



Short Communication

Kinetics and thermodynamics of heavy metal ions sequestration onto novel *Nauclea diderrichii* seed biomassMartins O. Omorogie^{a,b}, Jonathan O. Babalola^{b,*}, Emmanuel I. Unuabonah^{c,d}, Jian Ru Gong^{a,*}^a National Center for Nanoscience and Technology (NCNST), Beijing, People's Republic of China^b Department of Chemistry, University of Ibadan, Ibadan, Nigeria^c Department of Chemical Sciences, Redeemer's University, P.M.B. 3005, Mowe, Ogun State, Nigeria^d Institut für Chemie, Universität Potsdam, Germany

HIGHLIGHTS

- ▶ *Nauclea diderrichii* seed biomass as a new biosorbent.
- ▶ Biosorption of Cadmium and Mercury ions.
- ▶ Kinetics and thermodynamics of biosorption.
- ▶ Biosorption feasible, spontaneous and endothermic.

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ABSTRACT

This study reports the sequestration of Cd(II) and Hg(II) using a new biosorbent, *Nauclea diderrichii* seed biomass. Experimental data obtained were fitted into kinetic and thermodynamic models. Experimental data fitted best into pseudo-second order kinetic model among others. Results obtained kinetically revealed that the biosorption of Cd(II) and Hg(II) using *N. diderrichii* seed biosorbent increased with increase in temperature. At the highest temperature, which was 333 K, the highest amount of metal biosorbed, q_e , for Cd(II) and Hg(II) obtained were 6.30 and 6.15 mg/g respectively. The biosorption of Cd(II) was kinetically faster than that of Hg(II), the highest initial biosorption rates for Cd(II) and Hg(II) were 56.19 and 4.39 mg/g min respectively. Thermodynamic parameters obtained by Eyring equation from this study revealed that the biosorption process was spontaneous, feasible, endothermic with a decrease in the degree of chaos in the biosorption system.

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1. Introduction

Environmental pollution is now a global problem due to its impact both on humans and the entire ecosystem. The availability of potable water is a paramount requisite for human existence and the ecosystem at large (Waseem et al., 2011). Cadmium (Cd) and Mercury (Hg) are two of the most commonly known micropollutants in domestic and industrial wastewater (Waseem et al., 2011).

Cadmium mainly accumulates in the kidneys and liver, hence leading to kidney failure, renal stone formation, bone disease and persistent proteinuria as a sign of kidney damage. Other effects from acute cadmium exposures may include muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock, renal failure (Iqbal et al., 2007). Mercury is generally considered as the most toxic metal in natural ecosystems (Clarkson, 1993).

Over the years, various biomasses had been chosen and utilized by researchers to sequester toxic heavy metal ions from industrial wastewaters. Some biosorbents recently used by researchers are defatted *Carica papaya* {Pb(II) and Cd(II)} (Adie et al., 2011), *Mansonia* wood sawdust {Cu(II) and Pb(II)} (Ofomaja et al., 2010), *Tamarindus indica* seeds {Cu(II)} (Chowdhury and Saha, 2011) and Mustard oil cake {Ni(II)} (Khan et al., 2012). Adsorbents of biological origin have gained excellent credibility because of their ubiquity, good efficiency and cost economics.

Nauclea diderrichii (De wild) is a deciduous tree and one of the few indigenous species available in Nigeria which thrives excellently under plantation management in the humid tropical rainforest zone of south-western Nigeria (Adeoye and Waigh, 1983).

This study reports the use of *N. diderrichii* seed biomass as a new low cost biosorbent for the sequestration of Cd(II) and Hg(II) from aqueous solutions in a batch system. Until now, there is no report on the use of *N. diderrichii* seed biomass for the biosorption of micropollutants.

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2. Experimental

2.1. Methods

2.1.1. Preparation of *N. diderrichii* seed biomass

Nauclea diderrichii seed biomass was obtained from the Forest Research Institute of Nigeria (FRIN), in Ibadan (7° 23' 16" North, 3° 53' 47" East), Nigeria, West Africa. After collection, this seed biomass was dried in an oven at 60 °C for 3 h. Thereafter, it was pulverized and sieved to 450 µm particle size which was used in this research.

2.1.2. Biosorption studies

Fifty milligrams each of *N. diderrichii* seed biosorbent was weighed into various 3 mL plastic containers. Various experimental solutions were prepared by diluting stock solutions prepared from of Cd(NO₃)₂·4H₂O and Hg(NO₃)₂·1/2H₂O in Milli-Q water deionizer to the desired concentrations when needed. The pH study was done using 50 mg of *N. diderrichii* seed biosorbent in 50 mL of 20 mg/L solution of Cd(II) and Hg(II). The pH of solutions was adjusted within the range of 3.0–7.0 using either 0.1 M HNO₃ or NaOH. Kinetic study was conducted with 50 mg of *N. diderrichii* seed biosorbent in 20 mL of 20 mg/L of Cd(II) and Hg(II) in 100 mL conical flasks. Samples were collected at specific time with a range of 0.5–120 min.

The experimental data obtained for biosorption study were fitted into kinetic models; pseudo-first order (Lagergren, 1898), pseudo-second (Ho and McKay, 1999) and Morris–Weber (Weber and Morris, 1963) intraparticle diffusion equations.

Pseudo-first order, pseudo-second and Morris–Weber intraparticle diffusion equations are given respectively as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$t/q_t = t/q_e + 1/k_2 q_e^2 \quad (2)$$

$$q_t = k_i t^{1/2} + C \quad (3)$$

Where q_e is the amount of metal ion biosorbed by the biosorbent (mg/g), q_t is the amount of metal ion biosorbed at time t (min) by the biosorbent (mg/g), k_1 and k_2 are the pseudo-first (/min) and pseudo-second (g/mg min) order model rate constants, $h = k_2 q_e^2$ (mg g/min) is the initial biosorption rate, k_i is the Morris–Weber intra-particle diffusion rate constant (g/mg min^{1/2}) and C is the thickness of the boundary layer.

For thermodynamic study, similar experiment above was repeated at 303, 318 and 333 K for Cd(II) and Hg(II). Also, experimental data obtained were fitted into the Eyring equation (Ho et al., 2000) which is expressed as;

$$\ln(k_2/T) = \ln(k/h) + (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (4)$$

Where k_2 , k , h , R and T are pseudo-second order constant, Boltzmann constant, Planck constant, universal gas constant (J/mol K) and absolute temperature respectively.

The mixtures were equilibrated in a thermostatic shaker (THZ-C Chinese Model) at 125 rpm for 120 min. At equilibrium the suspensions were filtered using filter paper and pure supernatant liquids obtained were taken for the residual Cd(II) and Hg(II) ion concentrations in the solutions using Perkin Elmer Optima 5300DV Model of ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer).

3. Results and discussion

3.1. Physicochemical analysis

Fig. 1 shows the SEM image of NDS biosorbent. From the SEM image the particles of this biosorbent were observed to be more

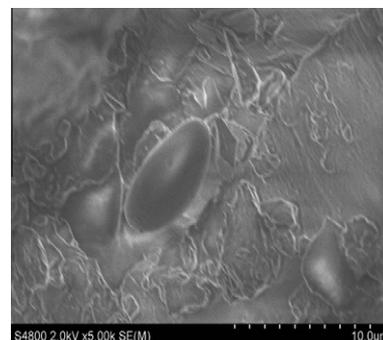


Fig. 1. Scanning Electron Microscopy (SEM) image of NDS biosorbent.

like stomata in plants with strands of fibres rather than criss-cross the surface of the material.

BET analysis indicates that NDS has a surface area of 5.36 m²/g, with a molecular cross-sectional area and average pore volume of 0.162 nm² and 0.00632 cm³/g respectively. The average pore diameter is got as 3.986 nm.

With thermogravimetric analysis (Fig. 2) there was weight loss of about 5% from 50 to 200 °C, 35% from 200 to 400 °C and 10% from >400 °C which can be assigned to loss in surface water, structural –OH and heat induced condensation reaction involving the hydroxyl groups on the surface of NDS adsorbent (Eren et al., 2011). For differential thermal analysis, NDS biosorbent showed a large endothermic peak (Fig. 2) at 20–510 °C with corresponding increase in heat flow. This may be due to bond breakage and dissociation (Park et al., 2006).

3.2. Effect of solution pH

Solution pH affects the degree of dissociation of the functional groups on biosorbent surface, the speciation and solubility of metal ions in aqueous solutions (Deng et al., 2007). This study showed that the optimum pH s of biosorption for Cd(II) and Hg(II) were obtained at 7.0 and 4.0 respectively. Similar optimum pHs of biosorption were obtained when green coconut shell powder (Pino et al., 2006) and chitin/cellulose composite membrane (Tang et al., 2011) were used for Cd(II) and Hg(II) uptake respectively. Fig. 3 shows the graphical representation of q_e (mg/g) against pH.

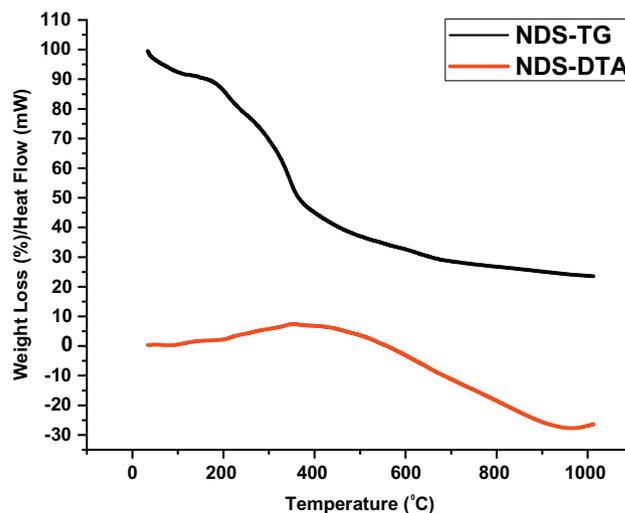


Fig. 2. Thermogravimetric/Differential Thermal Analysis (TG/DTA) thermograms of NDS biosorbent.

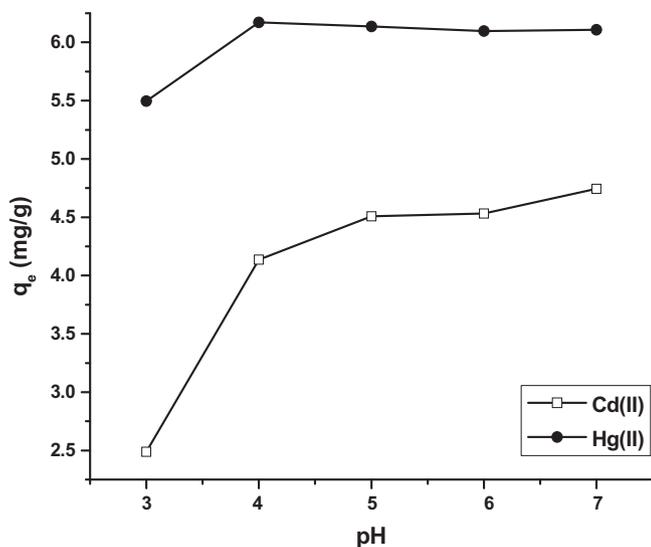


Fig. 3. A plot of q_e (mg/g) against pH for the bisorption of Cd(II) and Hg(II) onto *N. diderrichii* seed biosorbent (Cd(II) = pH 7, Hg(II) = pH 4; Biosorbent dose = 50 mg; Initial metal ion concentration = 20 mg/L; Agitation time = 0.5–120 min; Agitation speed = 125 rpm).

3.3. Effect of agitation time

The amount Cd(II) biosorbed q_t (mg/g), increased from 0.5–60 min at all the studied temperatures. The increase was from 5.70–6.11, 5.93–6.22 and 5.84–6.30 mg/g at 303, 318 and 333 K, respectively. For Hg(II), a similar increase was observed from 3.73–6.00, 2.54–6.01 and 4.14–6.14 mg/g at 303, 318 and 333 K, respectively. Increase in temperature may be responsible for the increased uptake of Cd(II) and Hg(II) onto the surface of *N. diderrichii* seed biosorbent with time due to increase the rate of collision of sorbates with the biosorbent surface, hence increase in the kinetic energy of the system (Gopal and Elango, 2007).

3.4. Kinetic modeling

The amounts of Cd(II) and Hg(II) biosorbed onto *N. diderrichii* seed biosorbent surface q_e , are 6.11, 6.23, 6.30 and 6.06 mg/g, 6.08 and 6.15 mg/g at the studied temperatures of 303, 318 and 333 K respectively. The initial biosorption rates h , for Cd(II) and Hg(II) are 45.23, 56.19, 22.27 and 3.78 mg/g min, 3.40, 4.39 mg/g min at 303, 318 and 333 K, respectively.

Some past works show that initial sorption rates h for Cd(II) and Hg(II) were less than those obtained in this study. For Cd(II), 0.87 mg/g min (Grassi et al., 2011) and Hg(II), 1.53–6.22 mg/g min (Sun et al., 2011). This indicates that the uptake of Cd(II) onto *N. diderrichii* seed biosorbent surface was kinetically faster than that of Hg(II). The pseudo-second order kinetic model requires a rate controlling step which may comprise chemisorption and diffusion processes (Ho and McKay, 1999).

Morris–Weber intraparticle diffusion model shows that the rate-limiting step required for a biosorption process includes external mass transport across the boundary layer surrounding the particle (film diffusion), and diffusional mass transfer within the internal structure of a biosorbent matrix by the surface or a pore, or a branched pore; and biosorption at surface sites, such as chemical or physical sorption (Ho and McKay, 1999). The values of intercept, C , obtained from the experimental data for the biosorption of Cd(II) and Hg(II) onto *N. diderrichii* seed biosorbent (see Table 1) were >0 . This suggests that intraparticle may not be the rate-limiting step, and chemisorption or ion exchange

Table 1

Kinetic Parameters for the bisorption of Cd(II) and Hg(II) onto *N. diderrichii* seed biosorbent.

	303 K		318 K		333 K	
<i>Pseudo-First Order Model</i>						
K_1 (/min)	Cd (II)	Hg(II)	Cd (II)	Hg(II)	Cd (II)	Hg(II)
	0.0353	0.0317	0.0322	0.0313	0.0261	0.0389
q_e (mg/g)	0.1859	0.5931	0.1515	0.5235	0.3071	0.6042
R^2	0.5106	0.8942	0.7689	0.8190	0.7096	0.9567
<i>Pseudo-Second Order Model</i>						
K_2 (g/mg min)	1.2120	0.1034	1.4489	0.0921	0.5611	0.1159
q_e (mg/g)	6.1087	6.0611	6.2272	6.0832	6.3011	6.1500
h (mg/g min)	45.2313	3.7844	56.1855	3.4041	22.2731	4.3872
R^2	1.0000	1.0000	1.0000	1.0000	1.0000	0.9994
<i>Morris–Weber Intra-particle Diffusion Model</i>						
K_1 (g/mg min ^{1/2})	0.0338	0.251	0.0260	0.336	0.0404	0.207
C	5.8316	3.8450	6.0055	3.2541	5.9242	4.2913
R^2	0.5040	0.7782	0.6566	0.6776	0.7717	0.7899

mechanism might have played a significant role in the biosorption process.

3.5. Thermodynamic modeling

In order to understand the impact of temperature, spontaneity and feasibility of this adsorption system with *N. diderrichii* biosorbent, there is need to calculate and evaluate the various thermodynamic parameters of this process. From various thermodynamic plots, ΔG° values decreased from -60.777 to -64.451 kJ/mol and -20.258 to -22.211 for Cd(II) and Hg(II) respectively as temperature rose from 303 to 333 K. Moreso, ΔH° (kJ/mol) values obtained are $+23.667$ and $+0.531$ kJ/mol for Cd(II) and Hg(II) respectively. ΔS° (J/mol K) values were calculated to be -122.474 and -65.107 J/mol K for Cd(II) and Hg(II) respectively. These suggests that the biosorption process for the biosorption of both metal ions was spontaneous, feasible, endothermically controlled and showing a decrease in the degree of disorderliness of the biosorption system. This suggests that the biosorption process was energy driven with respect to its endothermic nature. This is a requisite needed to overcome the energy barrier in this process (Gopal and Elango, 2007).

4. Conclusion

This study investigated the kinetics and thermodynamics of the uptake of Cd(II) and Hg(II) onto *N. diderrichii* seed biosorbent. The result revealed kinetically that *N. diderrichii* seed biosorbent showed greater capacity for Cd(II) than Hg(II), and that the process was kinetically faster for the uptake of Cd(II) than Hg(II). The thermodynamic parameters obtained showed that the biosorption was spontaneous and feasible, also, the process was endothermic with a decrease in the sorbate/biosorbent interface. *N. diderrichii* seed biosorbent has proved from this study to be an easily sourced and cheap biosorbent for the removal of Cd(II) and Hg(II) from industrial wastewaters.

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