

Removal of Ni(II), Zn(II) and Cr(VI) from aqueous solution by *Alternanthera philoxeroides* biomass

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Abstract

Alternanthera philoxeroides biomass, a type of freshwater macrophyte, was used for the sorptive removal of Ni(II), Zn(II) and Cr(VI) from aqueous solutions. Variables of the batch experiments include solution pH, contact time, particle size and temperature. The biosorption capacities are significantly affected by solution pH. Higher pH favors higher Ni(II), Zn(II) removal, whereas higher uptake of Cr(VI) is observed as the pH is decreased. A two-stage kinetic behavior is observed in the biosorption of Ni(II), Zn(II) and Cr(VI): very rapid initial biosorption in a few minutes, followed by a long period of a slower uptake. It is noted that an increase in temperature results in a higher Ni(II), Zn(II) and Cr(VI) loading per unit weight of the sorbent. Decreasing the particle sizes of the *Alternanthera philoxeroides* biomass leads to an increase in the Ni(II), Zn(II) and Cr(VI) uptake per unit weight of the sorbent. All isothermal data are fairly well fitted with Langmuir equations. The thermodynamic parameter, ΔG° , were calculated. The negative ΔG° values of Cr(VI), Ni(II) and Zn(II) at various temperatures confirm the adsorption processes are spontaneous. © 2006 Elsevier B.V. All rights reserved.

Keywords: Langmuir isotherm; *Alternanthera philoxeroides* biomass; Biosorption; Ni(II); Zn(II); Cr(VI)

1. Introduction

Heavy metal pollution of wastewater is a common environmental threat, since the toxic metal ions dissolved can eventually reach the top of the food chain and thus, become a risk factor for people's health. For instance, ingesting large amounts of Cr(VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. The World Health Organization (WHO) has determined that Cr(VI) is a human carcinogen [1]. The tolerance limit for the discharge of Cr(VI) into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L [2]. Although zinc is essential trace element, high levels can cause harmful health effects. The most common adverse health effect of nickel in humans is an allergic reaction. Large amounts of nickel can also cause lung and nasal sinus cancers. The US Environmental Protection Agency (US EPA) requires zinc and nickel in drinking water not to exceed 5 and 0.04 mg/L [3]. Therefore, various process and measurements such as chemical precipita-

tion, ion exchange, membrane separation and activated carbon adsorption have been employed to remove metal pollutants from aqueous solutions [2–4]. However, most of these methods suffer from some disadvantages including incomplete metal removal, toxic sludge generation and high costs when applied to dilute effluents on a large scale. Hence, there is a crucial need for the development of a method that is not only cost effective, but can be easily implemented. This leads to a search for cheaper, easily obtainable materials for the adsorption of heavy metals or organic pollutants [5–13]. Biosorption by inexpensive biomaterials promises to be an excellent alternative. During the past two decades, there has been interest in the use of aquatic plants in treating polluted effluents. The rapid, often excessive, growth of these plants allow a biomass production that far exceeds the yield of most productive agricultural crops. These species studied have been *Eichhornia crassipes* (water hyacinth), *Alternanthera philoxeroides* (alligator weed), *Pistia stratiotes* (water lettuce), and *Potamogeton crispus* [14]. Early studies concerning the use of these aquatic plants in pond systems to remove metal ions and other pollutants from wastewaters were conducted by National Space Technology Laboratories (NASA/ASTL) in United States in the 1970s and demonstrated at laboratory scale

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and at a wastewater treatment station that this freshwater plants efficiently remove dilute concentrations of heavy metals, including Co, Ni, Sr, Ag, Cd, Hg, and Pb [14]. However, in recent years, the nonliving forms have been proposed as potential sorbents, since these are essentially dead materials, which require no nutrition maintain the biomass. Problems associated with metal toxicity in living biomass and the need to provide suitable growth condition also do not arise. Indeed, many early studies have shown that nonviable biomass may be even more effective than living cells in sequestering metallic elements [3]. Up to now, many types of dead organisms have been studied for their heavy metal uptake capacities and suitability, which include seaweeds, molds, yeasts, bacteria, fungi. Nevertheless, there are very limited studies on application of the nonliving biomass of freshwater macrophytes grown worldwide for treatment of toxic heavy metals. André et al. [14] reported that the dried biomass of *Potamogeton lucens*, *Salvinia herzogii* and *E. crassipes* were excellent biosorbents for Cr(III), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II).

The *A. philoxeroides* (alligator weed), a type of freshwater macrophyte, is exotic species and easily available in large amounts in nature in China. The *A. philoxeroides* is a complex material containing proteins, carbohydrates and lipids as major constituents. Chemical sorption can occur by the polar functional groups of these constituents, which include carboxyl groups and phenolic hydroxyl as chemical bonding agents [14]. The present research described here was designed to test the characteristics of *A. philoxeroides* biomass as adsorbent for removing Ni(II), Zn(II) and Cr(VI) from aqueous solutions in batch system. The important factors affecting the biosorption efficiency such as solution pH, contact time, temperature, and particle size were investigated.

2. Materials and methods

2.1. Materials

The raw biomass, *A. philoxeroides*, was obtained from wild specimens growing in Lianyungang, China. The plant tissues were washed with copious quantities of deionized water for the removal of ions present, dried at 60 °C overnight and finally ground to various particle sizes for the use in the experiments.

The stock metal solutions at various concentrations were prepared by dissolving nickel nitrate, zinc sulfate and potassium dichromate, which are all of analytical reagent grade.

2.2. Methods

2.2.1. Effect of solution pH

The effect of pH on the adsorption capacity of *A. philoxeroides* biomass (particle size <125 μm) was investigated using solutions of 100 mg/L Ni(II), Zn(II), Cr(VI) for pH 2.0, 4.0, 6.0 and 8.0 at room temperature, respectively. Metal solutions at various initial pH were adjusted using 0.1 mol/L HNO₃ or 0.1 mol/L NaOH. 0.25 g of *A. philoxeroides* biomass was added to 50 mL of Ni(II), Zn(II), Cr(VI) solutions. Experiments could not be performed at higher pH values due to hydrolysis of metal ions.

After shaking the flasks for 5 h, the *A. philoxeroides* biomass was separated by filtration through a membrane filter (0.45 μm). The filtrates were analyzed for the remaining Ni(II), Zn(II) concentrations by atomic absorption spectrophotometry (AAS). The Cr(VI) concentrations were analyzed by a colorimetric method. Using a UV spectrophotometer, the filtrates were measured at 540 nm after complexation with 1,5-diphenylcarbazide (colorimetric method 3500-Cr D).

2.2.2. Effect of contact time

The effect of contact time on the adsorption capacity of *A. philoxeroides* biomass (particle size <125 μm) was investigated using solutions of 100 mg/L Ni(II) and Zn(II) for pH 6.0 and Cr(VI) for pH 2.0 at room temperature. 0.25 g of *A. philoxeroides* biomass was added to 50 mL of Ni(II), Zn(II), Cr(VI) solutions. The samples were withdrawn at periodic time intervals (5, 15, 30, 60, 120, 180 min) and centrifuged. The filtrates were analyzed.

2.2.3. Effect of temperature

A 50 mL of Ni(II), Zn(II), Cr(VI) solutions with a concentration in the range of 40–100 mg/L was placed in a 125 mL conical flask. 0.25 g of biomass with particle size <125 μm was then shaken at a constant speed of 200 rpm in a shaking water bath with temperatures 4, 20, and 40 °C, respectively. After shaking the flasks for 5 h, the samples were centrifuged and analyzed.

2.2.4. Effect of particle size

A 50 mL of Ni(II), Zn(II), Cr(VI) solutions with a concentration in the range of 40–160 mg/L was placed in a 125 mL conical flask. 0.25 g of biomass at two different particle sizes (<74 and 125–250 μm) was then shaken at a constant speed of 200 rpm at room temperature. After shaking the flasks for 5 h, the samples were centrifuged and analyzed.

3. Data evaluation

Biosorption of the metal ions (q , mg/g) in the sorption system was calculated using the mass balance:

$$q = \frac{V(C_i - C_e)}{W} \quad (1)$$

where V is the solution volume (L), W the amount of biomass (g), and C_i and C_e are the initial and final (equilibrium) metal concentrations (mg/L), respectively.

The Langmuir isotherm is used to fit the experimental data. The Langmuir isotherm can be expressed as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

where q_m and b are Langmuir constants (mg/g, L/mg), which reflect the maximum sorption capacity and the affinity between the ion and biosorbent, q_e the sorption capacity at equilibrium (mg/g).

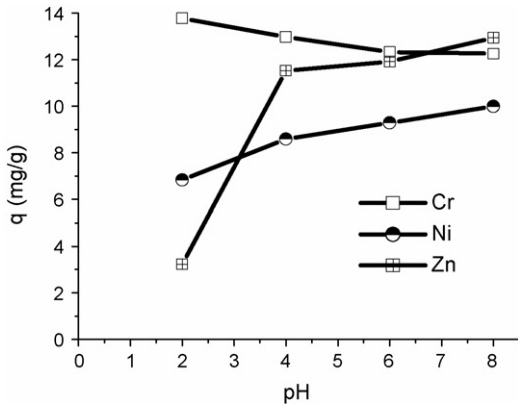


Fig. 1. pH effect on metal uptake.

4. Results and discussion

4.1. Effect of solution pH

It is well documented that solution pH is an important parameter affecting biosorption of heavy metal ions [2]. Biosorption of heavy metal ions (Ni(II), Zn(II) and Cr(VI)) onto *A. philoxeroides* biomass as a function of pH was studied and the results are shown in Fig. 1. The uptakes of Ni(II), Zn(II) increase sharply from pH 2.0 to 4.0; whereas, the uptakes of the Ni(II), Zn(II) by this biomass do not increase appreciably beyond 4.0. For Cr(VI), the pH influence is different compared to Ni(II), Zn(II). The uptake increases with a decrease in pH and the optimum pH is 2.0. Similar findings were reported for other types of biosorbents [1]. In addition, one can find that *A. philoxeroides* biomass has better metal biosorptive capacity for Zn(II) than that for Ni(II), suggesting that the organic functional groups such as phenolic hydroxyl and carboxyl in the biomass have a higher affinity for Zn(II).

The dependence of metal uptake on pH is related to both the surface functional groups on the cell walls of the biomass and the metal chemistry in solution. In the case of Ni(II), metallic ions are the dominant species below pH 6.0 (see Fig. 2(a)); Ni(II) sorption from pH 2.0 to 4.0 cannot be explained by the change in Ni(II) speciation. This implies that the functional groups on the cell walls and its ionic state in the pH range determine the extent of biosorption. The positively charged hydrogen ions may also compete with nickel ions for binding on the ligands on the cell wall. At lower pH, the higher concentration of the hydrogen ions effectively leads to fewer ligands being available for the binding of the nickel zinc ions. As the pH is increased (i.e. fewer H⁺ ions), more ligands are available for these two cations, thus resulting in an enhanced nickel ions removal. For Zn(II), the reason is similar to that of Ni(II).

Electrostatic attraction may play an important role in the biosorption of negatively charged metal ions by biosorbents [1]. Fig. 2(b) shows the dominant species of Cr(VI) is HCrO₄⁻ at pH < 5.5. As the pH is lowered, more functional groups such as phenolic hydroxyl on the biomass surface may carry much more positive charges, thus, more hexavalent chromium in the form of HCrO₄⁻ will be attracted electrostatically onto the surface with

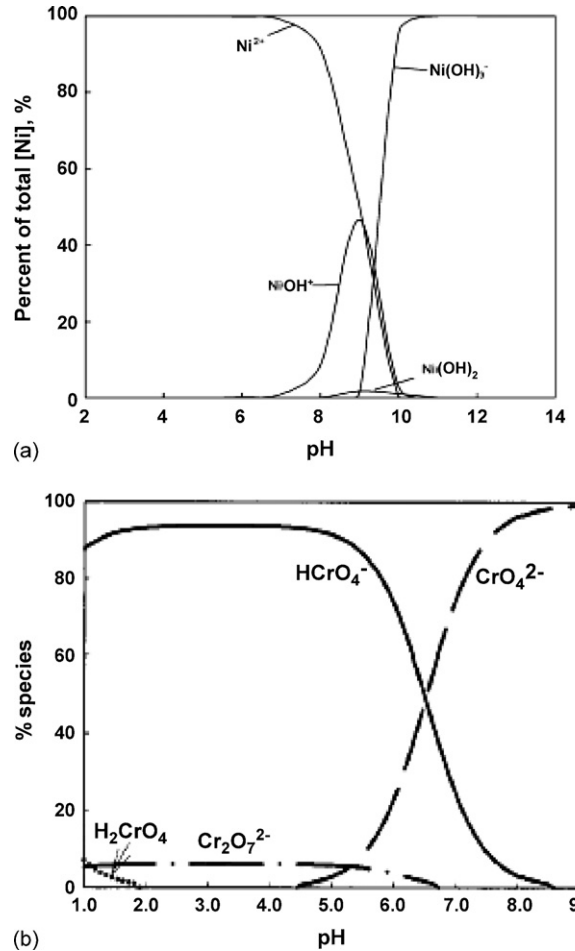


Fig. 2. Metal ion species in solution for (a) Ni(II) [15] and (b) Cr(VI) [1].

the decrease of pH, which result in higher uptake of the hexavalent chromium. In addition, chemical biosorption reactions can have a key role described as follows:



where the SOH represents a generalized organic functional group in the biomass surface.

Eq. (3) shows that a decrease of solution pH can shift the reaction to the right and cause higher adsorption.

In order to examine the biosorption potential of *A. philoxeroides* biomass and to ensure that the metal ions studied exist in their ionic states during biosorption, the pH in the subsequent experiments were controlled at 6.0 for Ni(II), Zn(II) and at 2.0 for chromium (VI).

4.2. Determination of equilibrium time

Equilibrium time is a function of many factors, such as type of biomass (number and kind of biosorption sites), size and form of biomass, physiological state of biomass, as well as the metal involved in the biosorption system [16]. The kinetic experiments of Ni(II), Zn(II) and Cr(VI) sorption onto *A. philoxeroides* biomass were carried out to determine the equilibrium time and the results are shown in Fig. 3. A two-stage kinetic behavior

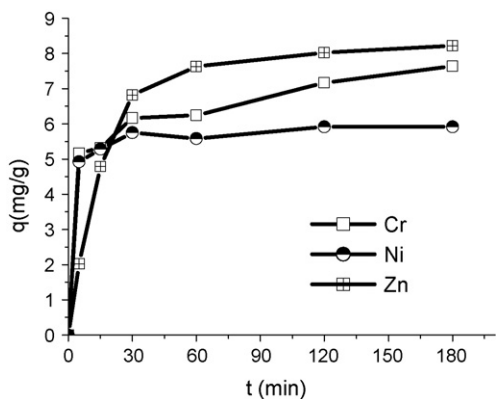


Fig. 3. Kinetic experimental studies of metal ion uptake.

is obvious: a very rapid initial sorption over a few minutes, followed by a long period of much slower uptake. In general, about 90% of the total metal ion sorption was achieved within 60 min. Therefore, in subsequent equilibrium experiments, 5 h was deemed sufficient to establish equilibrium.

4.3. Effect of particle size

Langmuir sorption isotherms of Ni(II), Zn(II) and Cr(VI) at two different particle sizes of *A. philoxeroides* biomass are shown in Fig. 4. Table 1 shows the maximum adsorption capacity (q_m) and the affinity constant (b) under the experimental conditions, i.e. pH 6.0 for nickel (II), zinc (II) and pH 2.0 for chromium (VI). It is clear that q_m increases with decreasing particle size for these three metal ions. This may be attributed to

the larger external surface available with smaller particles at a constant mass of *A. philoxeroides* biomass in the system.

The effect of isotherm shape can be used to predict whether a sorption system is “favorable” or “unfavorable” [17]. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R , which is defined by the following relationship:

$$K_R = \frac{1}{1 + bC_0} \quad (4)$$

where K_R is a dimensionless separation factor, C_0 the initial concentration (mg/L) and b the Langmuir constant (L/mg). This parameter indicates the shape of the isotherm accordingly:

Values of K_R	Type of isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

The values of K_R for Ni(II), Zn(II) and Cr(VI) at two different particle sizes are given in Fig. 5. The K_R values all indicate that sorption is more favorable for the higher initial ion concentrations than for the lower ones. However, it should be noted that the sorption process becomes more favorable with increasing particle size for Ni(II), Zn(II).

4.4. Effect of temperature

Sorption isotherms of Cr(VI), Ni(II) and Zn(II) at various temperatures of solutions are shown in Fig. 6 and the Langmuir

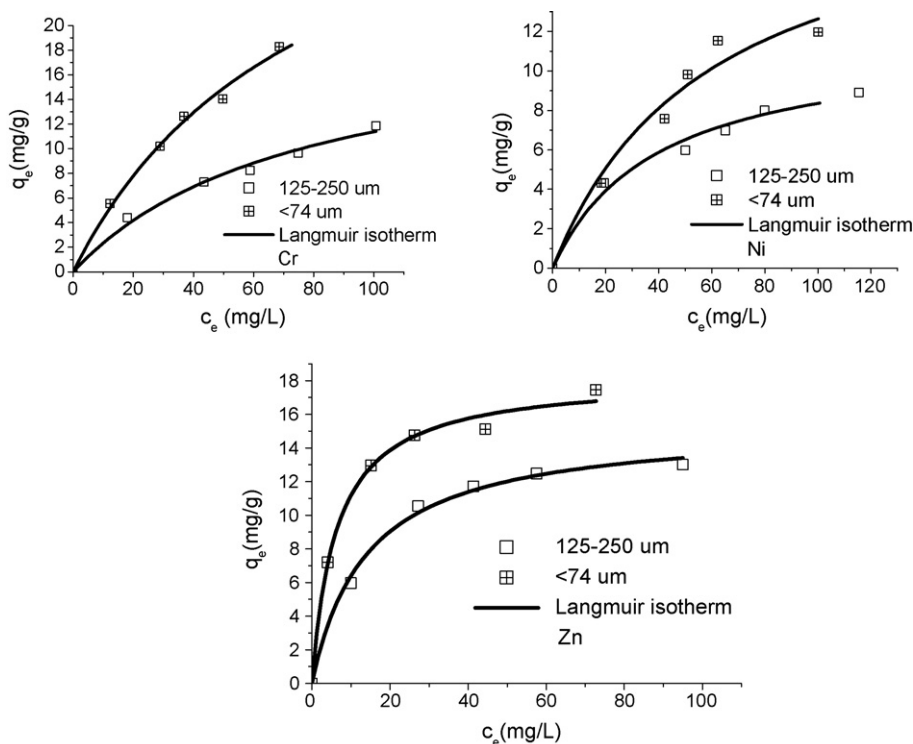


Fig. 4. Langmuir isotherms for the sorption of Cr(VI), Ni(II) and Zn(II) using *Altermanthera philoxeroides* biomass at two different particle sizes.

Table 1
Langmuir sorption isotherm constants and coefficient of determination (R^2) at two different particle sizes for Ni(II), Zn(II) and Cr(VI)

	Cr(VI)		Ni(II)		Zn(II)	
	<74 μm	125–250 μm	<74 μm	125–250 μm	<74 μm	125–250 μm
q_m (mg/g)	37.57	20.04	20.16	11.63	18.23	15.38
b (L/mg)	0.0128	0.0132	0.0168	0.0255	0.1584	0.0712
R^2	0.994	0.991	0.972	0.987	0.994	0.996

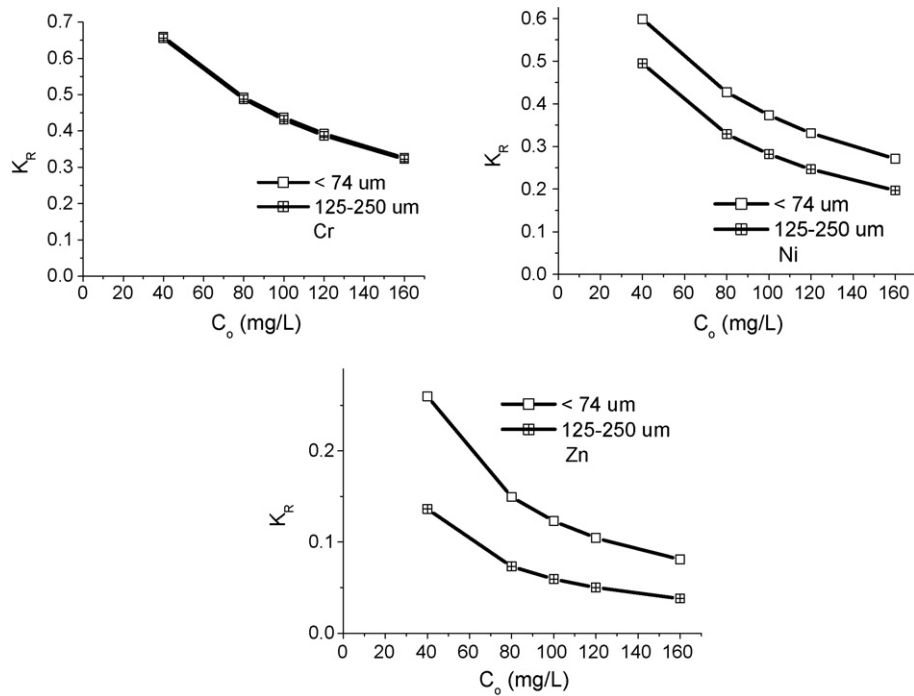


Fig. 5. Plot of K_R against initial concentrations of various particle sizes for Cr(VI), Ni(II), and Zn(II).

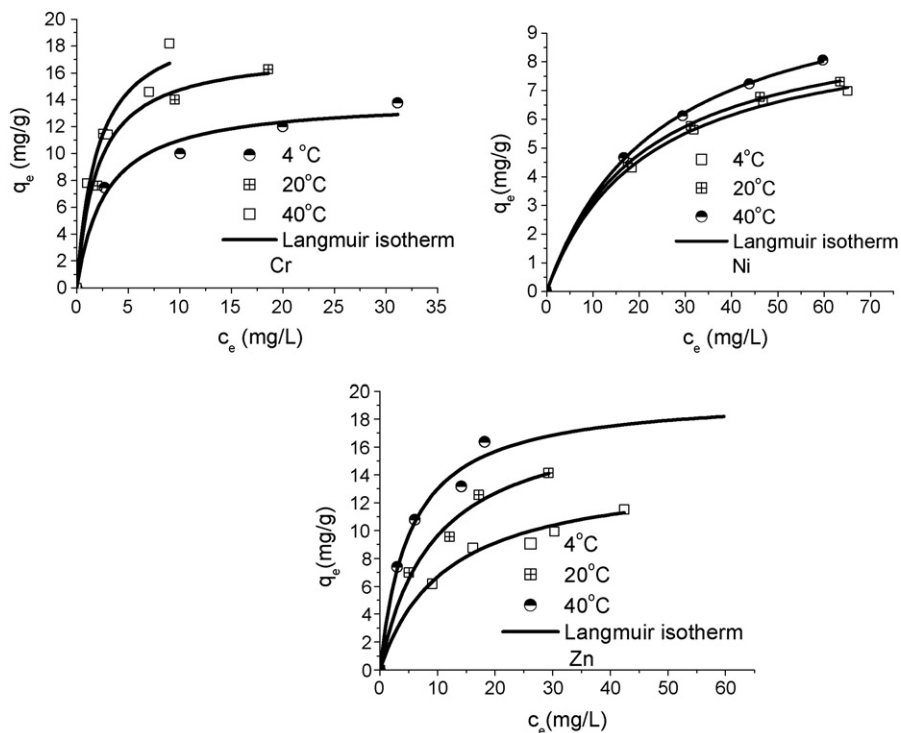


Fig. 6. Langmuir isotherms for the sorption of Cr(VI), Ni(II), and Zn(II) using *Alternanthera philoxeroides* biomass at various temperatures.

Table 2

Langmuir isotherm constants, coefficient of determination (R^2), and values of ΔG° for the adsorption of Cr(VI), Ni(II), and Zn(II) at various temperatures

	Cr(VI)			Ni(II)			Zn(II)		
	4 °C	20 °C	40 °C	4 °C	20 °C	40 °C	4 °C	20 °C	40 °C
q_m (mg/g)	14.06	17.71	20.45	9.44	9.73	11.25	14.34	18.57	19.78
b (L/mg)	0.356	0.497	0.498	0.0466	0.0482	0.0415	0.0871	0.1074	0.983
R^2	0.981	0.972	0.972	0.998	0.999	0.999	0.995	0.989	0.983
ΔG° (kJ/mol)	-22.63	-24.74	-26.46	-18.20	-19.37	-20.31	-19.93	-21.58	-27.06

Table 3

Previously reported adsorption capacities for various adsorbents for metal ion adsorptions

Adsorbent	Adsorption capacity (mg/g)			References
	Zn(II)	Ni(II)	Cr(VI)	
2-Mercaptobenzothiazole loaded clay	0.92			[18]
Low-rank Turkish coals	1.2			[18]
Silicagel modified with salicylaldehyde	2.61			[18]
SDDC-carbon column	9.9			[18]
Chabazite	5.5	4.5		[19]
Clinoptilolite	2.7	0.9		[19]
<i>Sargassum</i> sp.	32.5	35.3		[3]
<i>Ulva</i> sp.	35	16.8		[3]
<i>Gracillaria</i> sp.	26	16.2		[3]
Hazelnut shell activated carbon			17.7	[2]
Sugar beet pulp			17.2	[2]
Palm pressed fibres			14.0	[2]
Maize cob			13.8	[2]
Sugar cane bagasse			13.4	[2]
<i>Alternanthera philoxeroides</i> biomass	18.57	9.73	17.71	This study

isotherm constants are given in Table 2. The results show that sorption capacities of Cr(VI), Ni(II) and Zn(II) at equilibrium increase with increasing temperature from 4 to 40 °C, suggesting that the sorption process is endothermic. The Langmuir constant, b , represents the affinity between the adsorbent and adsorbate. The values of b increase with increasing temperature for Zn(II) and Cr(VI), but not for Ni(II). This may be due to that the interaction between adsorbent and Zn(II) or Cr(VI) is different from that between adsorbent and Ni(II). To estimate the effect of temperature on the adsorption of Cr(VI), Ni(II) and Zn(II) onto *A. philoxeroides* biomass, The free energy change (ΔG°) (Table 2) were calculated from the variation of the Langmuir constant, b (L/mg), with change in temperature using the following equations:

$$\Delta G^\circ = -RT \ln b \quad (5)$$

where R is the universal gas constant, 8.314 J/mol K and T is absolute temperature, K.

The negative ΔG° values of Cr(VI), Ni(II) and Zn(II) at various temperatures confirm the adsorption processes are spontaneous and the negative values of ΔG° (see Table 2) decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of Cr(VI), Ni(II) and Zn(II) are inversely proportional to the temperature. Enhancement of adsorption capacity at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface.

4.5. Comparison with other sorbents

In order to justify the validity of *A. philoxeroides* biomass as an adsorbent for adsorption, its adsorption potential must be compared with other various adsorbents used for this purpose. The values of maximum sorption capacity reported in the literature are given in Table 3. It shows that *A. philoxeroides* biomass has good adsorption capacity when compared with other adsorbents. The adsorption capacity differences of metal ions uptake are ascribed to the properties of different adsorbent such as structure, functional groups and surface areas [20].

5. Conclusions

Biosorption performance of *A. philoxeroides* biomass was studied for the removal of Cr(VI), Ni(II), and Zn(II) from aqueous solutions. The removal of Ni(II) and Zn(II) increases with an increasing pH whereas lower pH favors the biosorption of Cr(VI). The kinetic experiments show that a two-stage kinetic behavior is observed in the biosorption of Ni(II), Zn(II) and Cr(VI): very rapid initial biosorption in a few minutes, followed by a long period of a slower uptake. It is noted that an increase in temperature can result in a higher loading per unit weight of the biosorbent for these three metals studied. Decrease in the particle size of *A. philoxeroides* biomass can result in an increase in the metals uptake per unit weight of the sorbent. The results show that *A. philoxeroides* biomass can be

used for the removal of Cr(VI), Ni(II), and Zn(II) from aqueous solutions.

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