Biosorption of Cd\textsuperscript{2+} using an admixture of \textit{Ulva lactuca} and fly ash from coal-fired power plant

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Abstract. This study investigated the adsorption of Cd\textsuperscript{2+} in a simulated wastewater using green macro alga, \textit{U. lactuca} and fly ash from coal-fired power plant, individually and as an admixture (25:75, 50:50, and 75:25). The maximum adsorption capacities for 0:100, 25:75, 50:50, 75:25 and 100:0 ratios of \textit{U. lactuca} and fly ash were 6.47, 6.28, 6.27, 6.19, and 6.39 mg/g adsorbent, respectively. The optimum adsorption was found to occur at an initial Cd\textsuperscript{2+} concentration of 70 mg/L at 293 K, pH 5, 120-minute contact time, 300 rpm agitation speed, and 10 g/L biosorbent dosage. The obtained results fitted well with Langmuir Isotherm, suggesting a monolayer adsorption with adsorption capacity of 6.852 mg/g adsorbent. The highest adsorption capacity was observed using fly ash while the lowest was observed using 75:25 \textit{U. lactuca} to fly ash ratio.

1. Introduction

Cadmium is one of the widely-dispersed heavy metal pollutants found in the wastewater effluents released by various industrial plants such as electroplating, metal finishing, mining extraction, manufacturing of Ni-Cd batteries, manufacturing of phosphate fertilizers, textile operations, and manufacturing of dyes. As a contaminant, Cd\textsuperscript{2+} partakes in bioaccumulation in photosynthetic plants and animals, and eventually transferred to humans causing many diseases [1-4]. With these, several methods for the elimination of Cd\textsuperscript{2+} in wastewater had been topical in several studies and researches. Some of the conventional processes utilized today for the removal of Cd\textsuperscript{2+} are ion exchange, flotation, chemical precipitation, and adsorption [5,6]. Among these methods, adsorption appeared to be advantageous because of its relatively simple operating conditions, vast pH range, low cost operation, and high metal-binding capacities [7, 8]. Cd\textsuperscript{2+} adsorbents used in this process include activated carbon [9], chitosan [10], resins [11], zeolite, clay, agricultural wastes, industrial by-products, and biomass materials [12]. Biomass materials have been on the rise among these types of adsorbents and amid these materials, algal biomass is the most common. Marine green algae can be specific to addressing heavy metals, because of the polysaccharides, proteins, and lipids that exist on the surface of cell walls that easily binds with the metals [13]. This potential of marine green algae is significant in addressing algal bloom and eutrophication issues. A wide array of marine green algae including \textit{Spirulina platensis} [1], \textit{Sargassum tenerrimum}, and \textit{Chloroidium saccharophilum} [14] exhibited high Cd\textsuperscript{2+} adsorbing capacities but \textit{Ulva lactuca} is the most abundant representative of green algae with a Cd\textsuperscript{2+} adsorbing capacity [15,16]. Another potential biosorbent for Cd\textsuperscript{2+} is fly ash, which is an industrial by-product of coal-fired power plants [15]. Thus, this study made use of the two biosorbents to make an admixture adsorbent for the adsorption of Cd\textsuperscript{2+} from wastewater and determined their effect on Cd\textsuperscript{2+}. 
removal by varying the concentration of each biosorbent in an admixture system.

This study promotes the use of waste materials such as fly ash in the removal of contaminants. Unlike other techniques used in adsorption, this study will not pre-treat the adsorbent which could lessen the cost of the process. This study aims to compare the adsorptive capacities of both the pure fly ash and the pure *U. lactuca*, as well as in their admixture with varied proportions. In addition, this study aims to propose a predictive mechanism for the adsorption of Cd\(^{2+}\) sorbate onto the identified sorbents *U. lactuca* and fly ash from coal fired power plant based on the sorbent characterizations such as SEM, FTIR and XRD.

2. Materials and methods

2.1 Biosorbent preparation

The green alga (*U. lactuca*) biomass was used as one of the constituents of the binary biosorbent for the biosorption of Cd\(^{2+}\) in a simulated wastewater. Samples of the biomass for *U. lactuca* were collected from the sea coast of Seaweed’s Farm in Calatagan, Batangas whereas the fly ash sample was collected in DMCI Holdings Inc. Power plant. The Bureau of Plant Industry authenticated the samples of biomass. To remove extraneous and salts, samples of the two adsorbents were washed four times using deionized water. Both adsorbents were dried in an oven at 65°C for 24 h to totally dry the layer of each biomass and the fly ash [15]. The dried algae biomass was chopped, grinded using Thomas-Wiley Laboratory Mill Model 4 and sieved using electronic sieve shaker, and the particles with an average of Mesh No. 35 (0.5 mm) were used for biosorption experiments [17]. The dried fly ash was sieved using the same mesh number. The particle size of *U. lactuca* and fly ash, as mentioned, exhibited high adsorption capacities for Cd\(^{2+}\) [16].

2.2 Treatment of fly ash

The chemical heat-treatment of fly ash was done by subjecting it to a convection oven for 12 h and at 105°C and allowed the cooling of furnace. After undergoing to chemical treatment, chemical heat-treated fly ash was obtained from the process. The sample was mixed with a 1 M HCl solution (Sigma Aldrich) at a ratio of 1 g fly ash to 2 ml of acid, was filtered and subjected to heat treatment at 105°C for 12 h in a convection oven and was subjected to furnace afterwards.

2.3 Sorbate preparation

Cd\(^{2+}\) solution with corresponding concentrations (i.e., 10 mg/L, 30 mg/L, 50 mg/L and 70 mg/L) were prepared by dissolving Cd(NO\(_3\))\(_2\)•4H\(_2\)O with respective amounts (i.e., 0.01 g, 0.03 g, 0.05 g, and 0.07 g) in 1000 mL deionized water using a 1000-mL volumetric flask. The pH of the solution was adjusted using a 1 M NaOH and a 1 M HCl.

2.4 Characterization of biosorbent

The Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700 FTIR) was used in the analysis of biosorbents (*U. lactuca* and fly ash). Scanning Electron Microscopy (SEM, JSM-5310 Scanning Electron Microscope) was conducted to study the surface morphology of the two biosorbents.

2.5 Effect of initial Cd\(^{2+}\) concentration

The initial Cd\(^{2+}\) concentration was varied at 10, 30, 50, and 70 mg/L at a fixed pH of 5 and an adsorbent dosage of 10 g/L with the following ratios of *U. lactuca* to fly ash as 25: 75, 50:50, and 75:25, and at a fixed pH (6) with adsorbent dosage of 10 g/L and contact time of 120 min. This was set in a water bath shaker at a constant speed (300 rpm) and temperature (25°C). Furthermore, the solution was then filtered with a filter paper. The filtrate metal was analysed using Flame Atomic Absorption Spectrophotometer (Flame AAS). The amount of metal left, and the percentage of metal removed were calculated.
2.6 Equilibrium studies
For the analysis of the adsorption isotherm models, the results of the AAS analysis in biomass concentration were used. The adsorption isotherms gave the optimum correlation and projected a high number of available binding sites and the amount of cadmium adsorbed. Based on the dry biomass (m, g dry-wt), the metal uptake (Q, mg/g dry-wt) was determined by the difference between the initial cadmium concentration (C₀, mg/L) and the obtained final cadmium concentration (Cᵢ, mg/L), multiplied to the volume of the suspension (V) in liters, given by

$$Q = (C₀-Cᵢ)V/m$$

The percent adsorption of cadmium was given by the equation

$$%\text{adsorption} = (C₀-Cᵢ)/C₀ \times 100$$

2.7 Isotherm model studies
The biomass concentration results of AAS analysis were used for the study of different adsorption isotherm models. The different adsorption isotherm gave the best correlation and indicated a high number of available binding sites and the amount of cadmium adsorbed. The two isotherm models that were utilized in the experimental data fitting are the Langmuir and Freundlich isotherms. The linearized equation for Langmuir model is

$$1/Q = (k/Q₀)(1/Cₑq) + 1/Q₀$$

The linearized equation for Freundlich model is

$$\log Q = \log k_f + (1/n)\log C$$

3. Results and discussion
3.1 Characterization of biosorbents

For the qualitative assessment of the main functional groups responsible for the binding with Cd²⁺ ions, the biomass materials were subjected to infrared spectroscopy. This characterization method delivers information for the identification of the functional groups of the active components present in the adsorbents’ structure based on the peak values within the regions of the infrared radiation. The dried U. lactuca powder was subjected to the FTIR and the functional groups of its constituents were

![FTIR spectra for U. lactuca before and after Cd²⁺ adsorption.](image)
separated based on their peak ratios. Figure 1 reveals the FTIR Spectra and the frequencies obtained for *U. lactuca* before and after the adsorption process.

Before the adsorption, it is observable that the band at 3414.48 cm$^{-1}$ is strong and broad as seen from figure 1. This is characterized by the O-H vibration stretching of the hydroxyl groups present in carbohydrates, fatty acids, proteins, lignin units and absorbed water. The band at 2959.48 cm$^{-1}$ to 2869.01 cm$^{-1}$ characterizes the C-H stretch vibrations for methyl. At 2926.44 cm$^{-1}$, stretching of Methylene C-H can be observed. Alcohol can be ascribed to the C-H stretching at 1646.30 cm$^{-1}$. Lastly, primary alcohols were observed at frequencies 1646.3 cm$^{-1}$ and 1057.25 cm$^{-1}$. These functional groups can be attributed to the lignocellulosic nature of the biomass. These constituents are responsible for chemical bonding due to the polar functional groups present. These functional groups comprise macromolecules that have the capability to absorb metal ions by complexation phenomena or ion exchange, which takes place on the surface of the material through the interaction of these functional groups with the metal ions. With this, *U. lactuca* tends to possess a high cation capacity, which makes it a potential adsorbent. Comparing between pristine and Cd$^{2+}$-loaded *U. lactuca*, it was noticed that there were shifts in wave numbers of dominant peaks associated with the loaded metal as well as occurrence of new bands. The shift in the band 3414.48 cm$^{-1}$ and 3392.30 cm$^{-1}$ showed the changes in the amount of hydroxyl group during the adsorption of Cd$^{2+}$ [1]. This wavelength shift illustrated occurrence of metal binding on the surface of the algal species [16]. It can be observed that the IR spectra after the adsorption process retained the same functional groups present in the *U. lactuca* sample before the adsorption, and it only exhibited lower values of percent transmittance. Since lower percent transmittance corresponds to a higher population of bonds, the interaction between the Cs$^{2+}$ and biomass material during the adsorption process has been confirmed [18,19].

The before and after cadmium adsorption results of the FTIR spectra of the fly are shown in figure 2. Fly ash before undergoing adsorption shows transmission peaks at 3410.79 cm$^{-1}$, 1627.59 cm$^{-1}$, 1154.44 cm$^{-1}$, 1116.95 cm$^{-1}$, 798.48 cm$^{-1}$, 777.77 cm$^{-1}$, 675.31 cm$^{-1}$ and 598.83 cm$^{-1}$. These peaks constitute to the respective bonds and functional groups of the fly ash.

![Figure 2. FTIR spectra for fly ash before • and after • Cd$^{2+}$ adsorption.](image)

The 3410.79 cm$^{-1}$ peak is included, which indicates the O-H hydrogen bond intermolecular stretch. Also, this can be attributed to the O-H in the water molecular-OH. The bonds in these spectra propose that the newly loaded substance in the treated ash occurs as a hydroxyl. The band 1627.59 cm$^{-1}$ is attributed within the bracket of C=O stretching, indicating the presence of amides. The bands at
1154.44 cm\(^{-1}\) and 1116.95 cm\(^{-1}\) characterize the stretching vibrations of C-N Stretch of aliphatic amines. The bands 798.49 cm\(^{-1}\), 777.77 cm\(^{-1}\), 675.31 cm\(^{-1}\), and 598.83 cm\(^{-1}\) may be attributed to the vibration stretching of C-Cl stretch of alkyl halides brought by preliminary treatment of fly ash through hydrochloric acid. In addition, wave numbers 675.31 cm\(^{-1}\), and 598.83 cm\(^{-1}\) are associated with C-Br stretch of alkyl halides. The presence of an absorption band from 1080 cm\(^{-1}\) to 1090 cm\(^{-1}\) and 469-800 cm\(^{-1}\), shown in the IR spectrum, indicates the presence of SiO\(_2\) in the ash. Variation in spectral features of the IR bands of fly ash (before and after) suggests that Cd\(^{2+}\) bind to hydroxyl, amino, carbonyl, and phosphoryl functionalities. This was attributable to the presence of the following specific bands. A band at 3410.79 cm\(^{-1}\) in treated fly ash (before) while a broad band at 3421.50 cm\(^{-1}\) in treated fly ash with Cd\(^{2+}\) due to non-bonded and bonded O-H respectively. The intensity of the band at 1154.44 cm\(^{-1}\) in the fly ash before adsorption decreased drastically after cadmium treatment indicating carbonyl of COOH to be involved in metal chelation. A band at 1116.95 cm\(^{-1}\) for fly ash before adsorption and at 1089.46 cm\(^{-1}\) for fly ash with Cd\(^{2+}\) after adsorption is indicative of the involvement of the phosphoryl group in metal binding.

The surface morphology of \textit{U. lactuca} was examined by SEM analysis. In order to verify whether Cd\(^{2+}\) was adsorbed, SEM micrographs were taken before and after adsorption. Figure 3 shows the changes on the surface appearance through a 15 kV x 2,000 magnification.

![Figure 3. Micrographs of \textit{U. lactuca} before (left) and after (right) Cd\(^{2+}\) adsorption.](image)

![Figure 4. Micrographs of fly ash before (left) and after (right) Cd\(^{2+}\) adsorption.](image)

As observed in figure 3, the biosorbent – \textit{U. lactuca} (at the left side) was characterized by its fine powder-like surface before it undergoes adsorption. In addition, there is no certain pattern on the magnified image on the left side surface. The image at the right side shows the surface micrograph of \textit{U. lactuca} after the adsorption process. From the image, there was a certain circular pattern formed through the adsorbent’s surface. The changes on the surface structure of \textit{U. lactuca} indicate the binding of Cd\(^{2+}\) in the surface. In addition, the microstructure of \textit{U. lactuca} biomass (250-500 μm) indicates that the biosorbent had a multi-pore and circular- or fiber-like structure after adsorption.
Figure 4 shows the SEM micrograph of Fly Ash before and after adsorption of Cd$^{2+}$. Apparently, the investigation has shown that there were spherical-shaped, smooth-surfaced particles, which comprise most of the particles in the fly ash. Figure 4 (at the left side) shows sub-angular and spherical particles with relatively smooth grains consisting of quartz, while the right side shows fiber-spiral like particles formed due to the adsorption of Cd$^{2+}$.

3.2 Equilibrium studies
The results obtained from testing the percent adsorption and adsorption capacity of different biosorbents with varying U. lactuca to fly ash ratios among four different initial Cd$^{2+}$ concentrations of 10 mg/L, 30 mg/L, 50 mg/L, and 70 mg/L were summarized in figure 5.

![Figure 5](image)

**Figure 5.** Effect of Initial Cd$^{2+}$ Concentration on the (a) Percent Adsorption of Cd$^{2+}$ and (b) Adsorptive Capacity onto different ratios of Ulva lactuca and fly ash (U. lactuca to fly ash ratio: A – 0:100, B – 25:75, C – 50:50, D – 75:25, E: 100:0; Conditions: pH = 5, time = 120 minutes, biosorbent dosage = 10 g/L, T = 293 K and Agitation Speed = 300 rpm).

Percent adsorption values with their corresponding adsorption capacities started from 99.55% (0.99 mg/g), 96.84% (0.90 mg/g), 95.32% (0.86 mg/g), 94.82% (0.84 mg/g), and 96.44% (0.89 mg/g) for U. lactuca to fly ash ratios of 0:100, 25:75, 50:50, 75:25, and 100:0 respectively at an initial Cd$^{2+}$ concentration of 10 mg/L. As can be observed, these values are the highest percent adsorption values as well as the lowest points for all the ratios of U. lactuca and fly ash. These percent adsorption values continuously decreased while the adsorption capacity continuously increased as the initial Cd$^{2+}$ concentration was increased from 10 mg/L to 70 mg/L. The maximum adsorption capacity values were observed at 70 mg/L with values 6.47 mg/g, 6.28 mg/g, 6.27 mg/g, 6.19 mg/g, and 6.39 mg/g for the same order of ratios of the biosorbents. This behavior in which percent adsorption was highest at the lowest initial Cd$^{2+}$ concentration was expected since it is much easier to adsorb the majority of the metal ions when they are in a smaller amount. Also, the amount of Cd$^{2+}$ initially present in the solution could freely interact with the highly available unoccupied binding sites in low concentration of metal ions; thus, a high value of percent adsorption was achieved for all the biosorbent ratios. These values then decrease as the increased amount of Cd$^{2+}$ saturates the adsorption sites as the initial Cd$^{2+}$ concentration is increased from 10 mg/L to 70 mg/L. At low initial Cd$^{2+}$ concentration, specific binding sites efficiently adsorbs the Cd$^{2+}$ and as this increases, these specific binding sites become saturated leading to almost completely filled and covered binding sites. On the other hand, adsorption capacity increased with increasing initial Cd$^{2+}$ concentration due to the increasing concentration gradient which is considered as the driving force for the adsorption process. The initial Cd$^{2+}$ concentration gives the needed driving force to deal with the resistances associated with the mass transfer of Cd$^{2+}$ between the solid and aqueous phases. In addition, this can also be referenced to the stronger attraction between the negative sites of the biosorbents and the positive sites of the Cd$^{2+}$ as both amounts are increased.

It is evident that biosorbent A or pure fly ash exhibited the highest adsorption capacity and percent
adsorption. At 10 mg/L of initial Cd\(^{2+}\) concentration, the percent adsorption and adsorption capacity values for biosorbents A, B, C, D, and E are 99.55% (0.99 mg/g), 96.84% (0.90 mg/g), 95.32% (0.86 mg/g), 94.82% (0.84 mg/g), and 96.44% (0.89 mg/g) respectively. At 30 mg/L of initial Cd\(^{2+}\) concentration, the percent adsorption and adsorption capacity values for biosorbents A, B, C, D, and E are 97.56% (2.98 mg/g), 95.03% (2.95 mg/g), 93.63% (2.94 mg/g), 96.31% (2.94 mg/g), and 96.31% (2.95 mg/g) respectively. At 50 mg/L of initial Cd\(^{2+}\) concentration, the percent adsorption and adsorption capacity values for biosorbents A, B, C, D, and E are 97.36% (4.91 mg/g), 94.19% (4.71 mg/g), 92.58% (4.63 mg/g), 92.57% (4.63 mg/g), and 94.01% (4.54 mg/g) respectively. Lastly, at 70 mg/L of initial Cd\(^{2+}\) concentration, the percent adsorption values for biosorbents A, B, C, D, and E are 91.28% (6.47 mg/g), 88.54% (6.28 mg/g), 89.63% (6.27 mg/g), 89.49% (6.19 mg/g), and 92.46% (6.39 mg/g) respectively. From these data which were also plotted in figure 5a, it can be inferred that adsorption capacity values were highest at biosorbent A or pure fly ash for initial Cd\(^{2+}\) concentrations of 10 mg/L, 30 mg/L and 50 mg/L, while at 70mg/L, biosorbent E or pure U. lactuca exhibited the highest adsorption capacity. This is because fly ash has high content of silica and alumina, which are known to have high affinity towards Cd\(^{2+}\) [20].

Because of the high silica content of fly ash, it became an effective adsorbent for Cd\(^{2+}\). Due to the high silica and alumina content of fly ash, several past studies believe that metal ions could be adsorbed on ash as SiO\(_2\) and Al\(_2\)O\(_3\) oxidized functional groups. Furthermore, there is a high affinity of metal ions interaction in the silica surface. Silicon dioxide has very fine pores, which pores can absorb moisture through their physical interactions will retain moisture. Fly ash has a high amount of silicon dioxide based on the elemental analysis. Higher specific surface area, porosity, and narrow particle size distribution are some of the factors that influence the adsorption [21]. Based on the results, larger specific surface area corresponds to more carbon content. Furthermore, adsorption capacity was increased due to the presence of spherical fly ash particles. Apparently, the increase in the surface area leads to a large number of the adsorbed metals. This described the direct relationship of the adsorption and the surface area. Large surface area is catered by finely divided, porous components of fly ash. However, crystalline substances have a lesser surface as compared to finely divided substances which make the powdered fly ash more effective adsorbents than their crystalline forms.

### 3.3 Adsorption isotherms

The parameters and correlation coefficients acquired from the plots of Langmuir and Freundlich isotherm models are listed in table 1.

| Table 1. Parameters for the langmuir and freundlich isotherm. |
|---------------|----------------|
| Model         | Value          |
| Langmuir      |                |
| q\(_m\) (mg/g) | 9.5785         |
| K\(_L\) (L/g)  | 0.348          |
| R\(^2\)       | 0.9927         |
| Freundlich    |                |
| K\(_F\) (mg/g)(L/g)^\(1/n\) | 0.7024 |
| n             | 4.8450         |
| R\(^2\)       | 0.9429         |

Interpreting the correlation coefficient of each isotherm model, the Langmuir isotherm (R\(^2\)=0.9927) directs a better correlation of the experiment data of Cd\(^{2+}\) absorption onto modified ash adsorbent than the Freundlich isotherm (R\(^2\)=0.9870). From the result, it inferred that the adsorption occurred mainly through physical forces and that the surface of the adsorbent is consistent, and uptake of metal ions is by monolayer adsorption. This behavior is visible on the SEM micrographs of powdered fly ash through which its surface was uniformly covered and changed right after the adsorption. Moreover, the value of R\(^2\) for Freundlich isotherm (R\(^2\)=0.9429). However, the R\(^2\) obtained
in the Freundlich model is also high suggesting that not only monolayer adsorption occurred, but also multilayer adsorption occurred indicating a heterogeneous surface of the adsorbent. This can be supported by the FTIR analysis, in which it was found out that there were several functional groups present in both adsorbents primarily fly ash where most of the functional groups responsible for high adsorption intake is present.

4. Conclusion
The study investigated the adsorptive capacity of both pure *Ulva lactuca* and pure fly ash with admixture varying their proportions and was able to propose a predictive mechanism of the adsorption of Cd$^{2+}$ onto the pure fly ash and *U. lactuca* and their respective proportions based on different characterizations. Pure fly ash and pure *U. lactuca* has higher adsorptive capacity than the varied proportions of admixture of the two sorbents. Dosage D (75% Ulva lactuca, 25% fly ash) has the lowest adsorption capacity due to the small amount of fly ash, which has higher adsorptive power than U. lactuca. Maximum adsorption happens on biosorbent a containing pure fly ash at initial cadmium concentration of 10 mg/L and adsorptive capacity of 6.47 mg/g followed by pure *U. lactuca* at similar cadmium concentration with an adsorptive capacity of 6.39 mg/g. Thus, the higher the amount of fly ash utilized as adsorbent, the higher the amount of metal ion adsorbed. Pure fly ash has the optimum adsorptive capacity among the other biosorbent dosages. Biosorption behavior was also observed. It was investigated that the type of adsorption occurred was monolayer on a homogeneous surface. This was concluded since the experimental equilibrium data fitted well to the Langmuir isotherm model. However, based also on the R$^2$ obtained using the Freundlich model, which was also high, multilayer adsorption was also present. Based on the chemistry of the two adsorbents, the physical attributes of fly ash made it more competitive for adsorption than the *U. lactuca*. Fly ash has a higher surface area and more porous than the *U. lactuca* allowing Cd$^{2+}$ to be adsorbed by Fly ash first before *U. lactuca*. Moreover, the electronegative nature of silica and alumina strongly adsorbed Cd$^{2+}$ than the surface electrical charges of the algal species, *U. lactuca*. The proposed mechanism suggests that Cd$^{2+}$ will more likely to be adsorbed by pure fly ash due to its electronegative surface, porosity and surface area followed by *U. lactuca*, and the varied proportions with a higher amount of fly ash. Thus, surface area, porosity, and electronegativity of the sorbent are all directly proportional to the amount of sorbate adsorbed.

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