Short Communication

Kinetics and thermodynamics of heavy metal ions sequestration onto novel Nauclea diderrichii seed biomass

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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 Erying 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 wastewaters (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), Tamarndus 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 Nauclea 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 Nauclea 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 Nauclea 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 Nauclea diderrichii seed biosorbent in 20 mL of 20 mg/mL 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:

\[ \ln (q_e - q_t) = \ln q_e - k_1 t \]
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \]
\[ q_t = k_h t^{1/2} + C \]

where \( q_t \) is the amount of metal ion biosorbed by the biosorbent (mg/g), \( q_e \) 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 order and pseudo-second order model rate constants, \( h = k_2 q_e^2 \) (mg g/min) is the initial biosorption rate, \( k_h \) is the Morris–Weber intraparticle diffusion rate constant (mg/g 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 Erying equation (Ho et al., 2000) which is expressed as:

\[ \ln (k_h/T) = \ln (k/\rho) + (\Delta S^o/\rho) - (\Delta H^o/RT) \]

where \( k_h \), \( k \), \( h \), \( R \) 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 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 absorbent (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.
be the rate-limiting step, and chemisorption or ion exchange (see Table 1) were >0. This suggests that intraparticle may not sorption of Cd(II) and Hg(II) onto N. diderrichii C of intercept, as chemical or physical sorption (Ho and McKay, 1999). The values pore, or a branched pore; and biosorption at surface sites, such the internal structure of a biosorbent matrix by the surface or a particle (film diffusion), and diffusional mass transfer within rate-limiting step required for a biosorption process includes controlling step which may comprise chemisorption and diffusion of Hg(II). The pseudo-second order kinetic model requires a rate some past works show that initial sorption rates (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).

### 3.3. 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 \( q_s \) 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 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, \( AG^o \) 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. Moreover, \( AH^o \) (kJ/mol) values obtained are +23.667 and +0.531 kJ/mol for Cd(II) and Hg(II) respectively. \( AS^o \) (J/mol K) values were calculated to be –122.474 and –65.107 J/mol K for Cd(II) and Hg(II) respectively. These suggest 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 endothermically controlled and showed 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).

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![Fig. 3. A plot of \( q_t \) (mg/g) against pH for the biosorption 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).](attachment:image.png)
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References


