The effect of Ca-bearing contents in chitosan on Pb^{2+} , Cd^{2+} and Cu^{2+} adsorption and its adsorption mechanism

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Abstract

The preparation of chitosan has been investigated for more than half century; however, the application of chitosan for heavy metal (HM) adsorption is still under research. This study investigated the effects of chitosan with chemically controlled Ca-bearing contents (CBC) on Pb^{2+} , Cd^{2+} and Cu^{2+} adsorption in the solution with the initial pH values of 2.10, 4.14 and 6.13. Highly purified chitosan showed the optimum HM adsorption at the initial pH values of 4.14 and 6.13, and the adsorption mechanism was chemisorption involving valence forces through sharing or exchange of electrons between the chitosan and HM ions. Highly purified chitosan prepared from HCl treated chitin only showed effective for Pb^{2+} , however, those prepared from CH_3COOH treated chitin showed effective for Pb^{2+} , Cd^{2+} and Cu^{2+} adsorption due to a little amount of CBC. The HM adsorption mechanisms of partly purified chitosan were precipitation due to CBC and biosorption. Chitosan with 73% CBC showed the optimum adsorption of Pb^{2+} (755 mg/g) at an initial pH value of 2.10 while Cd^{2+} (979 mg/g) and Cu^{2+} (877 mg/g) at the initial pH values of 4.14 and 6.13. High $\text{Ca}(\text{OH})_2$ -bearing chitosan prepared from HCl and H_2SO_4 treated chitin showed the optimum Cd^{2+} (978 mg/g) and Cu^{2+} (852 mg/g) adsorption at an initial pH value of 2.10. Biosorption isotherm and kinetics models showed that the adsorption data of Pb^{2+} , Cd^{2+} and Cu^{2+} onto the surface of chitosan was well-fitted by Langmuir model and Pseudo-second-order model with correlation coefficient ($R^2 > 0.95$ and $R^2 > 0.91$, respectively). Pseudo-second-order model showed that the adsorption capacity strongly depended on CBC in chitosan and initial pH value of HM solution. It is concluded that the HM adsorption by the prepared chitosan is a chemical process that was supported by CBC of chitosan through elevating solution pH value.

Keywords Chitosan · Heavy metal · Adsorption · Biosorption · Precipitation · Crab

Introduction

Heavy metal (HM) contamination has become a serious environmental concern due to its toxicity, persistency and accumulation. A number of physical, chemical and physico-

chemical processes were developed over the years to remove toxic HM ions from wastewater [5, 17, 45]. Adsorption is the most popular method for the contaminated wastewater treatment and various inexpensive and high metal-binding capacity materials are used for HM adsorption [5, 28, 59]. Biosorption has gained more attention for the treatment of industrial wastewater [21, 51]. Use of crab shell wastes has emerged as a novel biosorbent for HM treatment due to their potentials for the preparation of chitin and chitosan [23, 42, 53, 56].

Raw crab shells [3, 23, 29], crab shell powders and washed or pre-treated crab shells [13, 51, 55], chitin only removing proteins but keeping minerals [45], chitin only removing minerals but keeping proteins [13, 16] and crude chitin removing both proteins and minerals [23, 44] were used to understand the roles of proteins, chitin and minerals in HM ions adsorption. The HM ions adsorption ability of crab shells derived different biosorbents followed the order: chitosan>calcareous chitin>chitin>Crab shell powder>Raw crab shell [43, 45].

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Chitin ($C_{18}H_{26}N_2O_{10}$) is a straight-chain polymer composed of β -1,4-N-acetylglucosamine and classified into α -, β - and γ -chitin based on the source of extraction [14, 30]. Chitosan is a hydrophilic, natural cationic polymer derived by partial N-deacetylation of chitin, is also a straight-chain polymer of glucosamine and N-acetylglucosamine [30, 47]. The biosorption of HM ions on the chitosan was based on several mechanisms such as ion-exchange, complexing physical adsorption by Van der Waals, and inter and/or intracapillary trapping [11]. The HM adsorption ability of chitosan was determined by the chemical nature of the chitosan: (i) hydrophilicity related to large number of hydroxyl groups, (ii) the presence of amine group, and (iii) flexible structure of the polymer chains that enable configuration [21, 38, 61].

The adsorption of HM ions also depended on the pH value and ion type of the solution [2, 32, 40]. The HM solution pH value affected both the dissociation degree of the functional groups from the chitosan surface and the solubility of HM ions. An initial pH range of 5.0–8.0 was usually suitable for the HM adsorption [10]. HM ions existed as free ions with an initial pH range of 4.0–5.0 and were adsorbed onto chitosan at higher pH value due to the decrease of H^+ concentrations. At lower pH value, H^+ concentration was high, so the protonation of amino group induced an electrostatic repulsion of HM ions [9, 26]. With the increase of pH value, there was a net negative charge on the surface of chitosan and the ionic point of ligands such as $-COOH$, $-OH$ and $-NH_2$ groups were free and thus promoted the interaction with the HM ions [8, 36]. Chitosan carried strong cationic charges at a pH value of lower than 6.5 and strong anionic charges when the pH value was higher than 6.5 [10, 33]. The efficiency of HM ions binding with chitosan followed this order: $Hg^{2+} > Cu^{2+} > Fe^{3+} > Ni^{2+} > Ag^+ > Cd^{2+} > Mn^{2+} > Pb^{2+} > Co^{2+} > Cr^{3+}$ [6, 34].

Literature reviews showed that previous studies investigated different influential factors on HM ion removal efficiency and adsorption capacity of raw crab shells, chitin and chitosan, such as initial concentration of HM ions, initial solution pH value, adsorbent dosage, reaction time, temperature, adsorbent size and agitation speed [7, 10, 29, 43, 44]. Most of them focused on the equilibrium and kinetic studies of HM ion adsorption on biosorbents [9, 18, 21]. There are several adsorption isotherm models (e.g., Langmuir, Freundlich, BET, Temkin and Dubinin–Radushkevich) and kinetic models (e.g., Pseudo-first-order, Pseudo-second-order, Intra-particle diffusion and Elovich) [4, 9, 50, 58] which have been widely applied to describe the adsorption of several HM ions onto chitosan or its derivatives [20, 57]. However, very few studies focused on the influence of chemical properties of the prepared chitosan such as Ca-bearing contents (CBC), proteins and chitin on HM ion removal efficiency and adsorption capacity (Anastopoulos et al., 2017; [26, 39, 45]). The CBC in

crab shell has neutralization ability in acid solution. Therefore, chitosan with high CBC has potential HM removal ability from acidic solution. However, there is no sufficient data to show the influence of CBC on HM ions adsorption of chitosan.

This study prepared different purities chitosan with varied CBC using HCl, H_2SO_4 and CH_3COOH , and investigated their Pb^{2+} , Cd^{2+} and Cu^{2+} adsorption in the solution with the initial pH values of 2.10, 4.14 and 6.13.

Methodology

Materials

Frozen sea crabs were purchased from Shanghai XueGuai Network Technology Co. Ltd., China. Meat from crab shell, head, jaw, leg and tail were separated manually. The collected sea crab waste (SCW) were washed through by tap water, followed by distilled water and vacuum dried at 60 °C for 24 h. Then dried SCW were grounded to make powder of 0.6 mm to 76 μm sizes by sieving.

The sodium hydroxide ($NaOH \geq 96\%$) used for deproteinization, hydrochloric acid (HCl , 36%–38%) and sulfuric acid (H_2SO_4 , 95%–98%) used for demineralization, and copper(II) sulfate ($CuSO_4$, $\geq 98.5\%$) used for the preparation of HM solution, were supplied by Shanghai Titan Scientific Co. Ltd., China. An acetic acid (CH_3COOH , 99.5%) from Shanghai Lingfeng Chemical Co. Ltd., China was also used for demineralization. A lead chloride ($PbCl_2$, 99%) was supplied by Nine-Dinn Chemistry (Shanghai) Co. Ltd., China and cadmium chloride hemi(pentahydrate) ($CdCl_2 \cdot 2.5H_2O$, 98%) was supplied by Shanghai Macklin Biochemical Co. Ltd., China were used for the preparation of HM solution. All the chemicals used in this research were AR grade.

Preparation of chitin and chitosan

The orthogonal experimental design was applied for the selection of crude chitin preparation from SCW powders. The adopted orthogonal experimental design was $L_8(2^7)$ and the different experimental parameters are shown in Table 1 (Appendix A). All the used crude chitin for preparation of chitosan was repeated twice to check for error in chitin preparation.

In the deprotenization process, 3.0 g SCW powder were put into 250 ml beaker soaked in a water-bath and then NaOH solution was added with L/S (v/w) ratio of 20. The mixture was filtered and washed until the pH value of the filtration reached to 6.0–7.0 and then the solid residues was vacuum dried at 60 °C for 8 h. The vacuum dried solids were subjected to demineralization process operated in a 250 ml beaker

Table 1 Preparation parameters, and degree of DP, DM and CY of selected crude chitin

Sample	Type of acid	Combination of preparation parameters		DP (%)	DM (%)	CY (%)
		Deproteinization*	Demineralization*			
Ch-HA-7	HCl	1.0 + 60 + 2	1.0 + 60 + 4	93.49	92.04	21.07
Ch-HA-3		0.1 + 60 + 12	0.1 + 60 + 24	25.51	22.37	71.23
Ch-AA-7	CH ₃ COOH	1.0 + 60 + 2	1.0 + 60 + 4	86.65	85.00	25.99
Ch-AA-1		0.1 + 25 + 2	0.1 + 25 + 4	29.75	26.79	74.49
Ch-SA-1	H ₂ SO ₄	0.1 + 25 + 2	0.05 + 25 + 4	34.64	33.89	72.91
Ch-SA-2		0.1 + 25 + 2	0.5 + 60 + 24	6.66	17.51	98.04

*The sequence of parameters in combination: NaOH/acid conc. (M) + Temp. (°C) + Reaction time (h)

soaked in a water-bath and subsequently HCl/H₂SO₄/CH₃COOH was added with L/S ratio of 20. The mixture was filtered and washed until the pH value of the filtration reached to 6.0–7.0 and then the solid residues (crude chitin) was vacuum dried at 60 °C for 8 h.

The extracted crude chitin was put into beaker and then 50% NaOH solution was added at a ratio (v/w) of 15. Then the beaker was kept to react at 110 °C for 12 h. After reaction, the mixture was filtered and washed until the pH value of the filtration reached to 6.0–7.0. Finally, the solid residues (chitosan) was vacuum dried at 60 °C for 8 h and then ground it to make powder.

Determination of deproteinization and demineralization degrees of chitin

The total proteins and minerals weight loss of the crude chitin was determined through Thermogravimetric (TG) analysis by a TG-DSC instrument (NETZSCH STA 449F3, Germany), which was heated from room temperature (RT) to 1200 °C at a rate of 10 °C/min under nitrogen gas (N₂) flow. The degree of deproteinization (DP) was calculated by the Eq. 1:

$$DP(\%) = \frac{W_s \times G_1 - W_c \times G_2}{W_s \times G_1} \times 100 \quad (1)$$

Here, W_s = Original sample weight, W_c = Crude chitin weight, G₁ = Weight of the ash remained after TG test of the raw material from RT to 591 °C, and G₂ = Weight of the ash remained after TG test of the extracted chitin from RT to 591 °C.

The degree of demineralization (DM) was calculated by the Eq. 2:

$$DM(\%) = \frac{W_s \times G_1 - W_c \times G_2}{W_s \times G_1} \times 100 \quad (2)$$

Here, G₁ = Weight of the ash remained after TG test of the raw material from RT to 1200 °C, and G₂ = Weight of the ash remained after TG test of the extracted chitin from RT to 1200 °C.

And the chitin yield (CY) was measured by the Eq. 3:

$$CY(\%) = \frac{\text{Chitin weight in the acid treated solid residue}}{\text{Original sample weight}} \times 100 \quad (3)$$

Adsorption experiments

To investigate HM adsorption capacity of the prepared chitosan, PbCl₂, CdCl₂·2.5H₂O and CuSO₄ reagents were used to prepare a 76 mg/L, 98 mg/L and 88 mg/L, respectively of HM solution with three initial pH value of each solution included 2.10, 4.14 and 6.13. The target pH values of the HM solution were adjusted by adding 1.0 M NaOH/HCl solution. Then 0.1 g chitosan was put into 250 ml beaker and subsequently 100 ml of the prepared Pb²⁺ solution was added. The mixture was kept to stir at 220 rpm speed for 60 min at 25 °C in water-bath. Then it was filtered to separate the Pb²⁺ adsorbed chitosan and the filtration was stored for Pb²⁺ analysis by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES). The same procedures were followed for the determination of Cd²⁺ and Cu²⁺ adsorption capacity by the prepared chitosan. The amount of HM ion adsorbed by the chitosan was calculated by using the Eq. 4:

$$Q = \frac{(C_i - C_f) \times V}{M} \quad (4)$$

Here, V is the volume of aqueous solution (L), M is the mass of chitosan (g) and Q is the HM adsorption capacity of chitosan (mg/g).

Adsorption isotherm and kinetics analysis

The well-established isotherm models Langmuir and Freundlich were used to analyze the experimental data to evaluate and compare the adsorption capacities of Pb²⁺, Cd²⁺ and Cu²⁺ onto chitosan. The Langmuir model is expressed as Eq. 5:

$$q_e = Q_{\max} K_L C_e / (1 + K_L C_e) \quad (5)$$

Here, q_e is the concentration on the solid phase (mg/g), C_e is the concentration on the fluid phase (mg/L), $Q_{\max}$ is the monolayer capacity (mg/g) and K_L (Langmuir constant) is the mass transfer coefficient (L/mg). The Langmuir constants K_L , $Q_{\max}$ and R^2 were calculated by using Origin 2019b software.

The Freundlich isotherm is expressed as Eq. 6:

$$q_e = K_F(C_e)^{1/n} \quad (6)$$

Here, K_F (L/mg) and $1/n$ are the Freundlich constants which represent the adsorption capacity and adsorption intensity, respectively. The Freundlich constants K_F and $1/n$, and R^2 were calculated by using Origin 2019b software.

Simplified kinetics models Pseudo-first-order and Pseudo-second-order models were used to evaluate the experimental data. The Pseudo-first-order equation is expressed by Eq. (7):

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

Here, q_e is the mass of HM ions adsorbed at equilibrium (mg/g), q_t is the mass of metal adsorbed at time t (min), and K_1 is the rate constant (L/min) for the Pseudo-first-order adsorption.

The Pseudo-second-order equation is expressed by Eq. (8):

$$q_t = K_2 q_e^2 t / (1 + K_2 q_e) \quad (8)$$

Here, K_2 is the rate constant (g/mg/min) for the Pseudo-second-order adsorption.

Characterization of chitosan

The characteristics of the synthesized chitosan were determined by Thermo Scientific Nicolet iS10 Fourier Transform Infrared (FTIR) Spectrometer. Spectral scanning was taken in the wavelength region between 4000 and 600 cm^{-1} at a resolution of 4 cm^{-1} with scan speed of 2 mm/s.

The mineral compositions of the prepared chitosan were determined via wide-angle X-ray diffraction (XRD, Rigaku D/MAX 2550 VB with a Cu target). The wide-angle XRD measurements were performed at 40 kV and 100 mA with a scan rate of 12°/min over the range of 10–80°.

The morphology of prepared chitosan was analyzed by a Field Emission Scanning Electron Microscope (FE-SEM) (GeminiSEM 500).

Results

Selection of chitin for chitosan preparation

The percentage of CY, DP and DM of SCW treated by HCl, H_2SO_4 and CH_3COOH are shown in Appendix A. The results

in Tables (2–4) (Appendix A) showed that only the acid concentration was highly significant in the DP of chitin preparation. Under the treatment of low concentration of HCl, H_2SO_4 and CH_3COOH , the prepared chitin showed 25%–36%, 22%–32% and 29%–35% DP, respectively, while 91%–93%, 5%–18% and 77%–86%, respectively under higher concentrated acid treatment. Acid concentration was highly significant under HCl and CH_3COOH treatment, and acid treatment time was highly significant under H_2SO_4 treatment in the DM of chitin preparation. Under the treatment of low concentration of HCl, H_2SO_4 and CH_3COOH , the prepared chitin showed 22%–34%, 19%–34% and 25%–29% DM, respectively, while 87%–92%, 17%–36% and 76%–85%, respectively under higher concentrated acid treatment. Both HCl and CH_3COOH demonstrated almost similar results in terms of DP, DM and CY that agreed with previous reports [15, 24, 46]; however, H_2SO_4 showed completely different results and its application in the preparation of chitin is also very limited. So there is no sufficient information about the influences of H_2SO_4 on the DM and CY from SCW.

Based on the highest and lowest CY, two chitins from each acid treated samples were selected for preparing chitosan used for HM adsorption: Ch-HA-3 and Ch-HA-7, i.e., treated by HCl; Ch-SA-1 and Ch-SA-2, i.e., treated by H_2SO_4 ; and Ch-AA-1 and Ch-AA-7, i.e., treated by CH_3COOH (Table 1). Samples Ch-HA-3, Ch-SA-1 and Ch-AA-1 were prepared under low concentrated acids treatment, and samples Ch-HA-7, Ch-SA-2 and Ch-AA-7 were under higher concentrated acids.

The selected 6 chitins were subjected to chitosan preparation. The chitosan prepared from sample Ch-HA-7 was denoted as CS-HA-7 and the other 5 chitosan samples were all denoted in the same format, i.e., CS-HA-3, CS-AA-7, CS-AA-1, CS-SA-2 and CS-SA-1.

Adsorption of Pb^{2+} onto chitosan

Chitosan prepared from HCl treated SCW

The results in Table 1 showed that the precursor chitin of sample CS-HA-7 contained less than 10% CBC and proteins of original SCW. Two characteristic peaks of chitosan at $2\theta = 10^\circ$ and 20° with high intensity were detected in the XRD analysis of sample CS-HA-7 (Fig. 1), which was in agreement with reported literature [1, 41, 47, 48, 60]. High intensity bands of $-\text{NH}_2$ group at 3435 and 3356 cm^{-1} and the band of $-\text{OH}$ group at 3285 cm^{-1} that is always overlapped with the band of $-\text{OH}$ (Fig. 2) showed the key characters of sample CS-HA-7 ([27, 31]; Qi and Xu, 2004). Therefore, sample CS-HA-7 can be thought as a purified chitosan [48, 60].

Sample CS-HA-7 showed around 94% Pb^{2+} removal and 712 mg/g of Pb^{2+} adsorption in the solution with an initial pH value of 4.14 and the final pH value reached to 6.96 (Table 2). It showed significantly decreased Pb^{2+} adsorption

Fig. 1 XRD pattern of the chitosan prepared from SCW treated by HCl

with the decrease of initial pH value from 4.14 to 2.10 but slightly decrease with the increase of initial pH value from 4.14 to 6.13 along with the similar trends in final pH values. It demonstrated higher Pb^{2+} adsorption than previous studies at the initial pH values of 4.3 [29] or 6.0 [23] (Appendix B). The adsorption mechanisms of Pb^{2+} on the chitosan surface was biosorption which is shown in Eqs. 9 and 10 [9, 37]. The low Pb^{2+} adsorption of sample CS-HA-7 at the initial pH value of 2.10 was because of (i) the active sites on the chitosan surface became positively charged at low pH value, thus increased the competition between H^+ and Pb^{2+} ions for the available $-\text{NH}_2$ groups [9, 38] and (ii) the lyophobic behavior of the chitosan [54]. The increased Pb^{2+} adsorption of sample CS-HA-7 at the initial pH values of 4.14 and 6.13 was due to more free $-\text{NH}_2$ groups available for the formation of $\text{NH}_2\text{-Pb}^{2+}$, and slight competitor effect and electrostatic repulsion, which was so called biosorption [29, 33, 36]. According to these results, sample CS-HA-7 was not recommended for Pb^{2+} removal from strong acid solution.

When a lower concentration of HCl (0.1 M) was used to treat SCW, the CBC and protein in the precursor chitin of sample CS-HA-3 increased to 78% and 75%, respectively (Table 1). High intensity characteristic peaks of Ca(OH)_2 and CaCO_3 were detected in the XRD analysis (Fig. 1), however, the characteristic peak intensities of chitosan at $2\theta = 10^\circ$ and 20° were much low [25, 27, 45, 60]. The intensities of $-\text{NH}_2$ group bands (3693 and 3638 cm^{-1}) and $-\text{OH}$ group band (3328 cm^{-1}) of sample CS-HA-3 were lower than those of sample CS-HA-7 (Fig. 2). The change of intensity of amide groups indicated the high protein contents in the chitosan [1, 27, 31]. The SEM observations showed that sample CS-HA-3 was a partly purified chitosan surrounded with hexagonal Ca(OH)_2 layers and cubic crystals or bunch of CaCO_3 (Fig. 3) [7, 39, 41, 43].

Sample CS-HA-3 removed around 96% Pb^{2+} and adsorbed 727 mg/g of Pb^{2+} in the solution with the initial pH value of 2.10, which was much better than sample CS-HA-7 did (Table 2). With the increase of initial pH value from 2.10 to 4.14 and 6.13, it showed a decreasing trend of Pb^{2+} adsorption. It can be found in Table 2 that the final pH values of the HM solution treated by sample CS-HA-3 exceeded the

Fig. 2 IR spectrum of the chitosan prepared from SCW treated by HCl

Table 2 Initial and final pH value of Pb^{2+} solution and its removal and adsorption by chitosan

Sample	pH value		Removal efficiency (%)	Adsorption capacity (mg/g)	Mechanisms	
	Initial	Final			Primary	Secondary
CS-HA-7	2.10	2.55	25.00	190	Biosorption	—
	4.14	6.96	93.68	712		
	6.13	6.66	88.82	675		
CS-HA-3	2.10	11.17	95.66	727	Precipitation	Biosorption
	4.14	11.74	86.84	660		
	6.13	11.72	72.37	550		
CS-AA-7	2.10	2.86	56.58	430	Biosorption	Precipitation
	4.14	10.97	98.29	747		
	6.13	11.00	95.13	723		
CS-AA-1	2.10	9.01	99.34	755	Precipitation	Biosorption
	4.14	11.26	85.53	650		
	6.13	11.30	77.63	590		
CS-SA-2	2.10	11.20	91.45	695	Precipitation	—
	4.14	11.60	69.74	530		
	6.13	11.68	67.11	510		
CS-SA-1	2.10	7.88	97.37	740	Precipitation	Biosorption
	4.14	11.23	88.03	669		
	6.13	11.33	90.66	689		

The bold marked ones are the optimum removal efficiency and adsorption capacity

highest pH value suitable for $\text{Pb}(\text{OH})_2$ precipitation. However, comparing with previous studies on purified chitosan, sample CS-HA-3 still showed much higher Pb^{2+} adsorption at the initial pH values of 4.3 and 6.10 [23, 29, 43] (Appendix B). Therefore, synergistic effect of CBC, protein and chitosan on Pb^{2+} adsorption occurred in the sample CS-HA-3. When the initial pH value of the HM solution was low, rapid neutralization of acid solution due to Eqs. 11 and 12 benefited the occurrence of Eqs. 9 and 10. At the same time the Eq. 13 helped the precipitation of Pb^{2+} . When the initial

pH value of the HM solution was bigger than 4, extra alkalinity due to higher CBC, especially $\text{Ca}(\text{OH})_2$, made the final pH value exceed the highest pH value suitable for $\text{Pb}(\text{OH})_2$ precipitation. Therefore, the Pb^{2+} adsorption of chitosan depended on not only its available $-\text{NH}_2$ groups but also its $\text{Ca}(\text{OH})_2$ content. The amount of $\text{Ca}(\text{OH})_2$ showed even more important role.

Fig. 3 Electron micrograph of sample CS-HA-3 with an energy of 10 KVA: **a** chitosan fiber/flakes, **b** thin hexagonal $\text{Ca}(\text{OH})_2$ layers, and **c** cubic/circular CaCO_3 crystals/chips

Chitosan prepared from CH_3COOH treated SCW

The results in Table 1 showed that the precursor chitin of sample CS-AA-7 also contained low but about twofold CBC and proteins than sample CS-HA-7. High intensity characteristic peaks of $\text{Ca}(\text{OH})_2$ and CaCO_3 were detected in the XRD analysis (Fig. 4), however, the characteristic peak intensities of chitosan were lower than sample CS-HA-7 [25, 27, 60]. Comparing to sample CS-HA-7 the IR band intensities of $-\text{NH}_2$ group and $-\text{OH}$ group were lower (Fig. 5). Sample CS-AA-7 was hence less purified than sample CS-HA-7.

Sample CS-AA-7 showed around 98% Pb^{2+} removal and 747 mg/g of Pb^{2+} adsorption at an initial solution pH value of 4.14 and the final pH value reached to 10.97 (Table 2). It showed the similar trend of Pb^{2+} adsorption with the increase of final pH values to sample CS-HA-7 but higher Pb^{2+} removal and adsorption, especially at the initial pH values of 4.14 and 6.13. The higher neutralization capacity of sample CS-AA-7 due to CBC increased the final pH value of the solution (Table 2) and benefited to the occurrence of Eqs. 9 and 10. The $\text{Pb}(\text{OH})_2$ precipitate and formed $\text{NH}_2\text{-Pb}^{2+}$ were physically adsorbed on the porous surface of chitosan. The results in Table 2 showed that the optimum initial pH value for Pb^{2+} adsorption was 4.14 when samples CS-HA-7 and CS-AA-7 were used as adsorbents, which was in consistent with previous studies in which purified chitosan was used [33, 36].

When a lower concentration of CH_3COOH (0.1 M) was used to treat SCW, the CBC and proteins in the precursor chitin of sample CS-AA-1 increased to 73% and 70%, respectively (Table 1), which were almost the same as those of sample CS-HA-3. High intensity characteristic peaks of $\text{Ca}(\text{OH})_2$ and CaCO_3 were also detected in the XRD analysis (Fig. 4), however, its characteristic peak intensities of chitosan were lower than those of sample CS-AA-7. The intensities bands of $-\text{NH}_2$ group (3693 and 3638 cm^{-1}) of sample CS-AA-1 were higher than sample CS-AA-7 but $-\text{OH}$ group band intensities (3328 cm^{-1}) were similar (Fig. 5). The high

intensity of amide groups in sample CS-AA-1 was attributed to its high proteins contents [1, 27, 31]. The SEM observations showed that sample CS-AA-1 was surrounded with $\text{Ca}(\text{OH})_2$ and CaCO_3 (Fig. 6).

Sample CS-AA-1 removed around 99% Pb^{2+} and adsorbed 755 mg/g of Pb^{2+} at an initial pH value of 2.10 and the final pH value reached to 9.01 (Table 2). It showed the similar trends of Pb^{2+} adsorption with the increase of initial pH value to sample CS-HA-3 due to possessing the similar physico-chemical properties (Fig. (1–6)) and (Table 1). It can be found in Table 2 that the final pH values of the HM solution treated by sample CS-AA-1 exceeded the highest pH value suitable for $\text{Pb}(\text{OH})_2$ precipitation at initial pH values of 4.14 and 6.13.

Chitosan prepared from H_2SO_4 treated SCW

There is no published study that used H_2SO_4 for the chitin preparation from SCW and the corresponding chitosan for HM ions adsorption. Sample CS-SA-2 showed distinct characteristics among the prepared samples according to TG, IR and XRD analysis (Table 1) and (Fig. (1–9)). It has the highest CBC and proteins among all the prepared samples. Only strong peaks of $\text{Ca}(\text{OH})_2$ and slight peaks of chitosan were detected in the XRD analysis (Fig. 7). A strong intensity band at 3638 cm^{-1} was observed, however, another band at 3576 cm^{-1} attributed to $-\text{NH}_2$ group was not detected (Fig. 8).

Sample CS-SA-2 showed around 91% Pb^{2+} removal and 695 mg/g of Pb^{2+} adsorption at an initial pH value of 2.10 and the final pH value reached to 11.20 (Table 2). With the increase of initial pH values from 2.10 to 4.14 and 6.13, the removal of Pb^{2+} decreased to 69.74% and 67.11%, which showed higher decrease degrees than samples CS-HA-3 and CS-AA-1. The biosorption of Pb^{2+} on sample CS-SA-2 was hence weak. It can be found in Table 2 that all the final pH values of the HM solution treated by sample CS-SA-2 exceeded the highest pH value suitable for $\text{Pb}(\text{OH})_2$ precipitation, which was attributed to the higher $\text{Ca}(\text{OH})_2$ content.

The results in Table 1 showed that the low concentration of H_2SO_4 (0.05 M) treated chitin of sample CS-SA-1 contained about 66% CBC and 65% proteins of original

Fig. 4 XRD pattern of the chitosan prepared from SCW treated by CH_3COOH

Fig. 5 IR spectrum of the chitosan prepared from SCW treated by CH_3COOH

SCW. The characteristic peaks of $\text{Ca}(\text{OH})_2$, CaCO_3 and chitosan (Fig. 7) of sample CS-SA-1 were similar to samples CS-HA-3 and CS-AA-1, so did the $-\text{NH}_2$ and $-\text{OH}$ groups (Fig. 8). The SEM observations (Fig. 9) showed sample CS-SA-1 was less porous than samples CS-HA-3 and CS-AA-1 (Fig. 3 and Fig. 6) and the chitosan was also surrounded with $\text{Ca}(\text{OH})_2$ and CaCO_3 along with some untreated crabs shells [7, 39, 41, 43, 45].

Sample CS-SA-1 removed around 97% Pb^{2+} and adsorbed 740 mg/g of Pb^{2+} at an initial pH value of 2.10 in the solution and the final pH value reached to 7.88 (Table 2). It showed almost the similar trend of Pb^{2+} adsorption with the increase of initial pH values to samples CS-HA-3 and CS-AA-1. Sample CS-SA-1 followed similar Pb^{2+} adsorption mechanisms to samples CS-HA-3 and CS-AA-1 (Table 2).

Most of the previous studies investigated Pb^{2+} adsorption on chitosan at an initial solution pH value range of 4.0–11.0. It was reported that the appropriate initial pH value was 4.0–5.0 for Pb^{2+} adsorption ([3]; Barriada et al., 2007; [23, 29]). However, according to this research, the Pb^{2+} solution pH and neutralization capacity of the chitosan due to CBC were the most influential factors affecting Pb^{2+} adsorption. The $-\text{NH}_2$ group played significant role in Pb^{2+} adsorption only when the solution pH value was between 4 and 6. Partly purified chitosan was a wise selection for strong acid solution.

Adsorption of Cd^{2+} onto chitosan

Highly purified chitosan samples CS-HA-7 and CS-AA-7 were unable to remove Cd^{2+} from the solution with an initial

Fig. 6 Electron micrograph of sample CS-AA-1 with an energy of 10 KVA: (a) chitosan fiber/flakes, (b) thin hexagonal $\text{Ca}(\text{OH})_2$ layers, and (c) cubic or circular CaCO_3 crystals

Fig. 7 XRD pattern of the chitosan prepared from SCW treated by H_2SO_4

pH value of 2.10 due to lack of sufficient neutralization capacity, i.e. less CBC (Table 3). Sample CS-HA-7 removed only 20%–29% Cd^{2+} and adsorbed 200–290 mg/g of Cd^{2+} at the initial pH values of 4.14 and 6.13, and the final pH value reached to 5.80 and 6.95, respectively (Table 3). It can be also observed from Tables 2 and 3 that sample CS-HA-7 showed significantly lower removal efficiency for Cd^{2+} than for Pb^{2+} at the initial pH values of 4.14 and 6.13. However, sample CS-AA-7, a purified chitosan with a few more CBC than sample CS-HA-7, showed around 100% Cd^{2+} removal and 979 mg/g of Cd^{2+} adsorption at the initial pH values of 4.14 and 6.13, and the final pH values were close to the optimum one for $\text{Cd}(\text{OH})_2$ precipitation. It showed extremely higher Cd^{2+} removal and adsorption than previous studies at the same pH values [23, 44] (Appendix B). Therefore, biosorption was not effective for Cd^{2+} removal, however, precipitation was.

High $\text{Ca}(\text{OH})_2$ bearing samples CS-HA-3 and CS-SA-2 removed around 100% Cd^{2+} and adsorbed around 979 mg/g of Cd^{2+} without the initial pH value influence and the final pH value reached to 10.48–11.67 (Table 3). Both samples showed higher Cd^{2+} adsorption than previous studies [23, 44] (Appendix B) which was attributed to high $\text{Ca}(\text{OH})_2$ content.

These findings were in agreement with previous studies which showed higher Cd^{2+} adsorption due to the synergistic effect of chitosan, proteins and CBC [18, 45].

High CBC-bearing samples CS-AA-1 and CS-SA-1 removed around 100% Cd^{2+} and 978 mg/g of Cd^{2+} adsorption at the initial pH values of 4.14 and 6.13 (Table 3). Both samples showed the increasing trend of Cd^{2+} adsorption with the increase of an initial pH value from 2.10 to 4.14 and 6.13. The formation of CdCO_3 also helped to remove Cd^{2+} (Anastopoulos et al., 2017; [48]).

The predominant Cd^{2+} adsorption mechanism was precipitation. Literature reviews showed the appropriate initial pH value was 5.0 for optimum Cd^{2+} adsorption [3, 7]. However, the results in this research showed the possession of CBC in chitosan helped to neutralize the acidic solution and improve the adsorption of Cd^{2+} .

Adsorption of Cu^{2+} onto chitosan

The Cu^{2+} adsorption mechanisms were also similar to Cd^{2+} adsorption (Tables 3 and 4). Highly purified samples CS-HA-7 and CS-AA-7 did not have enough acid neutralizing

Fig. 8 IR spectrum of the chitosan prepared from SCW treated by H_2SO_4

Fig. 9 Electron micrograph of sample CS-SA-1 with an energy of 10 KVA: (a) chitosan fibers/flakes, (b) thin hexagonal Ca(OH)_2 layers, (c) cubic/circular CaCO_3 crystals/chips, and (d) untreated crab shells

capacity, so could not remove Cu^{2+} in the solution at an initial pH value of 2.10 (Table 4). They showed an increasing trend of Cu^{2+} removal with the increase of the initial pH value from 2.10 to 4.14 and 6.13.

Sample CS-HA-7 showed the highest 68% Cu^{2+} removal and 600 mg/g of Cu^{2+} adsorption at the initial pH value of 6.13 (Table 4). Sample CS-AA-7 removed around 99%–100% Cu^{2+} and adsorbed 868–879 mg/g of Cu^{2+} at the initial

pH values of 4.14 and 6.13 (Table 4). It can be also found in Tables 2–4 that sample CS-HA-7 showed significantly lower removal efficiency for Cu^{2+} than for Pb^{2+} but higher than for Cd^{2+} . When the CBC increased a little, the Cu^{2+} removal efficiency of sample CS-AA-7 largely increased.

Samples CS-HA-3, CS-SA-2, CS-AA-1, and CS-SA-1 were all effective for Cu^{2+} adsorption and showed similar final pH values when treated solution with the initial pH values of

Table 3 Initial and final pH of Cd^{2+} solution and its removal and adsorption by chitosan

Type of chitosan	Sample	pH		Removal efficiency(%)	Adsorption capacity (mg/g)	Mechanisms	
		Initial	Final			Primary	Secondary
Highly purified	CS-HA-7	2.10	2.42	0.00	0	Biosorption	–
		4.14	5.40	20.41	200		
		6.13	6.95	29.59	290		
	CS-AA-7	2.10	2.39	0.00	0	Precipitation	Biosorption
		4.14	10.72	99.90	979		
		6.13	10.89	99.90	979		
High Ca(OH)_2	CS-HA-3	2.10	10.48	99.82	978	Precipitation	–
		4.14	11.53	92.04	902		
		6.13	11.66	99.90			
	CS-SA-2	2.10	11.19	99.79	978	Precipitation	–
		4.14	11.63	99.87	979		
		6.13	11.67	99.88	979		
High CBC	CS-AA-1	2.10	5.68	29.59	290	Precipitation	Biosorption
		4.14	11.29	99.73	977		
		6.13	11.38	99.82	978		
	CS-SA-1	2.10	6.14	30.61	300	Precipitation	Biosorption
		4.14	11.21	99.84	978		
		6.13	11.07	99.86	979		

Table 4 Initial and final pH of Cu^{2+} solution and its removal and adsorption by chitosan

Type of chitosan	Sample	pH		Removal efficiency(%)	Adsorption capacity (mg/g)	Mechanisms	
		Initial	Final			Primary	Secondary
Highly purified	CS-HA-7	2.10	2.33	0.00	0	Biosorption	—
		4.14	6.65	20.45	180		
		6.13	6.38	68.18	600		
	CS-AA-7	2.10	2.71	0.00	0	Biosorption	Precipitation
		4.14	9.94	98.64	868		
		6.13	10.83	99.88	879		
High $\text{Ca}(\text{OH})_2$	CS-HA-3	2.10	10.61	96.82	852	Precipitation	Biosorption
		4.14	11.73	97.16	855		
		6.13	11.70	98.52	867		
	CS-SA-2	2.10	6.07	67.05	590	Precipitation	Biosorption
		4.14	11.63	95.00	836		
		6.13	11.74	99.70	877		
High CBC	CS-AA-1	2.10	5.40	32.95	290	Precipitation	Biosorption
		4.14	11.06	99.11			
		6.13	11.24	99.06	872		
	CS-SA-1	2.10	5.22	17.05	150	Precipitation	Biosorption
		4.14	11.03	99.09	872		
		6.13	11.08	99.42	875		

4.14 and 6.13 (Table 4), which was in consistent with previous studies [9, 33, 52]. However, they showed different Cu^{2+} adsorption at the initial pH value of 2.10 due to the varied final pH value. High $\text{Ca}(\text{OH})_2$ -bearing samples CS-HA-3 and CS-SA-2 showed better Cu^{2+} adsorption than high CBC-bearing samples CS-AA-1, and CS-SA-1. The key Cu^{2+} adsorption mechanism of these samples was precipitation.

The reported studies showed that the preferred initial pH value was 4.3–6.0 for the effective Cu^{2+} adsorption when purified chitosan was used as an adsorbent [10, 29, 36, 37], which was in agreement with the results in this research. However, the results in this research showed that $\text{Ca}(\text{OH})_2$ or CBC of the prepared chitosan sample gave a big contribution to Cu^{2+} adsorption. Therefore, the acid neutralizing capacity of chitosan was the key influential factor for Cu^{2+} adsorption and biosorption ability was the secondary.

Different ionic strength of acid influenced the removal of CBC in the preparation of chitin from SCW and then influenced HM removal and adsorption of corresponding chitosan. Chitosan prepared from HCl and CH_3COOH acids treated chitin showed similar HM adsorption capacity because their ionic strength is very close. Besides, initial solution pH value, adsorption affinity ($\text{Cu} > \text{Cd} > \text{Pb}$) and initial HM concentration played the most important role in the HM adsorption [12, 22]. The non-uniformity in Pb^{2+} , Cd^{2+} and Cu^{2+} adsorption by the prepared chitosan was also possibly due to the differences in ionic potential, electronegativity, softness capacity for hydroxylation, and position in the Irving-Williams series, and hydration energy and hydrated ionic radius of HM ions [38].

Adsorption mechanisms

Samples with high CBC namely CS-HA-3, CS-AA-1 and CS-SA-1 were selected for adsorption isotherm and kinetics studies. The characteristic parameters for each isotherm and related correlation coefficients were determined by using Origin 2019b software. R^2 values are considered as a measure of the goodness of fit of experimental data by isotherm models. The parameters of the Langmuir and Freundlich isotherm models for Pb^{2+} , Cd^{2+} and Cu^{2+} are summarized in Table 5. It was observed that the Langmuir isotherm model better fitted to the experimental data for all three metal ions with high correlation coefficient ($R^2 = 0.97\text{--}0.99$ for Pb^{2+} and Cu^{2+} , $R^2 = 0.95\text{--}0.99$ for Cd^{2+}). The experimental q_{max} values are similar to those calculated using the Langmuir model. Therefore, the adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} on chitosan was a monolayer coverage process and the CBC homogeneously distributed on the surface of chitosan made the adsorption sites of chitosan have the same affinity. The high values of K_L imply strong binding affinity (strong interaction between adsorbate and adsorbent). The affinity of a HM ion for a binding site on the chitosan surface is likely to be affected by the chemical coordination characteristics of that HM ion. The efficiency of HM ions binding with chitosan followed this order: $\text{Cu}^{2+} \geq \text{Cd}^{2+} > \text{Pb}^{2+}$.

In Freundlich model, correlation coefficients of determination obtained from the results were low ($R^2 = 0.35\text{--}0.64$ for Pb^{2+} , $R^2 = 0.28\text{--}0.78$ for Cd^{2+} and $R^2 = 0.26\text{--}0.62$ for Cu^{2+}) and the obtained n value is less than 1 (Table 5). Therefore,

Table 5 Isotherm constants and regression data for adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} onto chitosan

Heavy metal	Sample	$Q_{\max}$ (mg/g) (exp)	Langmuir isotherm parameters			Freundlich isotherm parameters		
			$Q_{\max}$ (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	n	R^2
Pb^{2+}	CS-HA-3	727.609	729.801	18.318	0.973	3.037	0.935	0.645
	CS-AA-1	754.189	755.579	19.362	0.996	1.697	0.579	0.561
	CS-SA-1	740.633	743.656	19.586	0.983	2.661	0.780	0.356
Cd^{2+}	CS-HA-3	976.026	979.198	17.338	0.997	2.492	0.941	0.695
	CS-AA-1	978.341	980.035	13.567	0.956	1.872	0.489	0.781
	CS-SA-1	977.638	978.894	15.097	0.979	4.172	0.596	0.286
Cu^{2+}	CS-HA-3	866.981	868.221	16.003	0.982	3.083	0.877	0.629
	CS-AA-1	872.731	875.317	17.937	0.994	5.026	0.916	0.461
	CS-SA-1	874.802	876.008	16.098	0.979	2.996	0.863	0.263

these adsorption are not multilayer adsorption and not completely fit the Freundlich model [4, 19, 35, 49]. The calculated low value of n indicates that the adsorption process is chemically controlled by the functional groups present in chitosan.

The absorption kinetic is used for determining controlling mechanisms of adsorption processes. The kinetic parameters are important in predicting the adsorption operation. To identify the controlling mechanism during the adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} , three steps were considered: mass transfer of the HM ion from the bulk solution to the chitosan surface, adsorption of the metallic ions into sites and internal diffusion of the HM ions into chitosan.

The kinetic parameters for adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} onto chitosan are presented in Table 6. The values of q_e calculated using the Pseudo-first-order model for the three HM ions were quite different from the experimental values, and the correlation coefficients for the three HM ions were also relatively lower ($R^2 = 0.26–0.78$). Therefore, Pseudo-first-order kinetic model did not fit the experimental data well.

The results shown in Table 6 reveal that Pb^{2+} , Cd^{2+} and Cu^{2+} adsorption best can be described by the Pseudo-second-order equation ($R^2 = 0.91–0.99$). The calculated (theoretical) q_e values approached the experimental q_e values closely. These results indicated that the adsorption process was a chemical adsorption controlled process [4, 8, 9, 19]. CBC accompanied by $-\text{NH}_2$, initial pH of solution showed key roles in the adsorption.

Fast initial adsorption was observed in the first 10 min, with adsorption equilibrium being reached after approximately 60 min. Therefore, it was considered that chitosan prepared in this research can be used as an adsorbent for fast removal of toxic HM ions from wastewater, especially for application in emergency treatment for sudden pollution accidents.

Conclusion

The chitosan's HM adsorption capability depended on its precursor chitin preparation process from SCW. According to

Table 6 Kinetic constants for adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} onto chitosan

Metal ions	Sample	q_e (mg/g) (exp)	Pseudo first order			Pseudo second order		
			q_e (mg/g)	K_1 (L/min))	R^2	q_e (mg/g)	K_2 (g/mg/min)	R^2
Pb^{2+}	CS-HA-3	727.020	259.355	0.085	0.353	726.325	2.792	0.999
	CS-AA-1	754.980	298.068	0.056	0.782	754.992	1.815	0.918
	CS-SA-1	740.010	379.221	0.049	0.492	742.004	1.893	0.989
Cd^{2+}	CS-HA-3	979.020	548.306	0.073	0.398	980.029	3.457	0.995
	CS-AA-1	978.240	398.332	0.069	0.584	976.917	3.89 5	0.943
	CS-SA-1	978.630	678.550	0.039	0.679	978.630	2.807	0.984
Cu^{2+}	CS-HA-3	866.980	255.982	0.039	0.791	867.516	2.109	0.999
	CS-AA-1	871.730	398.045	0.033	0.681	870.934	1.248	0.982
	CS-SA-1	874.900	466.791	0.025	0.416	875.007	0.817	0.990

this research, the HM adsorption of chitosan depended on not only its available free -NH_2 groups but also its CBC, especially Ca(OH)_2 even a more important role. It was not necessary to use higher NaOH/acid concentration for the preparation of chitin that subsequently applied for HM adsorption. The most influential factors affecting Pb^{2+} , Cd^{2+} and Cu^{2+} adsorption were initial solution pH value, CBC and free -NH_2 group in chitosan. The appropriate initial pH value of Pb^{2+} solution was 4.14 for highly purified chitosan while acidic condition for partly purified chitosan. The convenient initial pH values of Cd^{2+} and Cu^{2+} adsorption were 4.14 and 6.13 for both highly purified and partly purified chitosan, however, 2.10 for high Ca(OH)_2 -bearing chitosan. The Pb^{2+} adsorption mechanism of highly purified chitosan was biosorption due to -NH_2 group which was promoted if chitosan possessed a little CBC. Precipitation due to CBC was the key Pb^{2+} adsorption mechanism for partly purified chitosan. Precipitation was the main mechanism of Cd^{2+} and Cu^{2+} adsorption, and biosorption only contributed to adsorption at the initial pH values of 4.14 and 6.13. The dissolution of CBC elevated HM solution pH value and thus promoted adsorption; however, additional alkalinity due to higher CBC, especially Ca(OH)_2 , made the final pH value exceed the highest pH value suitable for HM precipitation when the initial HM solution pH value higher than 4. The amount of CBC and proteins in chitosan should be controlled according to the target HM and the initial pH value of solution.

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Compliance with ethical standards

Conflict of interest There are no conflicts of interest in terms of authorship and funding.

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