Modified ion exchange jackfruit seeds resin for removal of selected trace heavy metal ions from aqueous solution: Thermodynamic evaluation

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ABSTRACT

Water is essential for every life processes. However, its quality is deteriorating every day due to the recent industrial advancements. Anthropogenic processes such as industrialization, mining and agricultural activities have led to alarming discharge of heavy metal ions to the aquatic bodies. This possess a greater threat to human, animal and the entire ecosystem wellbeing. Accumulation of heavy metal ions in drinking water beyond permissible limits is detrimental to human health. Therefore, their removal is paramount. Conventional remediation techniques have been employed but have remained expensive and not universally appropriate. This has therefore spurred research interests in the use of adsorption techniques from locally available materials as an environmentally sustainable alternative. Jackfruit seeds are discarded as wastes of a Jackfruit and can be utilized as an ion exchange resin in heavy metal ions removal from wastewater. The present study involved application of previously prepared raw and modified Jackfruit seed resins to study thermodynamics of copper (II), lead (II) and cadmium (II) ions adsorption from synthetic water. FTIR results showed presence of functional groups in raw and modified resins as important sites for studying thermodynamics of adsorption of copper (II), lead (II) and cadmium (II) ions. Thermodynamic data showed that standard Gibb's free energy (ΔG°) values for all metals were negative indicating that adsorption process was feasible and favourable. Standard enthalpy change (ΔH°), standard entropy (ΔS°) and activation energy (E_A) were positive ($> 40 \text{ kJ mol}^{-1}$) and in the order lead (II) > copper (II) > cadmium (II). This confirmed adsorption

of copper (II), lead (II) and cadmium (II) ions onto both raw and modified resins was predominated by chemical interactions between the metal ions and the resin active sites. This was confirmed by very low values of sticking probability (S^*). The findings indicated that ion exchange Jackfruit seeds resin is promising for heavy metal ions removal from wastewater in an optimized temperature controlled system.

Keywords: Jackfruit seeds, thermodynamics, ion exchange resin, chemisorption.

INTRODUCTION

With advanced rapid industrialization and technological advancements, industrial and agricultural activities have led to increased discharge of chemical pollutants to the environment (Chakraborty et al., 2015). Among these pollutants are different prevalent toxic heavy metals such as copper, lead and cadmium (O'Connell et al., 2008) which are released to water bodies through various industrial activities such as battery manufacturing, electroplating, petroleum refining, paper and pulp, ceramic and glass industries, pesticides and mining activities amongst others (Vijayaraghavan et al., 2016; Li et al., 2015; Biswas & Mishra, 2015). This makes water unsafe for use thereby threatening all life processes (Saini et al., 2019). Their accumulation is of great concern because they have a long persistence, cannot biodegrade and are toxic even at their low concentrations in water. Their toxicity is by how they react with protein and enzyme ligands such as nitrogen

(-NH₂ and > NH), sulphur (-S-S-, -SH) and oxygen (-COO-, -OH, >C=O, -OPO₃H) (Bathla & Jain, 2016) in their biomolecules to form stable complexes which alter the body metabolism (Engwa et al., 2019; Kaile & Nyirenda, 2016). This has led to various health effects associated with kidney damage, brain dysfunction, neonatal deaths, liver damage, reduced hemoglobin synthesis, cancer and death (Herrera et al., 2020; Liu et al., 2019; Khan et al., 2017). Maximum acceptable set levels of copper (II), lead (II) and cadmium (II) metal ions in drinking water are 2 mg/L, 0.01 mg/L and 0.003 mg/L (WHO, 2011); 1 mg/L, 0.01 mg/L and 0.003 mg/L (KEBS, 2007) and 2 mg/L, 0.01 mg/L and 0.005 mg/L (EU, 1998). Therefore, treating industrial effluents before being discharged to water bodies becomes necessary.

A number of technologies such as chemical coagulation, reduction, electrodialysis, membrane technology, oxidation and chemical precipitation have been explored (Tovar et al., 2018) but have remained costly and inefficient. Adsorption has emerged an alternative technique due to its high efficiency even at trace levels, cost effectiveness and use of locally available materials (Gusain et al., 2014). The use of biomass from agricultural wastes in the removal of heavy metal ions has been reported (Nthiga et al., 2021; Ndung'u et al., 2020; Goyal & Arora, 2016; Wanja et al., 2016; Omorogie et al., 2012). Use of biowaste in raw form has been reported to cause leaching of soluble organic compounds leading to high total oxygen demand (TOD), biological oxygen demand (BOD) and chemical oxygen demand (COD) in water (Abdolali et al., 2014). Therefore, to offer a solution to the above problem, biomass

needs to be stabilized by chemical modification. The study focused on application of an ion exchange resin material that was prepared by chemically modifying Jackfruit seeds adsorbent with ethylenediamine (Ndung'u et al., 2020). The raw and modified resins were used to assess thermodynamics of copper (II), lead (II) and cadmium (II) ions adsorption from aqueous solutions.

MATERIALS AND METHODS

Research Design

The study aim was to use raw and modified ion exchange resin to study thermodynamics of adsorption of copper (II), lead (II) and cadmium (II) ions from aqueous solution using optimized parameters of pH, time, speed, dose and initial concentration.

Adsorbent preparation

The fruits were collected locally from city park market, Nairobi Kenya and transported to Kenyatta University Chemistry laboratories, cleaned with distilled water and cut open to obtained seeds sample. The sample was cut to small pieces and oven dried at 105 °C for 1 day to a constant weight. They were then ground into fine powder, sieved and kept in a tightly labelled bottle awaiting subsequent experiments. The raw resin was chemically modified as described by Ndung'u et al. (2020) and Da Silva Filho et al. (2006). The sixth carbon of the cellulose molecule of Jackfruit seeds adsorbent was chlorinated with thionyl chloride forming chlorodeoxy cellulose intermediary. Reaction mechanism is as shown by the figure 1 below:

Figure 1: Jackfruit seeds cellulose chlorination

Figure 2: Modified Jackfruit seeds resin synthesis

Chlorinated Jackfruit seeds cellulose was treated with ethylenediamine where chlorine substitution by nitrogen atom from the chelating ligand occurred as shown by the figure 2 above. The modified resin was vacuum dried and kept in a labelled bottle awaiting FTIR analysis and thermodynamic adsorption studies. The adsorbents (raw and modified) were characterized using Fourier Transform Infrared (FT-IR) spectrophotometer (IRTracer-100, SHIMADZU made in Japan).

Adsorbate preparation

1000 mg/L of Cu (NO₃)₂, Pb (NO₃)₂ and Cd (NO₃)₂ (anal grade) stock solutions were prepared by dissolving 2.952 g of Cu (NO₃)₂, 1.599 g Pb (NO₃)₂ and 2.103 g of Cd (NO₃)₂ in sodium acetate solution to maintain constant ionic strength. Concentrations of working solutions were prepared from the 1000 mg/L metal solutions by dilution. 0.1 M of HCl and KOH were used for pH adjustments monitored by a calibrated pH meter (HANNA model).

Metal analysis

An atomic absorption spectrophotometer (AA-6200, SHIMADZU, Kyoto, Japan) instrument was used to determine the concentration of copper (II), lead (II) and cadmium (II) metal ions in the respective supernatant metal solutions.

Thermodynamic experiments

The experiments were conducted by batch mode in a temperature controlled water bath shaker using 120 mL plastic bottles. The experiments were performed by putting optimal dose of 15 mg (raw) and 10 mg (modified); 15 mg (raw and modified); 13 mg (raw) and 10 mg (modified) to 20 mL of 30 mg L⁻¹ optimal solutions of copper (II), lead (II) and cadmium (II) ions at optimal pH of 4.2 and 5.7; 5.0 and 6.4; 5.6 and 6.0 (raw and modified) respectively. Optimal agitation speed of 150 rpm (both raw and modified) for both copper (II), lead (II) ions; 175 rpm (raw) and 150 rpm (modified) for cadmium (II) ions. The mixtures were agitated at varying temperatures (298K, 308K, 318K, 328K and 338K) for 30 minutes at optimal agitation speeds of 150 rpm for copper (II) and lead (II) ions; 175 rpm (raw) and 150 rpm (modified) for cadmium (II) ions. The mixture was filtered and the amount of residual metal ions in the solution was determined by AAS. The amount of copper (II), lead (II) and cadmium (II) ions adsorbed was calculated by equation 1.

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

where q_e is the amount of cations adsorbed at equilibrium, C_i is initial adsorbate concentration and C_e is adsorbate final concentration of cations at equilibrium (mg/L), V is

the total volume of Copper (II), Lead (II) and Cadmium (II) cations solution and M is the dosage mass (Ndung'u et al., 2020).

Thermodynamic analysis

To evaluate thermodynamic parameters, experimental data was analyzed by distribution coefficient (K_d), calculation of Gibb's free energy (ΔG°) and thermodynamic Van't Hoff equation (Moftakhar et al., 2016) given by equations 2 – 4.

$$k_d = q_e / c_e \quad (2)$$

$$\Delta G^\circ = -RT \ln k_d \quad (3)$$

$$\ln k_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4)$$

where k_d is the distribution coefficient; q_e is the amount of Copper (II), Lead (II) and Cadmium (II) cations complexed at equilibrium (mg g⁻¹). C_e is the concentration of the residual cations at equilibrium (mg L⁻¹); ΔG° is the Gibb's free energy (J mol⁻¹); ΔH° is the enthalpy change (Jmol⁻¹) and ΔS° is the entropy change (J mol⁻¹K⁻¹) at standard conditions of temperature and pressure, T is the absolute temperature (K) and R is the Molar gas constant (8.314 J mol/K⁻¹). Van't Hoff plot of $\ln k_d$ verses reciprocal of temperature ($1/T$) yields a linear relationship with $\Delta H^\circ/R$ as the slope and $\Delta S^\circ/R$ as the intercept which can be used to calculate ΔH° and ΔS° respectively.

The E_A , activation energy and S^* , sticking probability can also be used to describe adsorption and can be calculated using Arrhenius equation (Ayawei et al., 2015) related to surface coverage θ as given in equations 5 – 7.

$$\theta = \left[1 - \frac{C_e}{C_i} \right] \quad (5)$$

$$S^* = (1 - \theta) e^{-\frac{E_a}{RT}} \quad (6)$$

$$\ln(1 - \theta) = \ln S^* + \frac{E_A}{RT} \quad (7)$$

S^* describes potentiality of adsorbed cations to remain on the binding sites in a temperature-controlled system (Sujata et al., 2014) and must lie in the range $0 < S^* < 1$. That is, if $S^* > 1$, no adsorption, if $S^* = 1$, a mixture of physi-adsorption and chemi-adsorption, if $S^* = 0$, chemi-adsorption predominates and if $0 < S^* < 1$ physi-adsorption predominates (Gongden et al., 2014). Negative activation

energy (E_A) values indicate that the adsorption process is exothermic (David et al., 2015) and positive values dictate an endothermic process (Sujata et al., 2014). E_A dictates the nature of adsorption: 5–40 kJ/Mol shows physisorption and 40–800 kJ/Mol shows that adsorption process is chemi-adsorption in nature (Heiba et al., 2018; Taha et al., 2016). A linear plot of $\ln(1-\Theta)$ against $1/T$ in Arrhenius equation yields a straight line with $\ln S^*$ as the intercept and E_A/R as the slope used to calculate sticking probability (S^*) and activation energy respectively.

RESULTS AND DISCUSSIONS

FTIR Results

The FTIR spectrum of raw and modified resins (figure shown by Ndung'u et al., 2020) showed functional groups capable of binding to metal ions. The FTIR results showed presence of functional groups; hydroxyl (-OH) at 3401.7 cm^{-1} (raw) and 3394.5 cm^{-1} (modified); carbonyl (-C=O) at 1651.0 cm^{-1} (raw) and 1665.2 cm^{-1} (modified) in ionic and non-ionic carboxylic (-COO-) acid derivatives and additional grafted amine groups (-NH₂) functional groups (shown by peaks at 1530.4 cm^{-1} and 656.5 cm^{-1}) in modified resin as important active sites for studying thermodynamics of adsorption of copper (II), lead (II) and cadmium (II) ions.

Optimization

Effect of temperature

The effect of temperature on the uptake of copper (II), lead (II) and cadmium (II) are shown by figure 3.

Figure 3: A plot of q_e (mg g^{-1}) against temperature for adsorption of copper (II) (A), lead (II) (B) and cadmium (II) (C) ions

The results presented in figure 3 show that increase in temperature increased adsorption capacity of the three metal ions from 288 K to 310 K with a maximum adsorption capacity of 13.97 mg g^{-1} (raw) and 15.96 mg g^{-1} (modified); 16.26 mg g^{-1} (raw) and 18.67 mg g^{-1} (modified); 15.41 mg g^{-1} (raw) and 17.11 mg g^{-1} (modified) for copper (II), lead (II) and cadmium (II) ions respectively beyond which a decrease was observed. The trend is expected for a chemisorption process which is mostly and endothermic

adsorption process (Mustapha et al., 2019). Increase in adsorption capacity as temperature is increased from 298 K to 310 K is due to activation of resin surface sites and mobility of metals ions from the metal solution to the resin active sites (Huang et al., 2018; Rahman et al., 2015). A decrease in adsorption capacity at temperature beyond optimum is attributed by a decreased stability of metal ion-resin complex (Alinnor, 2007) which decreases the adsorption interaction forces between resin surface and the metal ions making the metal ions adsorbed to desorb from the resin surface (Nyoni et al., 2017). The results are coherent with those reported in the literature (Gaur et al., 2018; Nyoni et al., 2017).

Thermodynamic results

The results for ΔG° , ΔH° , ΔS° , S^* and E_A were calculated from Van't Hoff and Arrhenius equations and are tabulated in Table 1.

Table 1: Thermodynamic parameters on copper (II), lead (II) and cadmium (II) ions adsorption

Metal ion	Resin	ΔG° (KJ mol ⁻¹) at different temperatures (K)								
		298	308	318	328	338	ΔH° kJ /mol	ΔS° J mol /K	S^*	E_A kJ /mol
Copper (II)	Raw	-0.37	-1.93	-4.23	-7.02	-8.64	63.64	214.17	2.72×10^{-09}	50.33
	Modified	-1.66	-3.76	-5.11	-8.26	-13.38	79.87	271.45	1.62×10^{-12}	68.85
Lead (II)	Raw	-0.77	-3.48	-5.18	-7.29	-10.06	65.16	221.82	5.86×10^{-10}	53.74
	Modified	-3.99	-7.92	-11.54	-14.16	-16.33	87.89	310.44	9.75×10^{-16}	83.98
Cadmium (II)	Raw	-0.23	-1.10	-3.70	-6.05	-8.31	62.16	207.77	2.35×10^{-08}	45.43
	Modified	-1.43	-3.10	-4.14	-7.75	-10.99	68.40	232.29	3.65×10^{-10}	55.55

Thermodynamic data showed that ΔG° values for the adsorption of cations were negative. This confirms the feasibility and spontaneity of adsorption of Copper (II), Lead (II) and Cadmium (II) ions (An et al., 2017). Van't Hoff and Arrhenius plots (Figure 4 and 5) shows positive values of ΔH° , ΔS° and E_A . Positive ΔH° values of 63.64 kJ/Mol and 79.87 kJ/Mol (copper (II)), 65.16 kJ/Mol and 87.89 kJ/Mol (lead (II)); 62.16 kJ/mol and 68.40 kJ/Mol (cadmium (II)) for raw and modified resins respectively are all above +40 kJ/mol dictating a chemisorption process. This is due to strong chemical

engagements between the metal ions and the resin surface (Ramdani et al., 2020). This was supported by positive E_A values of 50.33 kJ/Mol and 68.85 kJ/Mol (Copper (II)), 53.74 kJ/Mol and 83.98 kJ/Mol (lead (II)); 45.43 kJ/Mol and 55.55 kJ/Mol (cadmium (II)) for raw and modified resins and increase in negative ΔG° values with increase in temperature (Manzoor et al., 2019).

The order of ΔG° , ΔH° and ΔS° values for the complexation of the three metal ions on both raw and modified resins was in the order $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$. This is due to the

strong interaction between Pb^{2+} cations and the binding sites in both raw and modified resins and increased affinity to binding sites which require more ΔH° energy and major structural changes of the resin sites (higher values of ΔS°) (Ramdani et al., 2020) and this decreases in that order. The ΔS° values were positive which reflected increased affinity of cations on raw and modified resin sites and increased disorderliness at the resin/metal solution interface with some structural changes in the surface resin that occurred during the complexation of the metal ions (Maleki et al.,

2015). Higher values of ΔG° , ΔH° , ΔS° and E_a were registered in modified form compared to raw form. Very low values of S^* close to zero showed a greater affinity of the complexed metal ions on both raw and modified resins dictating a

chemisorption process (Sujata et al., 2014) with modified forms registering more lower values than in raw form. The

results for both raw and modified resins compare with those reported in the literature (Kumar et al., 2020; Sujata et al., 2014).

Figure 4: Van't Hoff plots of copper (II) (A), lead (II) (B) and cadmium (II) (C) ions respectively

Figure 5: Arrhenius plots of copper (II) (A), lead (II) (B) and cadmium (II) (C) ions respectively

CONCLUSIONS

In this study, thermodynamic interaction of Copper (II), Lead (II) and Cadmium (II) ions onto raw and modified Jackfruit seeds resin was investigated. The negative ΔG° values confirmed spontaneity and feasibility of the metal ions adsorption onto raw and modified resins. High positive values of ΔH° and E_A indicated that adsorption was endothermic and chemisorption process. This was confirmed by very low values of S^* . The findings of the study showed the potentiality of the Jackfruit seeds adsorbent to remove copper (II), lead (II) and cadmium (II) ions in a temperature controlled system.

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CONFLICT OF INTEREST

Authors declared no potential conflicts of interest regarding the research, authorship and/or publication of this manuscript.

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