

Adsorption of Zn²⁺ and Ni²⁺ in a binary aqueous solution by biosorbents derived from sawdust and water hyacinth (*Eichhornia crassipes*)

Willis Gwenzi, Tinashe Musarurwa, Phillip Nyamugafata, Nhamo Chaukura, Allen Chaparadza and Sharron Mbera

ABSTRACT

The Zn²⁺ and Ni²⁺ adsorption capacities of six biosorbents derived from water hyacinth (*Eichhornia crassipes*) (WH) and sawdust (SD) were investigated, with activated carbon as the control. The biosorbents were raw biomass (WH, SD), charred WH (BWH) and SD and sulphonated bio-chars of WH and SD. The effect of the initial solution pH and Zn²⁺ and Ni²⁺ concentrations on adsorption capacity was studied, and adsorption isotherms for Zn²⁺ and Ni²⁺ evaluated. The initial solution pH significantly influenced adsorption ($p < 0.05$) but the relationship was generally nonlinear. Zn²⁺ suppressed Ni²⁺ adsorption on all biosorbents. The adsorption capacities of the biosorbents were statistically ($p \leq 0.05$) similar to or higher than that of activated carbon. The effects of pyrolysis and bio-char sulphonation on adsorption were inconsistent and dependent on biomass type; in most cases bio-char was a better biosorbent than the original biomass, while sulphonation resulted in less or comparable adsorption. Adsorption data obeyed at least one of three isotherms (linear, Langmuir and Freundlich) ($r^2 = 0.90-0.995$, $p < 0.05$). The study revealed that low-cost biosorbents may be used as alternatives to activated carbon in applications including selective separation of Zn²⁺ from multi-metal ion solutions containing Ni²⁺, and water and wastewater treatment.

Key words | adsorption, biosorbents, sawdust, sulphonation, water hyacinth

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INTRODUCTION

Heavy metal contamination of water from sources including mining and mineral processing, electroplating and pesticide industries poses significant ecological, public and environmental health risks (Vijayaraghavan & Yun 2008). Traditional methods for removal of heavy metals in aqueous solutions include precipitation, redox reactions, floatation, ion exchange, ultrafiltration, membrane filtration and adsorption using activated carbon and synthetic resins (Gloaguen & Morvan 1997; Wang & Chen 2006). However, the high costs, operational difficulties (Homagai *et al.* 2009) and low removal efficiencies (Zheng *et al.* 2009) associated with conventional adsorbents such as activated carbon and synthetic resins constrain their large-scale application, particularly in developing countries.

Biosorption is attractive due to its simplicity, convenience and high removal efficiency (RE) even at low concentrations. Low-cost biosorbents can be derived from

inexpensive feedstocks including sawdust (SD) and bio-wastes from industrial processes such as fermentation, crop and forestry residues, and aquatic weeds, which are renewable and readily available in large quantities (Gwenzi *et al.* submitted). Aquatic weeds and macrophytes such as water hyacinth grow rapidly in nutrient-rich tropical aquatic ecosystems in Africa (Mahamadi & Nharingo 2010) and South America (Schneider & Rubio 1999) posing significant ecological, environmental and public health risks. The control of aquatic weeds through chemical, biological and physical methods is often expensive and ineffective (Magadza 2003). Therefore, the development of biosorbents from biowastes and aquatic weeds is economically and environmentally attractive.

Understanding adsorption kinetics and isotherms is important for large-scale application of biosorption technology. Biosorption occurs as either a pH-dependent (Pang

et al. 2011) or independent process (Gloaguen & Morvan 1997) depending on the type of adsorbent and metal ion under consideration (Vijayaraghavan & Yun 2008). Solution pH, initial concentration of the heavy metal ions, equilibrium or contact time, ionic strength and adsorbent dosage are among the factors influencing heavy metal adsorption (Wang & Chen 2006; Vijayaraghavan & Yun 2008). Several empirical and quantitative isotherms are used to provide information on heavy metal uptake capacities and differences in metal uptake between various adsorbents; amongst the prominent ones are the linear (partition), Langmuir, Freundlich and Brunauer–Emmett–Teller (BET) models (Stumm & Morgan 1996).

Although several studies have investigated the effect of physical and chemical pre-treatment of biomass on adsorption (Wang & Chen 2006; Vijayaraghavan & Yun 2008), little information is available on the effect of high temperature (300–700 °C) pyrolysis and subsequent sulphonation of biomass on heavy metal adsorption. Pyrolysis of biomass produces bio-char, an emerging carbon-rich biomaterial with multiple potential industrial and environmental applications. Pyrolysis and subsequent activation of biomass through sulphonation could potentially increase the cation exchange capacity and adsorption capacity compared to that of the original biomass. Batch experiments were used to investigate the hypothesis that the adsorption capacities of the six biosorbents developed from sawdust and water hyacinth (WH), an aquatic weed, are comparable to or higher than that of commercially available activated carbon (control). The specific objectives were to investigate the effect of initial solution pH and concentration of Zn²⁺ and Ni²⁺ on the adsorption capacity; and to evaluate the adsorption isotherms for Zn²⁺ and Ni²⁺ on the different biosorbents.

MATERIALS AND METHODS

Preparation of biosorbents

Two readily available and low-cost sources of biomass were used in this study: water hyacinth (*Eichhornia crassipes*) and sawdust. Whole plants of water hyacinth were manually harvested from the Ruwa River and sun-dried for three days to reduce the water content. Sawdust was obtained from a timber-making company in Ruwa, Zimbabwe. Both feedstocks were dried in an oven (model: Gruenthal and Bekker Pvt Ltd, Harare, Zimbabwe) at 70 °C for three days. Bio-char was produced by tightly packing the dried raw

biomass in closed steel canisters to ensure limited or no oxygen. The canisters containing biomass were then placed in a muffle furnace operated at 500 °C for 1 h following procedures in the literature (e.g., Brown 2009). Thereafter, the bio-char was allowed to cool in closed containers under room-temperature conditions (25–26 °C). Dried raw biomass (SD and WH) and bio-char SD and WH (BSD and BWH) were then ground to a particle size of 2 mm using an electric laboratory mill (model: Thomas Model 4 Wiley Mill, Thomas Scientific, Swedesboro, NJ, USA).

Portions of the BSD and BWH were activated through sulphonation. A 10 g portion of each sample was weighed into an Erlenmeyer flask. A 100-mL aliquot of concentrated (98%) sulphuric acid was added to each flask. The flasks with the bio-char/sulphuric acid mixture were placed on a magnetic stirrer (model: Framo-Geratetechnik M21/1, Eisenbach, Germany) in a fume hood and stirred at 1,400 rpm for an hour at 10 min intervals. Sulphonation was conducted at a temperature of 60 °C. Thereafter, the mixture was quenched with 2 L of distilled water and left overnight. The mixture was then vacuum-filtered and the residue washed several times with distilled water to remove excess acid. The sulphonated bio-char was oven-dried at 70 °C for 24 h.

Characterization of the adsorbents

Moisture content was determined using the gravimetric method by oven drying each biosorbent at 110 °C for 24 h. The pH and electrical conductivity (EC) were measured in a 1:5 biosorbent-water mixture using a pH and conductivity meter (model: Mettler Toledo, GmbH, Greifensee, Switzerland), respectively. Approximately 0.25 g of each adsorbent was agitated in 40-mL distilled water for 1 h. Cation exchange capacity (CEC) was used to evaluate the capacity of the biosorbents to adsorb cations onto their surfaces. CEC was determined by extraction using ammonium acetate followed by summation of exchangeable basic cations (Na⁺, Mg²⁺, Ca²⁺ and K⁺).

Effects of initial solution pH

The adsorption procedure by Dong *et al.* (2011) was used. A ratio of Ni²⁺ to Zn²⁺ of 10:1, typical of values reported for wastewater, was used (Hranova 2006). A standard binary aqueous solution of 1,000 mg L⁻¹ of Ni²⁺ and 100 mg L⁻¹ Zn²⁺ was prepared from Ni(NO₃)₂ and ZnCl₂, respectively. The pH values investigated were limited to 3–7 because precipitation of Zn²⁺ and Ni²⁺ occurs under alkaline

conditions (Mohan *et al.* 2007). The amount of Zn²⁺ and Ni²⁺ adsorbed at equilibrium (q_e) was calculated according to Mohan *et al.* (2007)

$$q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where V is the volume of the solution used, C_0 is the initial concentration of the solution, C_e is the final equilibrium concentration of the solution and M is the mass of the biosorbent.

Percentage RE of Zn²⁺ and Ni²⁺ was calculated according to Wang *et al.* (2011)

$$\text{RE (\%)} = \frac{(C_0 - C_e)}{C_0} * 100 \quad (2)$$

Effect of initial concentration Zn²⁺ and Ni²⁺

Batch adsorption experiments were conducted at the initial pH of the biosorbent at nine initial concentrations of Zn²⁺ and Ni²⁺ (5, 10, 20, 30, 40, 50, 60, 80 and 100 mg L⁻¹). For each biosorbent, 0.25 g was weighed into a 100-mL plastic bottle, and then 50-mL of each solution was added. The mixture was shaken for 24 h at 150 rpm at room temperature (23–24 °C) using a horizontal mechanical shaker. The samples were then filtered through a double ring filter paper. The filtrate was analysed for Ni²⁺ and Zn²⁺ using an atomic absorption spectrophotometer (model: Varian SpectraAA 50, Varian Inc, Palo Alto, CA, USA).

Data analysis

Data were first tested for the analysis of variance assumptions before testing for the effects of solution pH, initial concentration of metal ions and biosorbents on adsorption. Linear, Langmuir and Freundlich models were fitted to the adsorption data. Correlation analyses were used to evaluate the goodness of fit between observed data and isotherm models using the coefficient of determination (r^2). A probability level, p of 0.05, was used for all statistical comparisons. The statistical software GenStat® Release 14 was used for statistical analysis. A dimensionless separation factor (SF) ($0 \leq \text{SF} \leq 1$) was used to evaluate the nature of the adsorption process (Equation (3)) (Webber & Chakkravorti 1974; Vijayaraghavan & Yun 2008). Using the SF, adsorption was classified as unfavourable ($\text{SF} > 1$), linear ($\text{SF} = 1$), favourable ($0 < \text{SF} < 1$), and irreversible

($\text{SF} = 0$) (Webber & Chakkravorti 1974; Vijayaraghavan & Yun 2008)

$$\text{SF} = \frac{1}{(1 + K_L C_0)} \quad (3)$$

where K_L (L mg⁻¹) is the adsorption affinity or energy.

RESULTS AND DISCUSSION

Characteristics of biosorbents

Electrical conductivity (EC), pH, moisture content and CEC varied considerably among biosorbents. Biosorbent pH ranged from near-neutral (6.1–7.9) for WH, BWH, SD and BSD to acidic (3.9–4.3) for commercial activated carbon (AC), sulphonated bio-chars of WH (SWH) and sulphonated bio-chars of WH and SD (SSD). EC was low (2.3–3.9 mS m⁻¹) for SD, BSD, SSD and AC and relatively higher (103–173.1 mS m⁻¹) for WH, BWH and SWH. Initial moisture content was generally low (0.5–1.2%), except for WH (4.6%) and AC (10.5%). CEC increased in the general order: SSD > SWH > SD > WH > BWH ≈ BSD. Overall, pyrolysis of biomass lowered CEC, while sulphonation of bio-char increased CEC relative to the original biomass.

Effect of initial solution pH

The relationship between pH and adsorption was generally nonlinear for all adsorbents (Figure 1), except for Ni²⁺ adsorption on activated carbon and BSD and Zn²⁺ adsorption on WH and SD, which showed an increasing trend with increasing pH. The pH at which maximum adsorption occurred also varied among biosorbents. For most biosorbents, maximum adsorption for both metal ions occurred around pH 7, except for the following: (1) Zn²⁺ adsorption on BWH and BSD occurred around pH ≈ 3 and pH ≈ 6, respectively; and (2) Ni²⁺ adsorption on SD, SSD and SWH, which occurred around pH ≈ 6 for the first two and pH ≈ 5 for the last biosorbent. For a given pH and biosorbent, Ni²⁺ adsorption was more than two times higher than that of Zn²⁺, reflecting the effects of 10:1 Ni²⁺:Zn²⁺ concentration in the initial solution. However, the fact that the ratio of Ni²⁺:Zn²⁺ adsorbed was less than that of the initial solutions points to a possible preferential adsorption of Zn²⁺, which is also evident in Figures 2 and 3.

The influence of pH on Zn²⁺ and Ni²⁺ adsorption can be attributed to the altering of solubility and speciation of

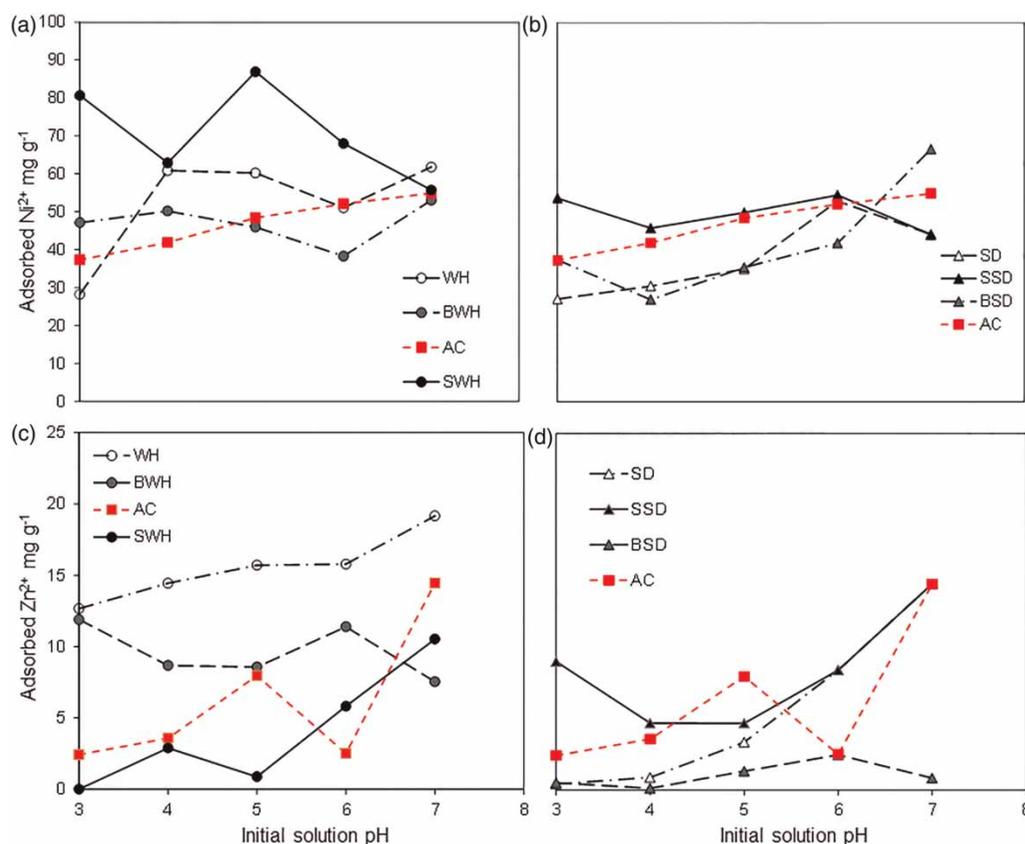


Figure 1 | Effect of initial solution pH on equilibrium adsorption (q_e) of Ni^{2+} ((a) and (b)) and Zn^{2+} ((c) and (d)) in aqueous solution. WH: water hyacinth (○), BWH: water hyacinth biochar (●), SWH: sulphonated water hyacinth biochar (●), SD: sawdust (△), BSD: sawdust biochar (▲), SSD: sulphonated sawdust biochar (▲), AC: commercial activated carbon (■). Initial concentrations: $\text{Ni}^{2+} = 1,000 \text{ mg L}^{-1}$, $\text{Zn}^{2+} = 100 \text{ mg L}^{-1}$, contact time: 24 h.

heavy metal ions, and to the nature of adsorption sites on biosorbents. The results point to the existence of both pH-dependent and non-pH dependent heavy metal adsorption sites on the biosorbents. High heavy metal adsorption at low pH is often due to non-pH dependent adsorption processes such as intra-particle diffusion. The current study made no attempt to continuously monitor and control the solution pH during equilibration, hence there is a possibility that solution pH could have changed during the adsorption process.

Effect of initial concentration of Zn^{2+} and Ni^{2+}

The RE of Zn^{2+} was generally higher (94–100%) than that of Ni^{2+} , which was highly variable among biosorbents (Figure 2). Ni^{2+} adsorption by SD, BSD and SSD approached a maximum at an initial concentration of approximately 60 mg L^{-1} (Figure 2(b)). Zn^{2+} adsorption, in contrast, increased linearly with initial concentration for all biosorbents (Figures 2(c) and 2(d)), suggesting a high

affinity for Zn^{2+} . Overall, the adsorption capacities of the biosorbents were comparable to or higher than that of activated carbon. An exception was SWH, which had a lower Ni^{2+} adsorption capacity than activated carbon. An anomalous selective adsorption of Zn^{2+} to Ni^{2+} was evident, contradicting the inverse relationship between cationic radii (i.e., 0.74 \AA for Zn^{2+} versus 0.70 \AA for Ni^{2+}) and adsorption affinity often reported (Pang et al. 2011). Although the exact mechanisms remain unclear, the results indicate that the adsorption behaviour of some transition metal ions on certain biosorbents may violate this relationship.

A study based on extended X-ray absorption fine structure spectroscopy showed that, unlike other divalent metal cations such as Ni^{2+} , hydrated Zn^{2+} has two adsorption sites on some adsorbents, arising from the change in coordination number from 6 to 4 and 5 when adsorbed (Zhang et al. 2006). Based on the Irving–Williams series, Ni^{2+} forms less stable complexes than other divalent transition metal ions such as Zn^{2+} (Stumm & Morgan 1996). This finding has implications on the removal of Ni^{2+} in the presence of Zn^{2+} , and should be

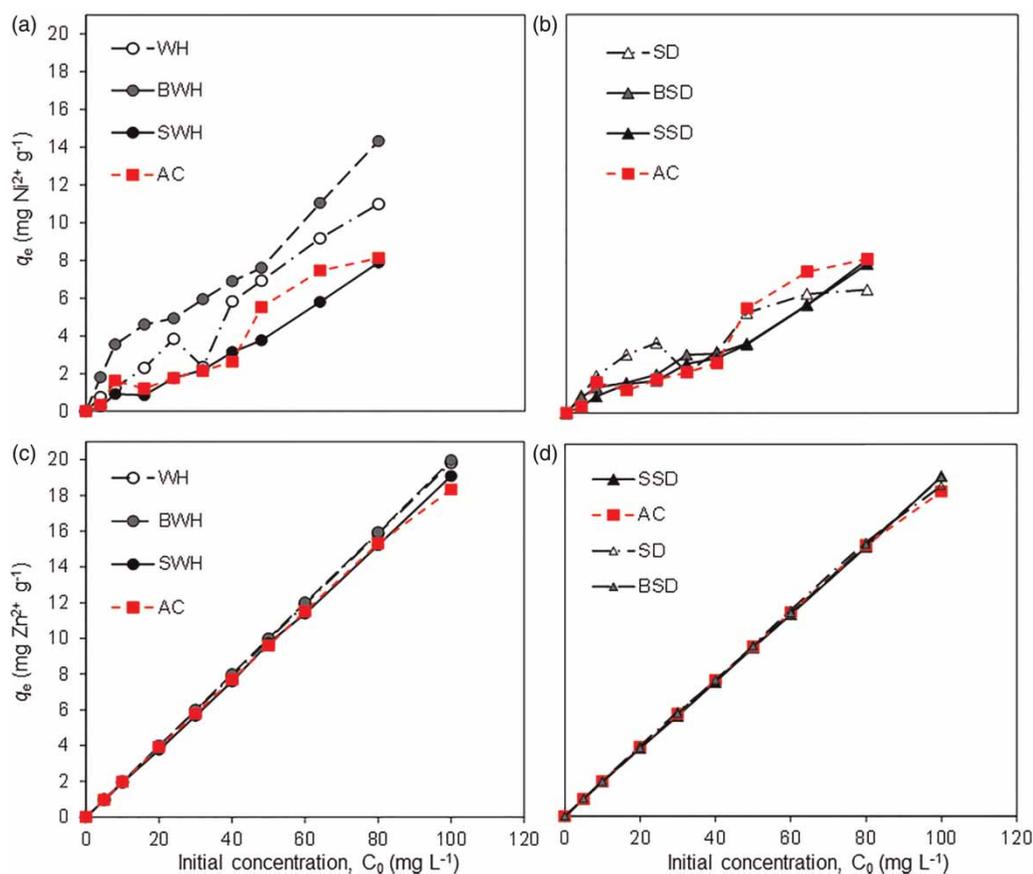


Figure 2 | Effects of initial concentration (C_0) on equilibrium adsorption (q_e) of Ni²⁺ ((a) and (b)) and Zn²⁺ ((c) and (d)) in aqueous solution. WH: water hyacinth (○), BWH: water hyacinth biochar (●), SWH: sulphonated water hyacinth biochar (●), SD: sawdust (△), BSD: sawdust biochar (▲), SSD: sulphonated sawdust biochar (▲), AC: commercial activated carbon (■). Initial concentrations: Ni²⁺ = 1000 mg L⁻¹, Zn²⁺: 100 mg L⁻¹, contact time: 24 h. Contact time: 24 h.

considered when designing remediation programs for aqueous media containing multi-component heavy metal ions.

Effect of biomass modification

At the initial pH of the adsorbent, the effect of pyrolysis and sulphonation on adsorption varied between the SD and WH, and Zn²⁺ and Ni²⁺ ions (Figure 3). Pyrolysis significantly ($p < 0.05$) increased the adsorption capacity of WH, but reduced or had no effect on the adsorption capacity of SD. Despite increasing CEC, sulphonation either lowered or had no effect on the adsorption capacity of both SD and WH. Correlation analysis showed no significant relationship between CEC and the adsorption capacity of the biosorbents.

Although pyrolysis and sulphonation altered the CEC of the biomass, Zn²⁺ adsorption on bio-chars was comparable to that of the original biomass. Two reasons could account for this: the unmodified SD and WH may have a Zn²⁺ adsorption capacity exceeding the initial concentrations

investigated here (5–100 mg L⁻¹), or Zn²⁺ may have specific adsorption sites or functional groups, which were not affected by both pyrolysis and sulphonation. Unlike for Zn²⁺, pyrolysis of WH significantly enhanced Ni²⁺ adsorption, but sulphonation lowered the adsorption capacity. The results suggest that increasing the functional groups on WH through pyrolysis enhances Ni²⁺ adsorption and reduces the suppressive effect of Zn²⁺. Pyrolysis of SD and subsequent sulphonation reduced Ni²⁺ adsorption capacity, although the effect was less pronounced compared to that of WH.

Based on adsorption data obtained at initial pH of the adsorbent, sulphonation did not consistently improve both Zn²⁺ and Ni²⁺ adsorption compared to the raw biomass. This inconsistency possibly reflects the competitive effects of H⁺ associated with the highly acidic sulphonate groups (Fourest & Volesky 1996). However, Figure 1 shows that the effect of pyrolysis and sulphonation is pH-dependent. For example, at pH ≈ 5 the Ni²⁺ adsorption capacity for SWH was higher than that of the original biomass, but

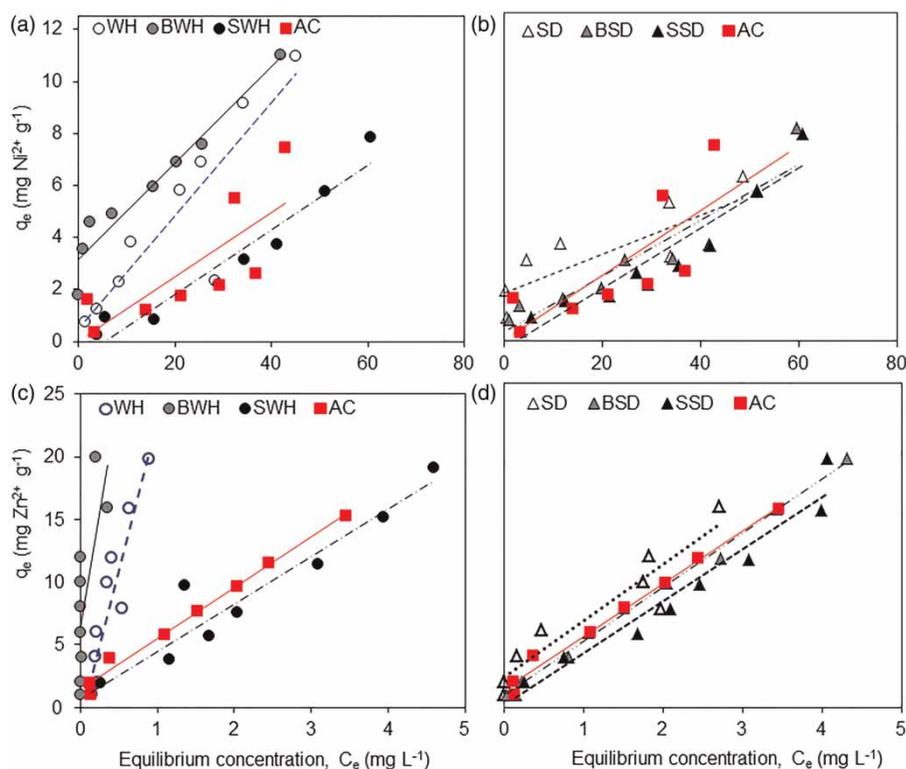


Figure 3 | Linear adsorption isotherms ($q_e = K_d C_e$) (solid and dotted lines) fitted to adsorbed (q_e) and equilibrium concentrations of Ni²⁺ ((a) and (b)) and Zn²⁺ ((c) and (d)). WH: water hyacinth (○), BWH: water hyacinth biochar (●), SWH: sulphonated water hyacinth biochar (◐), SD: sawdust (△), BSD: sawdust biochar (▲), SSD: sulphonated sawdust biochar (◑), AC: commercial activated carbon (■). Initial concentrations: Ni²⁺ = 1,000 mg L⁻¹, Zn²⁺: 100 mg L⁻¹, contact time: 24 h. Contact time: 24 h.

conversely the SWH had lower Zn²⁺ adsorption capacity than WH. This seemingly inverse relationship further supports the competitive adsorption between the two ions.

Adsorption isotherms

Linear, Langmuir and Freundlich isotherm models were fitted to the adsorption data (Figures 3–5). The degree of fit between the observed data and model predictions varied considerably between Zn²⁺ and Ni²⁺, and among biosorbents. The adsorption of Zn²⁺ on SWH, BSD and SSD was best described by all three models ($r^2 = 0.93–0.995$, $p < 0.05$). A similar trend was observed for Ni²⁺ adsorption on SSD ($r^2 = 0.92–0.98$, $p < 0.05$). Based on the Langmuir model, maximum Zn²⁺ adsorption capacity (q_m) decreased in the order: SSD (21.01 mg g⁻¹) > SWH (16.37 mg g⁻¹) > AC (14.6 mg g⁻¹) > BSD (7.36 mg g⁻¹) compared to SSD (43.38 mg g⁻¹) > SWH (20.41 mg g⁻¹) > WH (6.1 mg g⁻¹) for Ni²⁺. However, due to poor fit of the model to the data, evaluation of other biosorbents using the Langmuir isotherm was not possible. In general, the number of isotherm models that best described the adsorption data ($r^2 = 0.80–0.995$, $p < 0.05$) increased with the

number of pre-treatment processes in the order: the raw biomass (SD and WH) < bio-char (BWH and BSD) < sulphonated bio-char (SWH and SSD). For instance, Zn²⁺ and Ni²⁺ adsorption on SSD obeyed all the three models. In comparison, Zn²⁺ adsorption on both SD and WH followed a linear model ($r^2 = 0.85–0.88$, $p < 0.05$), while Ni²⁺ adsorption on WH was best described by Freundlich equation ($r^2 = 0.90$, $p < 0.05$).

The inconsistent performance of bio-char and sulphonated bio-chars compared to the raw biomass highlight the diversity in bio-char properties associated with different feed-stock types (Spokas & Reicosky 2009) and the need for further characterization of the biosorbents. The Langmuir maximum adsorption capacity (q_m) for Zn²⁺ on SWH, SSD, BSD and AC (7–21.1 mg g⁻¹) were within the range (3.45–25.6 mg g⁻¹) reported in the literature for other biomaterials (Bakkaloglu et al. 1998). However, the q_m values (3.16–43.8 mg g⁻¹) for Ni²⁺ adsorption on WH, SWH, BSD and SSD were generally higher than those reported in previous studies (1.11–2.85 mg g⁻¹) (Bakkaloglu et al. 1998), indicating the superiority of the biosorbents used in the current study. The adsorption capacities of sulphonated bio-chars, SSD (21.01 mg g⁻¹) and SWH (16.37 mg g⁻¹) were higher than

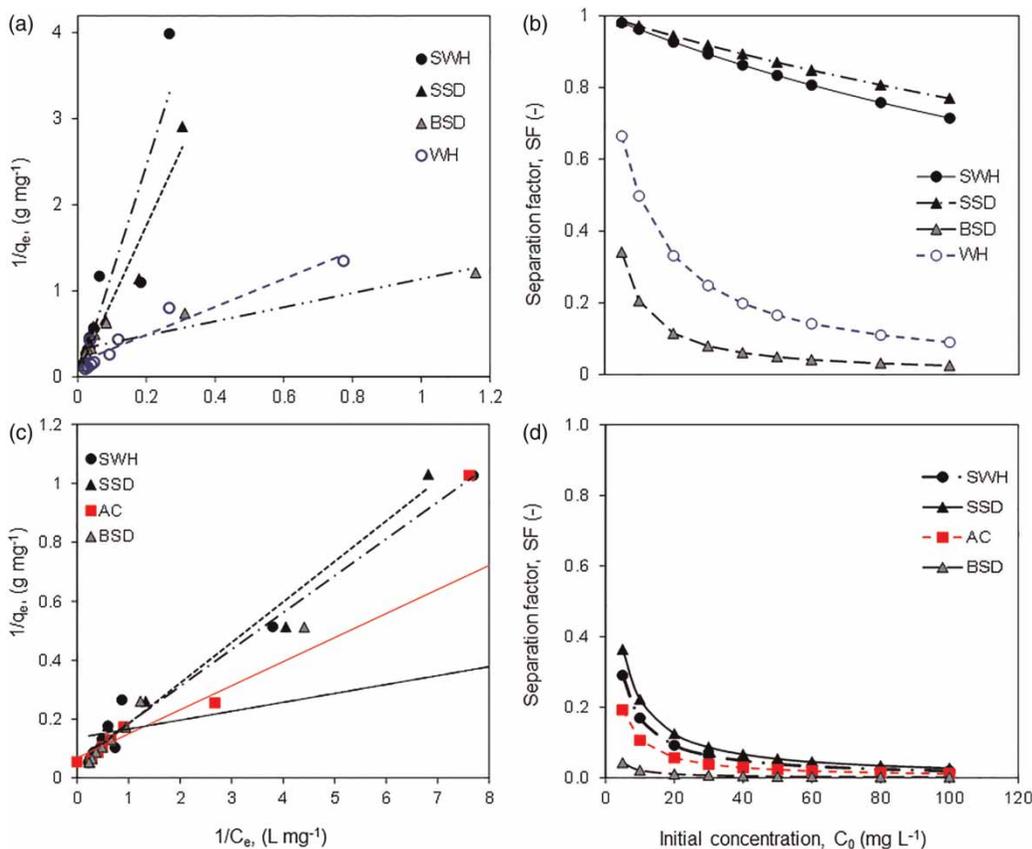


Figure 4 | Langmuir adsorption isotherms (left) and corresponding separation factor (SF) versus initial concentration (right) for Ni²⁺ ((a) and (b)) and Zn²⁺ ((c) and (d)). WH: water hyacinth (○), BWH: water hyacinth biochar (●), SWH: sulphonated water hyacinth biochar (●), SD: sawdust (Δ), BSD: sawdust biochar (▲), SSD: sulphonated sawdust biochar (▲), AC: commercial activated carbon (■). Initial concentrations: Ni²⁺ = 1,000 mg L⁻¹, Zn²⁺: 100 mg L⁻¹, contact time: 24 h. Contact time: 24 h. Data shown are only for adsorbents with good fit ($r^2 \geq 0.8$) between observed and predicted values.

that of the activated carbon (control) (14.6 mg g⁻¹). The Langmuir SF values ($0 < SF < 1$) obtained in the present study indicate that the adsorption process was favourable (Mahamadi & Nharingo 2010). Adsorption data obeying the Langmuir equation indicate homogeneous monolayer or surface adsorption of Zn²⁺ and Ni²⁺ on the biosorbents, while those that followed the Freundlich isotherm model suggest multilayer adsorption or the occurrence of both surface and intra-particle diffusion.

The weak relationship between CEC and Zn²⁺ and Ni²⁺ adsorption further highlights that, while ion exchange may contribute to the overall adsorption, other mechanisms are also involved. For sulphonated bio-char, adsorption capacities were less than or comparable to that of the original biomass and activated carbon, except for the data on pH effect for Ni²⁺. The failure of sulphonation to enhance heavy metal ion adsorption could be related to the competitive effects of H⁺ associated with sulphonate groups, which are known to be highly acidic and can release free H⁺ ions under aqueous conditions (Fourest & Volesky 1996). In

contrast, the higher adsorption capacity for bio-char (pH > 7) than sulphonated bio-char could be related to deprotonation and development of pH-dependent negative charges on the biosorbents. For sulphonated bio-char, a drop in pH following initial adjustment could also have occurred during the 8-hour adsorption process.

Overall, the nonlinear relationship between pH and adsorption, the preferential adsorption of Zn²⁺ relative to Ni²⁺, and the fact that the data obeyed multiple isotherms, highlights the complexity of the adsorption process. Indeed, the weak relationship between CEC and adsorption capacity, and limited changes in adsorption with solution pH, demonstrate that besides ion exchange, other processes could also be involved. These multiple mechanisms include surface adsorption, intra-particle or pore diffusion, micro-precipitation and formation of complex coordination species (Wang & Chen 2006), ion exchange and C π -cation interactions between metal ions and aromatic rings of biosorbents (Rivera-Utrilla & Sanchez-Polo 2003; Berber-Mendoza et al. 2013).

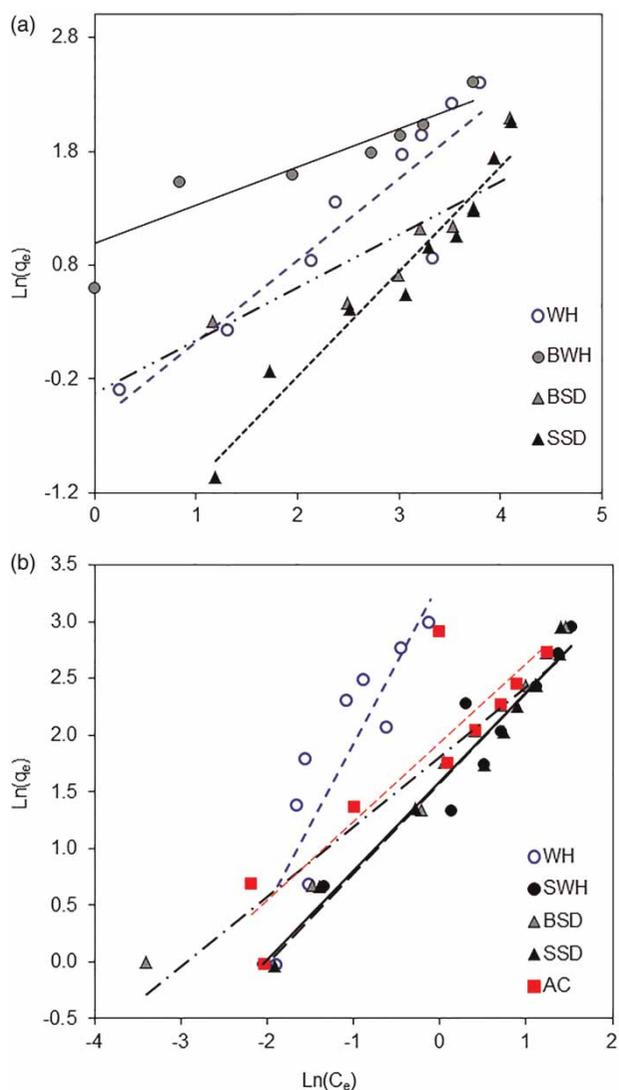


Figure 5 | Freundlich adsorption isotherms for Ni^{2+} (a) and Zn^{2+} (b). WH: water hyacinth (\circ), BWH: water hyacinth biochar (\bullet), SWH: sulphonated water hyacinth biochar (\bullet), SD: sawdust (Δ), BSD: sawdust biochar (\blacktriangle), SSD: sulphonated sawdust biochar (\blacktriangle), AC: commercial activated carbon (\blacksquare). Initial concentrations: $Ni^{2+} = 1,000 \text{ mg L}^{-1}$, $Zn^{2+} = 100 \text{ mg L}^{-1}$, contact time: 24 h. Data shown are only for adsorbents with good fit ($r^2 \geq 0.8$) between observed and predicted values.

CONCLUSIONS AND FUTURE RESEARCH

The six biosorbents had adsorption capacities similar to or higher than that of activated carbon (control). The findings have implications for the potential application of biosorption in environmental engineering, and separation and purification technology. Biosorption is critical in hydrometallurgy, permeable reactive barriers (Wang *et al.* 2011) for remediation of acid mine drainage, and treatment of storm-water, water and wastewater. While large-scale application

of activated carbon is constrained by the high cost of activated carbon, our results suggest that low-cost biosorbents developed from biowastes and aquatic weeds could be potential alternatives. Biosorbents have the capacity to achieve high removal efficiencies even at low concentrations. However, the suppression of heavy metal ions in binary or multicomponent aqueous solutions could present operational challenges in the remediation of aqueous media contaminated with multiple ionic species. One possible option to enhance removal of such competing ions includes sequential adsorption, entailing removal of Zn^{2+} followed by Ni^{2+} . However, preferential adsorption could be exploited in separation and purification technology such as hydrometallurgy (Homagai *et al.* 2009) for the selective separation of Zn^{2+} from multicomponent aqueous solutions containing Ni^{2+} . Overall, our findings demonstrate the complexity of biosorption, and emphasize the need for a detailed understanding of the process and its key controlling factors before large-scale application of the technology. Future research should focus on further characterization of the biosorbents and their potential application in hydrometallurgy and remediation of contaminated media. To this end, we are currently conducting further research on thermal analysis, BET surface area determination, zeta potential and desorption behavior of the biosorbents. In addition, we have initiated a pilot study using column and microcosm experiments to investigate the feasibility of using biosorption and phytoextraction to treat acid mine drainage.

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