Pb\textsuperscript{2+} biosorption on *Sargassum ilicifolium* in the presence of Na\textsuperscript{+} and quaternary ammonium cations

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**Abstract.** Quaternary ammonium cations (or quats) and Na\textsuperscript{+} were used as model interfering ions that could possibly influence the uptake of Pb\textsuperscript{2+} in wastewater by dead algal biomass of *Sargassum ilicifolium*. This biosorption study consisted of four sets of batch experiments: Pb\textsuperscript{2+}; Pb\textsuperscript{2+}/Na\textsuperscript{+}; Pb\textsuperscript{2+}/quats; Pb\textsuperscript{2+}/Na\textsuperscript{+}/quats. The effect of the presence of ions other than Pb\textsuperscript{2+} on the maximum extent of adsorption on the biomass was determined. Equilibrium data gathered suggested that improved Pb\textsuperscript{2+} adsorption could occur in the presence of quats. On the other hand, the presence of Na\textsuperscript{+} lowered the maximum extent of adsorption of Pb\textsuperscript{2+}, particularly at low initial concentrations of Pb\textsuperscript{2+}. In the presence of both Na\textsuperscript{+} and quats, more Pb\textsuperscript{2+} were adsorbed than when only one type of interfering ions was present.

1. Introduction

The wastewater that recent industrial activities produce may result in further deterioration of the environment and heightened risk exposure to human. There have been appropriate treatment processes for most types of wastewater. In removing or reducing heavy metals from wastewater, one of the most studied processes is biosorption by using microorganisms [1], dead plant [2-5], or algal biomass [6-9]. Pioneering studies were able to explain and report the mechanism of adsorption of heavy metals (e.g., Pb\textsuperscript{2+} and Cd\textsuperscript{2+}) on dead biomass of brown algae [10]. Recent studies considered designing continuous-flow packed-bed biosorption systems [11]. However, studies that report interference of other ionic species that might be present in wastewater are scant [12].

In this study, quaternary ammonium cations (quats) and a light metal cation (Na\textsuperscript{+}) were used as model interfering ions that could affect the maximum extent of biosorption of Pb\textsuperscript{2+} on *Sargassum ilicifolium* biomass. Quats are cationic surfactant commonly used as active component of cleaning solutions, laundry detergents, and household disinfectants. How the presence of one or both interfering ions affect the removal or reduction of heavy metal (i.e., Pb\textsuperscript{2+}) from simulated wastewater was the main focus of this study.

2. Materials and method

2.1. Materials

The seaweed samples, *Sargassum ilicifolium*, were collected from Sorsogon Bay, which is more than 500 km south of Manila. Immediately after collecting, the seaweeds were cleaned by soaking in tap water to take off attached shells, sand particles, small stones, and debris. The washed seaweeds were then sun-dried. The dried seaweeds were then milled and, using Ro-tap Sieve Shaker, the milled
product were separated according to particles size range (mesh number 20, 40, 70, 100, and 200). The seaweed particles with greatest fractions (mesh number 40, 70, and 100) were mixed and used in the subsequent experiments.

The source of Pb\(^{2+}\), Na\(^{+}\), and quats were lead chloride (Merck), reagent grade sodium chloride, and a quaternary ammonium compound \([\text{n-alkyl(C12-C18)} \text{ dimethyl benzyl ammonium chloride}]\) (Merck), respectively.

2.2. Protonation

The biomass particles were protonated by contacting with 0.1 M HCl solution (10 g biomass / 1 L HCl solution) for 24 h. Repeated washing of the protonated biomass with distilled water until the wash water attained a constant pH followed. The protonated biomass were the oven-dried at 60ºC, overnight. The dried biomass were then stored in a desiccator.

2.3. Batch equilibrium experiments

Each biosorption experiment was done by contacting 300 mg of protonated biomass with 100 ml of solution containing Pb\(^{2+}\), Pb\(^{2+}\)/Na\(^{+}\), Pb\(^{2+}\)/quats, or Pb\(^{2+}\)/Na\(^{+}\)/quats. The water used to prepare the solutions was distilled water, which did not contain Pb\(^{2+}\) and Na\(^{+}\) initially, based on FAAS analysis.

A magnetic stirrer was used to ensure uniform distribution of the biomass in the solution. The recorded temperature during the batch experiments ranged between 26 and 29ºC. Based on previous kinetic studies pertaining to Pb\(^{2+}\) biosorption on Sargassum of this group, equilibrium during batch experiments would be attained in 3 to 4 hours. Therefore, the allotted contact time for maximum adsorption used in this study were 6 hours in all samples to ensure equilibrium.

The experiments were performed at different initial Pb\(^{2+}\) concentrations (60 ppm, 70 ppm, 80, ppm, 90 ppm, 100 ppm). In treatments with Na\(^{+}\), the Na\(^{+}\) concentrations were varied: 0.1 M, 0.2 M, 0.3 M, and 0.5 M. In treatments with surfactant, amount of surfactant added was approximately 0.05 g. In all treatments, the initial pH was 5, and was adjusted to 5 every 30 minutes.

A supernatant sample of the equilibrated solution/biomass biosorption system was analyzed for lead using FAAS (Perkin-Elmer AAnalyst 100). Standard procedure for digestion of the sample was followed.

The Pb\(^{2+}\) uptake \((q, \text{ mg Pb}^{2+}/\text{g biosorbent})\), also known as loading, was computed using the mass balance equation:

\[
q = \frac{(C_i - C_f) V}{m}
\]

where \(C_i\) and \(C_f\) are the initial and final (total) lead concentration, respectively, \(V\) the solution volume, and \(m\) the mass of dry biosorbent used.

3. Results and discussion

3.1. Effect of Na\(^{+}\) in the Pb\(^{2+}\) uptake of Sargassum

The reported uptake of Pb\(^{2+}\) by algal biomass in a single metal system was more than 90%, which could reach as high as 99%. However, in this study, the presence of Na\(^{+}\) resulted in reduced equilibrium loading of Pb\(^{2+}\) on Sargassum. Na\(^{+}\) could have competed with Pb\(^{2+}\) on adsorption sites. Figure 1 clearly suggests that at all initial Pb\(^{2+}\) concentrations, equilibrium loading of Pb\(^{2+}\) would decrease as the concentration of competing Na\(^{+}\) ions increased. This also means lower reduction in Pb\(^{2+}\) concentration in solution as amount of Na\(^{+}\) increased. This observed effect, however, was most pronounced at the lowest initial concentration considered.
3.2. Effect of cationic surfactant (quats) on the biosorptive uptake of Pb$^{2+}$ by Sargassum

Figure 2 suggests that the presence of quats, without Na$^+$ in the solution, resulted in reduced Pb$^{2+}$ uptake by Sargassum.

It should be noted that Na$^+$ ions were also found in the in the aliquot of the supernatant despite no initial Na$^+$ ions were added in the solution. The ions must be coming from the protonated Sargassum. The unused Sargassum was analyzed using FAAS. It was found out that the protonated Sargassum had approximately 24 mg Na$^+$/g dry biosorbent. The biomass could have released Na$^+$ into the solution and the surfactant could have replaced the light metal ion preventing Pb$^{2+}$ ions to bind with the adsorption site first.

Biosorption availability would affect equilibrium loading; therefore, it would be expected that, in the presence of Na$^+$ in the solution, more Pb$^{2+}$ would be adsorbed than when only quats were present. The uptake was actually greater in the more occupied biosorbent (in the presence of added Na$^+$).

3.3. Effect of cationic surfactant (quats) on the uptake of Pb$^{2+}$ in the presence of Na$^+$

Figure 3 shows the fraction Pb$^{2+}$ adsorbed in systems with added Na$^+$ relative to the Pb$^{2+}$ adsorbed in system without added Na$^+$. All systems were with quats.
Figure 3. Effect of *quat* on the uptake of Pb (II) in the presence of Na⁺ relative to uptake of Pb (II) from solution without Na⁺.

At lower initial Pb²⁺ concentrations (60 and 70 ppm), lower relative fraction adsorbed (< 1) were observed in systems with 0.1 and 0.2 M Na⁺, while it was higher (> 1) in systems with 0.3 and 0.5 M Na⁺. At initial concentration 80 – 100 ppm, higher relative fraction adsorbed occurred in all systems with at least 0.1 NaCl. It was highest in system with 0.1 M NaCl, followed by 0.2 M, 0.3 M, and 0.5 M NaCl, in that order, at an initial Pb²⁺ concentration of 90 ppm. The surfactant and the interfering Na⁺ enhanced the sorbent’s performance. The maximum loading (at equilibrium) was greater when both quats and Na⁺ were present compared to when only the quats or Na⁺ were present. Thus, increasing the uptake of Pb²⁺ would result in remaining Pb²⁺ to diffuse from the solution into the biosorbent. This increase, however was only appreciable at low initial Pb²⁺ concentrations.

The increase in uptake of Pb²⁺ when quats were present compared to the results when no quats were present would establish the effect of the presence of cationic surfactant on the adsorption of Pb²⁺ in the presence of Na⁺. See figures 4(a)-4(c). Without quats or Na⁺, adsorption was still best. However, in the systems with both quats and Na⁺, maximum equilibrium loading was better than the system with Na⁺ but without quats. The quats would have prevented the release of Na⁺ from the biosorbent and the interaction with Pb²⁺. It would have interacted with Na⁺, making it avoid occupying binding sites, thus leaving more for Pb²⁺.
Figure 4. (a) Equilibrium loading of Pb (II) in the presence of 0.1 M Na⁺ without Na⁺, (b) Equilibrium loading of Pb (II) in the presence of 0.3 M Na⁺ without Na⁺ and (c) Equilibrium loading of Pb (II) in the presence of 0.5 M Na⁺ without Na⁺.

4. Conclusion
The cationic surfactant (quaternary ammonium compound) improved the biosorption performance of Sargassum. Equilibrium data gathered suggested that improved Pb²⁺ adsorption could occur in the presence of quats. On the other hand, the presence of Na⁺ only lowered the maximum extent of adsorption of Pb²⁺, particularly at low initial concentrations of Pb²⁺. In the presence of both Na⁺ and quats, more Pb²⁺ were adsorbed than when only one type of interfering ions was present.

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