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CALCIUM REMOVAL FROM AQUEOUS SOLUTION BY MARINE CYANOBACTERIUM, *GLOEOCAPSA* SPECIES: ADSORPTION KINETICS AND EQUILIBRIUM STUDIES

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ABSTRACT

Calcium is an essential macronutrient required for healthy human life. It is abundantly present in seawater and its extraction is possible through biological means by using cyanobacteria. Efficiency of the marine cyanobacteria in removal of calcium is little known. Hence, the present work analysed adsorption kinetics of calcium from aqueous solution by using the marine cyanobacterium (*Gloeocapsa* sp.) in batch culture methods. The effect of initial calcium concentration, temperature, and adsorbent mass on calcium removal was tested. The process of calcium adsorption followed pseudo second-order rate expression and obeyed the Langmuir's model with high correlation coefficient (R2>1). The results indicate that *Gloeocapsa* species is a potential adsorbent for calcium, as evident by its high calcium adsorption value under optimal culture conditions.

Key wards: Cyanobacteria; calcium removal; *Gloeocapsa* sp., phytoremediation

1. INTRODUCTION

Cyanobacteria are photosynthetic and nitrogen-fixing prokaryotes, and their salinity tolerance and other stress tolerance phenomena are dependent on calcium ions. These organisms also have a number of calcium-mediated processes, such as sporulation, akinete formation, heterocyst differentiation, and nitrogen fixation. The photosynthetic system-II of the cyanobacteria depends on the concentration of calcium, and this process may enhance photosynthesis to overcome the decreased photon flux. The role of calcium as a second messenger and calmodulin, a signal transducer protein in the osmoregulation is very vital in this process. Another indispensable role of calcium ions is protecting the oxygen sensitive enzymes like nitrogenase for the nitrogen-fixation. An increase in the inorganic phosphate has been reported by addition of calcium in the cultures of cyanobacteria. Hence, calcium is an essential nutrient element for the optimum growth and biochemical activities.

Marine cyanobacteria have been exploited for improving the process of brine purification *in situ* by removing the calcium impurity through biological means which is cost-effective and requiring no external source of energy, chemical or labor. There are series of steps carried out to develop this eco -friendly technology which does not liberate or produce any hazardous substance in the environment rather the extra biomass produced can be used as an aqua feed. The euryhaline species of cyanobacteria have a wide range of salinity tolerance as they can survive and function efficiently and it is also reusable. The unique biochemical properties of cyanobacteria in leaching the calcium without any extra effort provide them an ecological niche for future field trials in salt farms. In this regard, the present work analysed adsorption kinetics of calcium

from aqueous solution by using the marine cyanobacterium (*Gloeocapsa* sp.) in batch culture.

2. MATERIAL AND METHOD

2.1. Adsorbent

The microbial cultures were obtained from Marine Biology Microbial Culture Collection Centre, Annamalai University, India. Eight strains of microbes that included three strains of *Cyanobacteria* spp., three of *Tharustochytrids* spp., and two of *Trichoderma* spp., were cultured for biomass by using specific production media. They were screened for calcium adsorption and identified the strain *Gloecapsa* species (CAS211) as an efficient one for the process and, it was used for further kinetics study as an adsorbent.

2.1.2.Adsorbate

The synthetic stock solution of calcium (1000 mg/L) was prepared using $CaCl_2$ (Hi media Mumbai) by dissolving in double distilled water. The stock solution was diluted with distilled water to obtain desired concentrations ranging from 0 to 100 mg/L. Solutions of the 0.1M HCl and 0.1 M NaOH were used for pH adjustment.

2.1.3. Analytical method

Calcium analysis was conducted by titrimetric method [1]**.** All samples were analyzed after filtering within 24 h of collection.

2.2.Batch kinetics experiments

Batch experiments were conducted for optimum dose, equilibrium time and effect of concentrations. *Gloeocapsa* biomass was added as per dose requirements to Erlenmeyer conical flask of 100 ml capacity with 50 ml of calcium solutions of desire concentration (10-100 mg/L) and pH range of 7-8.5. The flasks were capped and placed on a mechanical shaker at a speed of 140 rpm at 24 °C, and the samples were taken at regular intervals. All samples were filtered by using a Whatman filter paper and analyzed for calcium. The amount of adsorbed calcium (Ca) was calculated using Equation (1) by the difference of initial and residuals amounts of Ca in solution divided by the mass of adsorbent. The removal efficiency, R_e (determined as the Ca removal percentage relative to initial concentration) using Equation (2) of the system,

$$q_e = \frac{(Co-Ce)}{M} X V \quad \text{----- (1)}$$

$$R_e = \frac{(Co-Ce)}{Co} X 100 \quad \text{------- (2)}$$

was calculated as:

Where, q_e (mg/g) is the amount of the calcium adsorbed per unit mass of *Gloeocapsa* sp. C_0 and C_e are the initial and equilibrium (or at any time) ion concentration (mg/L), respectively, V is the volume in liter of solution and M is the mass (g) of the *Gloeocapsa* sp. biomass.

2.3. Batch isotherms studies

After determining the optimum pH, temperature and equilibrium time, isotherm studies were conducted by varying the biomass of *Gloeocapsa* sp. Representative masses (0,5,10,15,20,25,30,35g/100) of *Gloeocapsa* sp. were added into 25 ml of solution containing 50 mg/L of calcium for 45 min as equilibrium time for calcium. The initial pH of the calcium solutions was adjusted to an optimum value of 8.5 with 0.1 M NaOH or HCl.

2.3.1. Effect of adsorbent dose

The experiment was carried out to find out the optimal dosage of adsorbent for the removal of calcium from the aqueous solutions. *Gloeocapsa*

sp. biomass dosage varied from 0 to 35 g/100ml and equilibrated for 45 min at an initial concentration of 50 mg/L.

2.3.2. Effect of contact time

The experiment was carried out to find out the equilibrium time for the removal of calcium for the different initial concentrations of 10, 20, 30, 40 and 50 mg/L. The optimum adsorbent dosage was taken as constant as 20 g/100ml and equilibrated for 45 min.

2.3.3. Effect of initial concentration

The effect of initial calcium concentration in the range of 10 to 50 mg/L on adsorption was investigated under the specified conditions (initial pH of 8.3; contact time of 45 min; adsorbent dosage of 20 g/L; and temperature of 24^{o}C).

2.4. Adsorption isotherms

The different initial concentrations of calcium were prepared and batch adsorption studies were carried out to check the Langmuir adsorption isotherms under the specified conditions (initial pH of 8.3; contact time of 45 min; adsorbent dosage of 20 g/L; initial Ca concentration varied from 10 to 50 mg/L; and temperature of 24^{o}C). The analysis of calcium was performed by titrimetric method.

2.5. Adsorption Kinetics

Kinetics measurements were performed in a glass vessel equipped with a mechanical stirrer in static conditions. The optimum dose of 20 g/L of adsorbent was contacted with 100 mL calcium solution of a known concentration (10 and 50mg/L) of calcium. The concentration of calcium from the aqueous solution was determined at known time intervals. The analysis of calcium was performed by titrimetric method.

2.6. Calcium removal from aqueous solution using *Gloeocapsa* sp.: adsorption kinetics and equilibrium studies

2.6.1. Effect of adsorbent dose

The effect of the adsorbent dose was studied at temperature (24^{o}C) by varying the adsorbent amounts from 5 to 35 g/100ml. For all these runs, initial concentration of calcium was fixed as 50 mg/L. The figure 1 expresses the adsorption of Ca which increased rapidly with increasing biomass of *Gloeocapsa* sp., due to greater availability of the surface area at higher biomass of the adsorbent. The significant increase in uptake was observed when the dose was increased from 5 to 20 g/100mL. Any further addition of the adsorbent beyond this did not cause any significant change in the Considering this fact the amount of adsorbent was taken as 20 g/100ml for the subsequent studies.adsorption. The maximum removal of calcium was obtained in the adsorbent dose of 20 g/100ml.

2.6.1.1. Effect of contact time

Adsorption of calcium was measured at a given contact time for five different initial calcium concentrations of 10, 20, 30, 40 and 50 mg/L. Biomass of *Gloeocapsa* sp. was used as an adsorbent in bench-scale studies. The figure 2 reveals that the per cent calcium removal was high at the beginning. This was probably due to larger surface area of the biomass being available at beginning for the adsorption of calcium. As the surface adsorption sites became exhausted, the uptake rate was controlled by the rate at which the adsorbate was transported from the external to the internal sites of the adsorbent particles. The maximum per cent calcium removal was attained after about 75 min of shaking time at different concentrations. The increasing contact time increased the calcium adsorption and it remained constant after equilibrium was reached in 45 min for different initial concentrations.

2.7. Kinetic studies

2.7.1. *Adsorption Kinetics*

The adsorption kinetic data of calcium were analyzed by using two kinetics models

$$\frac{dq_t}{Dt} = k_1 (q_e - q_t) \quad \text{--- (3)}$$

mainly, pseudo-first order, pseudo-second order rate equations. The pseudo-first order kinetics rate equation [3] is expressed as follows:

Where k1 is the pseudo-first order rate constant, qe represents adsorption capacity. The integrating rate law by applying the initial condition of t = 0 to t and qt = 0 to qt, Equation (3) becomes:

$$\text{Log}\,(q_e - q_t) = \log q_e - (k_1/2.303)\,t \quad \text{---- (4)}$$

Where, qe and qt both (mg/g) are the amount of calcium adsorbed per unit of biomass of *Gloeocapsa*. spp at equilibrium and time t. respectively, and K_1 the rate constant (1/min). The value for the K_1 was calculated from the slope of the linear plot of log (qe - qt) versus t [Figure 3. (a)]. The K_1 values and correlation coefficients R_2 are given in Table 1. The pseudo-second order reaction rate equation of Ho et al.[2] is used to study the kinetics of adsorption of calcium. This model was also applied to assess the kinetics of adsorption of calcium on biomass of *Gloeocapsa* sp. The equation is as follows:

$$\frac{dq_t}{Dt} = k_1 \quad (q_e^2 - q_t^2) \quad \text{---- (5)}$$

Where k_2 is the rate constant of pseudo second-order adsorption. The integrating rate law Eq.(5), after applying the initial conditions[5] and rearranging it gives as linearized form of pseudo second-order rate kinetics expressed as follows.

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

In addition, initial rate of adsorption is h is

$$h = k_2\, q_e^2 \quad \text{------- (7)}$$

Where, qe and qt both (mg/g) are the amount of calcium adsorbed per unit of mass of biomass of *Gloeocapsa* sp. at equilibrium and time t. respectively, and K_2 is the rate constant of pseudo second order adsorption (g/mg min). The kinetics plots between t/qt versus t were plotted for the different initial concentrations [Figure 4]. Slope and intercept values were solved to give the value of pseudo-second order rate constant (Table 1). Figure 3 and Table 1 show that highly significant regression line (R^2>1) and the data were well fitted only to the pseudo second-order rate equation. The straight line indicates that the process follows a pseudo second order kinetics for various concentration of calcium. While the initial calcium concentration increased from 10 mg/L to 50 mg/L, the adsorption capacity, qexp, decreased from 0.723 to 0.093 mg/g. This indicates that the initial calcium concentration plays a key role in determining the adsorption capacity of calcium by *Gloeocapsa* sp. It is also observed in table 1 that when initial calcium concentration increased from 10 to 50 mg/l, the rate constant, k_2 decreased from 80.01×10^{-3} to 0.013×10^{-3} g/mg/min.

2.7.2. Adsorption Isotherm

The equilibrium adsorption isotherm is of importance in the design of adsorption systems [6]. Several isotherm equations are available and the Langmuir isotherm was selected in this study. The Langmuir adsorption isotherms assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application to many sorption process of monolayer adsorption. The Langmuir adsorption isotherm can be written as:

$$q_e = \frac{q_m b c_e}{1 + b c_e} \quad \text{----- (8)}$$

The Langmuir parameters were obtained by fitting the experimental data to the linearized equation derived from Eq. (8):

$$\frac{C_e}{Q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad \text{---------- (9)}$$

$$\frac{1}{q_e} = \frac{1}{bq_m} \times \frac{1}{q_m} + \frac{1}{q_m} \quad \text{---------- (10)}$$

Where, qe is the adsorbent amount (mg/g) of the calcium, Ce is the equilibrium concentration of the calcium in solution (mg/L), qm is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption (L/mg). Based on Eq. (9) and Eq. (10) the isotherms were fitted to the adsorption data obtained. The Langmuir adsorption exponents for Eq. (9) and Eq. (10), the qm and b are determined from the linear plots of Ce/qe versus Ce and 1/qe versus 1/Ce and calculated correlation coefficients for these isotherms, are shown in Table 2. The values of the Langmuir constant were calculated from the slopes and intercepts of the plots. The magnitude of Langmuir constant b was small (1.616 L/mg) and the adsorption capacity qm was determined as 1.008 mg/g. In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter RL was determined by using the following equation [4]:

$$R_L = \frac{1}{(1 + bc_o)} \quad \text{---------- (12)}$$

Where, C_o is the initial concentration and b is the Langmuir isotherm constant. The parameter RL indicates the shape of isotherm. The process is irreversible if RL = 0, favorable if RL < 1, linear if RL = 1 and unfavorable if RL > 1. The Figure 5 shows that the RL values at different initial calcium concentration indicating a highly favorable adsorption. As shown in Table 2 and Figure 5, the Langmuir equation represents that adsorption process is very well and the correlation coefficient, R_2 value is in a very good mathematical fit.

3. Conclusions

Calcium removal was attained maximum after about 75 min of shaking time at different concentrations. The increasing contact time increased the calcium adsorption and it remained constant after attaining equilibrium in 45 min for different initial concentrations. Adsorption kinetics revealed that the initial calcium concentration plays a key role in determining the adsorption capacity of calcium by *Gloeocapsa* sp. When initial calcium concentration increased from 10 to 50 mg/l, the rate constant, k_2 decreased from 80.01×10^{-3} to 0.013×10^{-3} g/mg/min.

The pseudo-second order kinetic models fit very well with the adsorption behavior of calcium. The amount of calcium uptake at equilibrium increased with increasing concentration of calcium. The parameter RL indicates the shape of absorption isotherm. The process is irreversible if RL = 0, favorable if RL < 1, linear if RL = 1 and unfavorable if RL > 1. The present result showed the RL value of less than 1 at different initial calcium concentrations and it indicated a highly favorable adsorption by *Gloeocapsa* sp., The results of present investigations revealed that *Gloeocapsa* spp. biomass is a potential adsorbent to remove the calcium from aqueous phase (Sea brine). The pseudo-second order kinetic models fit very well with the adsorption behavior of calcium. The adsorption suggested that the adsorption was high at alkaline pH range 7-8.5. The amount of calcium uptake at equilibrium increased with increasing solution concentrations. The findings of the study showed that *Gloeocapsa* sp. biomass has excellent potential for use in the removal of calcium from sea brine and water.

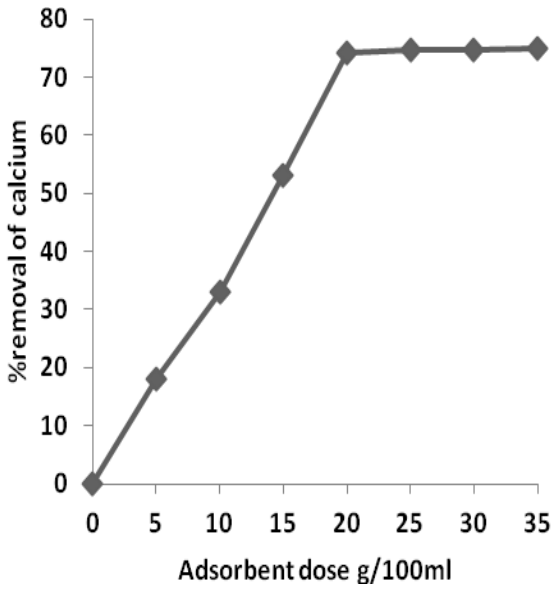

Fig 1. Effect of adsorbent dose on removal of calcium from sea brine solution

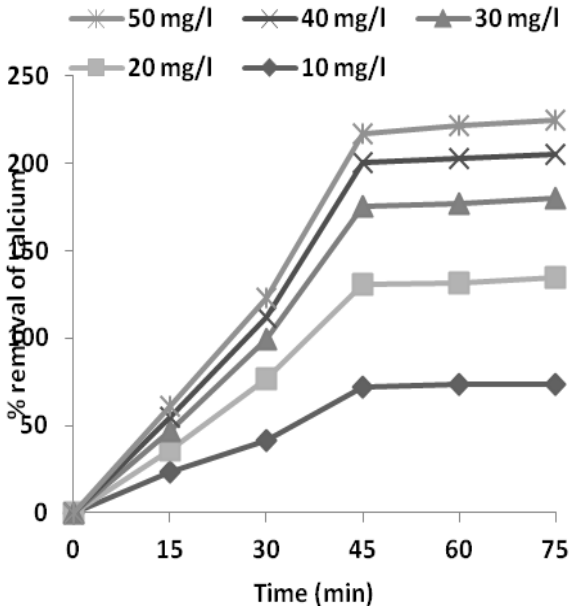

Fig. 2. Effect of contact time on removal of calcium in aqueous solution

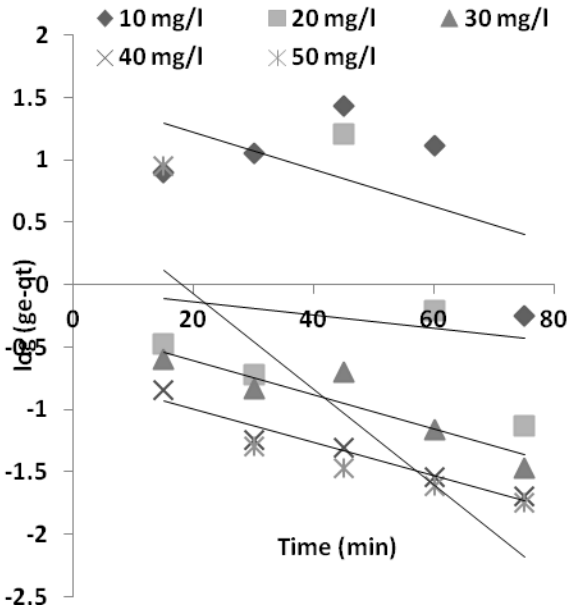

Fig.3 . Kinetics analysis of calcium adsorption by linear plots of (a) pseudo first-order rate equations

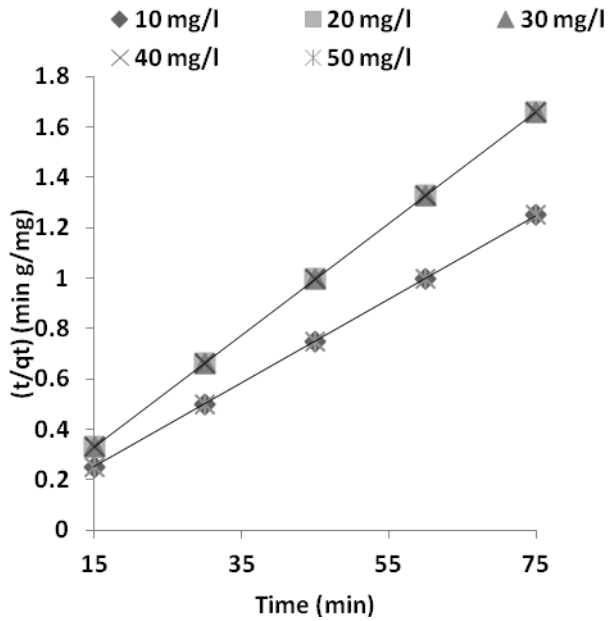

Fig.4. Kinetics analysis of calcium adsorption by linear plots of (pseudo second-order rate equations

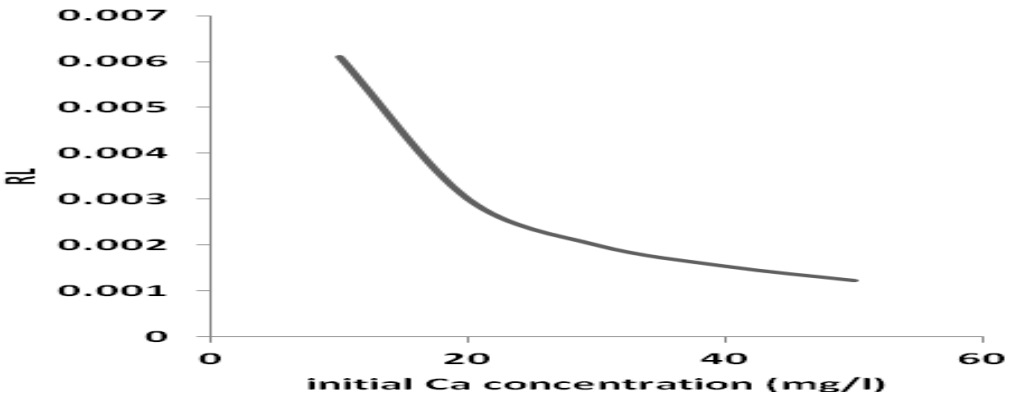

Fig. 12. Separation factor for calcium adsorption using *Gloeocapsa* sp.

Calcium mg/l	Lagergren constants			Pseudo second-order rate constants			
	qexp	K_1 X 10^{-3}	R^2	qe	K_2 X10^{-3}	h X10^{-3}	R^2
1	0.723	0.009	0.299	72.5	80.01	417.72	1
2	0.291	0.016	0.02	58.9	45.45	157.67	1
3	0.151	0.0153	0.83	42.8	45.45	157.67	1
4	0.062	0.0215	0.948	26.5	45.45	157.67	1
5	0.093	0.1961	0.649	16.9	0.013	8.712	1

Table.1. Lagergren constants, pseudo second-order rate constants constants for calcium

Langmuir isotherm parameters	C_e/q_e	1/qe
qm (mg/g)	1.008	1.008
b (L/mg)	1.616	1.616
R2	1	1

Table 2. Langmuir isotherm constant for adsorption of calcium by *Gloeocapsa* sp.

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