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A novel approach for the adsorption of cadmium ions in aqueous solution by dead calcareous skeletons

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ABSTRACT

Heavy metal contamination in water causes problems to the environment and the deterioration of human health. Various types of water remediation methods have been conducted to counter this problem and to reduce the toxicity risk in water. As the conventional treatment process does not completely remove pollutants in the water, alternative purification methods have been studied to improve the treatment process. In this present study, batch experiments were conducted to evaluate the ability of dead calcareous skeleton in removing cadmium ions (Cd(II)) from aqueous solution. The factors affecting adsorption were evaluated in respect of adsorbent size, contact time, adsorbent dosage, pH, and initial concentration to determine the optimum conditions for Cd(II) removal. The optimum size of CS was 710 μm and the equilibrium was achieved at 600 min. The most favorable dosage concentration was 20 g/L. The optimum pH for the Cd(II) adsorption was 6.42, which is the initial pH of Cd(II) solution. The adsorption capacity of CS appeared to be higher when the initial concentration Cd(II) increased above 1 mg/L. The experimental data fitted better in the Freundlich isotherm than in the Langmuir isotherm but the bonding was rather weak. The results from this study demonstrate that dead calcareous skeletons have considerable potential in water treatment applications for the metal removal process. In addition, the cost of chemical usage can be reduced due to the natural characteristics of adsorbents, which are able to alter the pH of the solution so that it is favorable for optimum adsorption capacity.

Keywords: Cadmium; Dead calcareous skeletons; Adsorption capacity; Removal efficiency; Batch experiment

1. Introduction

Increasing industrial development has caused a direct upsurge of pollution loading into the water bodies. Heavy metals are introduced into surface water and groundwater, thereby affecting the drinking water quality. The presence of metal ions in excessive concentrations in water, poses dangerous risks to human health and fauna. The consumption of contaminated water over a period of time leads to many health problems including acute or chronic illness. Cadmium is known to be a toxic metal because of its carcinogenic characteristics. Cadmium contamination in water occurs from the discharge of battery fluid, electronic components, fertilizers, and galvanized and

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cadmium-containing piping systems [1]. Long term exposure to cadmium causes damage to the human body, such as the case of *itai-itai* disease, in which the people who lived within a cadmium contaminated area in Japan suffered from osteomalacia with different types of osteoporosis and renal tubular disease [1].

Previously, water treatment has been conducted to control the pollutants from further deteriorating the water quality. The remediation has been performed through conventional methods, such as coagulation, flocculation, ion exchange, membrane filtration, and chemical precipitation [2–5]. The conventional treatment methods are rather costly because of the complex operation systems and high consumption of chemicals. In addition, sludge residues from the conventional plants are not able to completely remove all the pollutants. The current treatments are not able to entirely reduce the discharge concentration to the regulatory limit due to the high concentrations of pollutants. As a result, additional treatment to the partially treated water is required before final discharge [6]. Furthermore, the contact period required for the thorough treatment of high concentrations of pollutants is rather long and thus causes an upsurge in the operational costs [7].

In order to counter the conventional treatment problems, many researchers have started to look for alternatives to produce low cost and sustainable methods for water treatment to meet the effluent discharge regulations [8]. These efforts have involved the use of agricultural waste, food waste, and industrial waste to perform the removal of heavy metals in aqueous solutions and real wastewater. The common materials used include palm shell, coconut shell, rice husk, various types of nut shell, fruit seed, fruit bagasse, seashell, cement, and fly ash [2,3,9–12]. The advantages of using these materials are because of their availability and abundance, making them a new viable alternative for water purification. These natural waste materials are cost-effective and only require simple modification for the effective removal of metals [13]. The period for effective treatment is also shorter compared to the conventional method, in as much as more than 99% removal can be achieved in less than 24 h. Besides, making use of these by-products contributes to the waste disposal management, and also improves the economic value of these adsorbents, as they function as water treatment products [8].

For this present study, dead calcareous skeletons were utilized to remove Cd(II) from aqueous solution. Calcareous skeletons mainly contain $CaCO_3$ of the aragonite family, which has the ability to uptake metal ions. In the earlier literature, calcareous skeletons were an indicator of Cd(II) concentration in seawater as well as a potential pollution detector [14,15]. However, very few studies have been conducted on dead calcareous skeletons for heavy metal removal and limited information is available concerning their removal ability. Dead calcareous skeletons are scattered abundantly along the sandy beaches due to the bleaching or strong wave destruction. The hardened skeletons are required to be cleared from the living scleractinian skeleton as they can pose further destruction and inhibit the growth of the living scleractinian skeleton. The constituents of calcareous skeletons can provide water purification through a metal interaction mechanism, in which the surface of calcareous skeletons offers metal-sorption [16].

In the present study, the ability of calcareous skeletons for removing Cd(II) ions was investigated by evaluating the effect of contact time, adsorbent size, dosage concentration, pH, and initial concentration. This study adopted a green approach to the current treatment process and possible application for real acidic wastewater. Further understanding on this material was studied and evaluated to provide novel adsorbent and alternative material for heavy metal removal.

2. Materials and methods

2.1. Adsorbent preparation

The CS (dead calcareous skeletons) used in this study were collected from along the sandy shoreline in Malaysia. The main component of CS used in this study is $CaCO_3$ in the form of calcite and aragonite [17]. The CS obtained were first rinsed with distilled water to remove sand and debris. The CS were then pre-washed by sonicating with 2% of ammonium citrate solution (w/v) to remove tissue residue from the surface of the CS [17]. Then, the CS were rinsed again with distilled water to remove the washed solution residue and remaining tissue from the surface [17]. The washed CS were dried in an oven at 70°C for 72 h to remove moisture content in order to obtain constant weight. The dried CS were pulverized and sieved into uniform size of 1 mm, 710 μm, and 500 μm, respectively, according to the US Department of Agriculture to obtain, relatively, very coarse, coarse, and medium sizes. Furthermore, the fine size of CS was not used in this study to avoid aggregation during the experiment. Each size of CS was kept in an acid washed zip-lock bag for further usage.

2.2. Chemicals

All the chemical reagents used in this study were of analytical grade. A stock solution of Cd(II) ions of

1,000 mg/L was prepared by dissolving an appropriate amount of $CdN_2O_6{\cdot}4H_2O$, Sigma Aldrich (Switzerland) with deionized water from the Milli-Q system (Millipore Corp., USA). The desired Cd(II) working solution was prepared by further diluting freshly prepared stock solution. The solution pH was adjusted with 0.1 M NaOH and 0.1 M HNO_3 due to the solubility of the chemicals in water and to avoid generating high solids and machine interference.

2.3. Batch experiments

In batch experiment, all the work was performed using an orbital shaker with an agitation speed of 180 rpm to ensure homogenous contact was achieved. During the experiments, all the solutions were tightly cap-covered at all times until testing to prevent environmental contamination, evaporation, or spillage. The experiments were maintained at temperature between 24 and 25˚C. The effects of contact time, adsorbent size, adsorbent dosage, pH, and initial concentration of Cd(II) were studied. For the effect of contact time and size, 10 g/L of CS dosage with size 1 mm, 710 μm, and 500 μm, respectively, were added in 30 mL of Cd(II) working solution with a required interval time for a 24 h period. For the effect of dosage, 5, 10, 15, 20, 30, 40, and 50 g/L of CS, respectively, were added into 30 mL of Cd(II) working solution with known concentration. The pH of the Cd(II) solutions were adjusted to 3, 4, 5, 6.42 (initial pH), 7, and 8, respectively, prior to mixing with CS by the addition of 0.1 M HNO_3 and 0.1 M NaOH. The initial pH of the Cd(II) solution without the addition of CS and pH adjustment was 6.42. This was done to observe its effect at the natural pH of the metal. The effect of the initial concentration of Cd (II) solution was studied by using Cd(II) at concentrations of 1, 5, 10, and 50 mg/L, respectively. All samples were filtered through 0.45 μm filter membrane and kept at 4˚C prior to metal analysis. The Cd(II) concentrations from collected samples were determined using an Induced-Coupled Plasma Mass Spectrometer, ELAN DRC-e (Perkin Elmer, USA). Quality controls and accuracy checks were implemented in respect of reliable data by checking the blank samples and a five-point calibration curve for analysis of the elements. Triplicate results ensure the precision and consistency of measurement. Accreditation of the equipment was obtained for its annual maintenance.

2.4. Data analysis

The removal efficiency of the CS is calculated at time of the contact period and also at equilibrium. The removal efficiency is calculated as follows:

$$\text{Removal percentage at equilibrium } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$\text{Removal percentage at time } (\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

where C_o and C_e are the initial and final Cd(II) concentrations (mg/L). C_t represents Cd(II) concentration at each interval of contact time (mg/L).

The amount of Cd(II) adsorbed per unit mass of adsorbent, CS, is calculated as follows:

$$\text{Adsorption capacity} = \frac{(C_0 - C_e)V}{m} \tag{3}$$

where V represents the volume of working solution (L) and m is the mass of the CS used in each solution (g).

2.5. Sorption isotherm models

The equilibrium data obtained from the removal of Cd(II) were analyzed using the sorption isotherm, Langmuir and Freundlich models. A linear Langmuir isotherm model is applied in this study. The Langmuir equation given is as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{4}$$

b and q_m are Langmuir constants, which relate to the rate of adsorption (L/mg) and adsorption capacity (mg/g).

The Langmuir isotherm can also be expressed as a dimensionless constant, also known as the equilibrium parameter, R_L as follows:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

The R_L value indicates whether the isotherm is suitable for the CS. When $R_L = 1$, it indicates a linear relationship. The $R_L > 1$ value shows that the type of isotherm is not favorable, when $0 < R_L < 1$, the isotherm is likely to be favorable and $R_L = 0$ is an irreversible relationship.

The Freundlich isotherm is applied in this study to describe the heterogeneous surface sorption, the Freundlich equation is as follows:

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

k_f is an empirical Freundlich constant and n is a Freundlich constant for adsorption capacity and adsorption intensity.

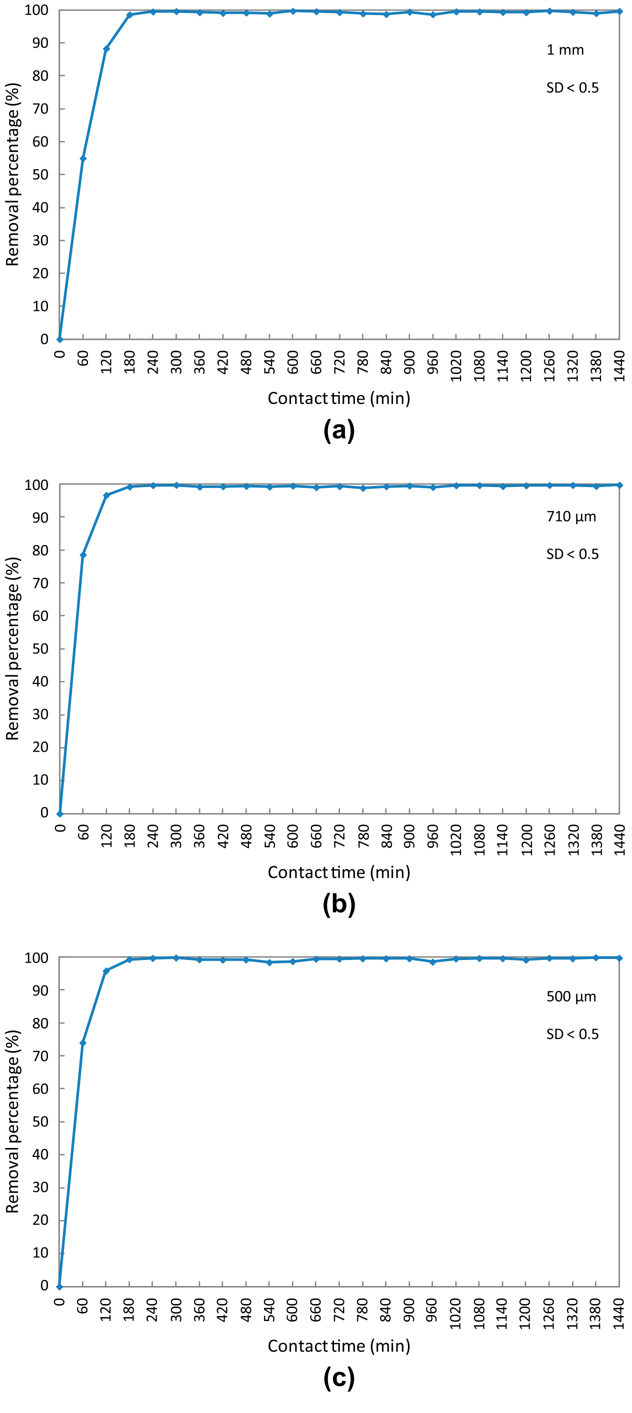
2.6. Characterization of adsorbent

For determination of the physical surface characteristic of the CS, BET (Brunauer, Emeett and Teller) method analysis was used to obtain the specific surface area and pore size of the CS. The CS were degassed at 300.0˚C for 21.8 h to eliminate surface impurities. Then, the degassed CS were left to adsorb N_2 gas at 77 K. The surface area of the CS was determined using the BET equation.

3. Results and discussion

3.1. Effect of contact time and adsorbent size

Three sizes of CS, 1 mm, 710 µm, and 500 µm, respectively, were used to determine the optimum size for Cd(II) removal. The three respective sizes of CS were able to remove up to 99.80% of Cd(II) in the aqueous solution, as shown in Fig. 1. The 1 mm CS had a slower removal rate compared to the 710 and 500 µm during the first and second hour ($p < 0.05$). As the time passed, each size of CS had an almost similar removal trend ($p > 0.05$). Based on the details of the removal efficiency of the three sizes on the adsorption of Cd(II), the CS of 710 µm were found to have the most stable removal throughout the whole contact period. During the first 60 min of contact, the 710 µm CS was able to reduce Cd(II) from 10 to 1.942 mg/L (Fig. 2). The removal of Cd(II) by 710 µm CS continued to increase until it reached equilibrium at the removal >99.0%. The smaller size of adsorbent showed better removal of metal ions due to the larger contact surface [18]. However, the smallest size used in this study did not agree with this phenomenon, which might be due to the agglomeration of the particles that caused the removal efficiency to be lower.



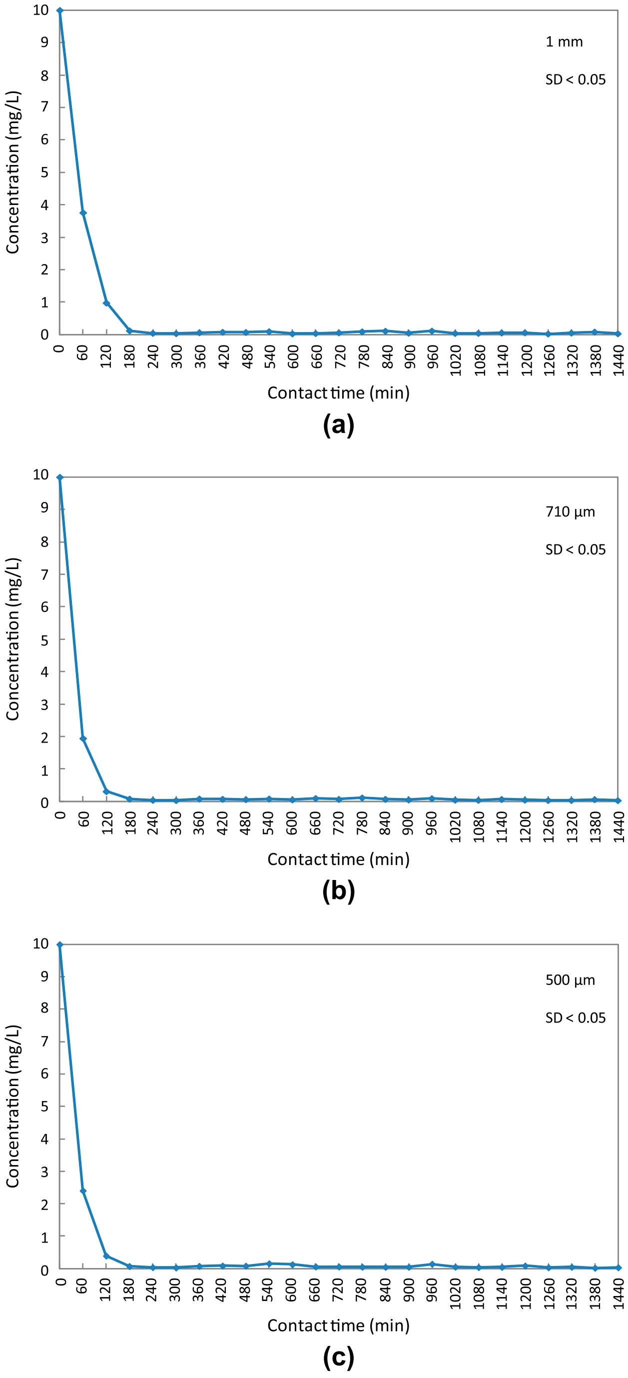
(a)

(b)

(c)

Fig. 1. Effect of contact time for three respective sizes of CS, (a) 1 mm, (b) 710 µm, and (c) 500 µm (initial Cd(II) concentration: 10 mg/L; dosage: 10 g/L, pH: initial state).

The results obtained from BET analysis showed that the surface area for 1 mm, 710 µm, and 500 µm, were 0.1063, 0.2115 and 0.3146 m^2/g, respectively. Although the surface area of these three sizes of adsorbents were found to be rather small compared to that found in the literature, these adsorbents were still able to reduce Cd(II) in the aqueous solution. This situation indicated that the surface area might not be an influential factor in the adsorption activities. Prieto et al. [16] proved that the BET surface area might not be a good estimation for adsorption efficiency, in that, although calcite has a higher active surface area, the adsorption capacity was lower than the abiogenic aragonite, which has a relatively small surface area. The relationship between metal-sorption and BET surface in this case was rather inconsistent because the small surface area of CS did not restrict the uptake of Cd(II) from aqueous solution. The available surface



(a)

(b)

(c)

Fig. 2. Effect of contact time on the reduction of Cd(II) concentration by three sizes of CS, respectively, (a) 1 mm, (b) 710 µm, and (c) 500 µm (initial Cd(II) concentration: 10 mg/L; dosage: 10 g/L, pH: initial state).

Table 1
Surface characteristics analysis of CS

	1 mm	710 µm	500 µm
BET surface area, m^2/g	0.1063	0.2115	0.3146
Total pore volume, cc/g	0.0031	0.0059	0.0057
Average pore diameter, nm	114.90	111.00	72.43

area tended to be filled with solution, which inhibited the ion exchange activity and reduces the sorption capacity [16,19]. Based on the BET analysis, the average pore diameters for the three respective sizes of CS were reported to be bigger than 50 nm, which is categorized as macro pore in IUPAC. The surface characteristics of CS are summarized in Table 1.

From Figs. 1 and 2, it is observed that Cd(II) removal increased as the contact time increased at the initial stage and equilibrium time was reached at 600 min by the three respective sizes of CS ($p > 0.05$). In order to ensure the equilibrium reaction was achieved, for the next batch experiment the contact time was set to 720 min.

3.2. Effect of adsorbent dosage

The adsorbent dosage is an influential factor for metal adsorption. The effect of CS dosage was investigated by varying the different dosages of 5, 10, 15, 20, 30, 40, and 50 g/L with the equilibrium time, 720 min. Fig. 3 show that when the CS dosage increased, the removal percentage of Cd(II) also increased, while the adsorption capacity decreased. At the equilibrium, the CS dosage of 20 g/L demonstrated the highest capability among the dosage concentrations with 99.68% of Cd(II) being removed. The highest CS dosage, 50 g/L also showed the same removal value and both dosages have no significant difference in removal efficiency ($p > 0.05$). At a certain point, when the adsorbent dosage was increased but the uptake of metal ions remained constant, it showed that the maximum uptake was achieved and no further removal was possible [20]. Therefore, 20 g/L CS dosage was chosen as the optimum dosage for further batch experiments because this amount of dosage saves the adsorbent sources. Although the 5 g/L dosage concentrations were also able to reduce Cd(II) in the aqueous solution, the efficiency was significantly lower than the 20 g/L dosage, which may be due to the insufficient binding surface ($p < 0.05$). By increasing the dosage concentration, metal removal efficiency can be improved because more active binding surface is available for metal adsorption [21]. The amount of adsorbent dosage determines the removal efficiency, and, thus, the available sites for the exchange of ions [22].

The adsorption capacity was observed to decline when the dosage concentration increased. The decreased of adsorption capacity indicates there is still

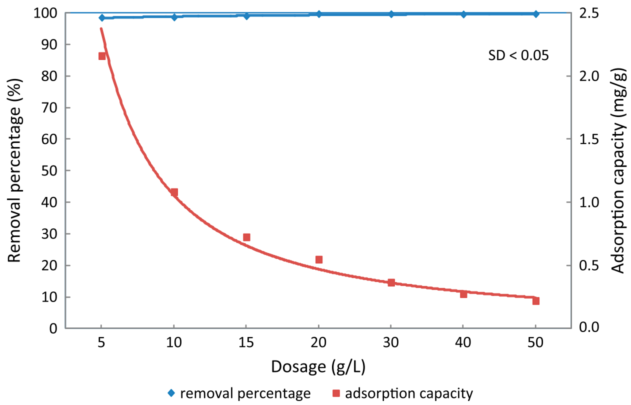


Fig. 3. Effect of dosage concentration on removal of Cd(II) ions (initial Cd(II) concentration: 10 mg/L; contact time: 720 min; pH: initial state).

remaining freely available sorption site. As observed in Fig. 3, the adsorption capacity continued to reduce with the addition of CS dosage ($p < 0.05$). The active exchangeable sites are not fully utilized in this case. The same conditions were applied as in the experiments of the previous work [22–24].

3.3. Effect of pH

Fig. 4 shows 90% reduction for each Cd(II) solution in the respective pH condition. The initial pH of each Cd(II) working solution was adjusted to 3, 4, 5, 7, and 8 with one remaining at its natural pH (initial pH 6.42). At the equilibrium, the final pH of the respective solution increased and shifted to alkaline condition (Table 2). From Table 2 and Fig. 4, the results show that the Cd(II) solution in its natural pH had the highest removal, 96.85%. The Cd(II) solutions with adjusted pH also showed 90% of removal because of the change of pH from acidic to alkaline condition. Due to the chemical compound of $CaCO_3$ in the CS, the dissolved calcium concentration from the CS directly contributed to the change of pH in the Cd(II) solution, as can be seen in Table 2. The dissolution of $CaCO_3$ in aqueous solution in Eq. (7) explains the increase in the pH of the solutions in the present study.

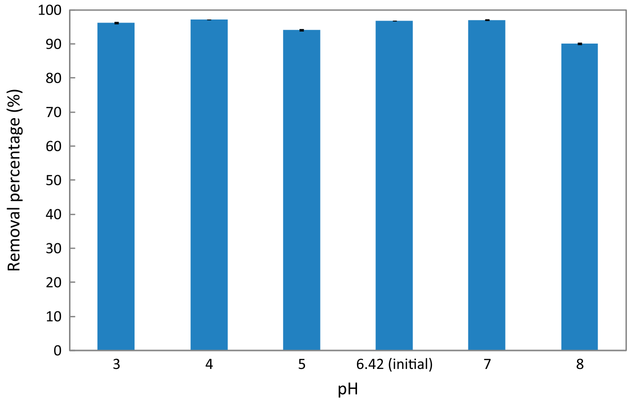


Fig. 4. Effect of pH on the removal of Cd(II) (initial Cd(II) concentration: 10 mg/L; dosage: 20 g/L; contact time: 720 min).

Table 2
Influence of CS in natural and adjust pH

Initial pH	Final pH	Removal (%)
3.00	7.68 ± 0.01	96.24
4.00	7.91 ± 0.02	97.20
5.00	8.16 ± 0.01	94.13
6.42 (original)	8.11 ± 0.01	96.85
7.00	8.29 ± 0.01	97.06
8.00	8.19 ± 0.01	90.20

$$H_2O + CaCO_3 \longrightarrow Ca^{2+} + HCO_3 + OH^- \tag{7}$$

From equation 8, the sorption of Cd(II) ions occurred by substituting the Ca (II) ions, which increased the pH of the solution. Similar results were obtained by Aziz et al. [25], in which the pH of the metal solutions shifted to alkaline condition after limestone was added. Metals also tend to precipitate to metal oxide or metal carbonate when the pH of the solution is higher than the solubility point [25].

$$CaCO_3 + Cd^{2+} \longrightarrow CdCO_3 + Ca^{2+} \tag{8}$$

It is preferable to remove Cd(II) at a higher pH value near to neutral or slightly alkaline condition [26–28]. An increase in pH causes an increase in the negative ions on the surface of the adsorbent, which results in better metal adsorption [26]. On the other hand, when the pH is reduced to an acidic condition, the positive ions also increase, which can cause competition between the metal ions to be adsorbed on the binding surface of the adsorbents [18,29].

However, at pH 8, the Cd(II) removal percentage was slightly lower than the others, which can be explained by hydrolysis of the Cd(II) ions in the aqueous solution. Kour et al. [29] explained that at higher pH, metal ions may undergo hydrolysis, which increases the anionic species in the solution and decreases the adsorption efficiency. Cadmium species, as such, $[Cd(OH)_3]^-$ and $[Cd(OH)_4]^-$, may exist when the solution pH increases from its buffer and reduces the adsorption capacity [30].

3.4. Effect of initial concentration

The effect of initial Cd(II) concentration was investigated to see the influence of metal ions in the removal process. Four independent initial Cd(II) concentrations consisting of 1, 5, 10, and 50 mg/L were prepared with a contact time of 720 min and CS dosage of 20 g/L. From the results in Fig. 5, the lowest initial Cd(II) concentration, 1 mg/L, had the lowest removal percentage among all, which is 87.54%. On the hand, as the initial Cd(II) concentration increased from 5 to 50 mg/L, the removal percentage and adsorption capacity also increased (Fig. 5). It can be said that the driving force was initiated by the initial concentration to reduce the mass transfer resistance, and, at the same time, improved the metal removal rate [27].

3.5. Adsorption isotherms

In order to determine the adsorption process that occurred on the adsorbent used in this study, two adsorption isotherms were applied—Langmuir isotherm and Freundlich isotherm. The Langmuir isotherm is commonly used to determine the monolayer adsorption mechanism. The Freundlich isotherm is generally represented by the adsorption mechanism that occurs in the heterogeneous layer. From Fig. 6, the R^2 value obtained from the Langmuir equation was 0.9032 with a negative rate of adsorption, which can also be observed in Fig. 5. The CS used in this study depicted an opposite result compared to the common literature as the CS had a higher removal efficiency and adsorption per mass when the initial concentration of Cd(II) increased. It was discovered that CS have a better adsorption capacity when the initial Cd(II) concentration is higher than 1 mg/L. The adsorption of Cd(II) was greater when the initial concentration of Cd(II) increased to 50 mg/L. The final Cd(II) concentrations from the respective initial concentrations were reduced to almost similar value. When the Cd(II) concentration was lower, the removal was also rather low, as seen in Fig. 5. The R_L values were not able to indicate the type of favorable isotherm for this adsorbent as the values were negative (Table 3).

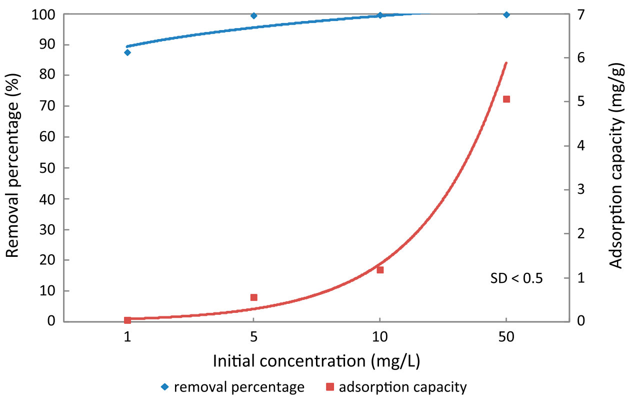


Fig. 5. Effect of initial concentration on the removal of Cd (II) (dosage: 20 g/L; pH: initial value; contact time: 720 min).

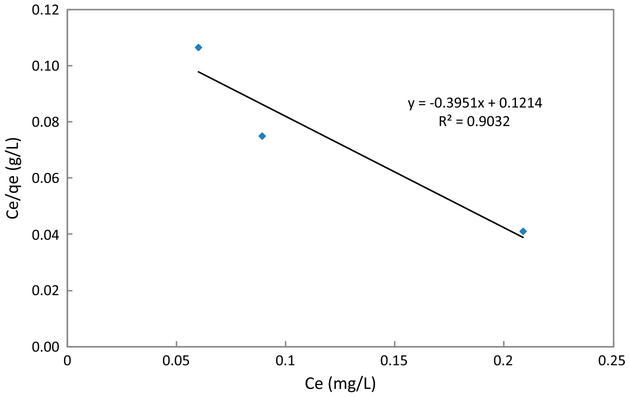


Fig. 6. Data fitting for adsorption of Cd(II) in Langmuir isotherm.

The coefficient obtained from the Freundlich isotherm was 0.9994, as shown in Fig. 7, which indicates that the adsorption of Cd(II) happened over heterogeneous layers rather than a monolayer. However, the Freundlich intensity obtained from the data fitting was unfavorable with $1/n > 1$, which indicated that the adsorption bond is weak, as seen in Table 3 [25,31]. A comparison with other studies on the removal of Cd(II) ions in aqueous solution is shown in Table 4. Even the CS adsorption capacity is not as high compared with previous studies, as the CS still exhibited great removal efficiency for Cd(II) in this study and potential application for a real system. This showed that the CS imposed unique characteristics as a metal adsorbent with high ability in removing Cd(II) ions in aqueous solution. The equilibrium isotherms did not adequately describe the adsorption that occurred between the CS and Cd(II) ions because of

Table 3
Adsorption model parameters for adsorption of Cd(II) by calcareous skeleton

Langmuir isotherm		Freundlich isotherm	
R^2	0.9032	R^2	0.9994
b (L/mg)	−3.2535	k_f	80.075
q_m (mg/g)	−2.5310	$1/n$	1.7546

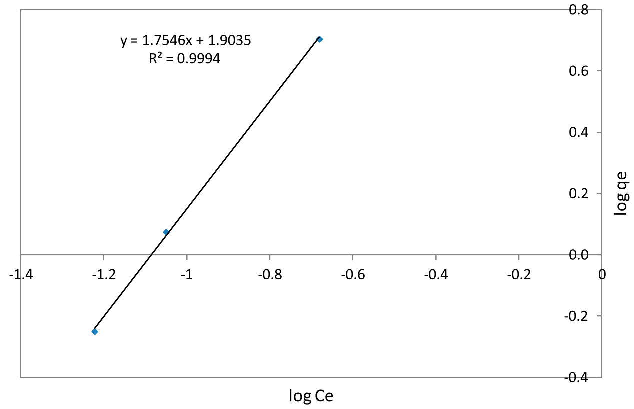


Fig. 7. Data fitting for adsorption of Cd(II) in Freundlich isotherm.

Table 4
Comparison of Cd(II) ions adsorption capacity

Adsorbents	Initial concentration (mg/L)	Adsorption capactity (mg/g)	Refs.
CS (present study)	50	5.068	Present study
Raw aragonite	200	470	[32]
Raw calcite	200	42	[32]
Treated aragonite	200	439	[32]
Treated calcite	200	40	[32]
Mollusk shell	209	1.62	[33]
Nano-sized aragonite mollusk shell	200	8.91	[34]

the peculiar characteristics of CS. The adsorption of Cd(II) ions by CS were seen to occur at a deeper level rather than on the surface layer of adsorbents.

4. Conclusion

The present study showed that CS could remove >99% of Cd(II) without adjusting the pH in 600 min. Consequently, the chemical cost can be reduced as CS itself acted as a pH adjuster to shift the solution pH. The natural characteristic of CS has added value for applications with real wastewater, especially in high acidic mine water where the use of chemicals to adjust pH can be reduced. The best size of CS was 710 µm, which is in the middle range of the three sizes. The BET surface area of CS was relatively small but the adsorption was still high, which indicates that the relationship of the BET surface area is not necessarily correlated with the adsorption efficiency, which made this adsorbent unique compared to the present literature. CS have the ability to remove Cd(II) at a higher concentration rather than a lower concentration, which appears to have different characteristics from the common literature in which most of the materials in the literature appear to have lower removal efficiency as the initial concentration increases. The output of this study provides a better understanding and cost-effective approach in metal removal phenomena. The Langmuir isotherm might not fit this application as the maximum adsorption capacity and Langmuir constant resulted as negative. This application fitted the Freundlich isotherm with weak adsorption bond. In conclusion, this adsorbent, CS, has the potential for application in water treatment as the removal efficiency is high and the material is environmentally friendly as not many chemicals are required for suitable removal conditions. In addition, a separation step, such as flocculation, is not necessary for this adsorbent as the size of CS used can be easily separated by gravity precipitation. Furthermore, this form of treatment promotes carbonate precipitation rather than hydroxide precipitation where sludge generation can be reduced. Thus, there will be no requirement for further addition of lime for neutralizing purposes. The promising results of this study provide an alternative approach for low-cost water treatment and promote influential factors for optimum metal removal. This is applicable for real water treatment plants to improve and enhance the operational efficiency for a more sustainable remediation system.

Acknowledgments

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