

ADSORPTION OF Pb(II) IONS FROM AQUEOUS SOLUTION USING LIGNIN FROM *HAGENIA ABYSSINICA*

Belete Tesfaw, Fekadu Chekol, Solomon Mehretie and Shimelis Admassie*

Department of Chemistry, Addis Ababa University, PO Box 1176, Addis Ababa, Ethiopia

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ABSTRACT. The adsorption of lead(II) ions from aqueous solution onto alkali lignin extracted from *Hagenia abyssinica* was investigated by electrochemical methods. The effect of solution pH, lignin dosage and contact time were investigated at room temperature in a batch system. Adsorption equilibrium was approached within 80 min. The adsorption kinetics data were described by pseudo-second-order kinetics model, while the equilibrium data were well fitted using the Freundlich model. A maximum adsorption capacity was found to be 80.41 mg g⁻¹ of the dry weight of lignin.

KEY WORDS: Lignin, Adsorption Capacity, Lead(II) ion, Square wave anodic stripping voltammetry

INTRODUCTION

Environmental pollution or introduction of undesirable substances from different sources to the environment is a serious challenge facing mankind in our century. Sources for environmental pollution can be natural processes like volcanoes or anthropogenic like industrial wastewater and the release of toxic compounds. Excessive levels of heavy metals in water are an environmental hazard because of their toxicity, accumulation in the food chain and persistence in nature [1-3]. Water contamination by heavy metals such as Cr, Cd, Hg, Cu, Ni, As and Pb, is a big environmental concern and it requires significant attention [4-8]. The major sources of heavy metal pollution are municipal waste, metal plating facilities, mining operations, fertilizer industries, tanneries, batteries and paper industries [9-12]. Heavy metals are non-biodegradable and they can be accumulated by tissues of living organisms [13]. If the metals are ingested beyond the permitted limit, they can cause serious diseases and disorders [13, 14]. Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge into the environment.

There are different techniques for heavy metal removal from aqueous effluents such as chemical precipitation [15], coagulation–flocculation [16], adsorption [17], ion exchange [18], oxidation [19], membrane filtration technologies [20], biological treatment [21, 22], electrochemical deposition [23] and chemical immobilization technique [24]. Among the various wastewater treatment techniques described, adsorption has become one of the alternative treatments because of its flexibility and simplicity of design, high efficiency, availability of different low cost adsorbents and ease of operation [25].

A lot of research works have been conducted on different types of adsorbents, such as those of mineral, organic or biological origin, magnetic nanoparticles [26, 27], nanosheet-structured materials [28], zeolites [29], industrial by-products [30], agricultural wastes [31, 31], biomass [33] and lignin and lignocellulose materials [8, 34, 35]. However, wastewater treatment technologies are still requiring new environmentally friendly, scalable, cheap and effective materials. The present study focuses on the removal of lead which is one of the most toxic heavy metals and is harmful to human beings and other creatures [36-40] using alkali lignin extracted from *Hagenia abyssinica*.

*Corresponding author. E-mail: shimelis.admassie@aau.edu.et; shimadm09@gmail.com

Lignin is one of the major constituent of wood and non-wood plants after cellulose and hemicellulose. It is a material that is available in large quantities in many parts of the world. As a three dimensional polymer, lignin is a polyphenolic, cell wall constituents [41] found exclusively in the plants kingdom. It is biosynthesized through enzyme-catalyzed dehydrogenative polymerization of three basic precursors: coniferyl, sinapyl and *p*-coumaryl alcohols. Each of the precursors is connected by series of ether and carbon-carbon linkage with other precursors to form the lignin polymer. Lignin contains various functional groups such as methoxyl, phenolic, aromatic carboxyl, alcohol and aldehyde, which increase its potential to adsorb heavy metals from aqueous solution [42, 43].

Alkali lignin can provide an environmentally safe and sustainable source of material for heavy metal removal. Despite its efficiency and eco-friendly character, to our knowledge, lignin from *Hagenia abyssinica* has not been previously investigated for heavy metal adsorption. In this paper we report the adsorption behaviors, kinetics and mechanisms of the alkali lignin for removal of Pb(II) ion from aqueous solution. In addition, the effects of different parameters such as deposition potential, deposition time, adsorbent dose and contact time were optimized.

EXPERIMENTAL

Apparatus

Square wave anodic stripping voltammetry (SWASV) measurements were performed using CH Instruments Electrochemical Analyzer (CHI840C). A three-electrode configuration consisting of bismuth film modified glassy carbon working electrode, Ag/AgCl/KCl (saturated) reference electrode, and a platinum wire as counter electrode was employed. All electrochemical experiments were carried out in one-compartment voltammetric cells (20 mL) at ambient temperature. Magnetic stirrer together with magnetic bar was used, when needed. FTIR spectroscopy and elemental analysis were carried out using Perkin Elmer Spectrum 65 FT-IR Spectrometer and Perkin-Elmer 240Q Elemental analyzer. Gallenkamp flask shaker was used for batch adsorption experiments. All pH measurement was carried out using a JENWAY 3510 pH-meter.

Reagents

Analytical grade reagents were used in this study. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Riedel-de Haen) and $\text{Pb}(\text{NO}_3)_2$ (Wagtech International Ltd. UK), were used for preparation of electrode modifier and analyte, respectively. CH_3COONa (BDH Chemicals Ltd, Poole, England) and CH_3COOH (Merck KGaA 64271 Darmstadt, Germany) were used to prepare supporting electrolyte. Deionized water was used to prepare all standard and sample solutions throughout the experiment. Lignin was extracted from *Hagenia abyssinica* using the procedure reported in the literature [44, 45]. Briefly: about 1 kg of ground wood sample was dried at 60 °C for 24 h and the wax was extracted with toluene and dry ethanol (2:1 v/v) for 6 h. The sample free of wax was treated with 7.5% (w/v) NaOH at 90-100 °C for 6 h and filtered. The filtrate was acidified by adding 5 M H_2SO_4 (pH = 5.5) and three times of ethanol by volume and then washed with 70% ethanol to precipitate the hemicelluloses. Ethanol was then evaporated from the filtrate and washed with 1% (v/v) H_2SO_4 and dried at 120 °C to obtain the pure lignin.

Solution preparation

Stock solutions of bismuth(III) and lead(II) (1 mM each) were prepared using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$, respectively, in 0.1 M acetate buffer, which was prepared from CH_3COONa and CH_3COOH using deionized water. Different desired concentrations of Bi(III) and Pb(II) were

prepared by diluting from the stock solution. Lignin solutions for adsorption were prepared using the target metal solution as required.

Preparation of bismuth film electrode (BiFE) and square wave anodic stripping voltammetry (SWASV) measurements

Glassy carbon electrode was first assiduously polished on a polishing pad using 0.05 μm alumina powder and thoroughly rinsed with distilled water. Then, BiFE were prepared by *in situ* potentiostatic method using a three electrode system on a glassy-carbon as a working electrode, the Ag/AgCl/Cl(satd) as reference electrode and platinum wire as a counter electrode from the 0.1 M acetate buffer solution (pH 4.6) containing 1 mg L^{-1} of bismuth(III) together with target heavy metal ion at a deposition potential of -1.2 V for 240 s. After the deposition step, the SWASVs were recorded by scanning the potential from -1.2 to 0.1 V with the frequency of 15 Hz, potential step of 4 mV, and amplitude of 25 mV. Prior to each measurement, the cleaning step was applied by holding the potential of working electrode at -0.3 V for 30 s. The experiments were carried out at room temperature in non-deaerated solutions.

Batch adsorption experiment

20 mg of powdered lignin were accurately weighed and treated with 10 mL solutions of 100 mg L^{-1} Pb(II) ion in 0.1 M acetate buffer using 100 mL Erlenmeyer flasks. The flasks were completely sealed and agitated in a shaker at room temperature for 80 min in all experiments while the mixture was shaken 5 to 160 min for contact time study. The equilibrium concentration (C_e , mg L^{-1}) of Pb(II) ion in the residual aqueous phase was measured using SWASV and determined from the calibration curve. Removal efficiency (R_E) and equilibrium adsorption capacity (q_e , mg g^{-1}) of the batch experiments were calculated using Eq. (1) and (2) [7].

$$R_E(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{V(C_o - C_e)}{m} \quad (2)$$

where V is the volume of the solution, m is the mass of lignin, C_o and C_e are the initial and equilibrium concentrations of lead ion, respectively.

RESULTS AND DISCUSSION

FTIR and elemental analysis

Fourier transform infrared (FTIR) was used to determine the main functional groups present on the adsorbent lignin extracted from *Hagenia abyssinica*. The strong broad peak at 3426 cm^{-1} was due to the stretching vibrations of aromatic and aliphatic OH groups and the characteristic shoulder peak at 2849 cm^{-1} is C-H stretch of O-CH₃ of coniferyl/sinapyl alcohols as shown in Figure 1. The strong peaks at about 1500 and 1609 cm^{-1} were related to aromatic ring vibrations of the phenyl propane skeleton in coniferyl alcohol. All these IR signals indicate that the alkali lignin is congruent with other lignin reported in the literature [46]. In addition, elemental analysis was performed and the lignin was found to contain C (46.3%), H (5.04%), S (2.25%) and O (46.4%).

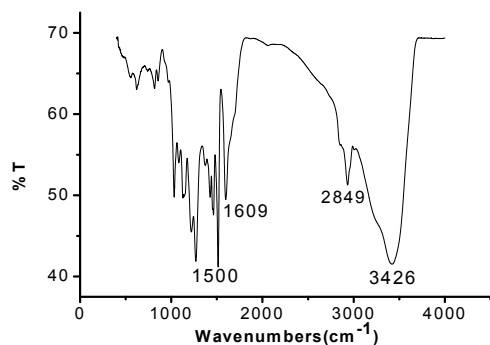


Figure 1. FTIR spectrum of lignin.

Effect of deposition time

The effect of deposition time on the anodic stripping signals of lead was studied in the range of 30–390 s in solutions containing $60 \mu\text{g L}^{-1}$ Pb(II) ions and the results are depicted in Figure 2. The peak current of the voltammetric stripping signals was found to increase significantly with increasing the deposition time due to an increase in the amount of Pb(II) deposited at the electrode surface. Since the peak current of Pb(II) ions is continually increasing with deposition time, a deposition time of 240 s was used for further analysis as a compromise between relatively short analysis time and high sensitivity.

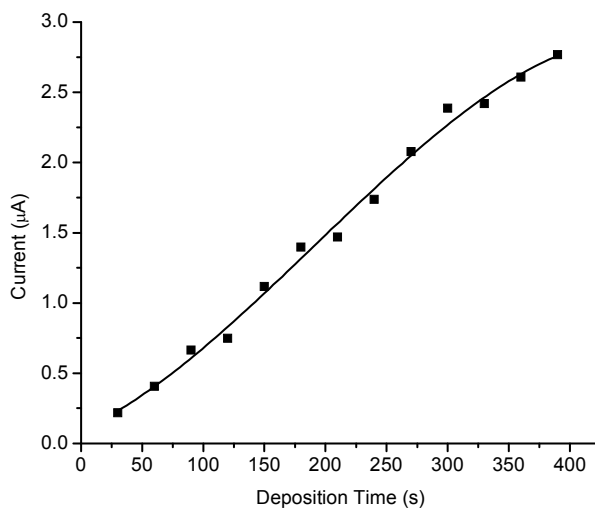


Figure 2. Effect of deposition time on the square wave anodic stripping voltammetric response of $60 \mu\text{g L}^{-1}$ Pb(II) at BiFE. Experimental conditions: 1 mg L^{-1} Bi(III) in acetate buffer with pH 4.6.

Effect of deposition potential

The effect of the deposition potential on the Pb(II) stripping signals was investigated by varying the potential between -0.6 and -1.4 V. The signals of Pb(II) increased with increasing potential

and reached a maximum at -1.2 V as depicted in Figure 3. When the potential was more negative than -1.2 V, the signals decreased slightly probably due to hydrogen evolution. Hence, -1.2 V was chosen as the optimum deposition potential for the determination of Pb(II).

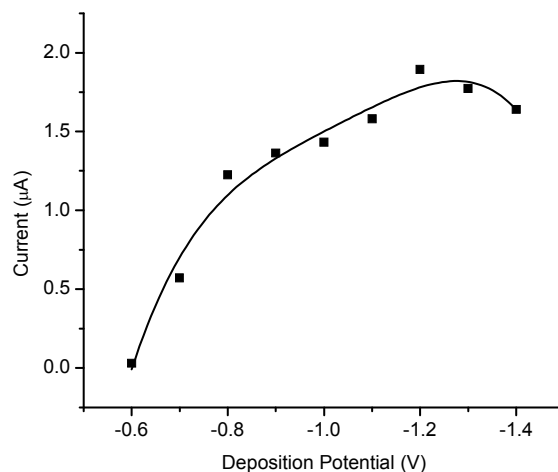


Figure 3. Effect of deposition potential on the square wave anodic stripping voltammetric response for $60 \mu\text{g L}^{-1}$ Pb(II) at BiFE. Experimental conditions: 1 mg L^{-1} Bi(III) deposition time 240 s, pH 4.6.

Calibration curve

After optimizing the electrochemical parameters like the deposition time and deposition potential a calibration curve was constructed to determine the concentration of Pb(II) for subsequent analysis. Using the optimized experimental conditions, anodic stripping voltammetric measurements were carried out for different concentration of Pb(II) (10 – $200 \mu\text{g L}^{-1}$) and the results are shown in Figure 4. The calibration curve obtained using a deposition potential of -1.2 V and a deposition time of 240 s was linear in the range examined (10 – $200 \mu\text{g L}^{-1}$, $R^2 = 0.9995$, $n = 11$) with sensitivity of $0.04389 \pm 0.00032 \mu\text{AL } \mu\text{g}^{-1}$. The limit of detection (LOD) was calculated using Eq. (3):

$$LOD = \frac{3SD}{m} \quad (3)$$

where SD is the standard deviation of blank solution and m is the slope of the calibration line. The standard deviation (SD) was calculated by measuring the anodic stripping signals of 20 samples of the blank solution. The detection limit calculated was found to be $0.24 \mu\text{g L}^{-1}$ with RSD of 1.1%.

Effect of pH and contact time

The effect of pH on the adsorption of $60 \mu\text{g L}^{-1}$ of lead ion on 2 mg mL^{-1} dose of adsorbent was carried out by varying pH in the range from 3.6 to 5.6. It was observed that the removal efficiency reached maximum at pH 4.6 as depicted in Figure 5. The poor removal efficiency at lower pH is attributed to the competitive nature of proton with lead ion while lower solubility of Pb(II) salt suppresses the percent removal at higher pH than 4.6 [47]. Therefore, pH 4.6 was taken as an optimum pH for the adsorption of lead ion for subsequent experiments.

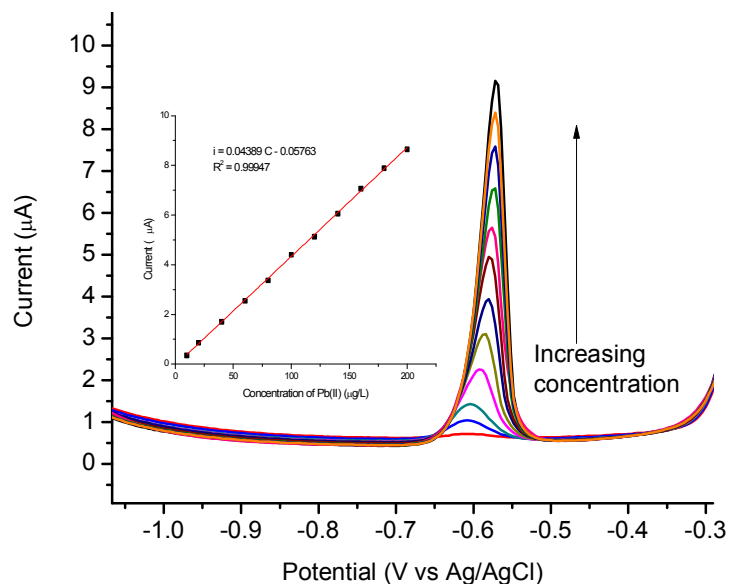


Figure 4. Square wave anodic stripping voltammograms for the linear range of calibration curve for standard addition of 10 to 200 $\mu\text{g L}^{-1}$ Pb(II) from bottom to top on glassy carbon electrode in 0.1 M acetate buffer with pH = 4.6 in the presence of 1 mg L^{-1} Bi(III). The inset is calibration curve peak current against the Pb(II) concentration from 10 to 200 $\mu\text{g L}^{-1}$ ($R^2 = 0.9995$).

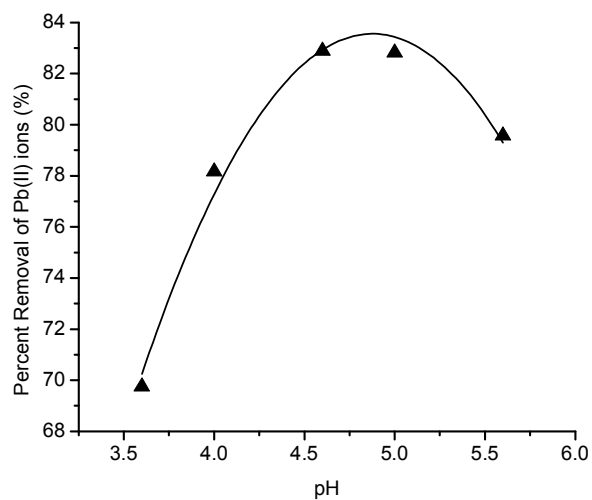


Figure 5. Effect of pH on the removal of Pb(II) with an initial concentration of 60 $\mu\text{g L}^{-1}$ in acetate buffer with 2 mg mL^{-1} adsorbent dose for adsorption time of 80 min.

The removal efficiency of lignin adsorbent was also investigated by varying the contact time with lead metal ion. A rapid adsorption of Pb(II) ion was observed in the first 40 min, then the

adsorption rate decreased gradually and finally got level off presumably due to the saturation of adsorbent sites (Figure 6).

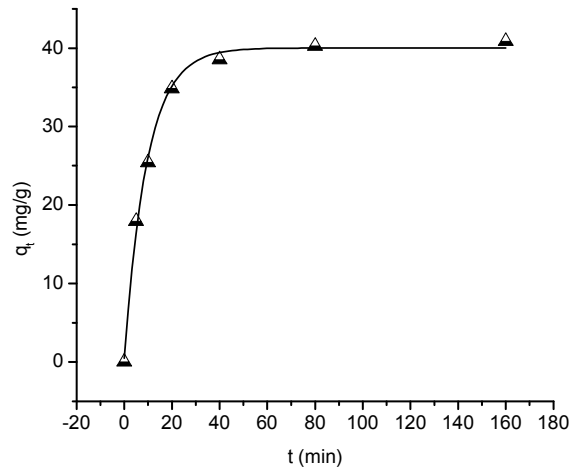


Figure 6. Adsorption capacity - time profile for lead ion in contact with lignin: $60 \mu\text{g L}^{-1}$ Pb(II) ion concentration in 0.1 M acetate buffer (pH = 4.6) with adsorbent dose of 2 mg mL^{-1} and contact time of 0, 5, 10, 20, 40, 80 and 160 min.

In addition, the effect of lignin dosage on Pb(II) ion adsorption was studied in the range of $0.5\text{--}5 \text{ mg mL}^{-1}$. The percentage of lead ion removal increases with lignin dosage from $0.5\text{--}5 \text{ mg mL}^{-1}$, starting from 40.2% to 88.2% as depicted in Figure 7. The rate of lead adsorption on lignin does not significantly increase larger than 5 mg mL^{-1} lignin dosage. This can be attributed to the overlapping of active sites of the adsorbent at higher dosage which results in reduced effective surface area [48].

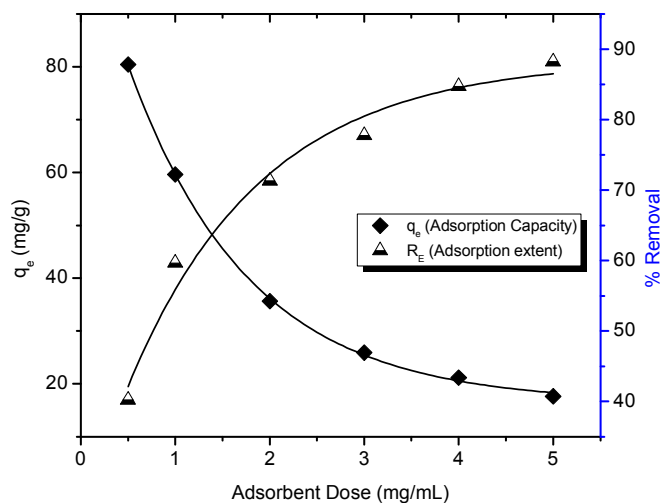


Figure 7. The effect of adsorbent dose on the removal of Pb(II) ion and its adsorption capacity: pH = 4.6, initial metal concentration of 100 mg L^{-1} and adsorption time of 80 min.

Adsorption isotherm models

The adsorption isotherms indicate the distribution of adsorbed molecules between the solid and liquid phases when the adsorption reaches equilibrium. One of the adsorption isotherms is the Langmuir isotherm which assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies [49]. Once the adsorbent sites are filled, no further adsorption can take place at the sites. The isotherm is represented by Eq. (4).

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \quad (4)$$

The constants K_L and q_{max} are related to the energy of adsorption and maximum adsorption capacity, respectively and their values were obtained from the slope and intercept of the plot of $1/q_e$ against $1/C_e$ and are summarized in Table 1. The linearity of this plot is not good as indicated in Figure 8. The adsorption capacity obtained from the Langmuir isotherm also significantly deviates from the experimental result.

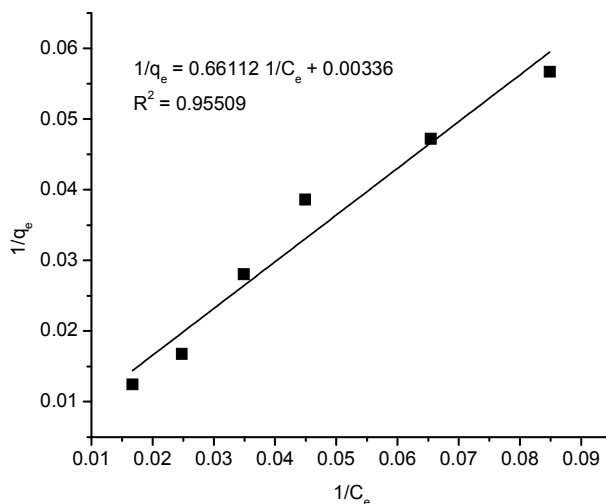


Figure 8. Langmuir fitting of adsorption of lead on to lignin.

The Freundlich isotherm has been derived by assuming an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich isotherm shows that the heavy metal ions adsorption occurs on a heterogeneous surface by multilayer sorption [50, 51]. The Freundlich isotherm is represented by Eq. (5) and Eq. (6) for nonlinear and linear, respectively.

$$q_e = K_F C_e^{1/n} \quad (5)$$

The equation can be linearized and temperature dependent constants K_F and $1/n$ are obtained by linear regression:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where K_F and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity, respectively. The plot of $\ln q_e$ versus $\ln C_e$ is used to determine K_F and n

values. The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if n = 1, then adsorption is linear; if n < 1, then adsorption is a chemical process; if n > 1, then adsorption is a physical process. The n value in Freundlich equation was found to be 1.03 (Table 1). Here, since n value lies between 1 and 10, adsorption of lead ion onto lignin is likely a physical adsorption process. The maximum adsorption capacity (q_{max}) from the Freundlich isotherm was calculated using Eq. (7) [52]:

$$K_F = \frac{q_{max}}{C_0^{1/n}} \tag{7}$$

where C₀ is the initial concentration of the solute in the bulk solution (mg L⁻¹) and q_{max} is the Freundlich maximum adsorption capacity (mg g⁻¹).

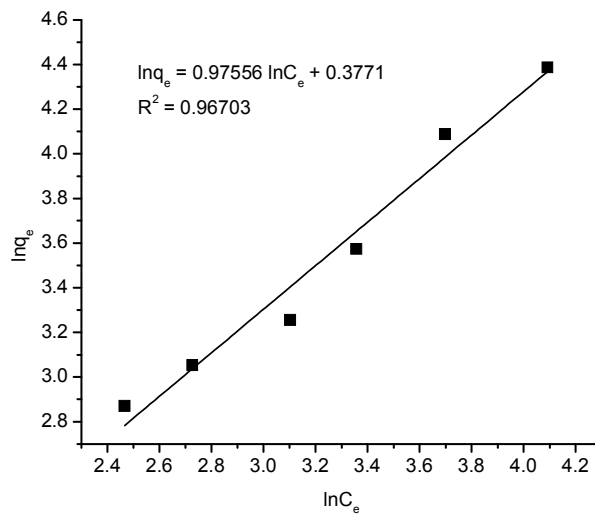


Figure 9. Freundlich fitting of adsorption of lead on to lignin.

Table 1. The Langmuir and Freundlich isotherm for the adsorption of lead ion onto lignin at 298 K.

Exp't	Langmuir			Freundlich				
	q _e (mg/g)	K _L (L/mg)	q _{max} (mg/g)	R ²	q _{max} (mg/g)	n	K _F ((mg/g)(L/mg) ^{1/n})	R ²
80.41		0.005	297.6	0.955	127	1.03	1.46	0.967

To obtain the most appropriate model for the lead ion adsorption, data were fitted to Langmuir and Freundlich isotherms. It was observed that the Freundlich adsorption isotherm was found to be a better model to describe the adsorption of lead ion onto lignin with a correlation coefficient R² of 0.967 as indicated in Figure 9.

Adsorption kinetics

The pseudo-first-order and pseudo second-order models were used to test adsorption kinetics of Pb(II) ion. The rate expression of Lagergren of pseudo-first-order is given by Eq. (8) [53].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{8}$$

Where q_t (mg/g) is the amount of adsorbed lead ion onto the lignin at time t, k₁ is the rate constant of first order adsorption and q_e is the equilibrium adsorption capacity. The plot of log (q_e

$-q_t$) versus t shows poor linearity (Figure 10A) and the values of q_e and k_1 was obtained from their intercept and slope, respectively (Table 2).

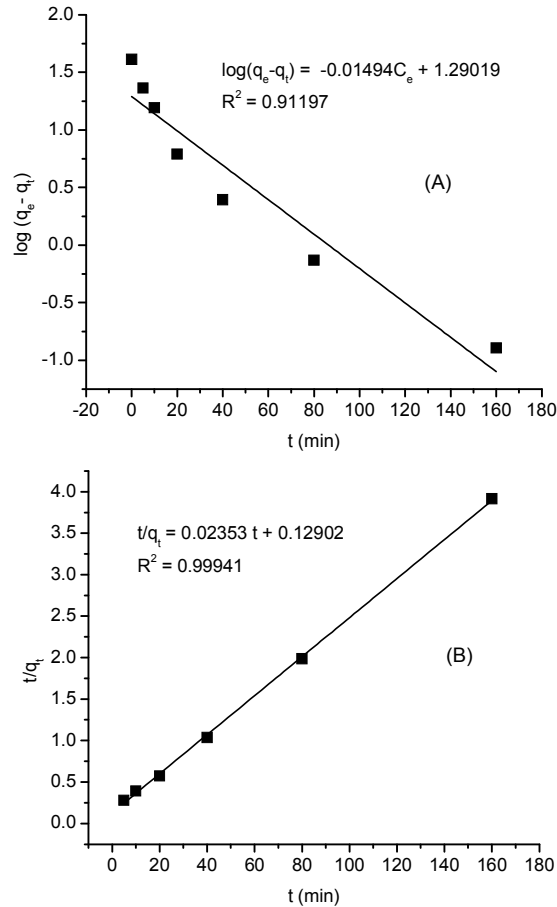


Figure 10. Kinetics models for Pb(II) ion adsorbed onto lignin : A) Pseudo first-order B) Pseudo second-order.

Table 2. Comparison between adsorption rate constants for the kinetics models.

Initial conc. (mg/L)	q_e exp. (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		k_1 ($\times 10^{-3} \text{ min}^{-1}$)	q_e cal. (mg/g)	R^2	k_2 ($\times 10^{-3} \text{ gmg}^{-1} \text{ min}^{-1}$)	q_e cal. (mg/g)	R^2
100	41	34.4	19.5	0.912	4.29	42.5	0.999

The pseudo second-order kinetic model in its linearized expression is also given by Eq. (9) [54]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. The plot t/q versus t exhibits linearity with a very good correlation coefficient R^2 of 0.9994 (Figure 10B), indicating that lead ion adsorption onto lignin obeys second-order kinetics. The values q_e and k_2 were obtained from the slope and intercept of the plot and presented in Table 2.

Table 3. Adsorption equilibrium time and adsorption capacities of some materials reported in the literature.

Adsorbent	Equilibrium time (min)	Adsorption capacity (mgg ⁻¹) of Pb (II)	Reference
Polar wood lignin	120	8.9	55
Kraft lignin	-	14.9	56
Alkaline lignin	30	69.8	7
Modified soda lignin	60	46.0	57
Amine modified lignin	60	61.0	58
Bi-functionalized lignin	-	53.9	59
Lignin from <i>Hagenia abyssinica</i>	80	80.4	Present study

CONCLUSION

Results from this study showed that the maximum adsorption capacity of Pb(II) ion onto the dry weight lignin was found to be 80.41 mg g⁻¹. This value is compared with other similar adsorbents (Table 3) and the alkali lignin extracted from indigenous plant *Hagenia abyssinica* is an effective adsorbent for lead ion removal. The adsorption equilibrium data fitted well to the Freundlich isotherm model with a better correlation coefficient of 0.967 compared to that of Langmuir model (0.955). The n value in the present investigation was greater than one, indicating that the adsorption of lead ion onto lignin is favorable. Besides, the adsorption kinetics follows pseudo-second order. This locally available lignin material has the potential to be used as an efficient and cost effective adsorbent for the removal of lead ion from waste water.

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