

COMPETITIVE METAL SORPTION AND DESORPTION ONTO *Kappaphycus Alvarezii*, SEAWEED WASTE BIOMASS

(Persaingan Penjerapan dan Nyah-Penjerapan Logam Berat ke atas Sisa Rumpai Laut *Kappaphycus alvarezii*)

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Abstract

Competitive metal sorption and desorption onto *Kappaphycus alvarezii* waste biomass were investigated. Metal sorption capacities were 0.82 mg Cr(III)/g, 0.73 mg Ni(II)/g, 0.67 mg Cd(II)/g, 0.65 mg Cu(II)/g and 0.64 mg Zn(II)/g in multi metal system. Whereas, desorption efficiencies were 66.08%, 71.50% and 80.44% using 0.1M HNO₃, 0.1M HCl and 0.1M H₂SO₄, respectively. The metal sorption sequence were Cr(III) > Ni(II) > Cd(II) > Cu(II) > Zn(II), while metal desorption sequence were Cd(II) > Zn(II) > Cu(II) > Ni(II) > Cr(III). Fourier transformed infrared spectroscopy (FTIR) technique was used to characterize the seaweed waste biomass. FTIR analysis shown that carbonyl (–C=O) and nitrile (–C≡N) groups interact with the metal ions. The experiments result revealed that *Kappaphycus alvarezii* waste biomass represent an attractive candidate to remove multi metal ions.

Keywords: Sorption, Desorption, *Kappaphycus alvarezii*

Abstrak

Persaingan penjerapan dan nyah-penjerapan logam berat ke atas sisa rumpai laut *Kappaphycus alvarezii* telah dikaji. Kapasiti penjerapan mencatat 0.82 mg Cr(III)/g, 0.73 mg Ni(II)/g, 0.67 mg Cd(II)/g, 0.65 mg Cu(II)/g dan 0.64 mg Zn(II)/g dalam sistem campuran logam berat. Sementara itu, kapasiti nyah-penjerapan masing-masing mencatat 66.08%, 71.50% dan 80.44% menggunakan 0.1M HNO₃, 0.1M HCl dan 0.1M H₂SO₄. Penjerapan logam berat mengikut turutan Cr(III) > Ni(II) > Cd(II) > Cu(II) > Zn(II). Selain itu, nyah-penjerapan logam berat mengikut turutan Cd(II) > Zn(II) > Cu(II) > Ni(II) > Cr(III). Teknik spektroskopi inframerah transformasi Fourier (FTIR) telah digunakan dalam mencirikan sisa rumpai laut. Analisa FTIR menunjukkan kumpulan karbonil (–C=O) dan nitrile (–C≡N) berinteraksi dengan logam berat. Hasil kajian mendapati sisa rumpai laut *Kappaphycus alvarezii* mempunyai keberkesanan tinggi dalam menyinkirkan campuran logam berat.

Kata kunci: penjerapan, nyah-penjerapan, *Kappaphycus alvarezii*

Introduction

Heavy metals are derived from various industrial activities viz. mining, tanning, smelting and electroplating [1]. Heavy metals are toxic, non-biodegradable and tend to accumulate in environment [2]. In recent years, heavy metals such as copper, cadmium and chromium are detected at elevated levels and pose a serious threat to environment [3]. Therefore, appropriate technologies are required to remove these metals to acceptable limits before discharging them into the environment.

New search technologies have been directed attention to biosorption process, with numerous biological material exhibit excellent biosorption capacities [4]. Among them, seaweed biomass have been proved to be the most efficient metal sorbent and examined in numerous biosorption studies [5]. Seaweed biomass such as *Sargassum* sp. and *Ulva* sp. have been shown to be effective and reliable metal sorbent to remove individual metal ions, such as Pb(II), Cu(II), Cd(II), and Zn(II) [4]. However, *Kappaphycus alvarezii* waste biomass have not been investigated as metal sorbent to remove metal ions.

Kappaphycus alvarezii is reliable and abundance waste biomass obtains from carrageenan extaction process. This waste biomass is rich in lignocellulosic material and its contain various chemical groups that able to interact with metal ions. Furthermore, this waste biomass is non-toxic, inert and ready to use in biosorption process [6].

In practice, various metal ions are encountered in wastewaters, and it is potentially impact the biosorption behavior: synergistic, antagonistic or non-interactive [2]. However, limited information is available to elucidate the competitive biosorption behavior [7]. It is important to provide better understanding to its application for real wastewater treatment.

In this work, competitive metal sorption onto *Kappaphycus alvarezii* waste biomass was investigated and their selectivity and competitive effect were compared with non-competitive metal system. Desorption using mineral acids (0.1M HCl, 0.1 M HNO₃ and 0.1 M H₂SO₄) were conducted. FTIR analyses were conducted to elucidate biosorption mechanisms.

Experimental

Seaweed waste biomass preparation

Kappaphycus alvarezii waste biomass was prepared in the laboratory using a common industrial process. The seaweed biomass was extracted with aqueous solution at 60°C for 6 hr. Then, the seaweed waste biomass was filtered using filter paper (Whatman No 2). The seaweed waste biomass was washed with distilled water and dried at 60°C for 24 hr. The dried seaweed waste biomass was ground in a blender and stored in a desiccator.

Metal solution preparation

The stock Cu(II), Cd(II), Cr(III), Ni(II) and Zn(II) solutions (1000 mg/L) were prepared by dissolving the metal nitrates (Merck) in deionised water. The metal solutions (10 mg/L) containing single and multi metal ions were prepared by diluting the stock solutions with deionised water. The metal solutions was adjusted to pH 3 by using 0.1 M NaOH.

FT-IR analysis

The untreated and Cr(III)-treated seaweed waste biomass samples were analysed using Fourier transform infrared spectroscopy. The seaweed waste biomass samples were encapsulated in KBr at a ratio of 1: 100. The IR spectra were collected using a Perkin Elmer spectrometer within the range 400--4000 cm⁻¹.

Biosorption experiment

Biosorption experiments were conducted by batch method using in shake flasks. Seaweed waste biomass (0.5 g) was added to a flask containing 50 ml mixed metal solution. The samples were agitated on a rotary shaker at 300 rpm for 3 hr. The samples were filtered using filter paper (Whatman No. 2), and the metal concentrations were measured using an AAS (PerkinElmer, USA).

The metal sorption capacities were calculated using the following equation:

$$Q_m = (C_0 - C_e).V / M \quad (1)$$

where, Q_m (mg/g) is the amount of metal adsorbed, V (L) is the volume of the solution, M (g) is the mass of the biomass, and C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of metal ions, respectively.

Desorption experiment

Desorption experiments were conducted in shake flasks. Multi metal treated seaweed waste biomass (0.5 g) was added to separate flask containing 50 ml of eluenting solutions (0.1M HCl, 0.1 M HNO₃ or 0.1 M H₂SO₄). The samples were agitated on a rotary shaker at 300 rpm for 1 hr. The samples were filtered using filter paper (Whatman No. 2), and the metal concentrations were measured using an AAS (PerkinElmer, USA).

Results and Discussion

FT-IR analysis

The FTIR analyses were conducted to identify characteristic functional groups and their possible interactions with metal ions.

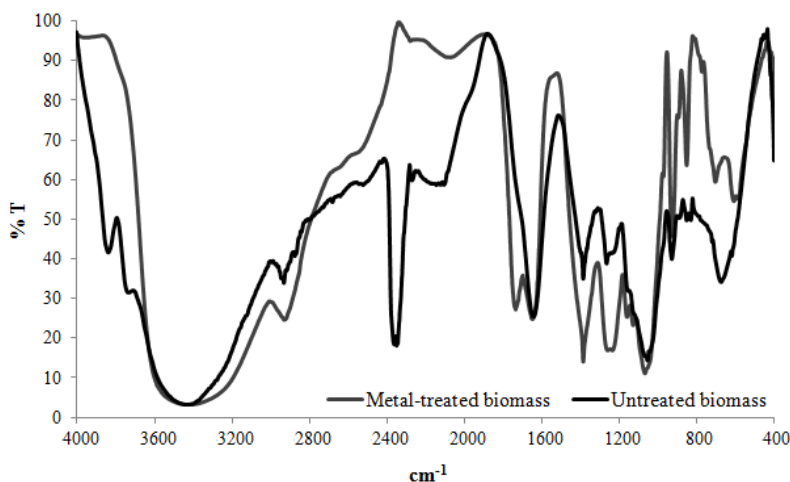


Figure 1: The untreated and metal-treated *Kappaphycus alvarezii* waste biomass FTIR spectra

The FTIR spectrum indicated several intense characteristic bands related with functional groups presented in the seaweed waste biomass. The absorption peaks at 3420 cm⁻¹ (–OH or –NH groups), 2930 and 1385 cm⁻¹ (–CH₃ groups), 2350 cm⁻¹ (–C≡N groups), 1646 and 1240 cm⁻¹ (–COOH groups) and 1050 cm⁻¹ (–C–O groups).

Table 1 displays the main vibration frequencies and functional groups responsible to metals sorption. It is observed that some vibration frequencies change after treated with metal ions.

Table 1: IR vibration wavenumber and functional groups observed on *Kappaphycus alvarezii* waste biomass

Wavenumber (cm ⁻¹)		Functional groups
Unloaded biomass	Metal-loaded biomass	
3430	3430	–OH and –NH stretching
2930	2930	–CH ₃ stretching
2350	–	–C≡N stretching
–	1730	–C=O stretching
1640	1645	–COO stretching
1385	1385	–CH ₃ bending
1240	1235	–C–O stretching
1065	1065	–C–O stretching

The absorption peak at 1640 and 1240 cm^{-1} corresponds to the $-\text{COO}$ groups shifted to 1645 and 1235 cm^{-1} , indicating that $-\text{COO}$ groups are involved in biosorption process. The peak at 2350 cm^{-1} corresponds to the $-\text{C}\equiv\text{N}$ groups disappeared, suggesting that $-\text{C}\equiv\text{N}$ groups are involved in biosorption process. A new peak at 1730 cm^{-1} corresponds to the $-\text{C}=\text{O}$ groups appeared, suggesting that $-\text{C}-\text{O}$ groups oxidize to $-\text{C}=\text{O}$ groups during biosorption process. However, the adsorption peaks around 2930, 1385 and 1065 cm^{-1} does not change, indicate that $-\text{CH}_3$ and $-\text{OH}$ does not involved in biosorption process.

The significant changes in the vibrational frequencies implicate that $-\text{CO}$, $-\text{COOH}$ and $-\text{C}\equiv\text{N}$ groups interacted with metal ions through ion exchange and complexation reactions.

Biosorption experiment

Metal sorption experiments were conducted in single metal system, and their selectivity and competitive effect were investigated in multi metals system. Metal sorption capacities were 0.82 Cu(II)/g, 0.83 mg Cd (II)/g, 0.86 mg Cr(III)/g, 0.76 mg Ni(II)/g and 0.84 mg Zn (II)/g in single metal systems, and 0.65 Cu(II)/g, 0.67 mg Cd (II)/g, 0.82 mg Cr(III)/g, 0.73 mg Ni(II)/g and 0.64 mg Zn (II)/g in multi metals system (Table 2). The metal sorption capacities was lower in multi metal system. This confirm that metal competition was occurred and caused antagonistic effect on biosorption process.

Cr(III) was favorably adsorbed on seaweed waste biomass over Cu(II), Cd(II), Ni(II) and Zn(II) in single and multi-metal systems. This confirms that Cr (III) bind more selective to seaweed waste biomass than other metal ions. However, it was difficult to find a common rule to determine how metal properties exactly affect the binding strength of metal ions to seaweed waste biomass [8].

In general, the binding strength increased with (1) increases in the ionic radius and decreases in the charge, (2) decreases in the hydrated radius and increases in the charge, or (3) decreases in the electronegativity [8].

Table 2: Biosorption capacities (mg/g)

Metal ion	Meta sorption capacities (mg/g)	
	Singel metal system	Muti metals system
Cu	0.82	0.65
Cd	0.83	0.67
Cr	0.86	0.82
Ni	0.75	0.73
Zn	0.84	0.64

The metals sorption sequence were Cr(III) > Zn(II) > Cd(II) > Cu(II) > Ni in single metal system, and Cr(III) > Ni(II) > Cd(II) > Cu(II) > Zn(II) in multi metal systems. The individual sequence were differed from those obtained in multi metals system.

It is obvious that different selectivity in multi metals system were diverse, and thus predictions on sorption selectivity should based on result obtained in multi metals system [9].

Desorption

Biosorption studies can be complemented with desorption to recover the metal retained and reuse the biomass. The desorption experiment were conducted using three different eluenting solutions. Hydrochloric, nitric and sulphuric acid were choose because mineral acids are the most feasible eluenting agents [10].

It is observed that 0.1M H_2SO_4 is a better eluenting agent than 0.1M HCl and 0.1M HNO_3 , although complete desorption were not achieve (Table 3). In practice, complete desorption is difficult to achieve in multi metal system [10].

In general, carbonyl and nitrile groups in seaweed waste biomass become protonated in acidic condition and does not attract the positively charged metal ions [11]. Meanwhile, some polysaccharides and mineral dissolve in acidic solution, and seaweed waste biomass become more fragile and loss its weight [12].

Table 3: Desorption percentage (%)

Metal ion	Metal desorption percentage (%)		
	0.1 M HCl	0.1 M HNO ₃	0.1 M H ₂ SO ₄
Cu	65.76	64.64	80.22
Cd	85.74	74.55	94.33
Ni	64.44	61.37	74.38
Zn	79.23	71.96	83.36
Cr	62.35	57.89	69.93

The metal desorption sequence were Cd(II) > Zn(II) > Cu(II) > Ni(II) > Cr(III). This revealed that desorption level were related to the affinity of metal to seaweed waste biomass [10]. In general, metal with higher affinity were more difficult to desorb, and thus retain into seaweed waste biomass. Cr(III) was the least desorbed from seaweed waste biomass. Cd(II), Ni(II) and Zn(II) are retain through electrostatic interactions, whereas Cu(II) and Cr(II) are retain through covalent interactions [13].

Conclusion

In this work, competitive metal sorption and desorption onto *Kappaphycus alvarezii* waste biomass were investigated. The metal sorption sequence were Cr(III) > Ni(II) > Cd(II) > Cu(II) > Zn(II), while metal desorption sequence were Cd(II) > Zn(II) > Cu(II) > Ni(II) > Cr(III).

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