

Cadmium (II) Biosorption onto Seaweed (*Kappaphycus alvarezii* and *Eucheuma denticulatum*) Waste Biomass: Equilibrium and Mechanism Studies

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Abstract: Cd(II) biosorption was investigated using seaweed (*Kappaphycus alvarezii* and *Eucheuma denticulatum*) waste biomass. The biosorption experiments were conducted at different pH values (pH 2 - 6), initial Cd(II) concentrations (10 - 100 mg/L) and the chemical compositions Cd-Cu and Cd-Ni. The biosorption capacities were dependent on pH solution and initial Cd(II) concentration. The biosorption capacities was suppressed by Cu(II) and Ni(II) present in the solution. The equilibrium biosorption data were fitted to Langmuir and Freundlich isotherms and the isotherm parameters were evaluated at different initial Cd(II) concentrations. The biosorption mechanisms were ion exchange and surface complexation. Overall, *K. alvarezii* waste biomass exhibited a better biosorption performance than *E. denticulatum* waste biomass.

Key words: Biosorption • Cadmium • Eucheuma Denticulatum • Kappaphycus Alvarezii

INTRODUCTION

Cadmium pollution has become a global phenomenon [1]. Cadmium pollution has caused a significant threat to the health and environment. Therefore, stringent environmental regulation has been imposed on industrial effluents [2]. The Environmental Protection Agency (EPA) has set maximum Cd(II) contaminate levels in industrial discharge at 0.01 mg/dm³.

Biosorption process has become a potential alternative method to conventional treatment technique such as chemical precipitation, ion exchange, membrane filtration and solvent extraction [3]. Biosorption process offers several advantages over conventional treatment methods include economic, efficient and practical [1, 4]. In general, biosorption performance depends on some operating factors such as solution pH, contact time, metal concentration and metal composition [2, 5]. The solution pH may influence biosorption performance through different mechanisms such as site dissociation and metal speciation [6].

Biosorption process could involve several mechanisms such as complexation, coordination, micro-precipitation and ion exchange and it is difficult to distinguish between the single steps [7, 8]. It is important

to understand in depth the biosorption mechanism to optimize operative conditions. However, biosorption mechanisms remain unclear and hence require further studies [9].

Several adsorption isotherms have been proposed to describe equilibrium biosorption data [10]. In addition, adsorption isotherms should be capable to predict the biosorption performance and reflect the biosorption mechanism [7]. Langmuir and Freundlich isotherms have been useful tools to compare results from different sources on the quantitative basis [11].

In this work, Cd(II) biosorption were investigated using seaweed (*Kappaphycus alvarezii* and *Eucheuma denticulatum*) waste biomass. Cd(II) biosorption experiment were conducted using the batch equilibrium technique and Cd(II) biosorption equilibriums were modeled using Langmuir and Freundlich isotherms. Cd(II) biosorption mechanism were investigated using different chemical techniques and instrumentation.

MATERIALS AND METHODS

Sample Preparation: *Kappaphycus alvarezii* and *Eucheuma denticulatum* waste biomass was prepared in the laboratory according to the industrial process.

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. The seaweed waste biomass was 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: The stock Cd(II), Cu(II) and Ni(II) solution (1000mg/L) were prepared by dissolving the metal nitrates (Merck) in deionized water. Cd(II) solutions with different concentrations and compositions were prepared by diluting the stock solutions with deionized water. The solution pH was adjusted to the desired value by using 0.1 mol/ L HCl and 0.1 mol / L NaOH.

Batch Experiment: Cd(II) biosorption experiments were conducted in a shake flask. Seaweed waste biomass (0.5 g) was added into a flask containing 50 ml Cd(II) solution and the solutions were agitated on a rotary shaker at 300 rpm for 3 hours. Cd(II) solution were then filtered using filter paper. Cd(II) concentrations were analyzed using Atomic Absorption Spectrometer (AAS) (Model AAnalyst 800, Perkin Elmer).

Cd(II) biosorption capacities were calculate using the following equation:

$$Q = \frac{(C_o - C_e)V}{m} \quad (1)$$

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_o (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.

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

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

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: Cd(II) biosorption mechanisms were studied using different chemical techniques and instrumentation. 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 Fourier transform infrared (FTIR) spectrometry (Perkin-Elmer). Spectra were recorded in the range 400-4000cm⁻¹. Morphology changes in the untreated and metal-treated seaweed waste biomass were elucidated using scanning electron micrometry (SEM). Micrographs were undertaken at moderate magnification (2000x).

RESULT AND DISCUSSION

Batch Studies: Cd(II) biosorption onto *K. alvarezii* and *E. denticulatum* waste biomass were studied at different pH values (2 - 6) and initial metal concentrations (10 to 100 mg/L). The highest biosorption capacity was obtained at pH 4 and then decreased with increase in pH value. This trend in pH dependence can related to chemical functional groups present in seaweed waste biomass and Cd(II) chemistry in solution [12,13]. Carboxyl groups would dissociate at pH higher than 3.0 and thus coordinate with Cd(II) ions through ion exchange and complexation reaction [14].

Biosorption capacity was increased with increase in initial Cd(II) concentration. In general, initial metal concentrations provided an important driving force to overcome mass transfer resistance. Hence, high initial heavy metal concentration will create high biosorption capacity [15, 16].

Biosorption capacity was reached a saturation point at Cd(II) concentration higher than 80mg/L. This biosorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations [13, 17].

Cd(II) biosorption onto *K. alvarezii* and *E. denticulatum* waste biomass was conducted in the binary systems containing Cd(II) and co-cation Cu(II) or Ni(II). Cd(II) biosorption capacities in the binary metals system was lower than that in the single metal systems. Cd(II) biosorption onto *K. alvarezii* waste biomass were 0.83 mg/g in the single metal system, 0.77 mg/g in the presence of Cu(II) and 0.76 mg/g in the presence of Ni(II). Meanwhile, Cd(II) biosorption onto *E. denticulatum*

Table 1: Langmuir and Freundlich isotherm parameters

	Langmuir isotherm			Freundlich isotherms		
	$Q_{max}(\text{mg/g})$	$K_L(\text{L/mg})$	R^2	$K_f(\text{L/mg})$	$1/n$	R^2
Seaweed waste biomass						
K. alvarezii	6.0680	0.1424	0.9502	0.7600	0.6509	0.9647
E. denticulatum	5.7603	0.0468	0.8578	0.2296	0.8588	0.9044

Table 2: Cations exchange

Seaweed waste biomass	Metal ion released into solution (meq/L)				
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Total
K. alvarezii	7.39 ± 0.33	8.27 ± 0.25	0.72 ± 0.23	0.87 ± 0.11	17.25
E. denticulatum	7.52 ± 0.30	8.82 ± 0.21	0.71 ± 0.09	1.36 ± 0.02	18.41
Seaweed waste biomass	Metal ion adsorbed onto seaweed waste biomass (meq/L)				
	Cd^{2+}	H^+	Total		
K. alvarezii	0.48 ± 0.01	15.79	16.27		
E. denticulatum	0.36 ± 0.01	15.79	16.15		

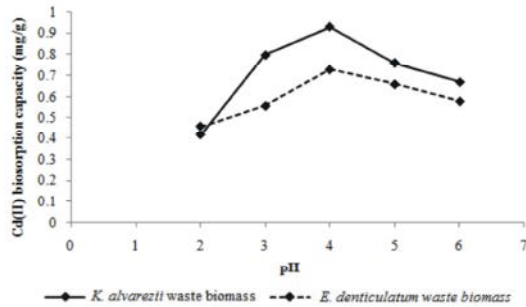


Fig. 1: Effect of pH on Cd(II) biosorption

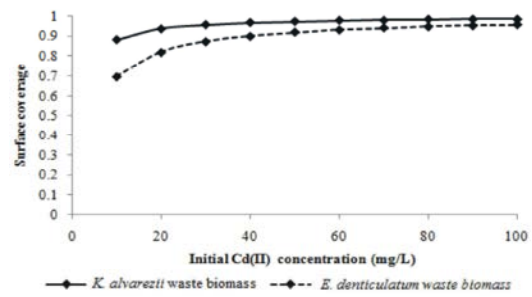


Fig. 4: Surface coverage (θ) profile

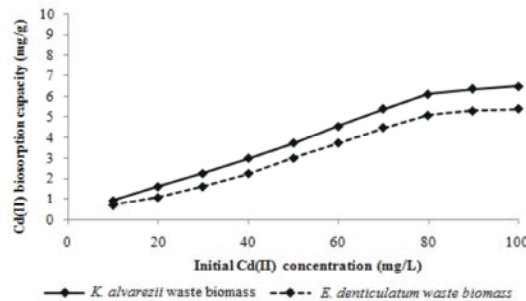


Fig. 2: Effect of initial metal concentration on Cd(II) biosorption

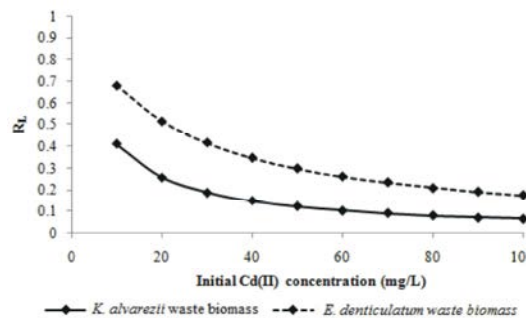


Fig. 3: Separation factor profile

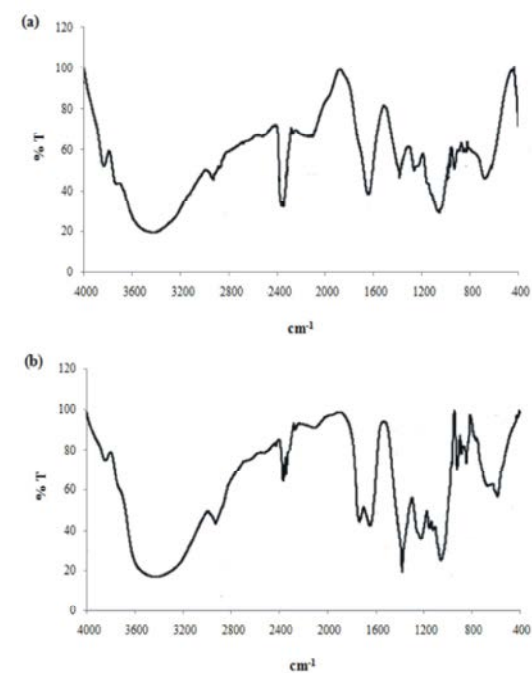


Fig. 5: FTIR spectra (a) untraeated and (b) Cd(II) treated *K. alvarezii* waste biomass

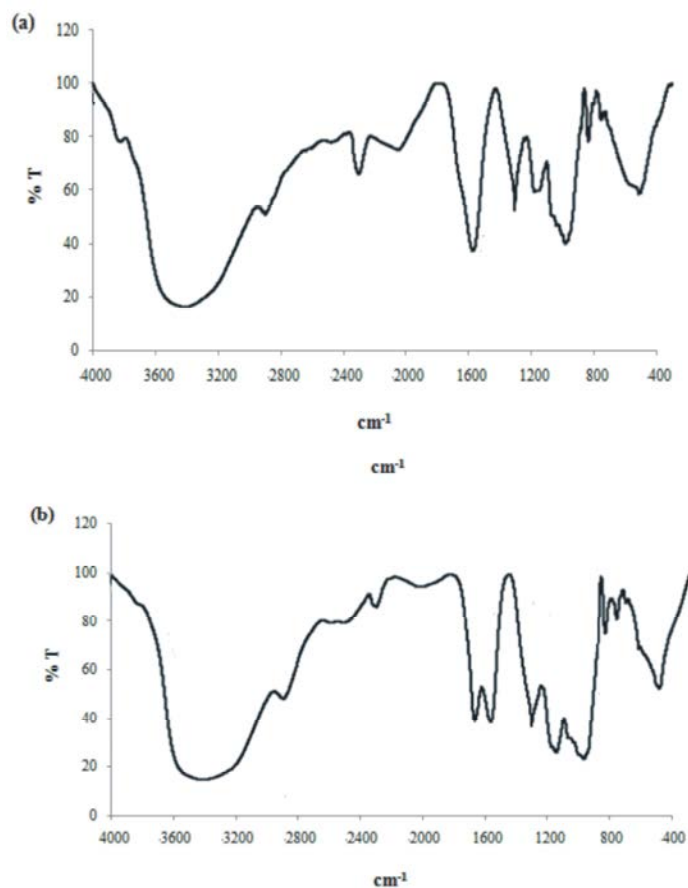


Fig. 6 FTIR spectra (a) untreated and (b) Cd(II) treated *E. denticulatum* waste biomass

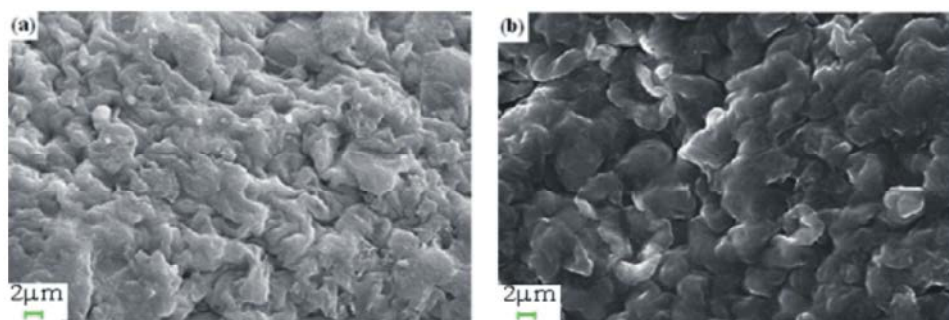


Fig. 7: SEM micrographs (a) untreated and (b) Cd(II) treated *K. alvarezii* waste biomass

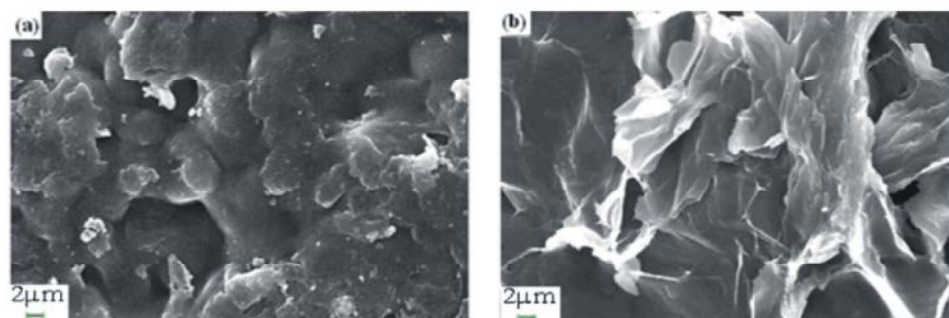


Fig. 8: SEM micrographs (a) untreated and (b) Cd(II) treated *E. denticulatum* waste biomass

waste biomass were 0.66 mg/g in the single metal system, 0.56 mg/g in the presence of Cu(II) and 0.54 mg/g in the presence of Ni(II). Suppression in Cd(II) biosorption capacities indicate an overlap in the biosorption site [18].

Biosorption Isotherms: Langmuir and Freundlich isotherms were employed to describe Cd(II) biosorption performance. Langmuir ($1/Q_e$ vs. $1/C_e$) and Freundlich ($\log Q_e$ vs. $\log C_e$) isotherm plots were conducted to derive Langmuir and Freundlich isotherm parameters and correlation coefficients (R^2).

The Freundlich model was better fit to the Cd(II) biosorption data than Langmuir model in the studied concentration range (10-100mg/L). Therefore, Cd(II) biosorption onto *K. alvarezii* and *E. denticulatum* waste biomass was monolayer sorption with heterogeneous surface [2].

Separation Factor (R_L): The Langmuir separation factor (R_L) was applied to estimate either the biosorption system favorable or unfavorable in a batch adsorption process. $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $0 < R_L < 1$ is favourable or $R_L = 0$ is irreversible [19].

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) Heterogeneous: Surface coverage (θ) was used to describe biosorption behavior. Surface coverage is expressed as follows:

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

Where K_F is the Freundlich equilibrium constant and C_o is the initial metal concentration.

The surface coverage values indicated that Cd(II) biosorption onto *K. alvarezii* and *E. denticulatum* waste biomass were effective at all initial metal concentrations (Fig. 4). In addition, surface coverage on seaweed waste biomass was increased with the initial metal concentration.

Metal Sorption Mechanisms

Ionic Balance: The simultaneous change in the ionic equilibrium indicated that chemical groups coordinate with Cd(II) ion through exchange with H^+ and/or other cations.

Overall, 17.25 meq/L K^+ , Na^+ , Ca^{2+} and Mg^{2+} were released into the solution and 16.27 meq/L H^+ and Cd^{2+} were adsorbed during Cd(II) biosorption onto *K. alvarezii* waste biomass. Meanwhile, 18.41 meq/L K^+ , Na^+ , Ca^{2+} and Mg^{2+} were released into the solution and 16.15 meq/L H^+ and Cd^{2+} were adsorbed during Cd(II) biosorption onto *E. denticulatum* waste biomass.

FTIR Analysis: The untreated and Cd(II)-treated seaweed waste biomass samples were analysed using FTIR. The untreated seaweed waste biomass spectrum showed six predominant peaks: 3430 cm^{-1} (-OH and -NH), 2930 cm^{-1} (-CH₂), 1642 cm^{-1} (-COO), 1385 cm^{-1} (-CH₃), 1264 cm^{-1} (-C-O-C) and 1053 cm^{-1} (-C-O).

Changes in vibration frequencies and absorbance intensities indicated that chemical groups coordinate with Cd(II) ions through ion exchange and complexation interactions. The absorption peak around -COO stretching shifted from 1642 cm^{-1} to 1647 cm^{-1} indicate that carboxyl groups formed complexes with the Cd(II) ions.

SEM Analysis: The untreated and Cd(II)-treated seaweed waste biomass samples were analysed using SEM. Differences in surface morphology indicated that Cd(II) ions deposited on seaweed waste biomass through surface precipitation. The mound-like structure indicates that Cd(II) ions precipitated on the seaweed waste biomass.

CONCLUSION

Overall, *K. alvarezii* and *E. denticulatum* waste biomass were able to remove Cd(II) ions from aqueous solution. Cd(II) biosorption process was pH dependant and biosorption capacities increased with increase in initial Cd(II) concentration. Cd(II) biosorption equilibrium data were fit to Langmuir and Freundlich isotherms. Cd(II) biosorption mechanisms were ion exchange, complexation and precipitation.

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