

A Systematic Review on Water Hyacinth *(Eichhornia crassipes)* as a Biosorbent of Cadmium

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Abstract: Water hyacinth has gained a noteworthy reputation as the worst invasive macrophyte for its alarming proliferation rates, threatening transportation and irrigation systems and ecosystem biodiversity. Sustainable efforts have found the plant to demonstrate efficiency in sequestering toxic heavy metals such as cadmium from marine environments. Cadmium presence in water, primarily caused by anthropogenic sources, poses public health risks due to its toxicity. Consequently, studies on the applications of Eichhornia crassipes and the removal of cadmium have become active research areas in recent decades. This review presents literature related to the Cd sorption capacity of water hyacinth biosorbents. The effects and optimization of parameters including treatment, temperature, pH, initial sorbate and sorbent concentration have been explored in classical and competitive adsorption models. Investigations on kinetics, equilibrium, and desorption studies have also been conducted. From the gathered literature, water hyacinth biosorbents show potential for industrial-scale applications, but its metal recovery and utilization in multi-metal and continuous sorption may require further evaluation.

Key Words: water hyacinth; biosorption; batch adsorption; cadmium; heavy metals

1. INTRODUCTION

Millions of cubic meters of untreated wastewater are disposed of in Manila Bay and Laguna Lake annually (International Water Association, 2018). Within these emissions are potential heavy metals that significantly impact the environment. Cadmium (Cd) is a naturally-occurring, heavy metal that bioaccumulates in organisms, causing adverse health effects such as cancer and toxicity in various organ systems (Rahimzadeh et al., 2017). Industrial effluents released from manufacturing processes are the primary anthropogenic pathway of Cd into the environment (Rao et al., 2010). Moreover, the Cd concentration of tap water sourced from Metro Manila 4.78ppm, exceeding the permissible reached concentration of 0.005ppm set by the WHO (Solidum & Solidum, 2012; World Health Organization, 2010).

To reduce its lethality, remediation techniques such as chemical precipitation, ion exchange separation, adsorption, filtration, reverse osmosis, solvent extraction, and electrochemical treatment have been developed, but most entail expensive operating costs (Wolowiec et al., 2019). Adsorption, however, has been preferred due to its low cost and high efficiency, particularly with the use of agricultural by-products (Lee et al., 2015).

Water hyacinth (Eichhornia crassipes) is regarded as the world's most invasive macrophyte for its alarming growth. It reduces oxygen levels in aquatic ecosystems and encourages diseases in nearby communities. Despite its disadvantages, its biomass has been reported by numerous valorization studies to be efficient in remediating polluted waters and removing toxic heavy metals like Cd. With the need for cost-efficient sustainable adsorbents, the high biomass production, tolerance to pollution, and adsorption capacity of water hyacinths qualify them as effective biosorbents (Priya & Selvan, 2017).

Through a systematic review of literature, relevant studies on Cd biosorption by E. crassipes were synthesized. Particularly, it aimed to evaluate the effects of sorbent treatments and experimental parameters, identify optimal conditions for Cd adsorption by water hyacinth (WH) biosorbents, and determine their applicability in industrial-scale operations.

The paper is solely centered on E. crassipes biomass as a sorbent of Cd. Different methodologies and adsorption systems were considered, where the biosorption capacity of WH was determined through real experiments. The relevance of output limited the reference articles to have been published within the last three decades.

2. METHODOLOGY

The Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines, which include a screening process for articles from



electronic databases, i.e., Scopus, ScienceDirect, and PubMed, were implemented. The keywords used in the initial search include the following terms and their combinations: "water hyacinth" OR "Eichhornia crassipes" AND "cadmium" OR "Cd" AND "adsorption" OR "biosorption". Following established inclusion and exclusion criteria, twenty-nine studies on Cd sorption by WH were deemed eligible (Figure 1).

A data extraction form was utilized to summarize and obtain specific information from the studies. The following items were included: (a) identification data; (b) adsorption type; (c) adsorbent parameters; (d) experimental parameters; (e) maximum sorption capacity; and (f) desorption data. Studies that had consistencies in variables, methodology, and results were sorted and tabulated. Analyses involved the comparison of results, particularly the influence of treatments and parameters on the adsorption capacity of the WH biosorbents.

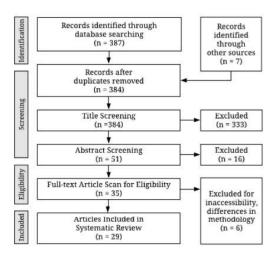


Figure 1. Adapted PRISMA screening process

3. RESULTS AND DISCUSSION

3.1 Classification of Sorbents

Three categories of sorbents were recognized in the studies: live, dried, and pyrolyzed WH biosorbents. Forty-eight percent were conducted using dried E. crassipes, while live biomass and biochar studies each comprised twenty-four percent of publications. One study conducted simulation studies (Soriano et al., 2016) which did not fit in any of the aforementioned classifications. All sorbent types exhibited effective Cd sorption capacity, with the highest removal rates for dried biomass, live water hyacinth and E. crassipes biochars being 99.9%, 100% and 99.24% respectively (Manju et al., 2016; Swain et al., 2014; Li et al., 2016).

3.2 Live Water Hyacinth Biomass for Cadmium Sorption

With the usage of live sorbents, phytoremediation studies precede the more common adsorption methods at present. Cd is primarily bound to WH via peptides (Romanova & Shuvaeva, 2015) while the cell wall and subcellular fractions of tissues account for most of the uptake (Fett et al., 1994b). Four studies applied live WH sorption for Cd removal (Table 1).

From the collated articles, untreated, raw and live E. crassipes biomass have been observed to perform well in terms of Cd sorption at near-neutral pH levels of 6.0-7.0. Acidic conditions have been found to be less ideal due to the binding competition between Cd2+ and H+ ions to WH adsorption sites. Similarly, Cd removal is most favorable in the absence of other metals; single-sorption systems produced the best Cd removal rates. (Hasan et al., 2007; Patel et al., 2014; Mishra & Tripathi, 2008). It was found that longer exposure times $(\geq 10 \text{ days})$ led to higher Cd accumulations. Moreover, the highest percent removal was at minimum initial Cd concentrations. While modifications might improve the metal uptake of E. crassipes, cadmium, at high concentrations, bears toxic effects on WH and suppresses plant growth and absorption (Fett et al., 1994a; Mishra & Tripathi, 2008). At larger scales where Cd is prevalent, live sorbents are not as reliable for removal.

3.3 Application of Dried Water Hyacinth Biomass in Cadmium Removal

Table 1. Batch cadmium sorption using live WH biomass.

Biomass Part	Optimal Parameters	Removal/Sorption Capacity	Reference
Roots, Shoots	pH 7.0; 1.0 mg L ⁻¹ Cd(II); 16 days	92.0% - single 73.2% - binary (vs Zn)	Hasan et al. (2007)
Whole Biomass	$2.0\ mg\ L^{-1}\ metal\ concentrations;$ 12 days	0.31 mg g ⁻¹ , 85% – quinary (vs Cu, Cr, Zn, Fe)	Mishra & Tripathi (2008)
Whole Biomass	pH 6; 10 mg L ⁻¹ Cd	20.54%	Patel et al. (2014)
Whole Biomass	pH 6.7; 0.27 mg L ⁻¹ Cd; 15 days	100%	Swain et al. (2014)

The Cd removal behavior of dried water hyacinth roots, shoots, and whole biomass has also been studied in various conditions (Table 2). To maximize surface area and available sites for adsorption, the biomass is usually dried and crushed into powder. According to Khatoon et al. (2016), pretreatment of biosorbents may result in the opening of biopolymer rings, increasing porosity and stability,



ultimately improving the heavy metal removal efficiency of the sorbent.

The effects of different pretreatment factors, including drying temperature and sorbent size on the

Table 2. Batch cadmium adsorption via dried WH biomass.

Biosorbent Treatment	Optimal Parameters	Removal/Sorption Capacity	Reference
Whole biomass, dried at 60°C		27 mg g ⁻¹ - quatemary (vs Pb, Cu, Zn)	Schneider et al. (1995)
Acid-treated biomass, oven-dried at 65°C for 12h	pH 7.10; 250 mg L ⁻¹ Cd; 3.5 g L ⁻¹ sorbent dose	87.54 mg g ⁻¹	Mahamadi & Nharingo (2006)
Acid-treated roots, wen-dried at 65°C for 2h	pH 5.8; 300 mg L ⁻¹ Cd	4.0 mg L ⁻¹ – quaternary (vs K, Ca, Mg)	Mahamadi & Zaranyika (2007)
Whole biomass, bried at 70°C for 48h	30 mg L ⁻¹ Cd	1.98 mg g ⁻¹ − single; 1.96 mg g ⁻¹ − <u>senary</u> (vs Cu, Zn, Ni, Pb, Cr); ≈98%	Verma et al. (2008)
Ash, air-dried and oven-dried, ournt at 220°C	$30~\mu g~mL^{-1}~Cd$	28.41 μg g ⁻¹	Mahmood et al. (2010)
Acid-treated roots, ann-dried for 2d, oven-dried at 65°C for 12h		9.92 mg g ⁻¹ - single 2.43 mg g ⁻¹ - binary (vs Pb); 6.42 mg g ⁻¹ - binary (vs Zn) 3.01 mg g ⁻¹ - ternary (vs Pb, Zn)	Mahamadi & Nharingo (2010)
Whole biomass, Iried separately at 80°C, 50°C	pH 5.0 30°C drying temperature; non-uniform sorbent size; 30°C; 60 min contact time	0.667 meq g ⁻¹ , >60% - binary (vs Zn)	Modenes et al. (2011)
Roots, shoots, kried at 65°C for 48h	pH 5.0; 50 mg L ⁻¹ Cd,	79.65% - roots; 79.22% - shoots	Ibrahim et al. (2012)
	5.0 g L ⁻¹ sorbent dose; 60 min contact time		
Acid-washed whole biomass, oven-dried at 60°C for 24h	pH 6.0; 0.2 g mL ⁻¹ sorbent dose; 300 mg L ⁻¹ Cd; 45°C; 175 rpm	104.16 mg g^{-1}	Murithi et al. (2014)
Emericella nidulans-immobilized biomass, dried at 50°C	pH 6.0; 1% sorbent dose; 100 mg L ⁻¹ Cd; 120 min sorption time; 40℃	99.9%	Manju et al. (2016)
Roots, dried at 70°C	pH 6.0; 0.267 mmol L ⁻¹ Cd and 0 mmol L ⁻¹ Cu - binary;	5.43% - single 0.62% - binary (vs Cd) (in Cd/biomass Wt%)	Zheng et al. (2016)
Leaves, dried in shade for 3d	pH 8; 250 mg L-1 Cd	96%	Hassoon & Najem (2017)
Sodium-alginate microspheres, oven-dried at 105°C	96h sorption time	94.2%	Grenni et al. (2019)
Shoots, oven-dried at 60°C	pH 6.5; 5 g L ⁻¹ sorbent dose; 10 mg L ⁻¹ Cd; 60 min sorption time	21.6 mg g ⁻¹	Li et al. (2020)

maximum adsorption of the WH have been taken into consideration. Modenes et al. (2011) observed greater adsorption capacity at the lower drying temperatures due to greater pore size contraction at high temperatures. Modenes et al. (2011) also found little variation in adsorption capacity of different sorbent particle sizes.

The studies on dried WH biosorption of Cd have determined different parameters to maximize adsorption rates. Several studies have found that a neutral acidity of pH 5.0 to 7.0 would be optimal for Cd adsorption due to a lower concentration of hydrogen ions competing for the sorption sites on the sorbent (Modenes et al., 2011; Manju et al., 2016; Zheng et al., 2016). Sorbent dose affects the electrostatic interactions between particles, and a ceiling of adsorptive capacity emerges at greater sorbent doses (Ibrahim et al., 2012). At 0.2 to 0.5mm, 5g L-1 of biomass reached maximum adsorption, while 1.0mm particle size plateaued at 0.2g mL-1; this signifies that the use of a smaller sorbent size requires less sorbent to reach the optimal amount (Ibrahim et al., 2012; Murithi et al., 2014; Li et al., 2020). Initial Cd concentration also affects the adsorption capacity of the biomass. With a greater amount of Cd ions present, the increased rate of adsorption reaction causes more amounts of the metal to be adsorbed but decreases the removal percentage of Cd (Mahamadi & Zaranyika, 2007; Mahamadi & Nharingo, 2006; Li et al., 2020; Murithi et al., 2014; Manju et al., 2016). The adsorption of Cd ions by WH consistently followed the pseudo-second-order model and fitted the Langmuir adsorption model. With the presence of other heavy metals, the competitive adsorption of Pb and Zn significantly hindered the adsorption of Cd, while Na, K, Mg and Ca had minimal to no impact (Mahamadi & Nharingo, 2010; Murithi et al, 2014).

3.4 Cadmium Biosorption via Water Hyacinth Biochar

The utilization of water hyacinth-derived biochars for Cd removal from aqueous solutions is relatively unexplored, with publications surfacing only recently (Table 3). However, it is a promising method to manage the invasive species and immobilize Cd effectively.

The heating temperature during biochar generation influences adsorption capacity. A pyrolysis temperature between 450°C to 700°C is found to be ideal (Zhang et al., 2015; Ding et al., 2016; Li et al., 2016). Ding et al. (2016) inferred that higher pyrolysis temperatures encouraged surface area and porous structure, but increasing the temperature beyond 600°C causes the loss of oxygen-containing groups. Increasing temperature results in greater Cd removal, but extreme heat dissipates functional groups essential for adsorption. Zhou et al. (2019) recommended a heating rate of 15°C min-1 for 2 hours, demonstrating a slow pyrolysis to be most effective.

Compared to dried and live biosorbents, WH biochars appear to be better accumulators of Cd at high and low initial concentrations in terms of adsorption capacity and metal removal. Higher concentrations of Cd require longer exposure times as presented by Zhang et. al (2015). Solution temperature heavily influences the adsorption behavior of biochars due to its endothermic characteristic (Ding et al., 2016; Liu et al., 2020),



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wherein increasing the temperature during sorption encourages Cd sorption mechanisms to occur. Solution pH has been considered as one of the most influential factors to the adsorption capacity of biochars. The surplus of H+ at low pH levels (>2.50) overwhelmed and protonated the negatively-charged biochar surface, repelling Cd2+; thus, a moderate pH level of 5.0-6.0 has been deemed optimal (Ding et al., 2016; Li et al., 2016; Liu et al., 2020).

Table 3. Batch cadmium adsorption by WH biochars.

Biochar Treatment	Optimal Parameters	Removal/Sorption Capacity	Reference
Acid-washed biochar	450°C pyrolysis; 24h sorption time	70.313 mg g ⁻¹	Zhang et al. (2015)
WH Biochar	450°C pyrolysis; pH 5.0; 100 mg L ⁻¹ Cd; 30°C	74.99 mg g ⁻¹	Ding et al. (2016)
WH Biochar	700°C pyrolysis; 1.0 g L ⁻¹ sorbent dose; pH 5.0; Imol L ⁻¹ Cd; 25°C	25.826 mg g ⁻¹ , 99.24%	Li et al. (2016)
Root biochar	500°C pyrolysis; 1.0 g L ⁻¹ sorbent dose;	39.81 mg g ⁻¹ , 96.24%	Li et al. (2018)
4 	100 mg L ⁻¹ Cd; 298K		77
Roots, leaves biochar pellets immobilized with <i>Chlorella</i> sp.	pH 6.0; 10 mg L ⁻¹ Cd(II); leaf biochar pellet immobilized with <i>Chlorella</i> sp.; 119 μmol m ² s ⁻¹ illumination	13.81 mg g ⁻¹ , 92.45%.	Shen et al. (2018)
Stem biochar 400°C pyrolysis; 2h heating time; 15°C min ³ heating rate;		20.175 mg g ⁻¹ , 80.70%	Zhou et al. (2019)

3.5 Cadmium Desorption and Recovery

Biomass regeneration potential and cadmium recovery are necessary determinants for the applicability of WH biosorbents at industrial scales. The practical efficiency of a biosorbent is determined not only by its adsorptive capacity but also by its accessibility and potential for reuse.

Shen et al. (2018) reported the use of nitric acid as an eluent at lower molar concentrations, wherein the Cd (II) removal efficiency of E. crassipes biochar pellets remained at 91.1% after three adsorption-desorption cycles. Meanwhile, Zheng et al. (2016) utilized Cu (II) ions, that have high affinity to sorption sites, to desorb over 90% of Cd (II) from dried biomass. Liu et al. (2020) demonstrated the sustainability of WH biochar-alginate capsules, which retained up to 70% of its initial adsorption capacity following 10 reuses.

As shown in Table 4, a number of studies accounted for the usefulness of the high Cd desorption capacity of WH for biomass regeneration and Cd recovery (Mahmood et al., 2010; Ding et al., 2016; Shen et al., 2018). However, at present circumstances, a survey of literature shows that WH-biosorption studies expounding on Cd recovery are limited. Table 4. Cadmium desorption by WH biosorbents.

Biosorbent Type	Eluent	Maximum Desorption Capacity	Reference
WH-derived ash	HNO,	27.54 μg g ⁻¹ , 96.9%	Mahmood et al. (2010)
WH biochar (450°C)	HCI	≈60%	Ding et al. (2016)
Dried WH roots	Cu	>90%	Zheng et al. (2016)
WH leaf biochar pellets	HNO3		Shen et al. (2018)

4. CONCLUSIONS

Water hyacinth biosorption is an effective means for cadmium remediation. Through biosorption applications, the environmental concerns associated with the toxicity of cadmium and the invasive property of E. crassipes are minimized. Several solution and sorbent parameters significantly impact its adsorption capacity. Cadmium sorption is favored at near-neutral pH levels to reduce competition with interfering ions, while lower initial sorbent and sorbate concentrations allow maximized adsorption without risk of precipitation. Unlike dried biomass, live biosorbents are hindered by metal toxicity. Pretreatment of biomass is advantageous as dried biosorbents have consistent efficient removal rates. However, biochar studies have become more prominent in recent years. The inclusion of pyrolysis high temperatures allows more sorbent at modifications such as the increased presence of functional groups, porosity, and surface area that aid in adsorption. Despite the accessibility, inexpensive cost, and excellent removal capacity of WH biomass, its usage in industrial scales requires further investigation, specifically on the themes of cadmium desorption, metal recovery, multi-metal, and continuous sorption systems.

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