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The Effect of the Presence of Cu^{2+} and Fe^{3+} Metal Ions on the Sorption of Mercuric Ion (Hg^{2+}) by Sargassum cristaefolium

Rochelle T. Alcantara
Dahlia C. Apodaca
Manuel R. De Guzman
School of Graduate Studies, Mapua Institute of Technology
Intramuros, Manila, PHILIPPINES

Previous studies have indicated that the seaweed *Sargassum cristaefolium* is capable of binding with metal ions. The metal sorbing property of *S. cristaefolium* suggests its possible participation in the removal of Hg^{2+} ions in water and wastewater. However, the potential application of *S. cristaefolium* for environmental remediation and precious metals recovery depends on the understanding of the other factors that could play a role in the sorption process.

This study illustrates the effects of some variables, such as pH and temperature, and that of the presence of other metal ions on the sorption process involving the binding of Hg^{2+} ions to *S. cristaefolium*. The uptake of Hg^{2+} ion was found to be affected by the initial concentration and the charge densities of the competing ions. Cu^{2+} ion shows a stronger affinity to Sargassum in the three metal systems of Hg^{2+}, Cu^{2+}, and Fe^{3+} ions. On the other hand, results show that Fe^{3+} ion is not a potential competitor for binding sites considering that no Fe^{3+} ion uptake by Sargassum has been observed.

Keywords: Bisorption; Hg^{2+}, Cu^{2+}, and Fe^{3+} metal ions; ion exchange; precious metals recovery; *Sargassum cristaefolium*; *and,* wastewater management.

INTRODUCTION

Biosorption has become a popular process or technology. Remediation of trace metals and recovery of precious metals are important applications of biosorption. Its advantages over conventional techniques—such as chemical precipitation and sludge separation, chemical oxidation or reduction, ion-exchange, reverse osmosis, electrochemical treatment, and evaporation—include being low-cost, metal-selective, regenerative, non-sludge-generating as well as its possible metal recovering properties, competitive performance, and high efficiency.

The method of biosorption takes advantage of the different unusual metal-binding properties of various algal species, such as seaweeds.

Among the seaweeds known to be effective for metals removal and recovery from wastewater streams, brown seaweeds have exhibited metal binding capacities higher than those of other types of absorbent materials derived from biomass (Matheickal 1999).

Moreover, biomass of brown seaweeds is a renewable biological resource, which is available in large quantities and can form a good base for the development of biosorbent materials (Schiewer and Volesky 2000). The mechanism of biosorption include mainly ionic interactions and the formation of complexes between metal cations and ligands contained in the structure of the cell wall biopolymers, as well as the precipitation on the cell wall matrix. Biosorption mechanisms are predominantly an ion-exchange process (2000).

Biosorption mechanisms differ qualitatively and quantitatively according to the species used, the origin of biomass, and its processing procedure (Holan and Volesky 1995). Therefore, further studies need to be done. Moreover, the complexities of the matrix that will be subjected to treatment by these biosorbents will greatly influence the efficiency of the sorption process. Other metal ions may manifest synergistic effect to give enhanced sorption efficiency but some would also tend to compete for binding sites and, therefore, would tend to reduce sorbent–metal interaction.

This study investigated the factors which affect the binding of Hg^{2+} with *Sargassum cristaefolium*. Specifically, this study was able to: (1) establish the ability of *S. cristaefolium* to bind with Hg^{2+} in the presence of Fe^{3+} and Cu^{2+} metal ions in artificially contaminated wastewater samples; and, (2) correlate pH and temperature on the binding of Hg^{2+} with *S. cristaefolium*.

This study utilized fresh, locally available *S. cristaefolium* seaweed samples. The water sample used in this study was artificially spiked with aqueous solutions of mercury, iron, and copper metal ions.

METHODOLOGY

Sample Collection and Preparation

Fresh *Sargassum cristaefolium* were collected from the coastal waters of Ilocos Sur, a province located on the northern part of the Philippines. The sun-dried material was washed with tap water and distilled water to remove sand and excess ions of sodium and potassium. After drying overnight at a maximum temperature of 50˚C to avoid degradation of the binding sites, the biomass was milled and sieved to 100 mesh.

Measurement of Metal Ions

The amounts of mercuric metal ions in the *S. cristaefolium* before and after sorption experiments were measured using an automatic mercury analyzer (AMA-254). On the other hand, a Perkin Elmer Atomic Absorption Spectroscopy instrument was used to determine the concentration of the competing ions (Cu^{2+} and Fe^{3+}).

A qualitative survey of the metal ions initially bound to *S. cristatefolium* was conducted using the Energy Dispersive X-Ray Spectroscopy.

Determination of the Binding Capacity of *S. cristaefolium* to Hg^{2+}

To investigate the binding of *S. cristaefolium* to Hg^{2+} ion in the presence of competing ions, such as Cu^{2+} and Fe^{3+} ions, equimass amounts of Cu^{2+} and Fe^{3+} ions and Hg^{2+} ion were allowed to bind with the biomass. Results of this experiment yielded information as to the effect of the initial concentration of the competing ions upon the binding of Hg^{2+} with *S. cristaefolium.* Another modification on the experiment was done by soaking the biomass in a solution containing equimolar amounts of Hg^{2+}, Cu^{2+}, and Fe^{3+} metal ions to determine the intrinsic properties of the metal ions upon binding; that is, to establish the preference of *S. cristaefolium* in binding with these metals regardless of their initial concentrations.

Morphological Studies

Surface morphologies of both unbound and bound *S. cristaefolium* were studied using the JEOL JSM-5310 SEM/EDX unit. The voltage used was 5keV and the magnification was 5000X.

FTIR/EDX Analyses of Samples

Sargassum samples were examined using the Nicolet Magna 550 FTIR spectrophotometer and the samples were incorporated with the KBr Pellets. FTIR was used to investigate the occurrence of some frequency shifts after the binding of Hg^{2+}, Cu^{2+}, and Fe^{3+} metal ions with the seaweed.

RESULTS AND DISCUSSION

Binding of Mercuric Ion (Hg^{2+}) to Sargassum

The influence of several operational parameters, such as pH and temperature, on biosorption of mercuric ions by *S. cristaefolium* was investigated to establish the optimum pH and temperature for this specific sorption study and to determine the influence of the initial metal concentration on the binding.

At Varying pH

Experiments involving different pH values were performed to establish the optimum pH at which maximum binding of Hg^{2+} ion to *S. cristaefolium* occurs. Binding of Hg^{2+} ion to the biosorbent was investigated at three pH values: 4, 7, and 9. The amount of Hg^{2+} ions bound to Sargassum, measured at different pH, can be seen in Figure 1.

The pH values were determined to evaluate if the system of Hg^{2+} ions favors an acidic, neutral, or a basic environment.

The sensitivity to pH of the sorption of Hg^{2+} ion to Sargassum was significantly evident in Figure 1. It was observed that the amount of Hg^{2+} ions bound to Sargassum decreased as the pH was increased. The reason for the lower extent of binding at an alkaline pH of 9, as explained by Noma (MAPUA 2003), suggest that electrolytes in the form of OH^- ions could serve as ionic screens around positively charged groups interacting with anionic carboxyl group and sulfate group of the Sargassum molecule. The excess OH^- ions present in the solution could have served as such ionic screens around the positive Hg^{2+} metal ions or possibly complexing with these Hg^{2+} ions reducing in turn the amount of metal ions available for binding.

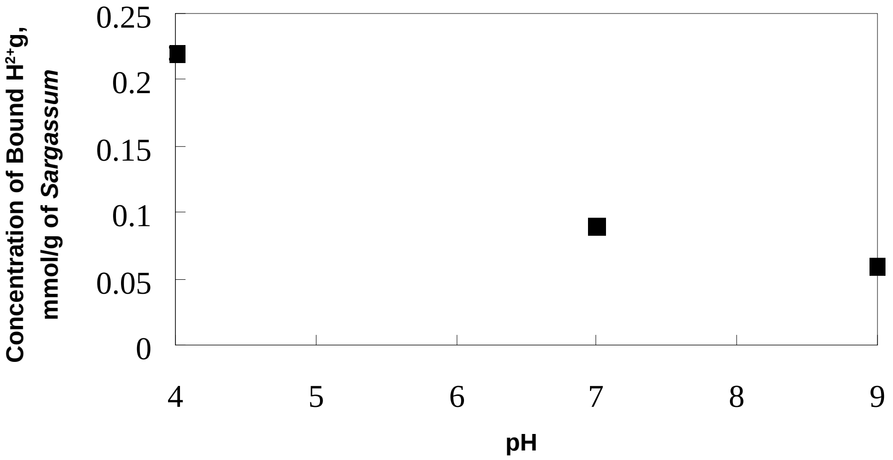

Figure 1. Binding of Hg^{2+} Ions towards Sargassum at Varying pH

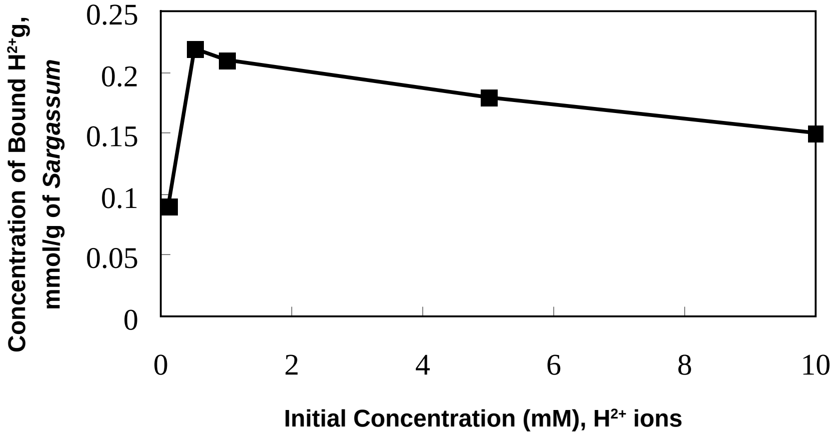

Figure 2. Binding of Hg^{2+} Ions towards S. cristaefolium at Varying Initial Concentrations

It can also be gleaned from Figure 1 that the maximum binding of Hg^{2+} ion to *S. cristaefolium* was found to be 0.2201 which occurred at pH 4 while only 0.0578 was found to bind with *Sargassum* at pH 9.

Binding of Hg^{2+} Towards Sargassum at Varying Concentrations

Varying concentrations of Hg^{2+} ions were use in determining the relative affinity of Hg^{2+} ions toward Sargassum biomass.

As could be noted from Figure 2, the sorption of Hg^{2+} ions to *S. cristaefolium* was found to be higher at 0.5mM. Also, it was observed that as the concentration of the Hg^{2+} ions in the solution increases from 0.5mM, the amount of Hg^{2+} ions bound to Sargassum tends to decrease only at small intervals; thus, at the initial concentration 0.5mM of Hg^{2+}, the Sargassum is said to have reached its maximum binding capacity.

Binding of Hg^{2+} Towards **Sargassum** *at Different Temperatures*

The effect of temperature on the removal of Hg^{2+} ions in aqueous solution by *S. cristaefolium* was studied by varying the temperature range from 20 to 40 ˚C. The data presented in Figure 3 showed that the Sargassum biomass prefers to

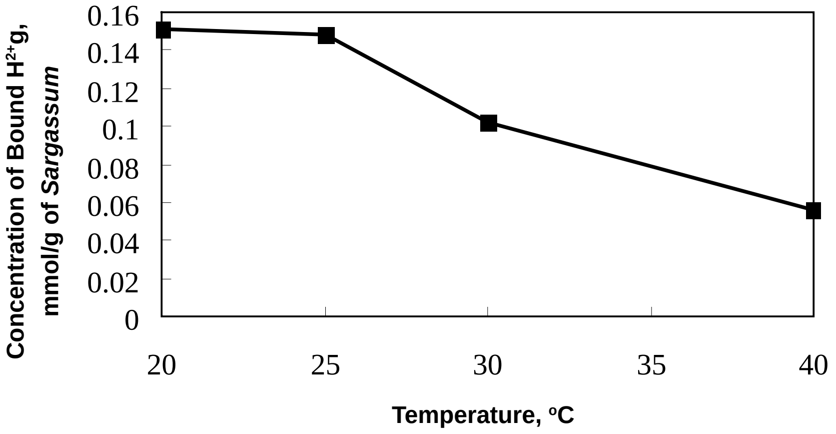

Figure 3. Binding Capacity of Hg^{2+} towards Sargassum at Different Temperatures

bind with Hg^{2+} ions at lower temperatures. The network of functional groups in the Sargassum somewhat trapped the ions; thus, when the temperature was increased, biopolymers have the tendency to be denatured causing some conformational changes to occur. This is because with increasing temperature, the intermolecular and intramolecular forces within the biomass surface were somewhat disrupted, thereby making the sorption process less efficient.

Binding Capacity of *S. cristaefolium* to Hg^{2+} Ions in the Presence of Competing Ions

Real wastewater samples contain several metal ions. Thus, this study sought to determine the effects of competing ions, such as Cu^{2+} and Fe^{3+} metal ions, on the uptake of Hg^{2+} metal ions by *S. cristaefolium*. Equimass amounts of binary metal system comprising Cu^{2+} and Hg^{2+} ions, binary metal system comprising Fe^{3+} and Hg^{2+} ions, and multi-metal system Cu^{2+}, Fe^{3+}, and Hg^{2+} ions were mixed accordingly: 50-mg each of the metal ion, which is equivalent to 0.7868mmol Cu^{2+}, 0.8953mmol Fe^{3+}, and 0.2493mmol Hg^{2+} were combined to ascertain the effect of initial concentration of competing ions on the uptake of Hg^{2+} ion by Sargassum. It could be observed from Figure 4 that the binding of Hg^{2+} metal ion had been affected by the initial concentration of the competing ions. It can be seen that the uptake of Hg^{2+} metal ion was relatively high when only Fe^{3+} metal ion had been introduced, which suggests that Fe^{3+} ion is not a potential competitor for binding sites considering that no Fe^{3+} ion uptake by Sargassum was observed.

Equimolar amounts of Hg^{2+}, Cu^{2+}, and Fe^{3+} ions were mixed with *S. cristaefolium* to determine the effect of the intrinsic properties of the metals upon binding. The same trend was observed in experiments involving equimolar amounts of Hg^{2+}, Cu^{2+}, and Fe^{3+} ions initially added to Sargassum. As given in Figure 5, results show the stronger affinity of Cu^{2+} ion to Sargassum in the three metal system of Hg^{2+}, Cu^{2+}, and Fe^{3+} ions.

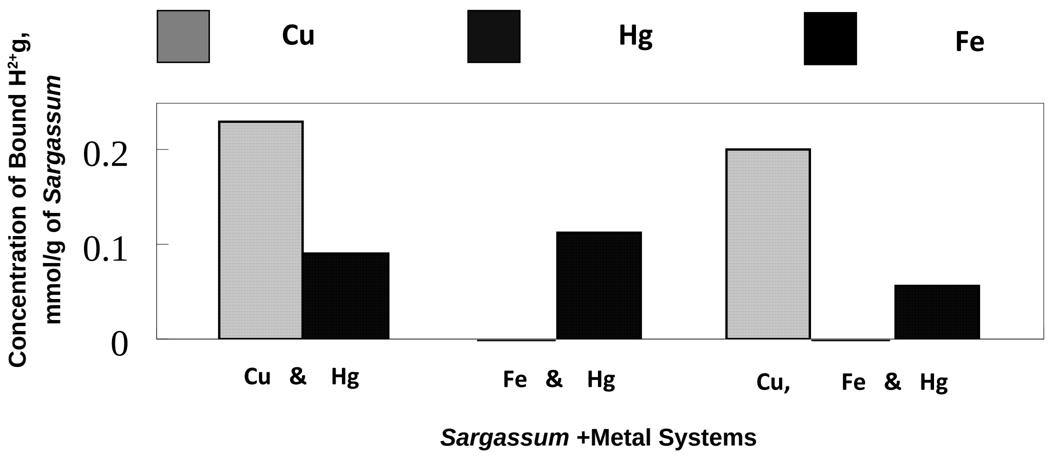

Figure 4. Comparison of the Amount of Hg^{2+} Ions bound to S. cristaefolium in the Presence of Competing Ions

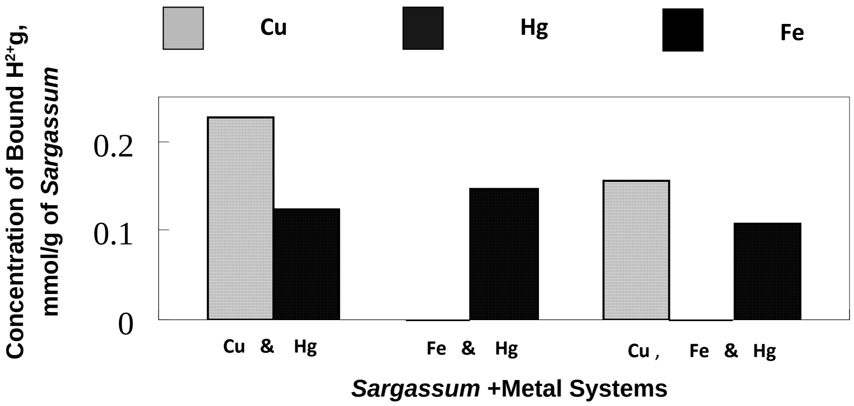

Figure 5. Comparison of the Amount of Hg^{2+} Ions Bound to *S. cristaefolium* **in the Presence of Competing Ions**

Table 1. Summary of the Total mmol of Hg^{2+}, Cu^{2+}, and Fe^{3+} Bound to Sargassum Involving Equimolar and Equimass Metals Systems

	Initial Concentrations of Metal Ions mmol/g *Sargassum*				**Concentrations of Bound Metal Ions mmol/g** *Sargassum*				
	Hg^{2+}	**Cu^{2+}**	**Fe^{3+}**	**Total**	**Hg^{2+}**	**Cu^{2+}**	**Fe^{3+}**	**Total**	**%**
Equimass Mixed System	0.2493	0.7868	0.8953	2.0	0.0573	0.2012	0	0.2585	13
Equimolar Mixed System	0.2	0.2	0.2	0.60	0.1080	0.1550	0	0.263	44

Table 1 gives the initial amount of Hg^{2+}, Cu^{2+}, and Fe^{3+} metal ions in *S. cristaefolium*. It can be observed from the table that the Sargassum biosorbent initially contained significant concentrations of Fe^{3+} ions. Also, Fe^{3+} metal ion was found to have zero affinity to Sargassum.

Experiment involving equimolar amounts of competing ions yielded quite high sorption efficiencies for Cu^{2+} and Hg^{2+} ions; that is, 78% and 50%, respectively. Thus, it may said that Hg^{2+} and Cu^{2+} ions indeed compete for binding sites in Sargassum. The ability of *S. cristaefolium* to accommodate more Cu^{2+} than Hg^{2+} metal ions could be attributed to the smaller size of Cu^{2+} ion resulting in higher charge density and better ionic interaction. Figure 6 shows the EDX spectrum of the multi-metal system comprising Fe^{3+}, Hg^{2+} and Cu^{2+} ions.

Morphological Studies

The SEM images give some idea on the surface structures of the bound Sargassum samples. The photographs shown in Figure 7 yield the surface topologies observed for both unbound and bound Sargassum biomass. In the presence of heavy metals, like Hg^{2+} ions, the intertwined network in the cell structure of *S. cristaefolium* was disrupted and, hence, accounts

Table 2. Binding Capacity of Sargassum to Hg^{2-} in Single and Mixed Metals System in the Presence of Cu^{2+} and Fe^{3+} Cations

Sargassum Cristaefolium	**Mixed Systems (mmol metal ion/g of *Sargassum*)**		
	Hg^{2+}	Cu^{2+}	Fe^{3+}
1. Unbound	0.0022	0.0047	0.9122
2. Equimass amounts of Hg^{2+}, Cu^{2+}, and Fe^{3+} added	0.0573	0.2012	0.8940
3. Equimolar amounts of Hg^{2+}, Cu^{2+}, and Fe^{3+} added	0.1080	0.1550	0.8996

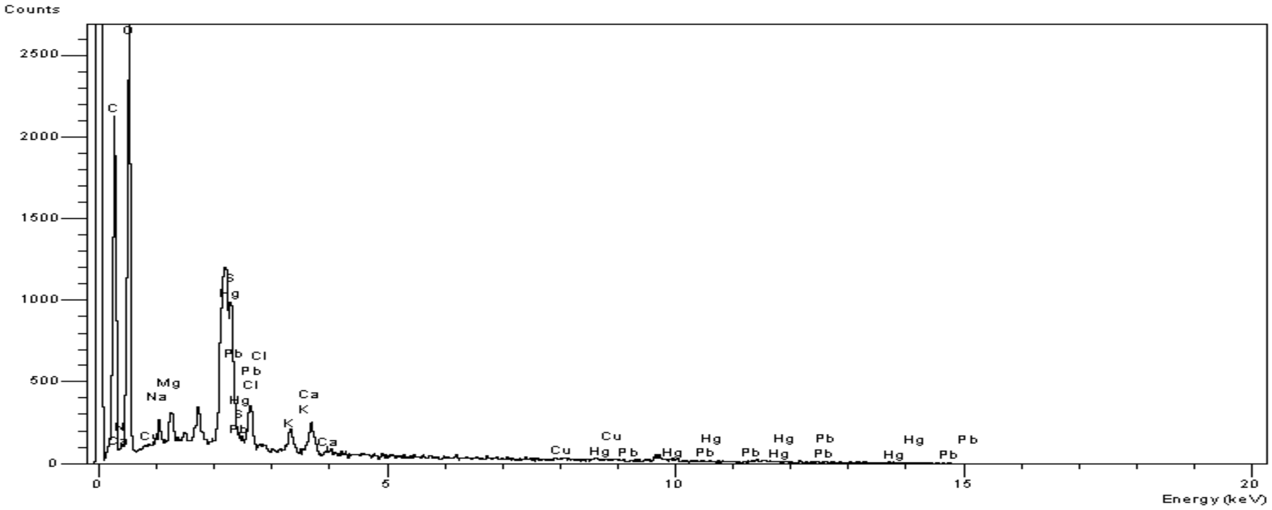

Figure 6. EDX Spectrum of Cu^{2+}, Fe^{3+} and Hg^{2+} Bound to Sargassum

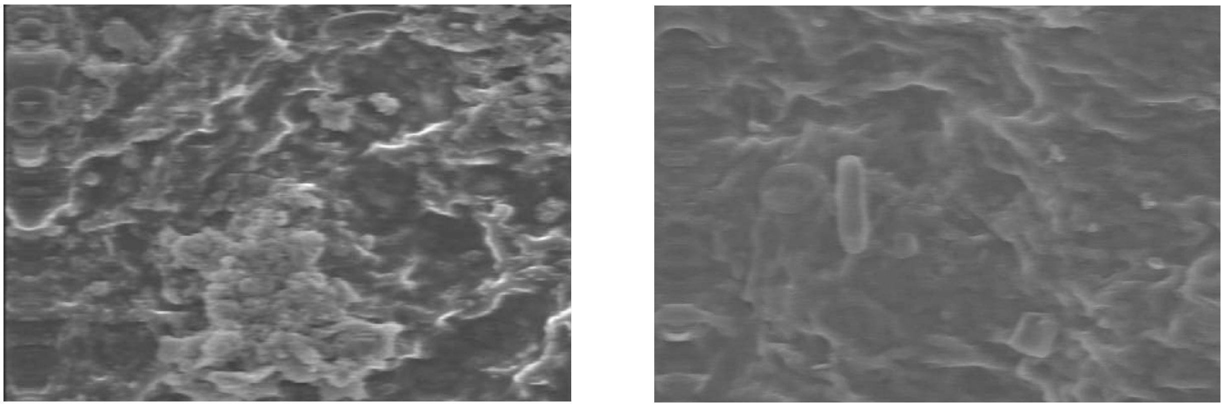

Figure 7. SEM Microphotographs of Unbound Sargassum (left) and Bound to Cu^{2+}, Fe^{3+}, and Hg^{2+} Ions (right)

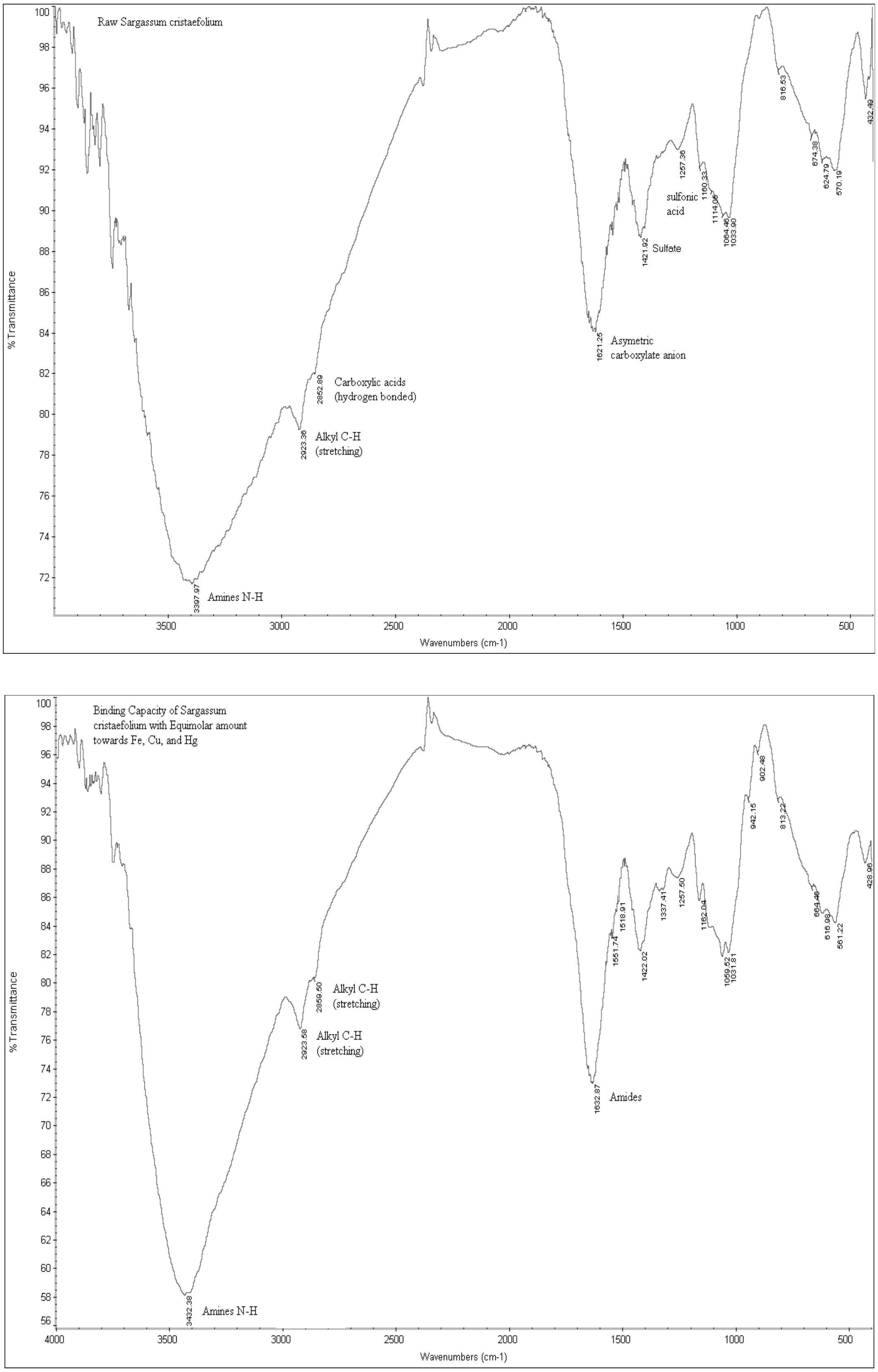

Figure 8. FTIR Spectra of Sargassum: Unbound (Left) and Bound to Cu^{2+}, Fe^{3+} and Hg^{2+} Ions (Right)

for the low metal uptake in the three-metal system. The more number of competing ions, the greater is the influence on the morphology of the Sargassum.

Fourier Transform Infrared (FTIR) Analysis

The unbound and metal-laden Sargassum samples were subjected to FT-IR analysis to qualitatively detect changes on the absorption frequency shift brought about by the presence of metal bonds. Atoms comprising the functional groups present in the biomass were found to be intact and that there were no significant interactions observed in the spectra. There is a need to confirm these metal bonds using other spectroscopic technique like XPS. The frequency between 3,300 and 3,400 has slightly weakened intensity and yielded less broad peak.

CONCLUSION

The factors that could affect the binding of Hg^{2+} ion towards *Sargassum cristaefolium* were investigated and the optimum conditions for pH, initial concentration, and temperature were validated. For pH, the maximum binding of Hg^{2+} ions occurred at pH 4 where 0.2201 of Hg^{2+} ions were bound to Sargassum while only 0.0578 of Hg^{2+} ions were found to bind with Sargassum at pH 9 since at alkaline pH there could be a competition between the solution hydroxyl groups and donor groups for metal ions. The Sargassum is said to have attained its maximum binding capacity at an initial concentration of 0.5mM of Hg^{2+} ion. A decrease in the sorption efficiency was observed with an increase in temperature which could be due to the intermolecular and intramolecular forces within the biomass surface that were possibly disrupted, thereby, making the sorption process less efficient.

Real wastewater may contain several metal ions, so the effect of competing ions such as Cu^{2+} and Fe^{3+} metal ions on the uptake of Hg^{2+} metal ion by *S. cristaefolium* was also established. It was found out that the uptake of Hg^{2+} ion is affected by the initial concentration and the charge densities of the competing ions. Cu^{2+} ion showed a stronger affinity to Sargassum in the three-metal system of Hg^{2+}, Cu^{2+}, and Fe^{3+} ions. On the other hand, results showed that Fe^{3+} ion is not a potential competitor for binding sites considering that no Fe^{3+} ion uptake by Sargassum had been observed.

SEM images of *S. cristaefolium*, unbound and bound to K^+, Na^+, Ca^{2+}, Cu^{2+}, and Fe^{3+} ions, display differences in the surface topologies, which gives some idea on the effect on the surface of *S. cristaefolium* upon introducing light and heavy metals.

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