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EQUILIBRIUM AND KINETIC STUDIES OF COPPER ADSORPTION BY HALOPHILIC *HALOFERAX* SP. GUSF-1

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Abstract The study was directed to examine the potential of haloarchaeal culture isolated from estuarine salt pan of Goa to adsorb copper ions from saline waters. The effect of certain physicochemical factors such as pH, initial metal concentration, salinity and contact time on adsorption was also assessed. The adsorption process was optimized; performance was evaluated by equilibrium and kinetic studies. The surface chemical functional groups of *Haloferax* sp. GUSF-1 biomass identified by fourier transform infrared (FTIR) were amino, carboxyl, hydroxyl, and carbonyl groups, which may be involved in the adsorption of heavy metals. This research showed that haloarchaeal biosorption had a potential to be used in the removal of heavy metal ions from saline wastewaters.

Keywords: *Haloferax*, Biosorption, Copper, Saline wastewater

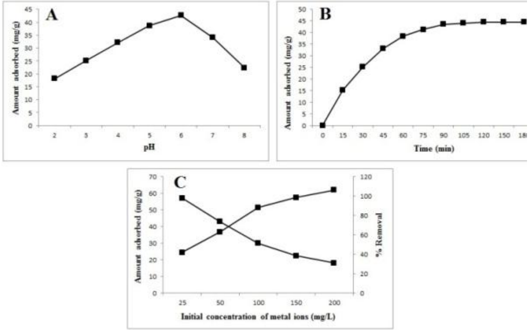
Introduction:

Copper (Cu) which is a heavy metal is essential for various biological functions, including photosynthesis and respiration. Although essential, but at high concentrations it is potentially toxic because of its chemical redox potential and ability to participate in free radical reactions which often causes oxidative stress [1]. It is extensively used in many industries including metal plating, storage batteries, ceramic, petroleum refining and Cu (II)-based fertilizers, fungicides and insecticides. Excessive intake of Cu (II) may lead to acute and chronic copper poisoning, Wilson's disease, and Indian childhood cirrhosis[2].

Materials and Methods: Cells of *Haloferax* spp. GUSF-1 grown in NTYE broth were harvested in stationary phase and washed three times with 15 % saline to remove media components if any. Biosorbent was then prepared by drying the biomass at 120°C followed by grinding using mortar and pestle to obtain a fine powder. Inactivated dead biomass of *Haloferax* spp. GUSF-1 was used as biosorbent for biosorption study. For optimization of pH, experiments were conducted with varying pH from 2.0 to 11.0 at concentration 50 mg/L of Cu(II) ions, 1.0 g/L of biosorbent dose in 10 mL saline metal solution and contact time 60 min. Effect of contact time was studied from 20 to 180 min at optimum pH from above experiments. The effect of the initial Cu(II) ions concentration on the biosorption was studied with varying metal ions concentration from 25 to 200 mg/L at optimum pH and contact time from above experiments. All optimization experiments were performed with 10 mL saline sample in 50 mL conical flasks at 150 rpm. Concentration of Cu(II) ions was determined by atomic absorption spectrophotometer and sorption behavior was analysed by statistical methods described by Oves et al. 2013[3].

Results and Discussion: pH is considered as the key factor in sorption studies as it influences metal binding sites on sorbent and nature of metal in solution. Fig. 1A shows the amount of Cu(II) ions adsorbed by biosorbent at different pH. The amount of all metal ions adsorbed was increased with increasing pH values. Maximum sorption was seen at pH 6. Less sorption at low pH is because of competitive inhibition between H^+ ions and metal ions towards sorbent at low pH. At high pH values deprotonation of functional groups on sorbent causes more negative charge which increases the binding with positively charge metal ions and thereby increases sorption [4].

Figure 1



Effect of contact time on adsorption of Cu(II) ions was studied and illustrated in Fig. 1B. It is clear from the plot that rapid and maximum sorption occurred in 60 min followed by gradual and minimal sorption thereafter. Rapid sorption at initial stage is due to abundance of free sites on sorbent available for metal binding. Later repulsive forces between solute molecules on solid and liquid phases hinder the binding of metal on remaining vacant sites on sorbent thus reducing the sorption. At equilibrium the amount adsorbed by dried biomass of *Haloferax* spp. GUSF-1 was 44.5 mg/g sorbent for Cu(II) ions [5].

It was observed that with increasing initial metal ion concentration sorption capacity (mg g^{-1}) of biosorbent was increased whereas percentage removal of metal ions from solution decreased (Fig. 1C). The maximum percentage removal of 97.84 % for Cu(II) ions was observed at low metal ions concentration (25 mg/L). The percent removal decreased with increasing initial metal ions concentration because at higher concentration, number of ions competing for the available binding sites whereas, at low concentration more binding sites are available for complexation of ions. However, maximum adsorption capacity of Cu(II) was 62 mg/g, at higher concentrations of metal ions at 200 mg/L [6].

The equilibrium data of Cu(II) sorption by dried biomass of *Haloferax* sp. GUSF-1 were evaluated using Langmuir and Freundlich models at different initial metal ions concentration (50 mg/L), sorbent mass (1 g/L), optimum pH (6) and constant temperature (30°C) is shown in Fig. 2. The maximum sorption capacity (Q_{max}) determined from the Langmuir isotherm was found to be 60.97 mg g^{-1} dried biomass for Cu(II). Higher Q_{max} values and lower b values are an indication of better adsorption capacity. Fig. 2B shows the Freundlich plots for Cu(II) sorption by dried biomass of *Haloferax* spp. GUSF-1. In case of Freundlich isotherm, the values of K_f is 15.12, for Cu(II). Further higher values of n (n > 1) confirmed higher intensity of adsorption. The view of high values of coreleation coeffiecients (r^2>0.90) adsorption data of Cu(II) is well described by both the isotherms but fitted best in Langmuir isotherm than Freundlich isotherm. In the Langmuir isotherm b is a Langmuir constant related to energy of sorption [7].

Figure 2

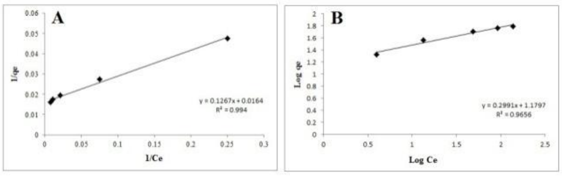


Table 1

Metal ions	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	b (L/mg)	r^2	K_f	n	r^2
Cu^{2+}	60.97	0.129	0.994	15.12	3.34	0.965

Fig. 3 represents the first order and second order kinetic models of Cu(II) sorption by dried biomass of *Haloferax* sp. GUSF-1. The values of constants were calculated from Fig 3 and are displayed in Table 2. The value of pseudo first order rate constant is 0.046 mg/g/min for Cu(II). The value of pseudo second order rate constant is 0.0003 mg/g/min for Cu(II), Value of correlation coefficient (r^2>0.90) indicated the fitness of data in both the models. The correlation coefficient values were higher in pseudo second order kinetic model as compared to pseudo first order kinetic model indicating adsorption of Cu follows pseudo second order kinetic model. Similar results were reported earlier for Mn adsorption by haloarchaeon adsorbent [8].

The biosorbent of *Haloferax* spp. GUSF-1 successfully removed Cu(II) ions from aqueous solution and was affected by initial metal concentrations, pH, and contact time. The maximum biosorption of heavy metals by biosorbent of *Haloferax* spp. GUSF-1 occurred at pH 6 within 90 min at 30 °C.

Figure 3

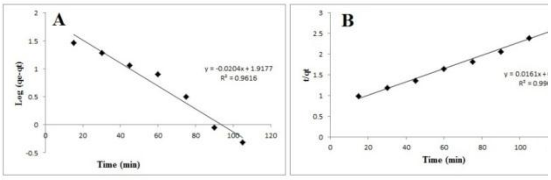
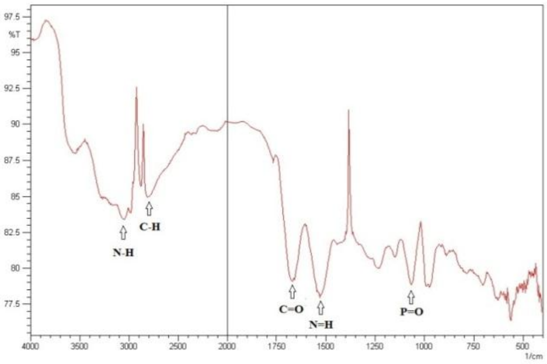


Table 2

Metal ions	Pseudo first order constants			Pseudo second order constants		
	q_e (mg/g)	K_L	r^2	q_e (mg/g)	K_2	r^2
Cu^{2+}	82.73	0.046	0.961	62.11	0.0003	0.990

Further IR spectra of adsorbent after Cu(II) adsorption (Fig. 4) revealed presences of bands at 3274, 2900, 1650, 1527 and 1100 cm^{-1} due to N-H bonds of amine (-NH) groups, $–CH_2$ groups, amide I (C=O), amide II (N=H) bands, and carboxyl (-COOH) or phosphate groups respectively[9] suggesting the involvement of these functional groups in adsorptionprocess.

Figure 4



In conclusion, a successful effort was done to formulate an adsorbent of *Haloferax* sp. GUSF-1 and to adsorb metal from saline solution. The process described herein is simple and can be extended to adsorb and recover metals from saline effluents.

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Figure Legends

Figure-1 Effect of (A) pH (B) Time and (C) Initial metal ion concentration on biosorption of Cu(II) ions on biosorbent of *Haloferax* spp. GUSF-1

Figure-2 Linearised Langmuir (A) and Freundlich (B) adsorption isotherm for Cu(II) ions on biosorbent of *Haloferax* spp. GUSF-1.

Figure 3 Kinetics for Cu(II) adsorption by Cu(II) at different initial Cu(II) concentrations: (A) pseudo–first-order plot; (B) pseudo–second-order plot.

Figure 4 FTIR analysis of adsorbent of Haloferac sp. GUSF-1 after Cu(II) adsorption

Table-1 Equilibrium parameters for Cu(II) adsorption by *Haloferax* spp. GUSF-1 calculated

Table-2 Kinetic parameters for adsorption of Cu(II) by *Haloferax* spp. GUSF-1

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