



Utilization of Reeds to Sequester and Recover Metals When Cu^{2+} and Ni^{2+} Present Individual or as a Binary Mixture in Simulated Wastewater

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Abstract This project evaluated the potential of common reed to recover heavy metals as valuable products. Common reeds were grown in 25, 50, or 75 ppm Ni^{2+} and/or Cu^{2+} solutions for 4 weeks to evaluate its potential to uptake metals followed by converting the contaminated biomass to valuable products by hydrothermal conversion (HTC). The higher concentration of metals in solution, the more metals accumulated in plants. Most metals were sequestered in the roots of reeds. Roots and stems treated with binary metals contained less $\text{Ni}^{2+}/\text{Cu}^{2+}$ than those cultured in single metal. The yields of bio-oils and hydrochars from reeds treated with different levels of metals were similar. About 6–10% of the total biomass were transferred to bio-oil, while 50–60% of the biomass were produced as hydrochars. The results suggest that metal accumulated in reeds does not affect the utilization of contaminated reeds via HTC. About 0.1–1.5% of Cu^{2+} and/or Ni^{2+} absorbed in biomass were transmitted from contaminated reeds to bio-oils after HTC at 250 °C.

Keywords Common reed · Phytoremediation · Hydrothermal conversion · Heavy metals · Ni^{2+} · Cu^{2+}

1 Introduction

Global energy demand is rapidly increasing due to population growth, urbanization, and economic development. Despite the large economic benefits, energy production technology receives negative attention for its impacts on the environment, including water consumption, wastewater generation, and heavy metal productions. Currently, coal is the primary global source to produce electricity (Our World in Data, 2023) while coal mining activities produce high levels of metals. Some heavy metals are essential as co-enzymes for human health (e.g., Fe^{2+} , Mn^{2+}) while other metals are toxic (e.g., Hg^{2+} , Cd^{2+}) (Rugnini et al., 2017). However, even necessary heavy metals if released in high levels from industrial process can be toxic to human and wildlife. For instance, the recommends level of Ni^{2+} in drinking water should not be more than 0.1 mg/L (ATSDR, 2005). However, Ni^{2+} is reported to be 20–200 mg/L in many industrial processes (Revathi, 2005). Exposure to high levels of Ni^{2+} may cause diseases like asthma and pneumonia (Genchi et al., 2020). National Pollutant Discharge Elimination System (NPDES) requires a daily maximum limit of 0.5 mg/L for total copper (Liu et al., 2023). However, copper concentrations ranging from 2.5 to 10,000 mg/L have been reported in industrial

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wastewater (Liu et al., 2023). Discharging water that exceeds NPDES limits is concerning as long-term exposure to high levels of copper through can lead to severe liver and kidney damage (Royer & Sharman, 2023). Thus, pursuing sustainable energy production with simultaneous recovery of heavy metals in effluent streams is essential. A unique way to accomplish these tasks is by using phytoremediation to uptake heavy metals from the contaminated environment followed by converting the biomass to produce bio-oils, hydrochars, and other valuable byproducts by hydrothermal conversion process.

Phytoremediation is an environmentally friendly treatment method that uses plants to uptake contaminants in the environment (Ghosh & Singh, 2005). More than 500 plant species from 101 families have been investigated to sequester and accumulate contaminants (Hemen, 2011). The common reed (*Phragmites australis*) has been widely used due to the advantages of being: widely distributed in the world; highly adaptable to harsh environmental conditions; able to grow in hydroponic or terrestrial habitat; able to yield high biomass; and tolerant to heavy metals and organic matters (Reale et al., 2012). *Phragmites australis* showed great potential to remove heavy metals from contaminated soils, synthetic soils, irrigation water, secondary treated wastewater, urban swages, urban waste leachate, and acid mine drainage (Rezania et al., 2019). For example, more than 60% of Fe^{2+} , Cu^{2+} , Ni^{2+} , and Mn^{2+} in paper manufacturing wastewater were removed by *Phragmites australis* (Rezania et al., 2019). Around 50–60% of Hg^{2+} was accumulated in *Phragmites australis* from Hg^{2+} contaminated soil after 36 weeks (Rezania et al., 2019). Similarly, Bonanno (2011) observed that *Phragmites australis* can accumulate various metals (e.g., Al^{3+} , Mn^{2+} , Ni^{2+} , Cu^{2+}) into its roots, stems, and leaves.

Although much research was done to evaluate the ability of reeds to uptake a variety of metals, how the concentration and type of metals influence metal sequestration in reeds still needs to be further studied. Another critical issue with phytoremediation is how to prevent secondary contamination to environment from the contaminated biomass. Two promising uses of phytoremediation biomass is to produce bioenergy which is more sustainable compared to fossil fuels; and hydrochars which could be used as fuels, sorbents, and/or catalysts. Different types of bioenergy can be

produced by different thermochemical treatments of biomass, which includes anaerobic treatment, pyrolysis, hydrothermal conversion (HTC), and gasification (Abdelsalam et al., 2009). Compared to other thermochemical treatments, HTC has several advantages. For instance, the yields of bio-oils generated from all biomass components, including lipids, proteins, and carbohydrates, from HTC are generally higher than other processes (Xu et al., 2018). In addition, most nutrients, such as N, P, and K, remain in the aqueous phase product of HTC and can be reused for growing biomass (Xu et al., 2018). However, the research related to the HTC process of contaminated common reed is very limited. Therefore, in this project, we evaluated the ability of reed to uptake Cu^{2+} and/or Ni^{2+} from wastewater followed by investigating the production of bio-oils and hydrochars from the contaminated reeds by HTC.

2 Materials and Methods

2.1 Hydroponic Solutions

Ni^{2+} and Cu^{2+} were the metals of interest as they are the most abundant metals produced by industrial process. The control solutions contained 1000 mL distilled (DI) water and 2 g commercial MaxiGro nutrients, which include 10.0% total nitrogen (N); 1.5% ammoniacal nitrogen (N); 5.0% available phosphate (P_2O_5); 14.0% soluble potash (K_2O); 6.0% calcium (Ca); 2.0% water soluble magnesium (Mg); 3.0% sulfur (S); 3.0% combined sulfur (S); 0.24% iron (Fe); 0.1% manganese (Mn). To study the capability of reeds to accumulate contaminants under the stress of single and binary metals, the treatment solution also contained nutrients and three levels of Ni^{2+} and/or Cu^{2+} (25, 50, and 75 mg/L) by adding analytical grade metal salts (Cu^{2+} as CuCl_2 , Ni^{2+} as NiCl_2). The initial pH of all the solutions was adjusted to 6.00 ± 0.05 . The selected levels were considered based on the common concentration in wastewater and the tolerance limits of plants (Ali et al., 2003; Baldantoni et al., 2009; Rzymiski et al., 2014; Sochacki et al., 2015). The water level was monitored. DI water was added into the hydroponic solutions to make sure the volume of the solutions was maintained at 1000 mL during the experiments.

2.2 Plant Sources

Rhizomes of common reed were purchased from Constructed Wetland Groups (CWG) and then cultured in commercial potting soil. After 30 days of growth in potting soil, seedlings of reeds with similar size were transferred into solutions to initiate the experiments. Reeds were cultured in the control and treatment solutions for 4 weeks.

2.3 Plant Digestion

After 4 weeks, plants were taken out from the solutions and cleaned by DI water. Plants were directly digested or processed by HTC as follows. First, plants were separated into roots, rhizomes, stems, and leaves and then air dried. Then plant tissues were weighed and crushed in a mortar and pestle. The milled tissues were then digested according to the methods presented in Guo and Cutright (2017): soaked 1 g of plant tissues in 20 mL of nitric acid (70%) for 6 h; boiled down the mixture to 10 mL; then added 4 mL of perchloric acid (70%); and heated for 90 min. Finally, the solution was diluted to 20 mL with distilled water. All plants digestion solution were filtered by 0.45 μm filters and analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy ICP-OES (Thermo Scientific™ iCAP™ PRO Series) which was purchased in 2021. To ensure data quality, all the samples analyzed by ICP-OES were repeated three times. The accuracy of ICP-OES for Cu^{2+} and Ni^{2+} was more than 98% based on the ICP standards.

2.4 HTC Process

The detailed HTC and product separation procedures are described in the previous publication (Haque et al., 2022). Briefly, the HTC process was carried out using a 30 mL High Temperature High Pressure (HTHP) batch reactor from Parr Instrument Company (Series 4590 Micro Stirred Reactor $\leq 5000\text{psi}$, $\leq 500^\circ\text{C}$). Tests included 1.5 g of dried control and contaminated reeds and 15 mL of DI water in the HTHP reactor and heated up to 250°C as quickly as possible (about 30 min) then cooled down immediately after reaching 250°C . After HTC, the gases were released without analysis. Other products were mixed with dichloromethane (DCM) followed by filtration to separate solids which are hydrochars

after washing and drying. The DCM portion was separated from the aqueous portion and evaporated under vacuum to recover bio-oils to determine the bio-oil yields. The yields of bio-oils and hydrochars are calculated based on the following equation:

$$\text{Yield}(\%) = 100\% \times \text{mass of bio-oils (or hydrochars)} / \text{mass of biomass}$$

2.5 HTC Product Analysis

The products from HTC of reeds were microwave digested. Ten mg of samples were mixed with 10 mL of concentrated nitric acid in SVT50 vessels and placed in the Anton Paar Multiwave 5000 microwave system where the temperature was ramped to 200°C in 20 min and stayed at 200°C for 10 min. After digestion, the samples were diluted to 25 mL using DI water followed by ICP analysis. Calibration was conducted using 0.1, 1.0, and 10 ppm standards of Cu^{2+} and/or Ni^{2+} .

2.6 Statistical Analysis

A completely randomized design was used to set up the pot experiments. All the treatments were replicated three times. Data were analyzed with one-way ANOVA using the Minitab statistical package (Minitab 16). Differences between specific metal levels were identified by Tukey's test at 5% significance level.

3 Results and Discussions

Reeds can successfully grow in all the metal solutions. Although the leaves of reeds cultured in solution with 75 mg/L Cu^{2+} and/or Ni^{2+} turned black, seedlings can still germinate from the rhizomes. The amounts of metals accumulated in reeds under different treatment were further analyzed as follows.

3.1 Metal Uptake in Reeds

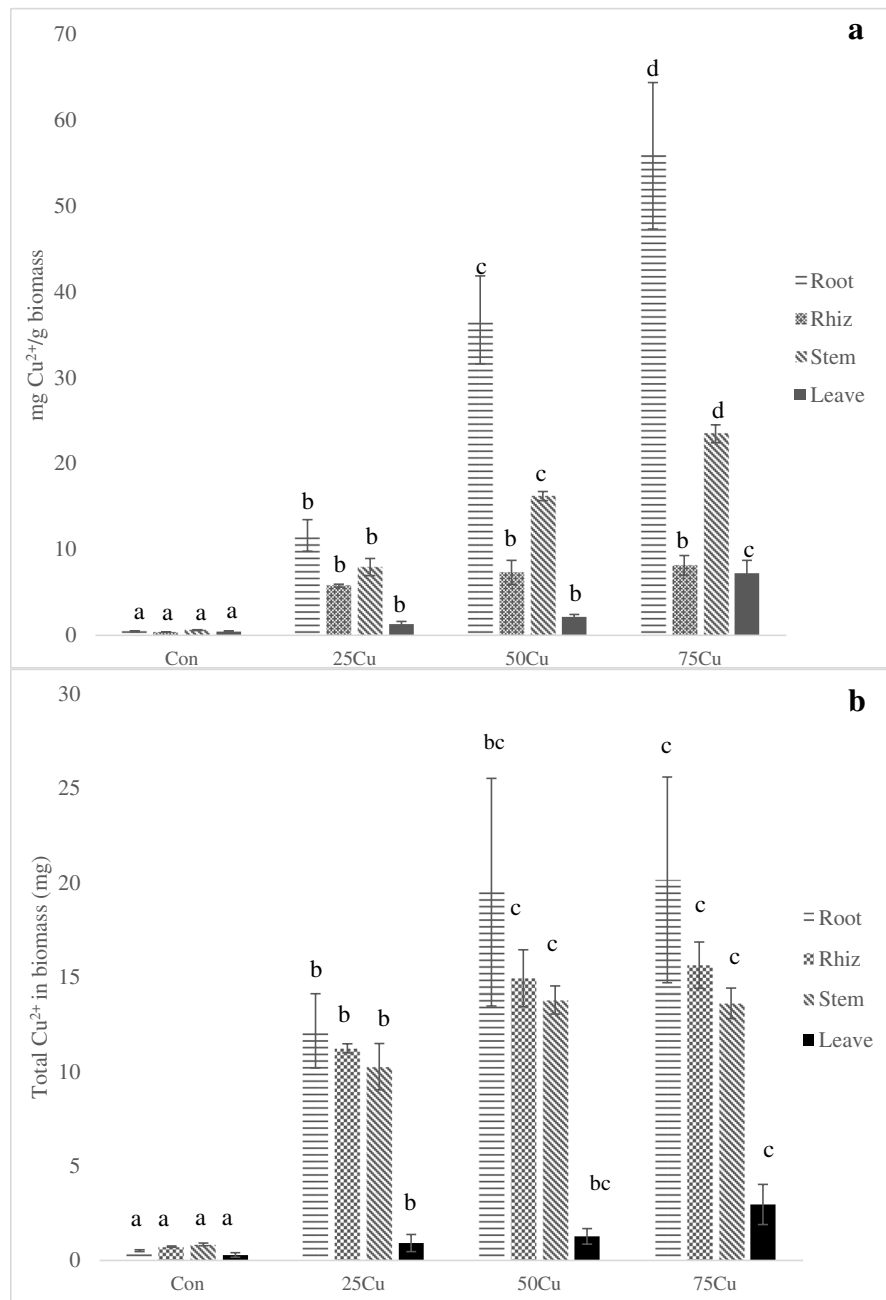
3.1.1 Reeds in Solutions with Single Metals

The content of Cu^{2+} in tissues of reeds cultured in solutions with different levels of metals were analyzed. As expected, the accumulation of metals in

plants was positively related to the concentrations of metals in solutions. The higher levels of Cu^{2+} in solution, the more Cu^{2+} was accumulated in different parts of reeds. For instance, the roots of reeds grown in solutions with 25 mg/L Cu^{2+} accumulated 11.62 ± 1.83 mg Cu^{2+} /g in dried biomass, while the roots in 75 mg/L Cu^{2+} solutions sequestered 55.82 ± 8.52 mg/g Cu^{2+} (Fig. 1a). The stem

of reeds in 50 mg/L Cu^{2+} solutions accumulated 16.22 ± 0.53 mg/g Cu^{2+} which was significantly higher ($p < 0.05$) than that in the stem of reeds grow in 25 mg/L Cu^{2+} (7.95 ± 0.99 mg/g Cu^{2+}) (Fig. 1a). The total amounts of metals in the tissues of reeds also increased with the metals in solutions. For example, reeds grown in solutions with 25 mg/L Cu^{2+} accumulated 11.23 ± 0.24 mg Cu^{2+} in rhizomes,

Fig. 1 A The concentrations of Cu^{2+} in each tissue of reeds (mg Cu/g biomass) and (b) the total Cu in each tissue of reeds cultured in solution with 25 mg/L, 50 mg/L, and 75 mg/L Cu^{2+} for 4 weeks. Error bar represented the standard deviation of triplicate samples. Different letters on the same plant organ indicate a significant difference at $p < 0.05$



while the rhizomes in solutions with 75 mg/L Cu^{2+} sequestered 15.63 ± 1.23 mg Cu^{2+} in total (Fig. 1b). A previous report also indicated that the levels of metals accumulated in reeds was directly related to the amounts of metals in environment (Ghassemzadehas et al., 2008). The amounts of metals in reeds were higher than some other plants cultured in Cu^{2+} contaminated medium. For example, *C. esculentus* was reported as a root accumulator for Cu^{2+} which took up 0.30 ± 0.04 mg/g Cu^{2+} from 50 mg/L Cu^{2+} solutions; *T. angustifolia* cultured in 50 mg/L Cu^{2+} solutions also sequestered most Cu^{2+} in the roots (0.35 ± 0.07 mg/g Cu^{2+}) (Chandra & Yadav, 2011).

Most Cu^{2+} in reeds was stored in the roots of reeds in our project. The concentration of Cu^{2+} (mg Cu^{2+} /g biomass) in different tissues was root > stem > rhizome > leave while the total amounts of Cu in each tissue was root > rhizome ~ stem > leave. Previous studies also found that large amounts of heavy metals (e.g., Mn^{2+} , Pd^{2+} , Zn^{2+}) were preferentially accumulated in the roots and rhizomes of reeds (Ali et al., 2002; Rzymiski et al., 2014). Cu^{2+} sequestered in reeds grown in a wetland also followed the order of root > rhizome > shoot (Bonanno and Giudice 2010). Similarly, Fawazy et al. (2012) reported that most of Cu^{2+} was stored in the roots of reeds while some other metals, such as Pb, were found in the shoot. However, some other research indicated that the amounts of Cr^{3+} , Cu^{2+} , and Zn^{2+} in rhizomes and stems of reeds were very similar (Bragato et al., 2009). The contents of heavy metals accumulated in various parts of reeds are affected by many factors, such as the growth stage of the reeds, the culturing time, and the availability of metals (Eid et al., 2020; Guo & Cutright, 2017). For example, the tendency of reeds storing more toxic metals in roots is a protection mechanism of plants (Baldantonni et al., 2009). By immobilizing metals in roots, less toxins would be transferred to rhizomes which are the only persistent part of the plant for growth (Baldantonni et al., 2009). The below ground to above ground translocation system in reeds may also act differently in different seasons (Bragato et al., 2009). During the growth of reeds, more metals may be translocated into stem, but less into leaves to protect the photosynthesis organ (Bragato et al., 2009). Our experiments were conducted during summer, which is the growing season of reed. Thus, it is not surprising to note that the levels of metals in leaves were low.

The translocation factors (TF), the ratio of metal in plant shoots to that in roots, were calculated (Bragato et al., 2008). TF of Cu^{2+} in reeds cultured in all solutions were less than 1 (Table 1) which further indicates that most Cu^{2+} were sequestered in the roots of reeds but was not a hyperaccumulator for Cu^{2+} . Previous research also reported that the TF of Cu^{2+} in reeds sampled from a lake was around 0.7 (Eid et al., 2020). TF of Cu^{2+} in reeds grown in constructed wetlands with electroplating wastewater was also found in the range of 0.31–1.28 (Sochacki et al., 2015). Cu^{2+} is an essential element needed for the plant health but may pose toxicity when the level is too high (Bragato et al., 2008), which may limit its mobility into the shoots of reeds. In addition, the low TF of Cu^{2+} may also be due to its tendency to precipitate (Bonanno, 2011). Although reed is not a hyperaccumulator for Cu^{2+} , it still can be efficiently used in restoration of sites contaminated by heavy because of its vigorous roots, fast growth rates, and high biomass (Prica et al., 2019; Reale et al., 2012). Abundant research has further confirmed its phytoremediation potential for metal-contaminated sites (Perna et al., 2023; Reale et al., 2012; Rezanian et al., 2019).

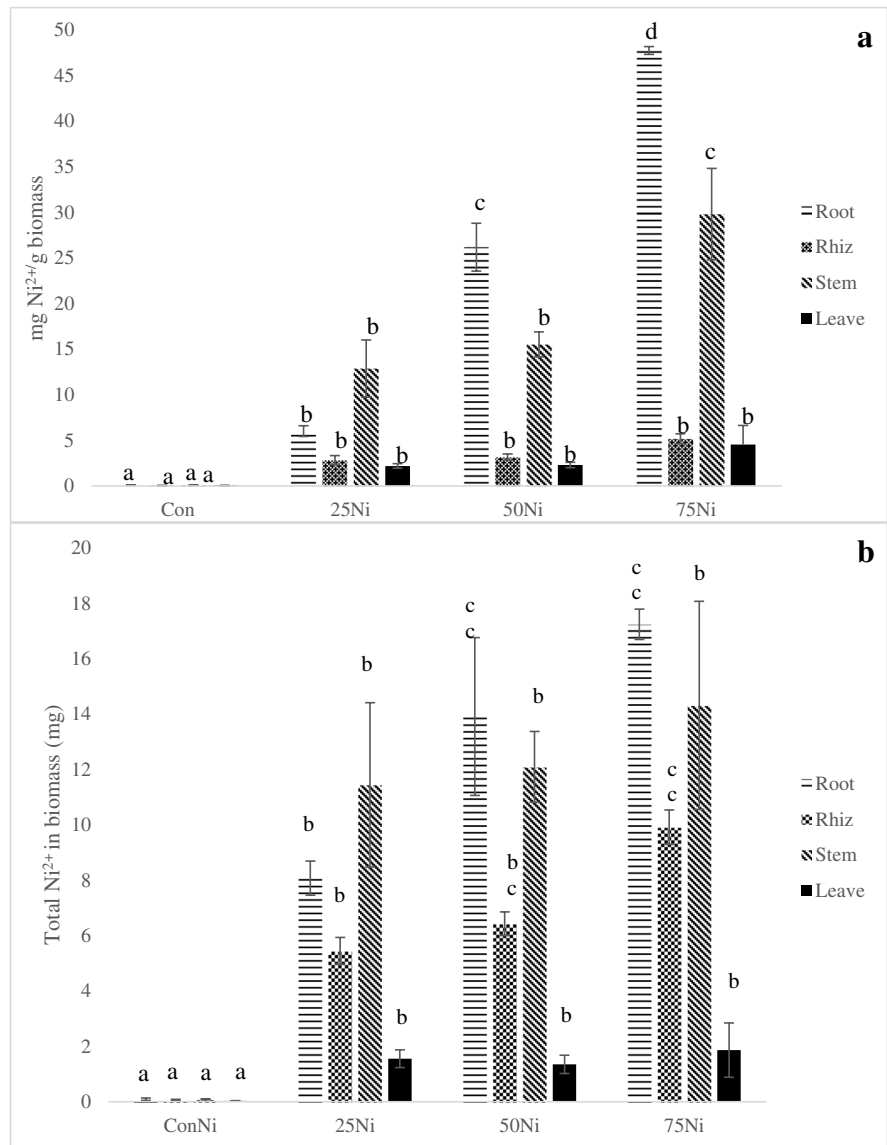
Similarly, with the increase of aqueous Ni^{2+} concentration, the Ni^{2+} contents in roots of reeds also increased. For instance, the roots of reeds grown in solutions with 25 mg/L Ni^{2+} accumulated 6.00 ± 0.58 mg/g Ni^{2+} , while the roots in solutions with 75 mg/L Ni^{2+} sequestered 47.75 ± 0.43 mg/g Ni^{2+} (Fig. 2a). The roots treated with 75 mg/L Ni^{2+} sequestered 17.24 ± 0.55 mg Ni^{2+} in total which was also higher ($p < 0.05$) than those in roots cultured in 25 mg/L Ni^{2+} solutions (8.07 ± 0.62 mg Ni^{2+}) (Fig. 2b). The concentrations of Ni^{2+} (mg Ni^{2+} /g

Table 1 Translocation factor (TF) of Cu^{2+} in different solutions

Solutions	TF of Cu^{2+}
25 mg/L Cu^{2+}	0.83 ± 0.30 a
50 mg/L Cu^{2+}	0.51 ± 0.10 a
75 mg/L Cu^{2+}	0.57 ± 0.15 a
25 mg/L $\text{Cu}^{2+} + \text{Ni}^{2+}$	0.84 ± 0.05 a
50 mg/L $\text{Cu}^{2+} + \text{Ni}^{2+}$	0.61 ± 0.23 a
75 mg/L $\text{Cu}^{2+} + \text{Ni}^{2+}$	0.24 ± 0.07 b

The TF of Cu^{2+} in reeds treated with different levels of metals; Different letters in the same column indicate a significant difference at $p < 0.05$

Fig. 2 A The concentrations of Ni^{2+} in each tissue of reeds (mg Ni/g biomass) and (b) the total Ni^{2+} in each tissue of reeds cultured in solution in solution with 25 mg/L, 50 mg/L, and 75 mg/L Ni^{2+} for 4 weeks. Error bar represented the standard deviation of triplicate samples. Different letters on the same plant organ indicate a significant difference at $p < 0.05$



biomass) in the tissues also followed the same order as Cu^{2+} : root > stem > rhizome ~ leave, while the total amounts of Ni^{2+} in tissues also depicted the similar trend of root > stem > rhizome > leave. For example, the stems of reeds cultured in the 75 mg/L Ni^{2+} solution accumulated 29.81 ± 5.01 mg/g Ni^{2+} which was significantly ($p < 0.05$) higher than that in the stems grown in 25 mg/L Ni^{2+} (12.86 ± 3.14 mg/g Ni^{2+}) (Fig. 2a). The total amounts of Ni^{2+} in leaves of reeds grown in 75 mg/L Ni^{2+} were 1.86 ± 0.98 mg which were lower ($p < 0.05$) than that in the rhizomes of reeds cultured in 75 mg/L Ni^{2+} solutions (9.91 ± 0.62 mg) (Fig. 2b). The levels of Ni^{2+}

found in reeds in our study were similar to previous research, which reported that the concentration of Ni^{2+} in belowground tissues of reed grown in a wetland ranged between 6.26 and 67.27 mg/g Ni^{2+} , while the amounts of Ni^{2+} in aboveground tissues can be from 5.13 and 50.02 mg/g Ni^{2+} (Cicero-Fernández et al., 2017).

TF of Ni^{2+} in reeds cultured in solutions with 50 mg/L Ni^{2+} and 75 mg/L Ni^{2+} are similar which are less than 1 (Table 2). It is very interesting to find that TF of Ni^{2+} in reeds cultured in solutions with 25 mg/L Ni^{2+} is more than 1 (2.47 ± 0.40). Previous research also found the TF of Ni^{2+} in the reeds grown

Table 2 Translocation factor (TF) of Ni^{2+} in different solutions

Solutions	TF of Ni^{2+}
25 mg/L Ni^{2+}	2.47 ± 0.40 a
50 mg/L Ni^{2+}	0.69 ± 0.16 b
75 mg/L Ni^{2+}	0.72 ± 0.07 b
25 mg/L $\text{Cu}^{2+} + \text{Ni}^{2+}$	0.66 ± 0.46 b
50 mg/L $\text{Cu}^{2+} + \text{Ni}^{2+}$	0.96 ± 0.36 b
75 mg/L $\text{Cu}^{2+} + \text{Ni}^{2+}$	0.32 ± 0.08 c

The TF of Ni^{2+} in reeds treated with different levels of metals; Different letters in the same column indicate a significant difference at $p < 0.05$

in a heavy metal contaminated lake were > 1 (Eid et al., 2020). As mentioned earlier, the age of plants and the availabilities of metals may vary by season which will impact the TF. The translocation of metals into different parts of reeds can also vary with many factors such as the species, environmental conditions, and growth rate of plants (Justyna et al., 2020).

In general, the concentrations of Cu^{2+} in the belowground tissues of reeds were higher than Ni^{2+} . For instance, the heavy metal uptake by different parts of reeds in a constructed wetland of North Italy was reported to have the order of $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cr}^{3+}$ at the roots and leaves (Bragato et al., 2009). The amounts of Cu^{2+} in both roots and shoots of *Phragmites australis* in a constructed wetlands that were used to polish electroplating wastewater were also higher than the Ni^{2+} levels (Sochacki et al., 2015). However, the levels of Cu^{2+} and Ni^{2+} were similar in the shoots in our experiment. This is not surprising as the metal accumulation in plants is mainly site specific (Guillaume et al., 2012; Sanchez et al., 2002). The physiological mechanisms and the concentrations of metals can affect metal sequester in plants (Hamidia et al., 2016; Guo & Cutright, 2017). Different plants also possess different tolerant levels and uptake mechanisms toward different metals (Taylor & Crowder, 1983). For instance, Fe was mainly sequestered in the roots, but Pb was usually found in the leaves of reeds (Rzyski et al., 2014). Metals also play different roles in the metabolisms of life. For example, Cu is needed to form hemocyanin which is important for oxygen transport; Mn is a cofactor for enzymes while Zn is required by metalloenzymes (Prca et al., 2019). So the uptake of those essential metals are mainly controlled by biological demand

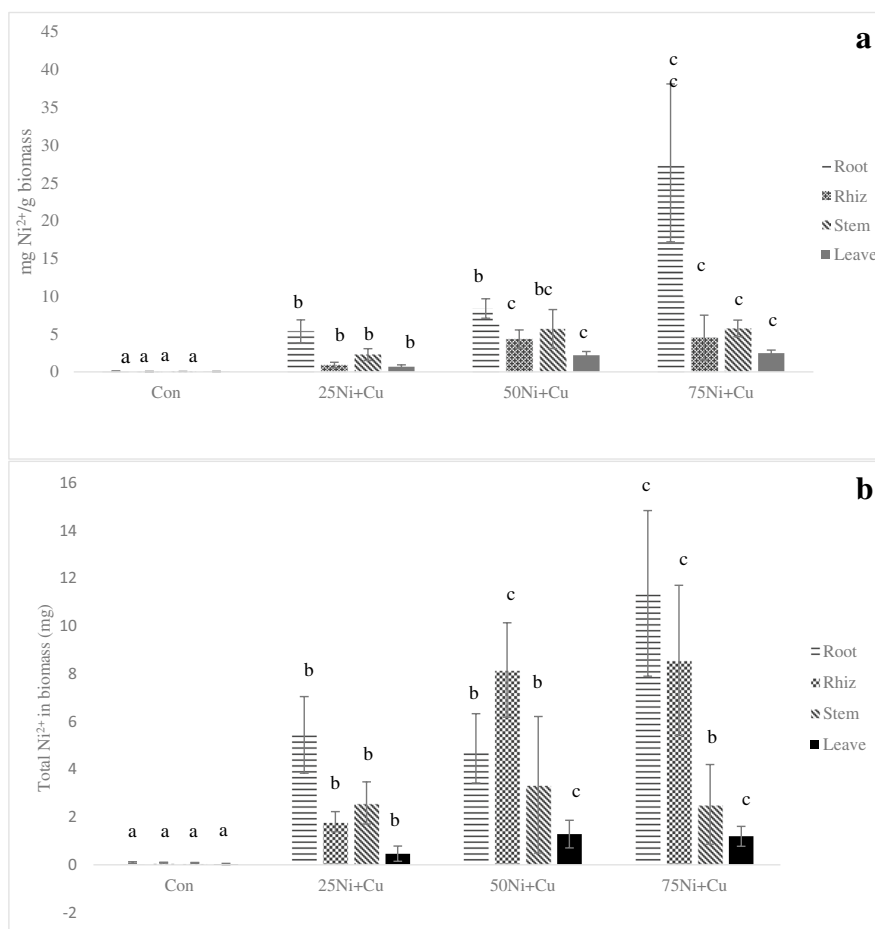
but the accumulation of other metals like Cd and Cr which are not necessary for the growth of plants would depend on the environmental levels (Prca et al., 2019).

3.1.2 Reeds Cultured in Solutions with Binary Metals

Compared with reeds treated with single metals, reeds treated with binary metals resulted in relatively lower Ni^{2+} contents in roots and stems. For instance, the roots of reeds treated with 75 mg/L Ni^{2+} solutions sequestered 47.75 ± 0.43 mg/g Ni^{2+} which is significantly ($p < 0.05$) higher than that of the roots of reeds treated with 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ (27.67 ± 10.45 mg/g Ni^{2+}) (Fig. 3a). The total Ni^{2+} in roots treated with 75 mg/L Ni^{2+} solutions were 17.24 ± 0.55 mg which is significantly ($p < 0.05$) higher than that in the roots of reeds treated with 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ (11.37 ± 3.47 Ni^{2+}) (Fig. 3b). Similarly, less Cu^{2+} accumulated in roots and stems cultured in solutions with binary metals, compared to reeds cultured in solutions only contained Cu^{2+} . For example, the stems of reeds treated with 75 mg/L Cu^{2+} solutions accumulated 23.46 ± 1.05 mg/g Cu^{2+} which was significantly ($p < 0.05$) higher than that of the stems treated with 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ (8.22 ± 1.05 mg/g) (Fig. 4a). The total Cu^{2+} in the stems cultured in 75 mg/L Cu^{2+} solutions (13.81 ± 0.61 mg) were also significantly ($p < 0.05$) higher than the total Cu^{2+} in stems treated with 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ (5.26 ± 1.23 mg) (Fig. 4b). Previous research reported the existence of competing elements, even the nutrients can affect the targeting metal sequester in plants (Guillaume et al., 2012; Sanchez et al., 2002). In addition, plants treated with more metals may develop protection mechanisms to avoid too much metal uptake in the roots (Ernst, 2006).

However, it was interesting to find that the metal contents in rhizomes and leaves of the reeds treated with binary metals were similar to reeds treated by single metals which were relatively lower than those of roots and shoots. As mentioned earlier, this may be due to the protection mechanism of reeds. In general, reeds tend to sequester less metals in rhizomes and leaves: the restriction of metals in rhizomes is important to the production of plants as rhizome is the only persistent organ for growth; and the relatively lower levels of metals in leaves is to prevent toxicity to the

Fig. 3 A The concentrations of Ni^{2+} in each tissue of reeds (mg Ni/g biomass) and (b) the total Ni^{2+} in each tissue of reeds cultured in solution with 25 mg/L, 50 mg/L, and 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ for 4 weeks. Error bar represented the standard deviation of triplicate samples. Different letters on the same plant organ indicate a significant difference at $p < 0.05$



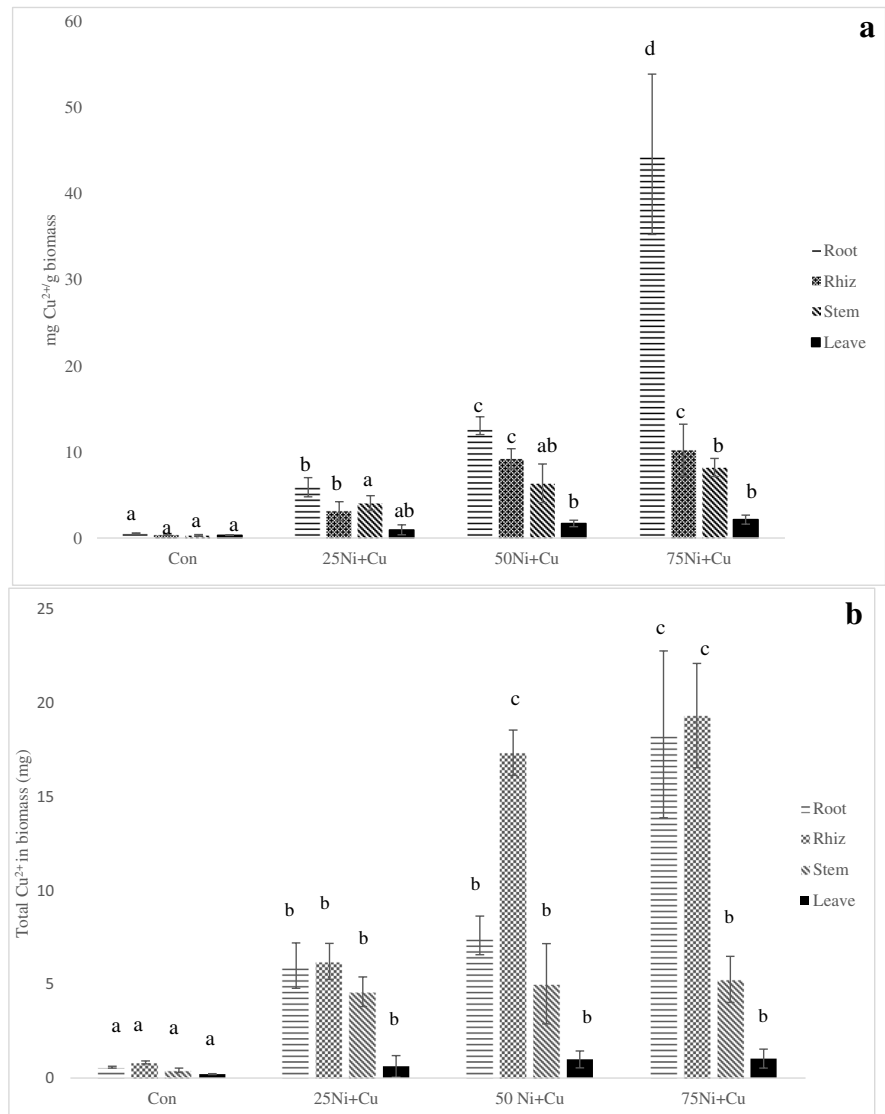
photosynthetic organs which are essential to plant health and growth (Bragato et al., 2009). So, it is reasonable to expect that the metal levels in rhizomes and leaves in reeds were limited in both binary and single metal solutions.

As mentioned above, the concentrations of Cu^{2+} in the belowground tissues of reeds treated with single metals were higher than Ni^{2+} . The total amount of Cu^{2+} in reeds cultured in solutions with binary metals were also higher than Ni^{2+} . For instance, reeds treated with 50 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ accumulated 30.98 ± 4.86 mg Cu^{2+} in the whole plant which was higher than Ni^{2+} (18.81 ± 4.95 mg) (Fig. 5). The amounts of Cu^{2+} (43.96 ± 9.97 mg) in reeds cultured in 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ solutions were also higher ($p < 0.05$) than the contents of Ni^{2+} (24.81 ± 5.67 mg) (Fig. 5). This mainly due to that different metals possess different characteristics and toxicity (Taylor & Crowder, 1983). It is well known that Cu^{2+} is essential

to the growth of plants, but Ni^{2+} was considered as a toxic element to plant in the past century (Guo et al., 2010). However, it was found later that Ni^{2+} is also essential nutrient to plants but just in small quantities (Guo et al., 2010). Plants also have different transportation mechanisms and transporters for various metals. For example, Cu^{2+} transported in plants by the two types of transporters P-type ATPases and RAN1 (Responsive-to-Antagonist) while TjN-RAMP4 is used to transport Ni^{2+} (Arif et al., 2016). The maximum Ni^{2+} uptake in other plants like giant reed was also lower than Cu^{2+} (Shaheen et al., 2019). *Phragmites australis* (common reed) and *Typha orientalis* (bullrush) collected from a wetland were also reported to be more efficient in taking up Zn^{2+} and Cu^{2+} than Ni^{2+} (Wang et al., 2018).

The TF of Ni^{2+} in reeds treated with 25 and 50 mg/L $\text{Cu}^{2+} + \text{Ni}^{2+}$ were all less than 1 (Table 2), similar to TF of Ni^{2+} in reeds in single metal

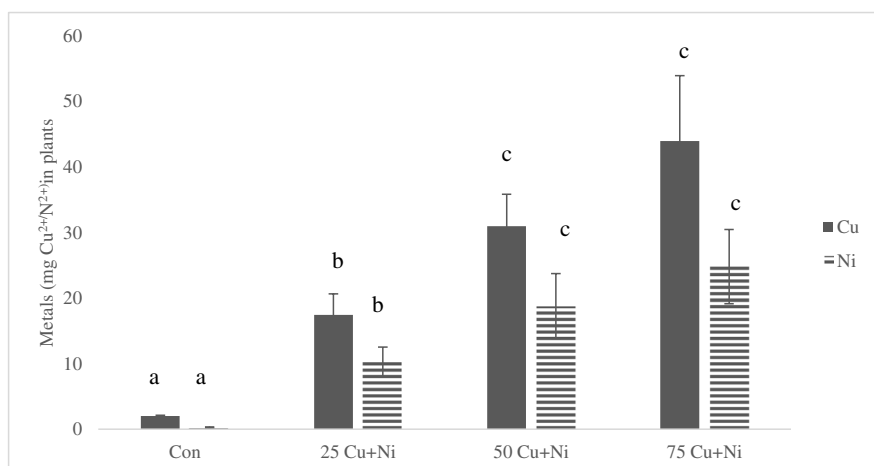
Fig. 4 A The concentrations of Cu^{2+} in each tissue of reeds ($\text{mg Cu}^{2+}/\text{g}$ biomass) and (b) the total Cu^{2+} in each tissue of reeds cultured in solution with 25 mg/L , 50 mg/L , and 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ for 4 weeks. Error bar represented the standard deviation of triplicate samples. Different letters on the same plant organ indicate a significant difference at $p < 0.05$



solutions. However, TF of Ni^{2+} in solutions with 75 $\text{mg/L Cu}^{2+} + \text{Ni}^{2+}$ were significantly less than TF of Ni^{2+} in reeds only treated with 75 mg/L Ni^{2+} ($p < 0.05$). The TF of Cu^{2+} in reeds cultured in solutions with 25 $\text{mg/L Cu}^{2+} + \text{Ni}^{2+}$ and 50 $\text{mg/L Cu}^{2+} + \text{Ni}^{2+}$ (Table 1) were similar to TF of Cu^{2+} in reeds in solutions with 25 or 50 mg/L Cu^{2+} . TF of Cu^{2+} in solutions with 75 $\text{mg/L Cu}^{2+} + \text{Ni}^{2+}$ were significantly less ($p < 0.05$) than TF of Cu^{2+} in reeds only treated with 75 mg/L Cu^{2+} . These differences of TF may reflect the fact that the translocation of metals in plants can change

with the concentrations and types of target elements and metal toxicity (Stoltz & Greger, 2005; Ye et al., 1998). The heavy metal uptake process in plants is related to metal uptake rate (k) (Vlyssides & Bouranis, 1998), while metal uptake rate (k) depends on the types and levels of metals in solutions (Vlyssides & Bouranis, 1998). The higher metal levels, the more metals and the more severe toxicity of metals may slow down the diffuse and translocation of metals in plants (Guillaume et al., 2012; Nigam et al., 1998; Sanchez et al., 2002) which leads to lower TF.

Fig. 5 The total amounts of Cu^{2+} or Ni^{2+} in the whole plants of reeds (mg $\text{Cu}^{2+}/\text{Ni}^{2+}$) in reeds cultured in solution with 25 mg/L, 50 mg/L, and 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ for 4 weeks. Error bar represented the standard deviation of triplicate samples. Different letters on the same plant organ indicate a significant difference at $p < 0.05$



3.2 Products from HTC Processes

Products of HTC include bio-oils, the solid hydrochars, the aqueous phase, and the gases. The yields of bio-oil and hydrochar were measured and analyzed in this study as they are the most valuable products of HTC. With HTC under the condition used, the yields of bio-oils and hydrochars from reeds treated with different levels of metals were similar. About 6–10% of bio-oils and 50–60% of hydrochars were produced from reeds under different treatments (Fig. 6). In other words, the yields of bio-oils and hydrochars were not negatively affected by the existence of metals accumulated in plant tissues. This was not surprising as plant species is one of the primary factors that determined the yields of the products from hydrothermal processing. Different plants with different compositions (e.g., cellulose, hemicellulose, lignin, protein) can produce different amounts of bio-oils. For instance, it was reported that maize, oats, and ryegrass had bio-oil yields of 27.6%, 25.1%, and 22%, respectively. For the same type of plant biomass, the yields of bio-oils or other products should be similar under similar HTC conditions. Rodriguez-Dominguez et al. (2021) also reported that there was no significant difference in the bio-oil yield from common reeds grown in different environmental conditions under the same HTC process.

The possible maximum yield of bio-oil and gases can reach 70% in total and the yield of biochar can be less than 30% through the pyrolysis of common reed, which is at much higher temperatures than HTC (Garrido et al., 2017). Rodriguez-Dominguez et al.

(2021) found that common reed can produce about 20% bio-oil and 20% hydrochars under a relatively more demanding HTC condition, at 340 °C for 15 min. In our study, at 250 °C and 0 min, less bio-oil (6–10%) but more hydrochars (50–60%) were obtained from common reed. However, our goal is not only to produce bio-oils but also hydrochars for future application in biosorption and/or catalysis. The yields of bio-oils and hydrochars are strongly related to HTC temperature, atmosphere, time, and catalyst used as they played important roles in the output and characteristics of HTC products. For instance, the yields of bio-oil of *Porphyridium* can be 5–25% depending on the parameters of the hydrothermal liquefaction process (Gollakota et al., 2018). It is worthwhile to conduct experiments to further study the complexities of different parameters to optimize product distribution and quality via HTC in future.

Besides the yields of bio-oils, another serious concern for bio-oil is that the heavy metals in biomass will be redistributed to bio-oils during HTC. In this study, ICP analysis detected very limited Cu^{2+} (0.1–0.7%) and Ni^{2+} (0.5–1.5%) in reeds grown in different levels of Ni^{2+} and/or Cu^{2+} (Figs. 7 and 8), were released into bio-oils. According to the results of Zhu et al. (2019) who analyzed the distributions of metals after HTC of *Rhus chinensis* treated with Pb, most of Pb remained in the hydrochars (contained around 30% of metals) and liquid products (contained 70% of metals) rather than bio-oils. Huang et al. (2018) also reported that only about 5% of the initial heavy (<3% in the case of Cu^{2+}) transmitted to bio-oils, while most of them are stabilized and remained in hydrochars or the aqueous phase. The critical factors

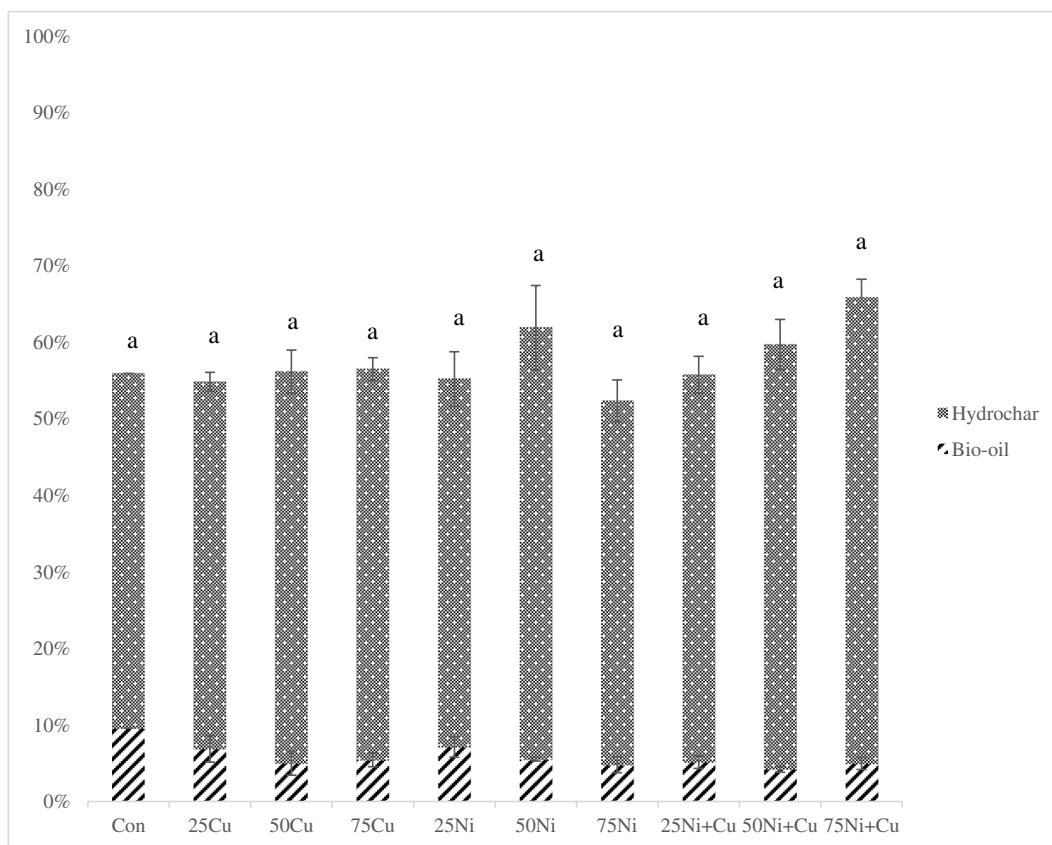


Fig. 6 The yields of bio-oil and hydrochars from reeds treated with different levels of metals via HTC process; Error bar represented the standard deviation of triplicate samples

Fig. 7 The percent of Cu^{2+} transmitted to bio-oils from contaminated reeds treated by different Cu^{2+} and/or Ni^{2+} levels; Error bar represented the standard deviation of triplicate samples. Different letters on the same treatment indicate a significant difference at $p < 0.05$

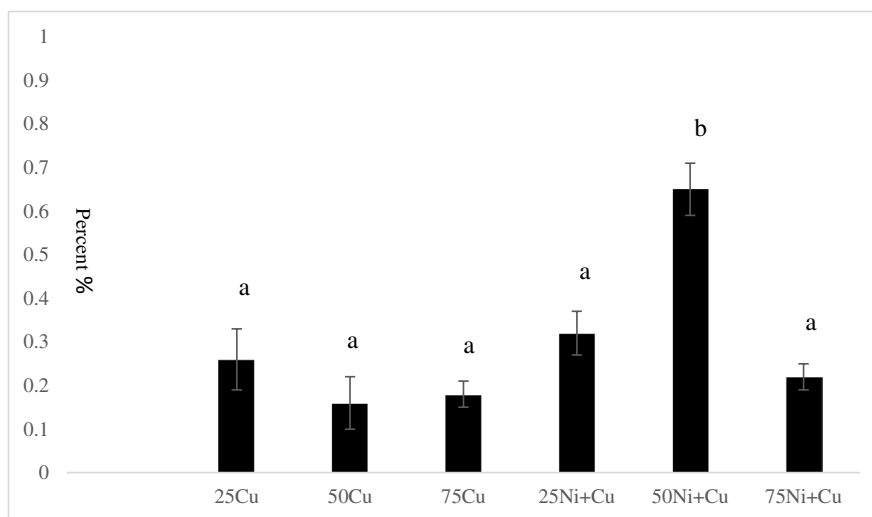
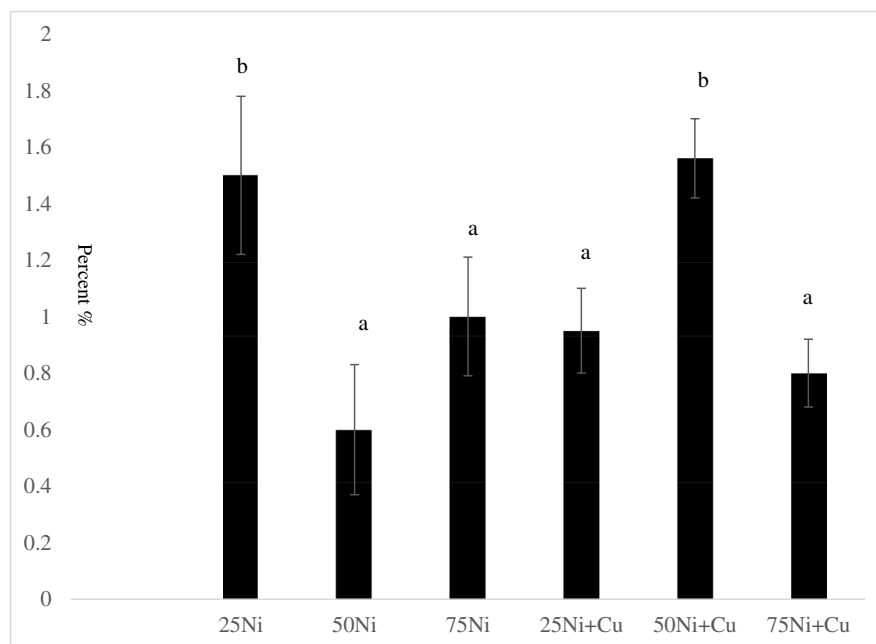


Fig. 8 The percent of Ni^{2+} transmitted to bio-oils from contaminated reeds treated by different Cu^{2+} and/or Ni^{2+} levels; Error bar represented the standard deviation of triplicate samples. Different letters on the same treatment indicate a significant difference at $p < 0.05$



that affect metal distribution during the HTC process include temperature and the type of metal involved (Li et al., 2020). Some metals, such as Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , and Cr^{3+} , presented a similar tendency to be distributed in hydrochars during HTC conducted at 300 °C while some other metals, such as arsenic, were mainly released into bio-oils (Wang et al., 2016). Metals sequestered within hydrochars are usually in immobile forms which may pose less risk to the environment (Wang et al., 2016). Further research is needed to investigate the potential environmental and economical applications of hydrochars which has great potential in energy production and pollutant adsorption (Zhang et al., 2022).

4 Conclusions

This project evaluated the potential of common reed to uptake Ni^{2+} and Cu^{2+} from wastewater and then investigated the feasibility of converting the resulted biomass to valuable products via HTC. Common reeds were cultured in solutions with 25, 50, or 75 ppm Ni^{2+} and/or Cu^{2+} for 4 weeks. Parts of plants were digested to measure the amounts of heavy metals in different tissues by ICP while some of the plants were used to produce bio-oils and hydrochars through the HTC process.

The results indicated that reeds can be successfully grow in the Cu^{2+} and Ni^{2+} solutions. When reeds were cultured in solutions with single Cu^{2+} or Ni^{2+} , the higher levels of Cu^{2+} or Ni^{2+} in solution, the more Cu^{2+} or Ni^{2+} was accumulated in the biomass of reeds. Most Cu^{2+} and Ni^{2+} were stored in the roots of reeds. Reeds cultured in solutions with 75 mg/L Ni^{2+} sequestered 47.75 ± 0.43 mg/g Ni^{2+} in roots, while the roots in solutions with 75 mg/L Cu^{2+} sequestered 55.82 ± 8.52 mg/g Cu^{2+} . The TF of Ni^{2+} and Cu^{2+} in reeds treated with all different levels were all less than 1, except the TF of Ni^{2+} of reeds cultured in 25 mg/L Ni^{2+} solutions was more than 1. In general, the concentrations of Cu^{2+} in reeds were higher than Ni^{2+} . Compared with reeds treated with single metals, relatively less Cu^{2+} and Ni^{2+} were sequestered in roots and stems of reeds treated with binary metals. For example, the roots of reeds treated with 75 mg/L $\text{Ni}^{2+} + \text{Cu}^{2+}$ accumulated 27.67 ± 10.45 mg/g Ni^{2+} and 44.6 ± 9.32 mg/g Cu^{2+} which were lower than the amounts of metals in single Ni^{2+} or Cu^{2+} solutions. The contents of metals in rhizomes and leaves in reeds treated by binary metals were similar to reeds treated by single metals.

The amounts of Cu^{2+} and Ni^{2+} in solutions or in plant tissues did not significantly affect the yields of bio-oils and hydrochars. About 6–10% of the biomass of reeds under different treatment were transferred to bio-oil, while 50–60% of the biomass were produced

as hydrochars. Very limited metals (less than 2%) sequestered in plants were released into bio-oils, 0.1–0.7% for Cu^{2+} and 0.5–15.% for Ni^{2+} . Using phytoremediation technology to clean heavy metal contaminated environments has become more and popular globally, but the safe disposal and use of the metals enriched biomass is a challenging. HTC can be a promising technique to produce valuable products from phytoremediation biomass. Future investigation should be conducted to further increase the metal accumulation in plants and study the impact of HTC parameters on the yields and quality of valuable products and to effectively recycle all products to significantly increase the sustainability of the process.

Author Contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Ken Vudang, Valeria Duran, Michael Brdecka, Julia Seigerroth, Ben Jang, and Lin Guo. The first draft of the manuscript was mainly written by Ken Vudang, Ben Jang, and Lin Guo. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data Availability Data are available from the corresponding author on reasonable request.

Declarations

All the authors are in compliance with publication ethical standards. No human participants and animals were involved in the research.

Consent to Participate All authors of the manuscript made substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data; or the creation of new software used in the work; drafted the work or revised it critically for important intellectual content; approved the version to be published; and agreed to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

Consent for Publication All the authors of the manuscripts give consent for the publication of identifiable details within the manuscript to be published in the Journal “Environmental Science and Pollution Research.”

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