

Copper (II) and Nickel (II) Sorption onto Seaweed (*Kappaphycus alvarezii*) Waste Biomass: Equilibrium and Mechanism Studies

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Abstract: Cu (II) and Ni (II) sorption were investigated using seaweed (*Kappaphycus alvarezii*) waste biomass. The metal sorption experiments were conducted at different pH values (pH 2-6) and initial metal concentrations (10-50 mg/L). The equilibrium sorption data were fitted to Langmuir and Freundlich isotherms and the isotherm parameters were evaluated at different initial metal concentrations. The metal sorption capacities were found to be pH dependent and increased with initial metal concentration. The maximum observed Cu (II) and Ni (II) sorption capacities (Q_{max}) were 4.5872 and 12.3460 mg/g (according to the Langmuir isotherm). The metal sorption mechanisms were determined to be ion exchange and complexation. In combination, *Kappaphycus alvarezii* waste biomass represents a cost-effective and efficient metal sorbent to remove metal ions.

Key words: Sorption • Copper • Nickel • *Kappaphycus alvarezii*

INTRODUCTION

In recent decades, metal contamination has represented a serious environment concern, as it poses a significant threat to the health and environment [1, 2]. For example, copper pollution in Zambia caused a serious detrimental impact on living organisms [3]. It is therefore necessary to impose stringent regulations on industrial effluents discharged into the environment. The EPA has set maximum Cu(II) and Ni(II) contaminate levels in industrial discharge at 1.0 mg/L.

Metal sorption has become a significant research area in environmental treatment. Metal sorption onto cheap or even waste materials has been proposed as an effective and affordable solution to this global problem [4, 5]. Metal sorption onto seaweed biomass, in particular, has been highlighted due to its favourable metal-binding properties [2, 6]. Numerous reports have been published on metal sorption onto seaweed biomass with varied sorption efficiencies and characteristics [6]. However, limited

studies have been conducted on metal sorption onto seaweed waste biomass generated from hydrocolloid industries.

Metal sorption occurs through interactions including ion exchange, complexation and coordination [7]. Metal sorption performance depends on several parameters such as the pH of the solution, metal concentration and metal composition [8]. For example, Cr(III) sorption onto *Fucus* sp., *Ulva* sp., *Palmaria* sp. and *Polysiphonia* sp. depends on pH and initial metal concentration [9]. Metal sorption onto seaweed biomass could therefore be attributed to cell wall properties i.e., chemical and physical interactions among the ligands on the cell wall surface and metal cations. However, sorption mechanisms remain unclear and hence require further studies [10].

In this work, Cu(II) and Ni(II) sorption were investigated using seaweed (*Kappaphycus alvarezii*) waste biomass arising from the carrageenan extraction process. Cu(II) and Ni(II) sorption experiment were conducted using the batch equilibrium technique and

Cu(II) sorption equilibriums were modeled using Langmuir and Freundlich isotherms. Cu(II) and Ni(II) sorption mechanism were investigated using different chemical techniques and instrumentation (FTIR and SEM).

MATERIALS AND METHODS

Sample Preparation: *Kappaphycus alvarezii* waste biomass was prepared in the laboratory according to the industrial process. Briefly, the seaweed biomass was extracted with aqueous solution at 60°C for 6 hour. The seaweed waste biomass was then separated from the aqueous solution using filter paper (Whatman No 2). The seaweed waste biomass was subsequently washed with distilled water and dried at 60 °C for 24 hours. The dried seaweed waste biomass was then ground in a blender.

Solution Preparation: Cu (II) and Ni(II) stock solution (1000mg/L) was prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ in deionised water. Cu(II) and Ni(II) working solutions with different concentrations were prepared by diluting the stock solution with deionised water. These Cu(II) and Ni(II) solutions were adjusted to the desired pH using 0.1 M HCl and 0.1 M NaOH.

Batch Experiment: Cu(II) and Ni(II) sorption experiments were conducted in a shake flask. The seaweed waste biomass (0.5 g) was added into a flask containing 50 ml metal solution and the solutions were agitated on a rotary shaker at 300 rpm for 3 hours. The samples were then filtered using filter paper (Whatman No 2) and Cu(II) concentrations were analyzed using Atomic Absorption Spectrometer (AAAnalyst 800, Perkin Elmer).

The metal sorption capacities were calculate using the following equation:

$$Q = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where Q (mg/g) is the amount of the metal adsorbed, V (L) is the volume of the metal solution, m (g) is the mass of the biomass, C_0 (mg/L) is initial concentrations of the metal ion, and C_e (mg/L) is the equilibrium concentrations of the metal ion.

Equilibrium Studies: Equilibrium sorption data acquired at different initial metal concentrations were fit to Langmuir (2) and Freundlich (3) isotherms.

$$Q_e = \frac{Q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

$$Q_e = K_F C_e^{1/n} \quad (3)$$

where Q_e (mg/g) is the equilibrium metal concentration on the metal sorbent, C_e (mg/L) is the equilibrium metal concentration in the solution, Q_{max} (mg/g) is the theoretical monolayer maximum metal uptake and K_L (L/mg) is the Langmuir equilibrium constant and K_F (L/g) and n is the Freundlich equilibrium constant.

Mechanism Studies: Cu(II) and Ni(II) sorption mechanisms were studied using different chemical techniques and instrumentation (Fourier transform infrared (FTIR) spectrometry and scanning electron micrometry (SEM)). The ion-exchange equilibriums between the metal solution and metal sorbent were determined using Induced Couple Plasma-Mass Spectrometer (ICP-MS) (Verma *et al.*, 2008). Frequency changes in the untreated and metal-treated seaweed waste biomass were detected using FTIR (Perkin-Elmer). Spectra were recorded in the range 400-4000 cm^{-1} . Morphology changes in the untreated and metal-treated seaweed waste biomass were elucidated using SEM. Micrographs were undertaken at moderate magnification (2000x).

RESULT AND DISCUSSION

Batch Studies: In the present research, Cu (II) and Ni(II) sorption onto *Kappaphycus alvarezii* waste biomass were studied at different pH values (2-6) and initial metal concentrations (10 to 50 mg/L). It was observed that the metal sorption capacity increased with pH but then decreased when the pH was higher than the optimum pH of 3 (Fig. 1).

Specifically, the metal sorption was low at pH less than 2 because active sites were protonated and associated with hydronium ions. The metal sorption was higher at pH in the range 3--4 because more active sites were deprotonated and carried negative charges, which attracted metal ions [11]. Furthermore, Cu (II) and Ni (II) ions were hydrolysed at this pH and facilitating metal sorption.

It was also found that metal sorption capacities increased with initial metal concentration, (i.e., higher metal concentrations created a concentration gradient and hence provided an important driving force to overcome mass transfer resistance between metal sorbent and sorption medium) [12] (Fig. 2). Interestingly, the maximum metal sorption was not reached within the experimental range (10 to 50 mg/L), indicating that active sites were not saturated.

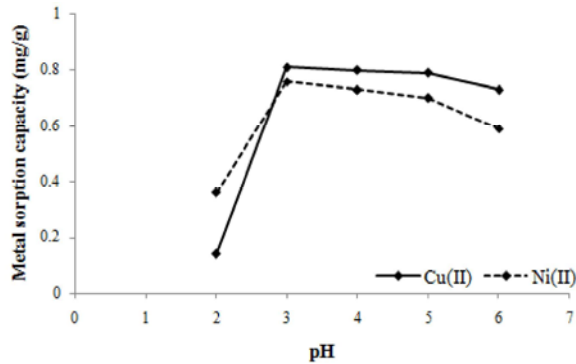


Fig. 1: Effect of pH on Cu(II) and Ni(II) sorption

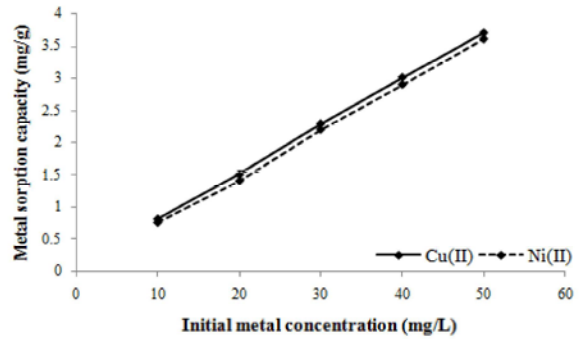


Fig. 2: Effect of the initial metal concentration on Cu(II) and Ni(II) sorption

Table 1: Langmuir and Freundlich isotherm parameters

Metal	Langmuir isotherm			Freundlich isotherms		
	$Q_m(\text{mg/g})$	$K_L(\text{L/mg})$	R^2	$K_f(\text{L/mg})$	$1/n$	R^2
Cu^{2+}	4.5872	0.1466	0.9600	0.6990	0.5929	0.9710
Ni^{2+}	12.346	0.0254	0.9770	0.9070	0.3266	0.9740

Table 2: Cations exchange

Metal solution (50mg/L)	Metal ion released into solution (meq/L)				
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Total
Cu^{2+}	7.38±0.60	8.54±0.02	0.73±0.09	1.40±0.02	18.05
Ni^{2+}	7.53±0.45	8.42±0.19	0.72±0.09	1.46±0.05	18.13
	Metal ion adsorbed onto seaweed waste biomass (meq/L)				
	Cu^{2+}	Ni^{2+}	H^+	Total	
Cu^{2+}	0.37±0.02	-	15.79	16.16	
Ni^{2+}	-	0.34±0.02	15.76	16.10	

Metal Sorption Isotherms: Langmuir and Freundlich isotherms were employed to describe sorption performance. Using these methods, it is possible to characterize metal sorbents under various operational conditions and to optimize the operating procedure.

Langmuir ($1/Q_e$ vs. $1/C_o$) and Freundlich ($\log Q_e$ vs. $\log C_o$) isotherm plots were therefore conducted to derive Langmuir and Freundlich isotherm parameters and correlation coefficients (R^2).

It was observed that equilibrium sorption data fit well to Langmuir ($R^2 > 0.96$ and Freundlich isotherms ($R^2 > 0.97$), indicating that the Cu(II) and Ni(II) sorption using *Kappaphycus alvarezii* waste biomass was monolayer sorption with heterogeneous surface conditions.

Separation Factor (R_L): The Langmuir separation factor (R_L) was applied to estimate either the sorption system favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$).

R_L is calculated from the Langmuir isotherm based equation as follow:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (4)$$

where K_L is the Langmuir equilibrium constant and C_o is the initial metal concentration.

The calculated R_L values indicated that Cu(II) and Ni(II) sorption were favorable ($0 < R_L < 1$) at all initial metal concentrations (Fig. 3).

Surface Coverage (θ): Surface coverage (θ) is expressed as follows:

$$\theta = K_L C_o (1 - \theta) \quad (5)$$

where K_L is the Langmuir equilibrium constant and C_o is the initial metal concentration. The surface coverage values indicated that Cu(II) and Ni(II) sorption were effective at all initial metal concentrations (Fig. 4).

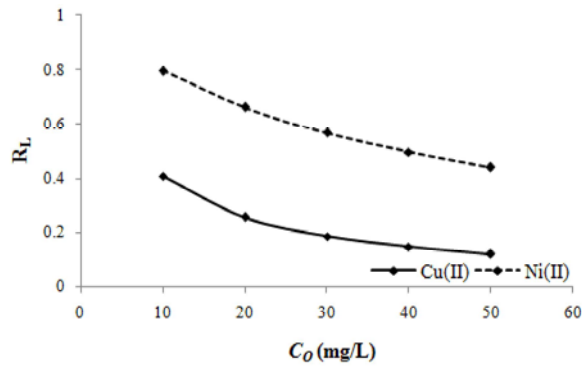


Fig. 3: Separation factor profiles

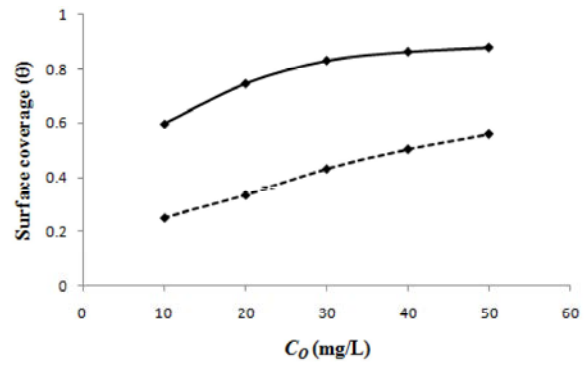


Fig. 4: Surface coverage (θ) profiles

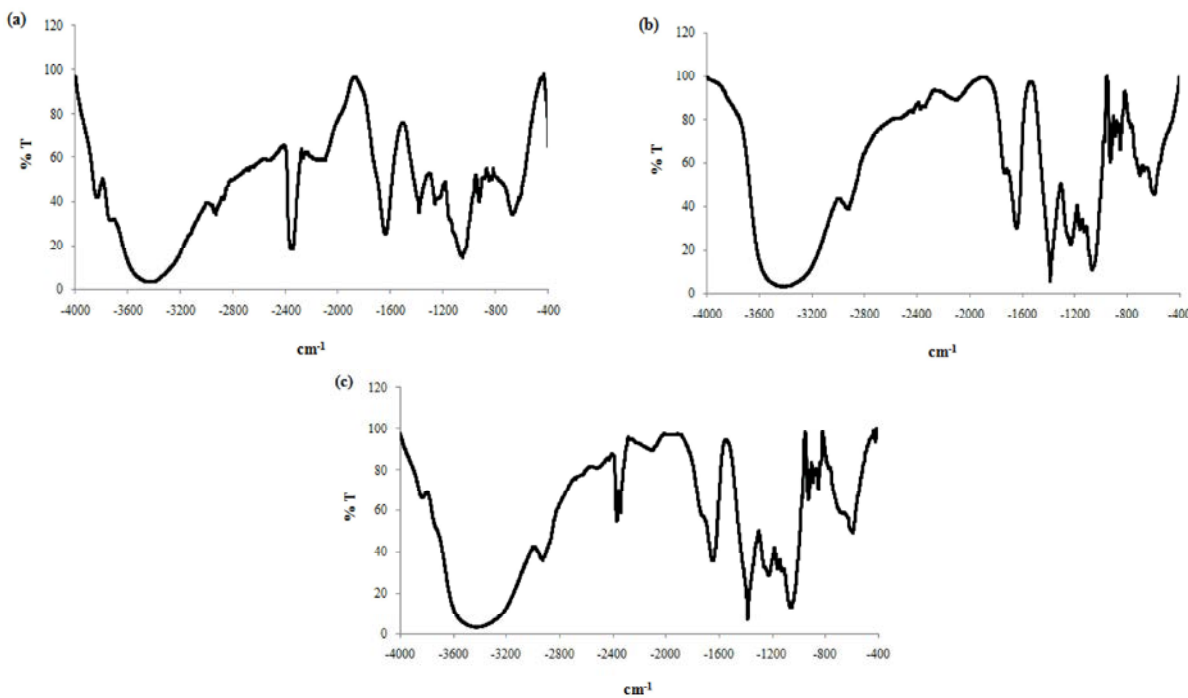


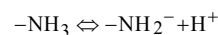
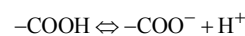
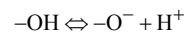
Fig. 5: FTIR spectra of (a) untreated, (b) Cu(II) treated and (c) Ni(II) treated *Kappaphycus alvarezii* waste biomass

In addition, surface coverage on seaweed waste biomass was found to increase with the initial metal concentration.

Metal Sorption Mechanisms

Ionic Balance: The simultaneous change in the ionic equilibrium indicated that the metal sorption occurred through an ion exchange mechanism. However, non-stoichiometric ion exchange showed that ion exchange was not the sole mechanism [10]. It was subsequently found that 18.05 meq/L K^+ , Na^+ , Ca^{2+} and Mg^{2+} were released into the solution and 16.16 meq/L H^+ and Cu^{2+} were adsorbed during Cu(II) sorption. Meanwhile, 18.13 meq/L K^+ , Na^+ , Ca^{2+} and Mg^{2+} were released into the solution and 16.10 meq/L H^+ and Ni^{2+} were adsorbed during Ni(II) sorption.

FTIR Analysis: FTIR analyses were conducted to identify functional groups present in the seaweed waste biomass to explain their possible interactions with Cu(II) and Ni(II) ions (Fig. 5). These functional groups were deprotonated at pH value greater than their acidic dissociation constants and thus interacted with metal ions [11].



Changes in vibration frequencies and absorbance intensities indicated that the metal sorption occurred through complexation interactions (Jha *et al.*, 2009).

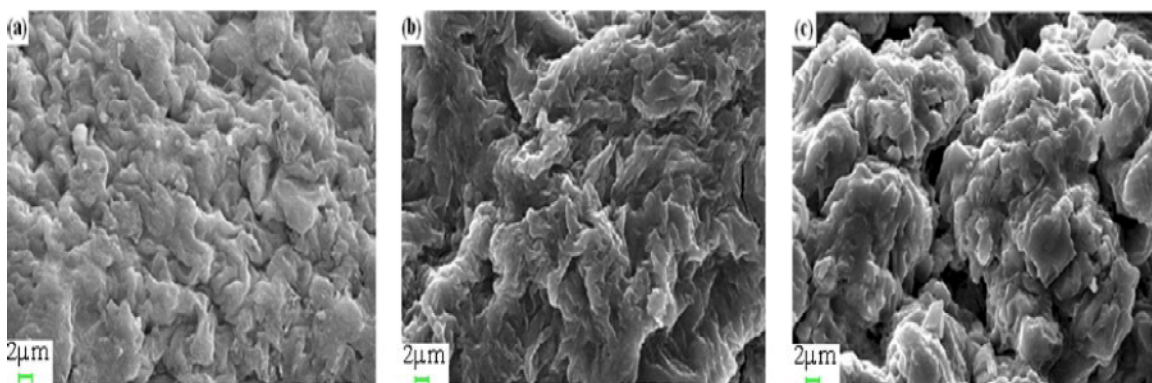


Fig. 6: SEM micrographs of (a) untreated (b) Cu(II) treated and (c) Cu(II) treated *Kappaphycus alvarezii* waste biomass

In addition, -COO stretching shifted from 1642 cm^{-1} to 1647 cm^{-1} , indicating that carboxyl groups formed complexes with the Cu(II) and Ni(II) ions. Furthermore, -C=N peak at 2350 cm^{-1} almost disappeared, indicating that the nitrile groups formed complexes with the Cu(II) ions.

SEM Analysis: SEM analyses were conducted to examine the seaweed waste biomass surface morphologies. Differences in surface morphology indicated that metal sorption further occurred through precipitation. Specifically, Cu(II) and Ni(II) treated biomass was observed to become aggregated, indicating that the Cu(II) and Ni(II) deposited on the surface.

CONCLUSION

The experimental results indicated that *Kappaphycus alvarezii* waste biomass was suitable metal sorbent for the removal of Cu(II) and Ni(II) ions. The metal sorption process was pH dependant and sorption capacities increased with initial metal concentration. Additionally, the equilibrium sorption data were fit to Langmuir and Freundlich isotherms. Furthermore, the main sorption mechanisms identified were ion exchange, complexation and precipitation.

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