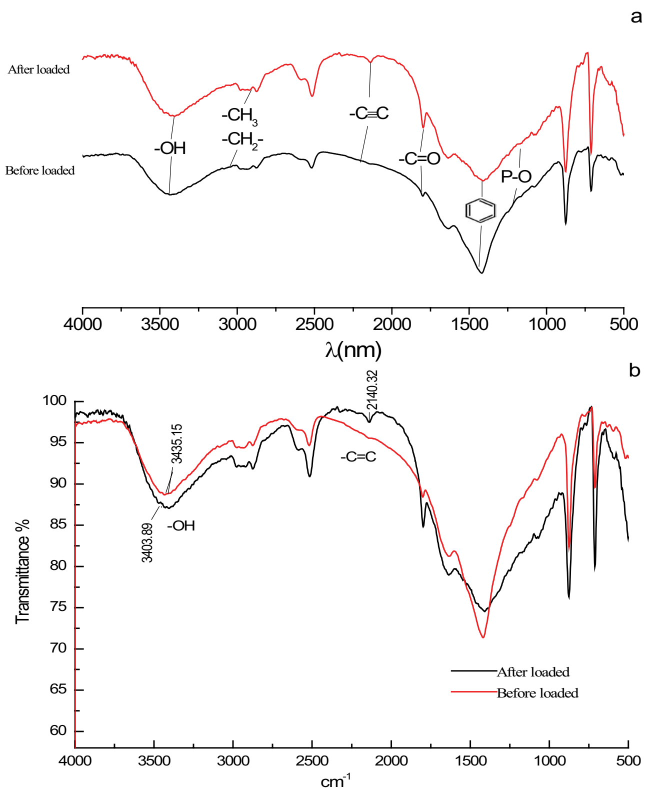


Fig. 9. FTIR spectra of the eggshells: (a) functional groups in eggshell and (b) interactions between functional groups before and after adsorption.

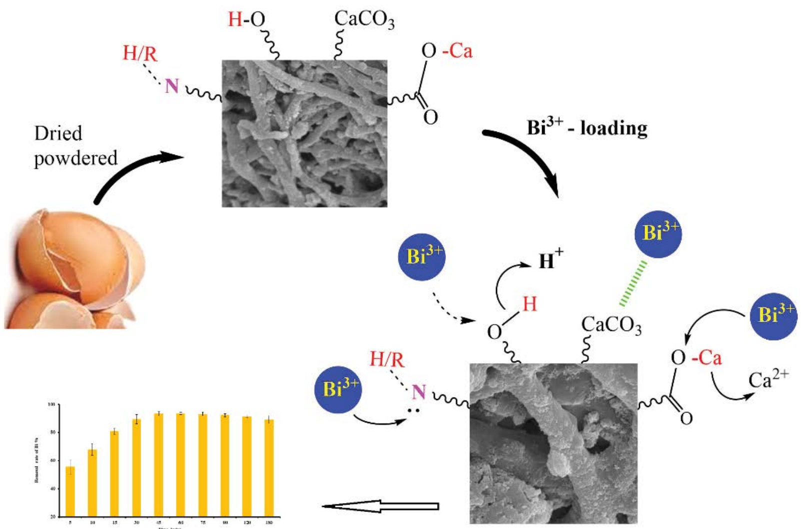


Fig. 10. Adsorption mechanism of Bi ion by the eggshells.

3.9. Adsorption mechanism

Based on the EDS analysis, the eggshell powder possessed elements of N, O, C, and Ca that proposed functional groups as shown in Fig. 10. The proposed mechanism of Bi ion uptake onto the eggshell might follow the three possible interactions: (1) the interaction or coordination of Bi ion with N, (2) exchange of Bi ion with H from O–H and (3) functional groups of the C≡C bond in the adsorption process. Hence, the high removal efficiency of Bi ion by the eggshell is probably due to the combination of above interactions.

4. Conclusion

The efficiency of the eggshell pulverized as an adsorbent for removal of Bi ion from contaminated water was determined using the batch technique. The eggshell is effective for the removal of Bi ion from aqueous solution, and the maximum removal efficiency of the eggshell was determined in the treatment of 50 mg/L of Bi ion with 6.25 g/L of eggshell at pH 8 at 40°C for 45 min. The removal efficiency was strongly dependent on the contact time, initial pH of the solution, adsorbent dosage, and initial Bi ion concentration. A high specific surface area of the eggshells was observed by SEM and EDS, which resulted in the considerable adsorption. The FTIR analysis revealed the main functional group of the C≡C bond involved in the adsorption process of Bi ion by the eggshell. The coexistence of Mg^{2+} and Zn^{2+} ions in the present solution leads to a notable decrease of the adsorption of Bi ion. The adsorption of Bi ion on the eggshell was better defined by Langmuir model. The interaction was endothermic according to the thermodynamic study. Overall, the pulverized eggshell can represent an excellent low-cost adsorbent for the treatment of Bi wastewater.

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