Desalination and Water Treatment
www.deswater.com

16 (2010) 74–82
April

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doi: 10.5004/dwt.2010.1047

Alkaline treatment of seashells and its use for the removal of Cu(II) from aqueous solution

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Received 19 March 2009; Accepted 25 November 2009

ABSTRACT

Natural aragonite, NA, (in the form of crushed seashells) has a limited capability to remove Cu(II) from an aqueous solution at ambient temperatures (removal = 22.5% at 25°C). At higher temperature, removal increases (removal = 83.5% at 50°C). Ion exchange is proposed as the mechanism of removal in this case. However, the treatment of NA by 4% $NaOH^-$ solution produced Na-modified aragonite, NA^-Na, which has higher capability for Cu(II) removal at ambient temperatures (removal = 76% at 25ºC). This is practically preferred. X–ray fluorescence of Na-modified aragonite showed presence of Na element on its surface with about 1% which suggests inclusion of Na in the NA lattice structure and this is in agreement with the results of the X–ray diffraction measurements. It is suggested that the modification occurs due to the replacement of some calcium ions by sodium ions over the outer layers of NA lattice, (i.e. facial and sub-facial isomorphous-substitution). This substitution causes deficiency in positive charge which is compensated facially by $Ca^{++}OH^-$ moieties. It is believed that these moieties are responsible for the micro-precipitation of Cu(II) upon removal process. Cu(II) removal by batch method (at pH value of 6.5) was carried out to assess NA^-Na removing performance in terms of capacity (the Langmuir and Freundlich isotherm models) and rate (the pseudo-first and second order models). The Langmuir model gives Cu-Adsorption capacity of 108.7 mg/g at 25°C. For kinetic study, the pseudo-second-order model is the one that best represents the Cu(II) removal by NA^-Na. This suggests that removal is one-step chemisorption, reversible and initial concentration-dependent process.

Keywords: Aragonite; Ion-substitution; Micro-precipitation; Isotherm; Kinetics

1. Introduction

Many industrial activities produce aqueous waste effluents containing ions of heavy metals. Most of these ions are toxic and their removal from aqueous effluents is an essential task. The objective of many studies is to introduce practical and cost effective materials that are able to eliminate this hazard. Several materials can meet these demands deploying conventional elimination methods such as adsorption, ion exchange, complexation, electrostatic attraction and precipitation [1]. Adsorption is the main method of removal especially in the case of low concentration and most of used materials are synthetic (e.g. polymeric ion exchangers) whose production is expensive, to some extent, and passes through several chemical and physical steps to fulfil the needed application conditions [2]. Some natural materials can be used for ion-elimination purpose (agricultural wastes, zeolites and clays), but a chemical and/or physical modification prior use are occasionally required [3--6]. These modification processes, in many cases, are tedious and costly. Finding a material that is natural, abundant and simply-treated

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(to enhance its removing capability) is important to face the heavy metal ion-contamination of increasingly spread industrial sites, especially in the developing countries.

The aim of this work is to elucidate that a simple treatment of an available and cheap matter, natural aragonite in the form of crushed seashells, can considerably enhance its metal-removal performance which facilitates the decontamination process. Seashells, as a natural source of calcium carbonate in aragonite form, can be used for metal ion decontamination purposes. Tremendous amounts of this matter are present over several beaches of the Egyptian northern cost. In this study, this natural aragonite (NA) was treated by a solution of sodium hydroxide to produce sodium-modified aragonite (NA-Na). This modification enhances its removing power towards Cu(II) from water at ambient temperature. It is expected that many others of heavy metals can be removed by NA-Na and Cu(II) is only employed in this work as a representative. Copper was selected to be studied because of its widespread use in many industrial activities: fertilizer production, paints and pigments, wood pulp production, and metal plating, etc. It was found out that the mechanism of removal was changed due to modification. The work comprises assessment of removal by studying the adsorption isotherm and kinetics using standard models.

2. Materials and methods

2.1. Aragonite modification

The natural aragonite, NA, in the form of seashells was collected from the Egyptian northern cost. Seashells pieces were ground and sieved to ~0.3 mm. NA was then washed with bi-distilled water to remove soluble foreign-matters that may be present. The modification of NA grains was simply performed by alkaline treatment: each single NA-sample of 0.5 g was treated by NaOH solution of (4%, 50 mL) for 30 min using a shaker at 150 rpm at ambient temperature producing modified natural aragonite, NA-Na. The modified samples were then washed several times by fresh distilled water (50 mL) to remove NaOH remains and the pH of last washing solution was monitored to decrease to about 6.5.

2.2. Characterization of NA and NA-Na

To understand the effect of modification on the aragonite grains, several techniques have been used for characterization: (i) a Perkin-Elmer Series II CHNS/O Analyser to elementally-analyse dried samples of NA and NA-Na (ii) Powder samples were characterized by scanning electron microscopy (SEM; Model S–900, Hitachi, Ltd) operated at 8 kV to get images of the outer surface of NA and NA-Na grains which elucidate their surface morphologies and associated X–ray fluorescence analysis for the determination of its elemental percentages, (iii) Powder XRD data of the samples was determined by means of a Philips X–Pert diffractometer with Bragg–Brentano geometry having Cu K_α radiation (λ= 1.5418°A) and (iv) Corning Photometer 400 to determine the degree of ion exchange between sodium and calcium after modification of NA by NaOH solution.

2.3. Cu(II)-removal process

All reagents used were of analytical purity. $CuCl_2.2H_2O$ was used to prepare synthetic concentrated stock aqueous solution (1000 mg/L, 0.5% HCl). Standard diluents were freshly prepared from this stock solution for removal experiments and were pH-adjusted using concentrated and diluted HCl and NaOH solutions.

The batch technique was applied for examining the adsorption behaviour: (1) for NA, two samples each of 0.25 g was used to treat 50 mL Cu(II)-solution of 20 ppm at 25 and 50°C; (2) for NA-Na, the factors considered were the temperature (5, 25 and 50°C), the contact time (10, 20, 30, 40, 50, and 60 min) and the initial Cu(II) concentration (10, 15, 20, 25 and 30 mg/L). The shaking speed (200 rpm), grain size (~ 0.3 mm), Cu(II)-solution volume (50 mL) and NA-Na mass (0.25 g) were kept constant for all experiments. The pH at which removal was performed was adjusted at 6.5 to avoid misleading precipitation phenomenon. The Perkin-Elmer atomic absorption spectrometer 3100 with Cu-element hollow cathode lamp and an air-acetylene burner was used for determining the metal-ion concentration (λ =324.8 nm).

3. Results and discussion

3.1. Characterization of NA and NA-Na

The Elemental analysis indicates the presence of carbon in NA and NA-Na as 12 and 11.5% respectively which agrees with its atomic percentage in $CaCO_3$.

X–ray diffraction: Fig. 1(A) gives $CaCO_3$ to be the main material of NA grains and aragonite is its lattice form. For

Table 1
Elemental percentage* of NA, NA-Na and Cu-loaded NA-Na determined by X–ray fluorescence analysis.

Element (%)	NA	NA-Na	Cu-loaded NA-Na
X	18	12	14
O	18	16	17
Si	1	9	2
Ca	63	62	65
Na	–	1	~1
Cu	–	–	~1

*Values were approximated.

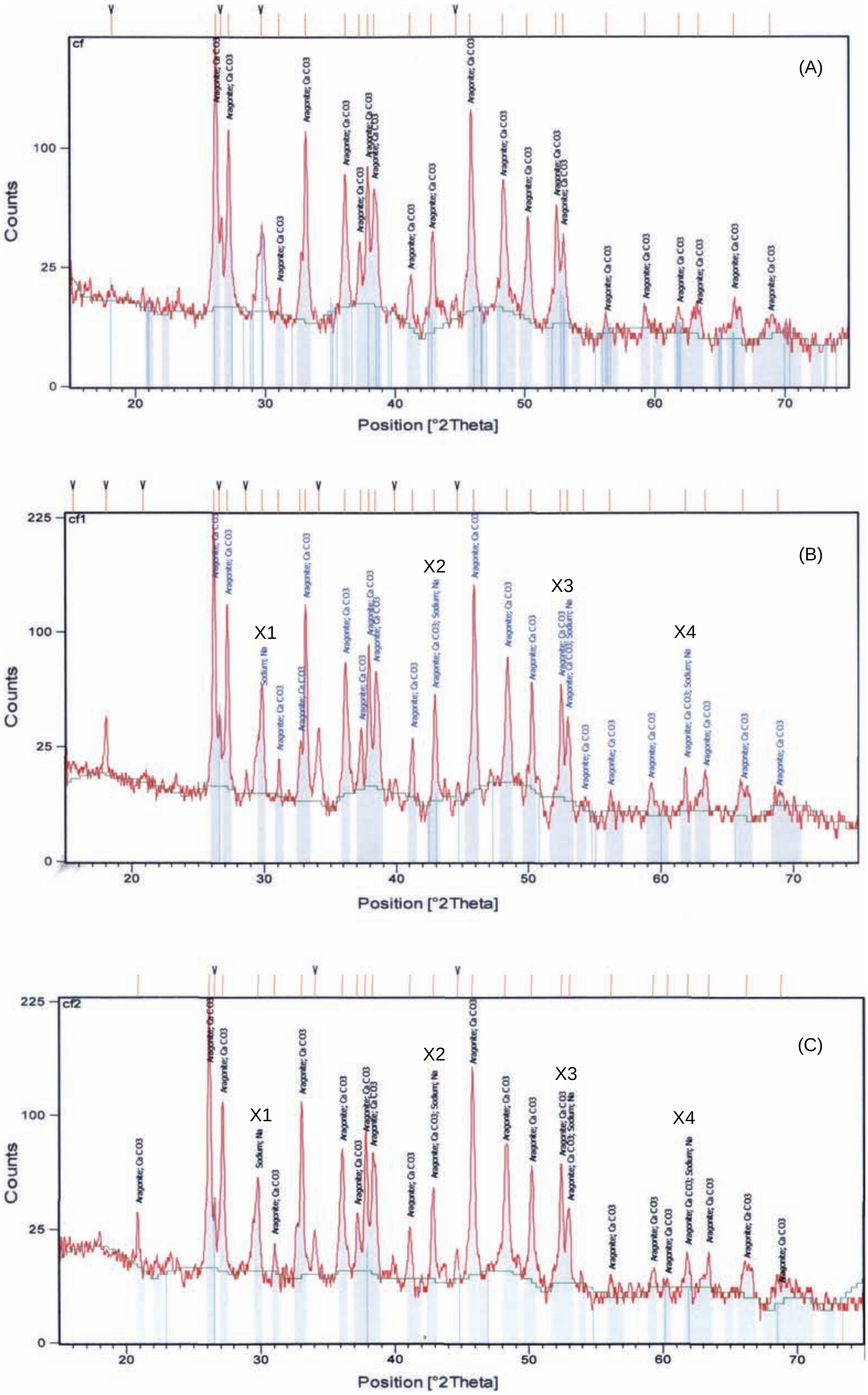

Fig. 1. X–ray diffraction of (A) NA, (B) NA–Na and (C) Cu-loaded NA–Na.

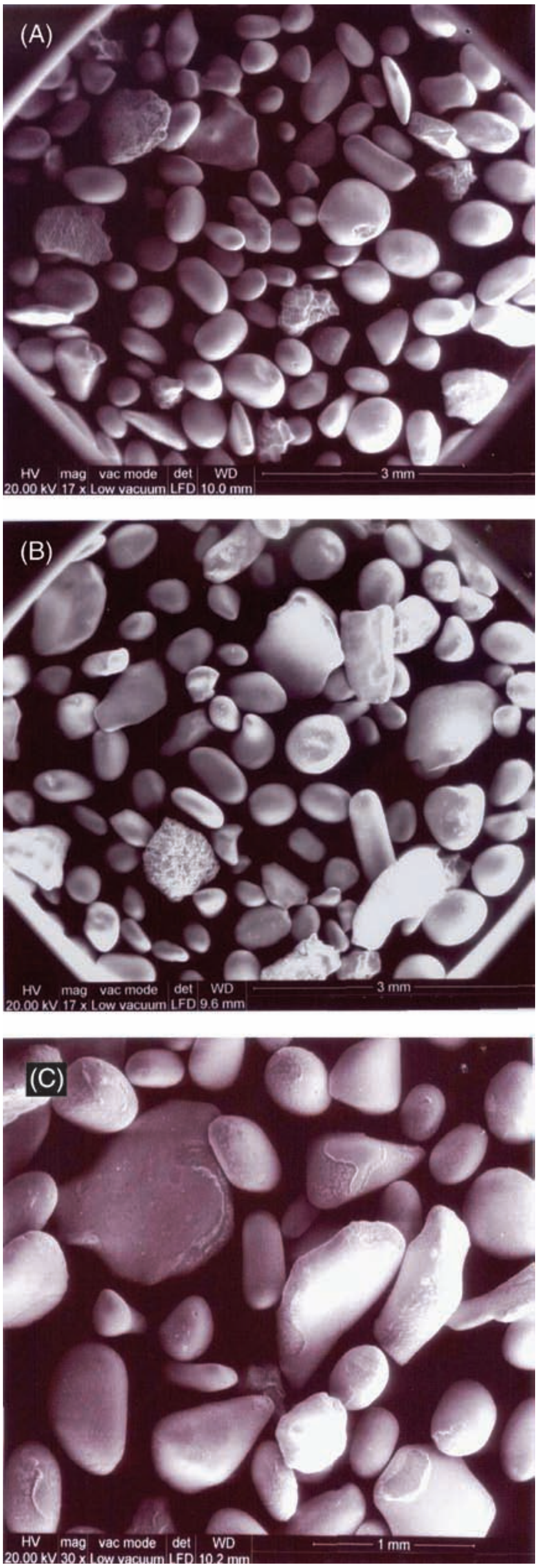

Fig. 2. SEM images: (A) NA (B) NA-Na and (C) Cu-loaded NA-Na.

NA-Na, Fig. 1(B), sodium was indicated to present at positions: X1, X2, X3, and X4. For Cu(II)-loaded NA-Na, Fig. 1(C), sodium ion was recorded at the same positions with intensities as for NA-Na. This observation gives: first, stable substitution of sodium ion in the lattice; second, sodium ion was not replaced by Cu(II), i.e. ion exchange cannot be suggested. The Cu(II)-removal does not affect the lattice (Cu did not give any signal) and removal can be suggested to be amorphous Cu-precipitation on the NA-Na surface.

X–ray fluorescence analysis: Table 1, indicates the presence of Si element in the samples of NA, NA-Na and Cu(II)-loaded NA-Na. X–ray diffraction does not give the same indication. This observation may be due to the presence of some insoluble foreign material in the sample (e.g. sand). X–ray fluorescence analysis gives marked different carbon-percentage with respect to elemental analysis for NA. This may be due to the exposure of NA-grain surface to different random erosion and interaction events with the surrounding materials whereas elemental analysis investigates the bulk mass. Although NA-Na was washed several times after treatment, X–ray fluorescence showed presence of Na element on its surface with about 1% which suggests inclusion of Na in the NA lattice structure and this is in agreement with X–ray diffraction result. This substitution is suggested to be facial and/or sub-facial where Na ions replaced some Ca ions. For Cu element, X–ray fluorescence shows that this element is present in Cu(II)-loaded NA-Na sample by about 1% with no significant change in Na elemental percentage.

Flame-photometer measurements showed that the amount of Na ions entered the aragonite matrix upon modification were about 0.17 mole, and the released amount of Ca ions into solution are 0.02 mole. This means that about 0.062 mole of substituted Ca (~76% of exchanged-Ca) are still stuck on the aragonite surface.

SEM images of NA and NA-Na, Fig. 2(A) and (B), are almost identical which may indicate no NaOH-accumulation on NA-Na surface. The grains of Cu(II)-loaded NA-Na sample, Fig. 2(C), has some contours on the surface and this may be due to Cu(II) precipitation.

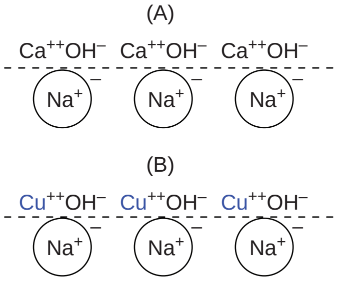

Fig. 3. Aragonite grain surface: (A) after treatment with NaOH and (B) after precipitation of Cu(II).

According to the previous argument, it can be suggested that NaOH treatment of NA causes insertion of some Na ions inside the facial layer of $CaCO_3$ lattice and this insertion follows certain routes after which Na ions occupy specific locations in NA lattice. These locations are mostly that of some exchanged Ca ions. In this case, each site occupied by Na ion is in fact deficient in positivity, i.e. the site is now negative and can be electrically balanced by one positive charge of $Ca^{++}OH^-$ moiety on the outer surface. Hereafter, $Ca^{++}OH^-$ moieties are responsible for the micro-precipitation of heavy metal ions when NA-Na grains were treated by Cu(II) solution. Fig. 3 elucidates this proposal. Imad A.M. Ahmed *et al*. suggested a similar proposal for cadmium fixation by calcite and discussed the Diffusion mechanism [7].

3.2. Cu(II)-removal by NA-Na, general discussion

NA showed a limited capability to remove Cu(II) from an aqueous solution at ambient temperature; 25°C, where the removal was 22.5%. At a higher temperature; 50°C, the removal increased to 83.5%. Accordingly, ion exchange is proposed as the mechanism of removal and higher temperature is favourable to enhance the process [1]. The higher temperature is not favoured for many applications due to unsuitability and/or power consumption. Besides, ion exchange works successfully for mild concentrations (~700 ppm) which is not the case for trace-contamination cases (≤50 ppm), especially for heavy metals, in which the presence of competing alkali and alkaline earth ions may diversely affect the removal process [8].

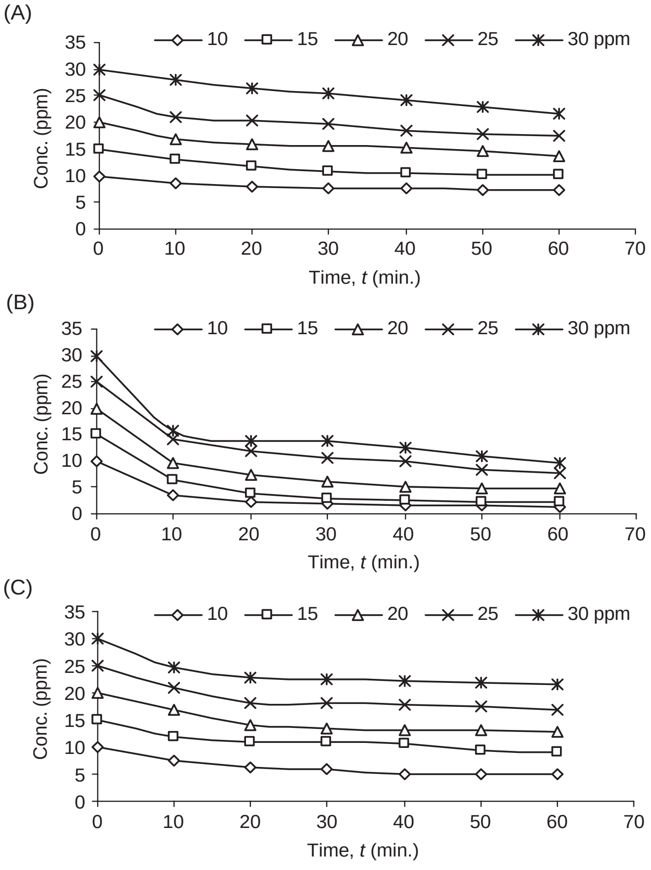

Fig. 4. Decrease in concentration of Cu(II) with time at different initial concentration values for different temperatures: (A) 5, (B) 25 and (C) 50°C.

In comparison with NA, NA-Na showed enhanced removal performance with respect to temperature. Fig. 4 clarifies that the decrease of Cu(II) uptake follows the following order: 25, 50 and 5°C, i.e. ambient temperature is favoured over higher or lower temperatures. This can be explained as follows: at higher temperature (50°C), the solubility of Cu(II) increases which inhibit considerable micro-precipitation which causes less significant removal compared to ambient one (25°C), but ion exchange may contribute for some Cu(II)-removal and that is why at 50°C the removal is higher than at 5°C. At 5°C, ion exchange is not preferred and micro-precipitation process is very slow. It is likely that NA-Na retains some of its ion exchange characteristics and that is why 50°C case showed notable removal when compared to 5°C case. A similar conclusion was given by köhler *et al*. [9]. They found that cadmium removal by aragonite occurs by surface precipitation of otavite, $CdCO_3$.

In general, we can conclude that for NA-Na, micro-precipitation is the main mechanism of adsorption with some contribution of ion exchange.

3.3. Effect of initial concentration (adsorption isotherm)

Fig. 5 shows the equilibrium capacity of Cu(II)-removal, q_e, against equilibrium concentration of Cu(II), C_e, at 5, 25 and 50°C. At 25 and 50°C, the Cu(II)-isotherms are regular, positive and concave (initial rapid increase) to the concentration axis, C_e, and these are of type I according to Brunauer's classification which represents the Langmuir adsorption model [10]. At 5°C, smooth and slow increase of q_e with C_e is in contrast to the other two temperatures and clearly implies that low temperature diversely affect the adsorption [8].

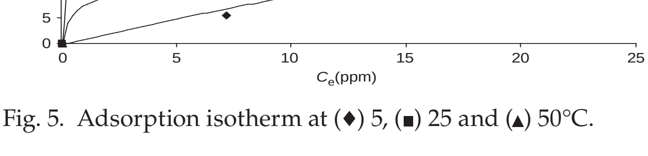

Fig. 5. Adsorption isotherm at (◆) 5, (■) 25 and (▲) 50°C.

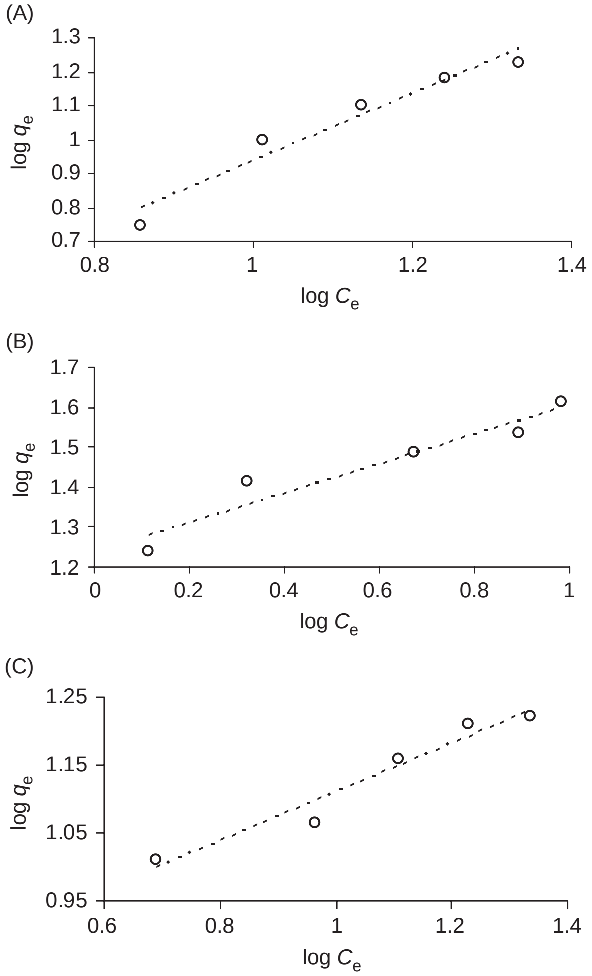

Fig. 6. Freundlich adsorption isotherm of Cu(II) for different temperatures: (A) 5, (B) 25 and (C) 50°C.

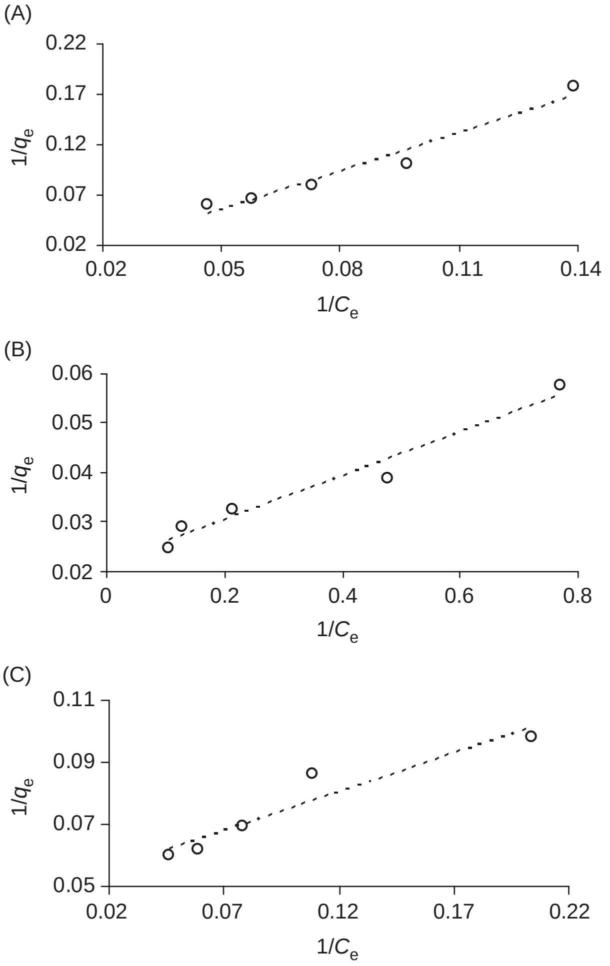

Fig. 7. Langmuir adsorption isotherm of Cu(II) for different temperatures: (A) 5, (B) 25 and (C) 50°C.

The initial rapid increase in equilibrium capacity, especially at 50°C reflects the probable positive effect of ion exchange mechanism in the whole adsorption process, i.e. there are NaOH-free areas of NA grains which can effectively contribute to the adsorption process.

Figs. 6 and 7 present the linear plots of the data of adsorption isotherms according to the Freundlich and Langmuir models respectively. From these plots, related constants were calculated. The known linear forms of these two models are given below:

Freundlich [11,12]:

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

Langmuir [13,14]:

$$\frac{1}{q_e} = \frac{1}{Q_\circ} + \frac{1}{bQ_\circ C_e}$$

The Freundlich model parameters q_e, C_e, K_F and n represent the amount of adsorbate adsorbed at equilibrium (mg/g), equilibrium concentration (mg/L), constant related to adsorption capacity and adsorption intensity respectively. The Langmuir model parameters parameters Q_o and b are the adsorption capacity (mg/g) and constant related to the energy of sorption (l/mg) respectively. The parameter b reflects quantitatively the affinity between the sorbent and the sorbate at considered conditions [8]. For each experimental data set, the parameters of each equilibrium model, correlation factor and standard error were determined by linear regression applying Microsoft Excel programme and are presented in Table 2. The two models, for each data set, showed that all correlations were significant (probability that variables are uncorrelated <5%) [15]. The values of parameters, slope and intercept of the two models given by regression, where analysed and linearity with 95%-confidence was concluded. The standard deviations

Table 2
Data-fitting of Cu(II)-adsorption isotherm by Freundlich and Langmuir models*:

Temp. (°C)	Freundlich	Langmuir
5	k_F ((mg/g)(mg/l)^n) = 1.1 (±0.1496) $1/n$ = 0.980 (±0.1326) r = 0.9739 SE = 0.050	Q_o (mg/g) =19.8 (±0.0147) b (l/mg) = 0.204 (±0.1649) r = 0.9761 SE = 0.012
25	k_F ((mg/g)(mg/l)^n) = 17.3 (±0.0397) $1/n$ = 0.367 (±0.0582) r = 0.9643 SE = 0.043	Q_o (mg/g) = 108.7 (±0.0023) b (l/mg) = 0.481 (±0.0054) r = 0.9789 SE = 0.003
50	k_F ((mg/g)(mg/l)^n) = 5.6 (±0.0511) $1/n$ = 0.36 (±0.0470) r = 0.9752 SE = 0.024	Q_o (mg/g) = 46.5 (±0.0052) b (l/mg) = 0.007 (±0.0459) r = 0.9522 SE = 0.006

*Standard deviation values of the models' parameters, according to fitting, are given in parentheses.

of these parameters are comparatively low. Recommended model that best represents these data sets was selected according to the argument about correlation factor, *r*, and standard errors, *SE*.

Langmuir model gives less standard error, *SE*, for all cases, which imply better prediction of q_e values than prediction by Freundlich model. The correlation factor, *r*, gives indication that adsorption process follows Langmuir model at 5 and 25°C and this is due to predomination of micro-precipitation mechanism, i.e. the NA-Na surface can be considered energetically homogenous in this case. However, at 50°C, Freundlich model gives notable better fit, according to correlation factor, and this is in agreement with the proposal declared earlier that ion exchange contribute in the adsorption process beside micro-precipitation, i.e. NA-Na surface can be considered heterogeneous in this case. It can be concluded that mechanism of removal is temperature sensitive.

According to Freundlich model, the values of $1/n$ parameter fulfil the condition of favouring the adsorption process ($0<1/n<1$) for three temperatures studied. The values of k_F indicate that maximum adsorption occurs at 25°C. The Langmuir parameter *b* has highest value for the same temperature. This suggests highest chemical adsorption at this temperature. The Langmuir model gives capacity of 108.7 mg/g at 25°C.

3.4. Effect of shaking time on adsorption

The variation of adsorbed amounts of Cu(II) with time at different temperatures (5, 25 and 50°C) is shown in Fig. 4. The figure clearly indicates that removal is effective at 25°C and fast during the first 10 min where about half of initial concentrations were removed.

Data from plots of Fig. 4 was employed for the investigation of adsorption kinetics using two models: pseudo-first order, and pseudo-second order. The linear form of these models can be expressed as follows [16]:

pseudo-first order:

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303}$$

pseudo-second order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where q_e and q_t (mg/g) are the solute amounts adsorbed by the resin at equilibrium and time *t* respectively. The parameters k_1 (min^{-1}) and k_2 (g/mg min) are the adsorption rate constants. The experimental adsorption capacity (q_{exp}) at equilibrium was calculated using the following equation:

$$q_{exp} = \frac{(C_o - C_e)V}{M}$$

where *V* (L) is solution volume and *M* (g) is the mass of the adsorbent. The values calculated from this equation were compared to those estimated by the kinetics models.

Linear regression using experimental data was performed to determine the parameters of each kinetic model. Correlation factor, *r*, and standard errors, *SE*, were also determined. The two models, for each data set, showed that all correlations were significant [15]. The linearity with 95%-confidence was concluded according to analysis of the values of parameters slope and intercept given by regression of the two models. The standard deviations of these parameters are comparatively low. To recommend a model to best represent these data sets, correlation factors, *r*, and standard errors, *SE*, were considered.

The linear plots of the two models are shown in Figs. 8 (pseudo-first order) and 9 (pseudo-second order), and corresponding parameters, correlation factors and standard errors are summarized in Table 3.

From the table, the correlation factor, *r*, indicates pseudo-second-order model better fits most data sets (except two conditions) than pseudo-first-order model and may be assigned to represent the kinetic Cu(II) removal by NA-Na. On the contrary, standard errors, *SE*, are less for pseudo-first-order model except for 25°C cases. This may be due to contribution of more than one mechanism in removal process. Each capacity value of the pseudo-first-order model (q_e) is considerably higher than the corresponding experimental capacity (q_{exp}). Although those of pseudo-second-order are still higher than experimental capacities, we can say that they are more representative. Assigning pseudo second-order to represent the kinetic Cu(II) removal by NA-Na suggests one step chemisorption, reversible and initial concentration-dependent removal process [8,17]. The dependency on initial concentration is clear from Table 3, as C_i increases, q_e increases and this may reflect the driving force of initial concentration on the adsorption process which also indicates its reversible nature [18,19]. Although micro-precipitation was suggested to be the dominant mechanism of removal, it seems that as initial concentration increases, another mechanism (ion exchange) may contribute in the process.

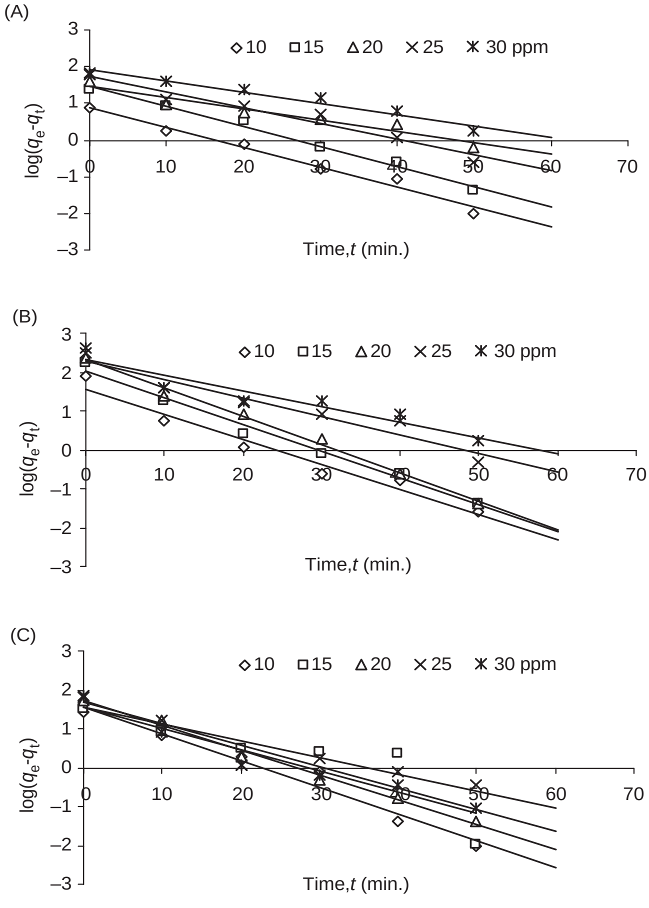

Fig. 8. Removal kinetics according to pseudo-first-order model of Cu(II) for different temperatures: (A) 5, (B) 25 and (C) 50°C.

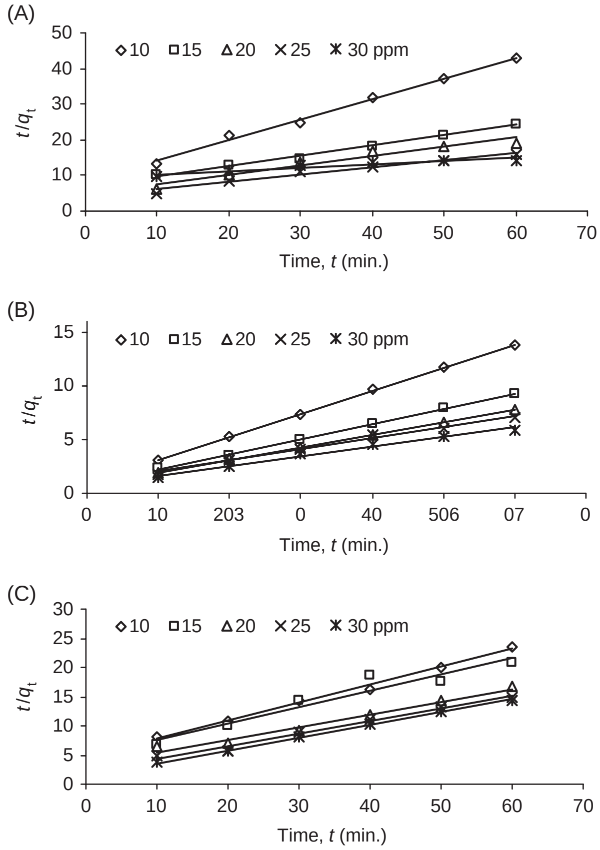

Fig. 9. Removal kinetics according to pseudo second order model of Cu(II) for different temperatures: (A) 5, (B) 25 and (C) 50°C.

4. Conclusion

Tremendous amounts of natural aragonite are present in Egyptian northern cost, in the form of crushed seashells. This material can be used for the removal of heavy metal traces from waste water. The mechanism is ion exchange and favours higher temperature over ambient temperatures in the country. By simple modification through alkaline treatment, using NaOH solution, the

Table 3
Kinetics-data fitting of Cu(II)-removal according to pseudo first and second order models.

Tem. (°C)	C_i	q_e (exp.)	pseudo first order				pseudo second order			
			k_L	q_e	r	SE	k_H	q_e	r	SE
5	10	0.56	0.13 (±0.0040)	7.7 (±1.3)	0.9890	0.17	0.04 (±0.77)	1.7 (±0.02)	0.9976	0.83
	15	0.98	0.13 (±0.0029)	29.7 (±1.2)	0.9945	0.12	0.01 (±0.48)	3.5 (±0.01)	0.9964	0.51
	20	1.26	0.07 (±0.0039)	28.5 (±1.3)	0.9695	0.16	0.01 (±1.28)	3.8 (±0.03)	0.9700	1.38
	25	1.52	0.10 (±0.0044)	55.3 (±1.4)	0.9797	0.19	0.01 (±0.73)	4.9 (±0.02)	0.9836	0.79
	30	1.68	0.07 (±0.0030)	85.7 (±1.2)	0.9811	0.13	0.001(±0.60)	10.7 (±0.02)	0.9490	0.65
25	10	1.74	0.15 (±0.0063)	36.6 (±1.6)	0.9813	0.26	0.05 (±0.06)	4.7 (±0.01)	0.9999	0.07
	15	2.58	0.16 (±0.0042)	105.1 (±1.3)	0.9927	0.18	0.02 (±0.06)	7.1 (±0.01)	0.9998	0.07
	20	3.06	0.17 (±0.0033)	200.8 (±1.3)	0.9958	0.14	0.02 (±0.05)	8.5 (±0.01)	0.9998	0.06
	25	3.44	0.11 (±0.0062)	197.0 (±1.5)	0.9686	0.26	0.01 (±0.18)	9.7 (±0.01)	0.9958	0.2
	30	4.08	0.09 (±0.0068)	204.2 (±1.6)	0.9477	0.28	0.01 (±0.23)	11.1 (±0.01)	0.9918	0.24
50	10	1.02	0.16 (±0.0061)	36.8 (±1.7)	0.9847	0.17	0.02 (±0.41)	3.3 (±0.01)	0.9976	0.44
	15	1.16	0.13 (±0.0163)	46.2 (±4.3)	0.8622	0.12	0.02 (±1.57)	3.6 (±0.04)	0.9602	1.69
	20	1.44	0.15 (±0.0030)	51.2 (±1.3)	0.9955	0.16	0.01 (±0.66)	4.6 (±0.02)	0.9878	0.71
	25	1.62	0.10 (±0.0083)	34.7 (±2.1)	0.9334	0.19	0.02 (±0.52)	4.7 (±0.01)	0.9923	0.56
	30	1.66	0.12 (±0.0065)	34.4 (±1.8)	0.9721	0.13	0.04 (±0.17)	4.5 (±0.01)	0.9992	0.18

* Standard deviation values of the models' parameters, according to fitting, are given in parenthesis.

mechanism changed to micro-precipitation which suits the dominant temperature. It is suggested that NaOH-treatment causes inclusion and fixation of Na$^+$ ions inside the CaCO$_3$ lattice and an isomorphous substitution with Ca^{++} ions occurred. Sites of Na$^+$ ions, which are positive-deficient, were balanced by a hydroxyl groups on the grain surface in the form of Ca^{++}OH$^-$ moieties. Presence of OH$^-$ on the surface is responsible for Cu(II) removal from water through micro-precipitation.

The values of correlation factor give indication that Cu(II) adsorption process follows Langmuir model at 5 and 25°C and this is due to micro-precipitation, and grain surface is considered energetically homogenous in this case. Whereas at 50°C, Freundlich model gives better fit due to contribution of ion exchange with micro-precipitation in the removal process. For ambient temperature (25°C), the Langmuir model gives capacity of 108.7 mg/g which is promising value for the metal-treatment of wastewater. In general, the correlation factor and standard error values indicate pseudo second-order model to fit the kinetic data better than pseudo-first-order. This suggests that the removal process is one step chemisorptions, reversible, and initial concentration-dependent removal process.

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