A Systematic Review on Biosorption of Copper (II) ions in using Water Hyacinth as a Biomass

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Abstract: Due to the recent increase in the concentration of heavy metals in urban bodies of waters in the Philippines due to industrialization, the study sought to determine ideal methods of adsorbing these substances and prevent them from posing adverse health effects to surrounding communities. The method in the study reviewed the literature on using water hyacinth biomass as an adsorbent of heavy metals, specifically copper (II) or Cu(II), in contaminated areas susceptible to polluted wastewater runoff. With this, the ideal adsorbent was determined through factors of particle size, initial ion concentration, adsorption time, ideal conditions, and the adsorbent structure. From the reviewed studies, water hyacinth is an effective biosorbent for copper ions and can reduce copper concentrations in wastewater bodies. Ideal factors for maximum adsorption in terms of wastewater characteristics were conclusive amongst the chosen literature. Other parameters, however, require further investigation to determine if there are trends in how they affect adsorption capacity and removal percentage of the biomass.

Key Words: adsorption; batch process; biosorption; copper; water hyacinth

1. INTRODUCTION

The rise of industrialization has coincided with the increasing presence of heavy metal pollution. This increase occurred rapidly in the latter part of the 20th century in the 1980s and 1990s. A study conducted by Zhou and colleagues (2020) from 1972 to 2017 had determined that sources of the global increase in heavy metal concentration were mining, manufacturing, rock weathering, and agricultural runoff, depending on the region. It was also noted that these increases were more prevalent in developing areas, such as Africa, Asia, and South America, compared to developed regions like Europe and North America.

This development is detrimental to the Philippines as a country heavily reliant on its agricultural and fishery resources. In 2017, Perelonia and colleagues found that heavy metals lead (Pb), cadmium (Cd), and mercury (Hg) had the most notable presence in aquaculture farms and coastal areas in Manila Bay. Although there had been standards set by the Department of Environmental and Natural Resources (DENR) concerning what level of heavy metal presence is considered "safe," in both the water itself and fish samples, several regions had failed to meet these standards during the country's dry and wet seasons respectively.

In the past, water hyacinth has been used as an alternative, cost-efficient method of extracting heavy metals, specifically Cu(II). Research conducted by Saraswat and Rai (2010) examined and experimented on the adsorption capacities of water hyacinth to other heavy metals such as Cd, zinc (Zn), and chromium (Cr). Like these elements, Cu(II) has also shown the potential to be adsorbed by the water hyacinth under different conditions.

The study explored the capabilities of water hyacinth as biomass in the adsorption of heavy metals; specifically, Cu(II), an element found in high amounts in industrialized areas, is easily transmitted and poses serious health threats in high doses. It utilized quantitative studies that tested the capabilities of water hyacinth as an adsorbent of Cu(II) under varying conditions, such as the initial concentration of the heavy metal, the particle size of the water hyacinth biomass, and the amount of time which the adsorbent is placed in the heavy metal solution.

2. METHODOLOGY

The data from other related studies were compared and analyzed for accuracy in creating an effective water hyacinth adsorbent model. The criteria adapted from the data involved the following factors: initial metal ion concentration, ideal water conditions, adsorbent structure, adsorbent particle size, and adsorption time. These factors were chosen as they were related to the adsorption process of the water hyacinth and the efficiency in making the ideal model. Following the methods from similar literature, the study focused on a batch procedure for the analysis.

Electronic studies were searched through available databases. The following databases were searched without language, publication year, or publication status restrictions:

- EBSCO Research Databases via the De La Salle University Libraries (Searched March 22, 2021)
- ScienceDirect via the De La Salle University Libraries (Searched March 22, 2021)
- Scopus via the De La Salle University Libraries (Searched March 22, 2021)
- Google Scholar (March 22, 2021)

3. RESULTS AND DISCUSSIONS

3.1. Water Hyacinth Biomass as an adsorbent for copper(II) ions

Many biosorption studies involving Cu(II) ions utilized dried and groundwater hyacinth. Grinding the biomass increases the surface area, which results in optimal metal adsorption. Gandhimati and colleagues (2013) also used the acid treatment on the biomass. All forms of biosorbent showed effective adsorption of Cu(II) ions, the highest removal percentages at 98.8%, 98.19, and 95.1%, as seen in Table 1. (Gandhimathi et al., 2013; Oktaviyana Lussa et al., 2020; Sadeek et al., 2015; Singa & Das., 2013).

Table 1. Batch Process Adsorption using Water Hyacinth Biomass

Biosorbent Form	Optimal Parameters	Adsorption Capacity	Removal Rate	Reference
Acid-treated	pH 7 10mg/L Cu(II) solution (100 mL) 0.1g/100 mL biomass concentration 300µm - 600µm particle size 75 minute contact time	6.56 mg g^{-1}	89.04%	Gandhimathi et al. (2013)
Leaves, Shoots	250 mL Cu-wastewater 10 g biomass Sieved with 100 meshes 1 hour contact time	22.19 mg g^{-1}	98.19%	Oktaviyana Lussa et al. (2020)
Roots	pH 5 100 mg/L Cu(II) concentration 1 g/100 mL biomass concentration 300µm - 600µm particle size 30°C 20 minute contact time	32.51 mg g^{-1}	80%	Li et al. (2013)
Roots	pH 5.5±0.5 20 mg biomass 50 mL Cu(II) solution, varying concentrations Biomass cut into segments	22.7 mg g^{-1}	>75%	Zheng et al. (2009)
Roots	25 mg/L Cu(II) concentration adsorbent 10 g/L biomass concentration 250–350 µm particle size 5 hour contact time	21.80 mg g^{-1}	>95%	Singha & Das (2013)
Whole Biomass	pH 7 10mg/L metal ion solution, 100 mL 0.1g/100 mL biomass 300µm - 600µm particle size 60 minute contact time	0.49 mg g^{-1}	65.93%	Gandhimathi et al. (2013)
Whole Biomass	pH 7 0.5-1mm particle size 25°C 4 hour contact time	181.8 mg g^{-1}	95.1%	Sadeek et al. (2015)
Whole Biomass	pH 9 0.5-1mm particle size 25°C 3 hour contact time	181.8 mg g^{-1}	98.8%	Sadeek et al. (2015)

When exposed to solutions with several metal ions, the biomass also tends to adsorb ions with a higher ionic radius as they have a greater affinity for adsorption binding sites (Saraswat & Rai, 2010). Compared to other biosorbents, water hyacinth achieves a higher removal percentage at lower pH levels and reaches equilibrium at pH 5 (Husoon et al., 2013; Singa & Das, 2013).

3.1.1 Roots versus Aerial Parts for Adsorption

Table 2. Accumulation of Cu(II) in Water Hyacinth parts

	Concentration in Water Hyacinth (µg g^{-1} dry matter)						
Heavy Metal Concentration	1 mg l^{-1}	3 mg l^{-1}	5 mg l^{-1}	7 mg l^{-1}	10 mg l^{-1}	50 mg l^{-1}	100 mg l^{-1}
Aerial Part	57	68	252	1105	700	1525	1900
Roots	1750	2110	2710	2750	2900	2950	2800

Note. Data was retrieved from Soltan and Rashed (2013).

Several studies utilize either roots or aerial parts; however, limited studies compare the adsorption capabilities of different water hyacinth parts under similar conditions. Soltan and Rashed (2003) explored the adsorption capacities of both root and aerial parts in mixed metal solutions containing Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn at different metal concentrations. They concluded that roots have higher adsorption capacity than aerial parts as seen in Table 2.

3.1.2 Effect of Biomass Concentration on Cu(II) Adsorption

Biomass concentration may also affect the removal rates during metal adsorption. Gandhimathi and colleagues (2013) found that the Cu(II) adsorption percentage increases as the biomass concentration increases from 0.2 g/L until reaching an optimal concentration of 1.6 g/L with a removal percentage of 74.12% for whole biomass and 92.01% for acid-treated biomass, as seen in Figure 1. Increasing the biomass concentration greater than 1.6 g/L yields almost no increase in removal percentage. This is supported by Oktaviyana Lussa and colleagues (2020), who tested three amounts of biomass (10 g, 15 g, 20 g) for copper adsorption in 250mL wastewater mainly containing Cu(II) ions. Although there were minimal differences in adsorption percentage, as seen in Table 3, these two studies depict a trend wherein increasing the biomass concentration beyond a certain point will negatively affect the resulting adsorption percentage due to interference in the number of active bonding sites of the adsorbent.

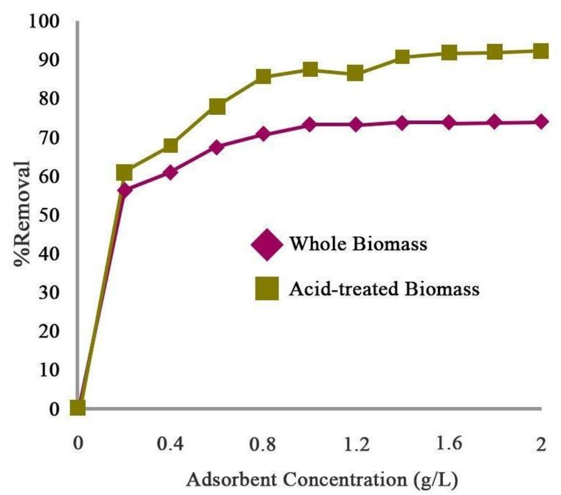

Figure 1. *Effect on Biosorbent concentration on Adsorption Percentage*
Note. Data retrieved from Gandhimathi et al. (2013).

Table 3. *Effect of Mass adsorbent on Cu(II) Adsorption*

	Adsorption Percentage		
Mass Adsorbent	30 min contact time	60 min contact time	90 min contact time
10 g	97.9626 %	98.1918 %	97.9741 %
15 g	96.7479 %	98.1345 %	97.9282 %
20 g	97.6990 %	98.0886 %	97.9168 %

Note. Data retrieved from Oktaviyana Lussa et al. (2020).

3.2 Ideal Wastewater Conditions

From the various studies gathered within the review of related literature, the ideal wastewater conditions revolve primarily around the pH level and initial metal ion concentration. These factors affect the quantity of water hyacinth capable of adsorbing until it reaches the maximum capacity (Saraswat & Rai, 2010). By manipulating how the water hyacinth attracts and binds to the ions, the ideal wastewater conditions will provide an optimal medium for the adsorption of Cu(II) and the adsorbent. Choosing the most favorable condition for the water hyacinth increases the maximum capacity, contributing to greater adsorption capabilities.

3.2.1 pH Level

The pH level of the wastewater can manipulate the surface charge and the solubility of the adsorbent (Smičiklas et al., 2008). Li et al. (2013) used pH levels 1-7 for Cu(II) adsorption using water hyacinth root powder. Throughout the adsorption process, they observed an optimal pH level of 5; however, pH 6 and 7 also followed a similar yield in adsorption percentage as the optimal pH level. This dependence may be attributed to the accessible hydroxide or carboxylic acid. Zheng et al. (2009) determined that the adsorption of copper (II) through water hyacinth roots with an initial pH of 4.5 was optimal in reaching maximum capacity due to the hydrogen ions that act upon the surface charge of the adsorbent. Additionally, another observation suggested that a decrease in maximum capacity starts after pH goes beyond 5.7. Pisitsak et al. (2019) explained the adsorption efficiency at the pH of 4.63 that was determined through a batch adsorption technique. In another study, Lu et al. (2014) used live water hyacinth plants for copper removal and wastewater maintenance. Due to water loss caused by evaporation, transpiration, and water testing, the pH had to be consistently maintained at a pH of 6 daily by adding 1.0 M HCl and NaOH to produce optimal results. A 2016 study by Zheng et al. tested a lowered pH of 3 and noticed a complete lack of adsorption amount for cadmium and a significant decrease in copper and found a range of 5.5 $\pm$ 0.05 to be optimal. The summary of the optimal pH used by the studies is shown in Table 4.

Table 4. *Optimization of pH Level*

Biosorbent Form	Optimal pH Used	Reference
Live Plants	6	Lu et al. (2014)
Plant Fibers	4.63	Pisitsak et al. (2019)
Roots	5.7	Zheng et al. (2009)
Roots	5.5 ± 0.05	Zheng et al. (2016)
Root Powder	5	Li et al. (2013)

The various studies showed that optimizing the pH level can be narrowed down for the adsorption process, with each study presenting an optimal pH range of roughly 4.5 to 5.5. Through experimentation, Li et al. (2013) determined a pH level of 5 as optimal with only minor outliers using 6 and 7. Lu et al. (2014) was an outlier using a pH level of 6, possibly because of the use of live water hyacinth instead of its biomass forms.

3.2.2 Initial Metal Ion Concentration

Saraswat & Rai (2010) mentioned initial metal ion concentration as an essential adsorption parameter because it is dependent on the absorptive surface area of the water hyacinth biomass. In turn, this would affect the saturation of the binding sites if the initial ion concentration were to be increased. This is evident in the study of Singha & Das (2013), which observed that an increase from 5 mg/L to 300mg/L would result in a lower percentage removal, showing a lower concentration would result in the majority of the ions stuck to the binding sites; whereas, a higher concentration would saturate the binding sites and leave excess copper ions in the solution.

A 2008 study by Mishra & Tripathi tested the adsorption capabilities of water hyacinth on five different heavy metals using 100g of live water hyacinth in 10L of water with varying initial ion concentrations. Once again, this study showed that adsorption capacity increases as initial ion concentration decreases. It tested initial copper ion concentrations of 1.0, 2.0, and 5.0 mg/L, resulting i of 95%,, 89% and 86% adsorption capacities, respectively. Similarly, another study made by Mokhtar et al. (2011) also analyzed the initial ion concentration, the range including 1.5, 2.5, and 5.5 mg/L. Using 250g to 300g of live water hyacinths in 8 L of water with the metal ions, the best result was done with 1.5mg/L with 97.3%, and the worst observed concentration was 5.5mg/L with 61.6%.

3.3 Metal Ion Adsorption Process

The experimentation process itself provides several factors that could affect both adsorption percentage and efficiency. These variables are controlled, such as the contact time allowed between the adsorbent and adsorbate. Alternatively, this could also apply to a mechanical filtering process using a filtration column should the study choose to do so.

3.3.1 Contact Time

Contact between the solution and the biomass was often facilitated using incubator shakers at varying speeds and temperatures. While the agitation and its resultant heating of the solution would encourage adsorption, this did not guarantee the highest possible adsorption rate after the solution had reached equilibrium. Qe represented this in Table 5, the equilibrium adsorption capacity calculated from a pseudo-second-order kinetic model as this equation was used amongst all the chosen studies.

Table 5. *Effect of Agitation and Contact Time on Cu(II) Adsorption*

Rotation Speed	Temperature	Time	Q.	Reference
175 rpm	303K	20 min	13.15 ± 0.26	Li et al., (2013)
150 rpm	308K	20 min	24.3	Zheng et al., (2009)
150 rpm	-	5 hr	5.74 (RWH) 9.06 (TWH)	Gandhimathi et al., (2013)

According to the studies conducted by Li et al. (2013) and Zheng et al. (2009), respectively, the maximum adsorption rate was reached within 30 minutes, even peaking after as early as 20 minutes of reaction time. This was contested only by Gandhimathi et al.'s study that used a predetermined reaction time of 5 hours, which resulted in the lowest Q_e value for both types of water hyacinth used in that particular study (raw and acid-treated).

3.3.2 Filtration Column

Mahamadi and Zambara's (2013) study showcased how mechanical filtration could lead to build-up and exhaustion of the biomass before reaching its total adsorption capacity. This filtration setup used the same amount of adsorbent for bed depths of two different measurements: 6.5 cm and 14 cm. The more tightly packed bed depth of 6.5 cm had allowed for the rapid accumulation of Cu within the filtration setup and the exhaustion of the biomass at around 20 hours. However, using a higher bed depth prevented the premature exhaustion of the adsorbent as it was looser and had made more adsorption sites available.

4. CONCLUSION

Water hyacinth is an effective biosorbent for the reduction of copper concentrations in wastewater bodies. Maximizing adsorption capacity and removal percentage in applications requires several factors to be considered. Certain parts of the biomass may result in better outputs. Roots are often preferred over aerial parts; however, limited studies exist comparing the adsorption capacities of parts under the same conditions. The amount of biomass utilized must also be optimized for efficiency as excessive biomass will result in saturation of adsorption sites leading to a limited increase in adsorption and waste of material. Wastewater conditions are also vital. Optimal adsorption results are often produced within pH 4-7, with pH 5 commonly cited as the point of significant increase. Metal ion concentration in the water can also affect removal percentage. Longer contact time during agitation does not garner better adsorption results, thus requiring more studies under the same testing conditions. Alternatively, results while using a filtration column heavily depend on its bed depth. It recommends loosely packing the biosorbent at a higher bed depth, without much emphasis on the height of the setup itself or how much time was spent in contact with it.

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