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A Novel Approach for the Removal of Lead(II) Ion from Wastewater Using Mucilaginous Leaves of *Diceriocaryum eriocarpum* Plant

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Abstract: Lead(II) ion is a very toxic element known to cause detrimental effects to human health even at very low concentrations. An adsorbent prepared using mucilaginous leaves from *Diceriocaryum eriocarpum* plant (DEP) was used for the adsorption of lead(II) ion from aqueous solution. Batch experiments were performed on simulated aqueous solutions under optimized conditions of adsorbent dosage, contact time, pH and initial lead(II) ion concentration at 298 K. The Langmuir isotherm model more suitably described the adsorption process than the Freundlich model with linearized coefficients of 0.9661 and 0.9547, respectively. Pseudo-second order kinetic equation best described the kinetics of the reaction. Fourier transform infra-red analysis confirmed the presence of amino (–NH), carbonyl (–C=O) and hydroxyl (–OH) functional groups. Application of the prepared adsorbent to wastewater samples of 10 mg/L and 12 mg/L of lead(II) ion concentration taken from a waste stabilization pond showed removal efficiencies of 95.8% and 96.4%, respectively. Futhermore, 0.1 M HCl was a better desorbing agent than 0.1 M NaOH and de-ionized water. The experimental data obtained demonstrated that mucilaginous leaves from DEP can be used as a suitable adsorbent for lead(II) ion removal from wastewater.

1. Introduction

Heavy metal pollution has been one of the most challenging environmental problems due to their toxicity, persistence and bioaccumulation tendencies [1,2]. Most industries produce and discharge metal-containing wastes mostly into water bodies, which affect the aesthetic quality of the water and also increase the concentrations of metals present [3,4]. Activities such as mining and smelting operations, wastewater treatment facilities, various agricultural works and metal castings contribute significantly to the concentration of heavy metals in the environment [5,6]. Heavy metal contamination is not a recent problem, but its management and prevention is still of global concern [6].

Lead(II) ion has been implicated as being responsible for intellectual disabilities in children and causes about 143,000 deaths annually in developing countries [7,8]. Young children are more vulnerable to lead exposure because it affects the development of brain and nervous system [7,9]. It also causes kidney damage and high blood pressure in adults and can lead to miscarriage, low birth weight, stillbirth and premature birth in pregnant women [7–10]. Ingestion of lead contaminated water has been implicated as a major route of lead toxicity [8–10].

Several techniques have been designed for heavy metals removal from aqueous solutions and these include ion exchange, chemical precipitation/co-precipitation, filtration, coagulation, membrane technologies and commercial activated carbon [2,11–13]. The major disadvantages of these methods lie in the cost involved, the efficiency of the processes and disposal of wastes generated [11–13]. These shortcomings have made researchers seek alternative techniques for heavy metal remediation. Adsorption using naturally available materials has been reported to be efficient in the removal of hazardous metals from industrial effluents. The materials employed in this technique often range from the use of microbes and naturally abundant plant materials to dead waste biomass [12,14]. The sorption capacity of some biosorbents is high due to the presence of adequate functional groups that sequester metals from aqueous solutions [11]. The use of this technique is cheap, environmentally friendly and naturally available. These bio-based materials have shown the tendency to remove metals at trace levels, thus overcoming some of the major shortcomings of the conventional methods [14].

Several adsorbents from plant origin have been used and modified for heavy metal removal from wastewater and aqueous solution which include: maize tassels [15,16], watermelon shell [17], coffee beans [18], coconut shell [19], peanut shell [20], *Annona squamosa* shell [21], rice husks [22], rice bran [10], orange peels [23], sunflower stem [13], groundnut shells [12] and avocado seed [24]. The use of mucilage extracted from plant materials and parts of mucilaginous plants for heavy metals remediation has been recently reported [25–27]. This study presents the use of mucilaginous leaves of *Diceriocaryum eriocarpum* Plant (DEP) as a potential, novel, environmentally friendly and low cost adsorbent for the remediation of lead(II) ion from aqueous solution and wastewater samples.

2. Experimental Section

2.1. Preparation of Adsorbent

DEP was collected from farmlands and nearby bushes in Malamulele town, Limpopo Province, South Africa. The plant was identified by Botanists from Botanical Laboratory in the Department of Botany, University of Venda to be *Diceriocaryum eriocarpum* species of the *Pedecialeace* family. The leaves were carefully detached from the stem of the plant and washed thoroughly with tap water to remove dirt, soil particles and debris and subsequently sun dried for 4 days. The dry biomass was ground to fine powder using a hammer mill and weighed [28]. The resulting powder was fractionated using analytical sieves. Particles of 20–150 μm were used for both simulated and wastewater samples. The wastewater samples were collected from the effluent of Siloam waste stabilization ponds located between latitudes 22°53′15.8″ S and 22°54′5″ S and longitudes 30°11′10.2″ E and 30°11′23.5″ E in Vhembe District of South Africa.

2.2. Instrumentation

The concentration of lead(II) ion in aqueous solution was analysed using a Varian 520 Atomic Absorption Spectrometer (PerkinElmer, USA). Fourier transform infra-red (FT-IR) spectra of the adsorbent was obtained using a PerkinElmer 100 FTIR (Waltham, MA, USA) with accessories. The pellets of the adsorbent used was prepared on a KBr press (Spectra Lab, Mumbai, India) in a ratio of 1:10. The spectra were scanned over the wavelength range of 4500 to 400 cm^{-1}. The surface area and pore width were determined by the N$_2$ gas Brunauer-Emmett-Teller method of analysis using a Micromeritics Chemisorption ASAP 2020 (Norcross, GA, USA) [29]. A Stuart mechanical shaker with adjustable speed and time was used for agitation (SSL1, Lasec (pty), Johannesburg, South Africa). A Sartotius pH meter was used for all pH measurements (PB-11. Goettingen, Germany. The chemical composition of the adsorbent was analysed using ZSX Primus II X-ray Fluorescence spectrometer (Rigaku, USA). The pressed powdered method was used in the preparation of the sample. Ten grams of powdered DEP was placed in a ring placed on a cylindrical die pressed under the pressure of 100 kN using a sample support ring made of PVC. The pellet was then loaded on Rigaku's Primus Wavelength dispersive XRF system and run in a vacuum atmosphere. The analysis was done using Rigaku's standardless analysis program "SQX" and EZ scan routine. A full semi-quantitative elemental analysis was performed.

The surface morphology of the adsorbent was analysed using a scanning electron microscope (SEM) (TESCAN, VEGA 3 SBU, Brno, Czech). Powdered samples of DEP were oven dried at 105 °C for 6 h. The samples were coated with thin layer of carbon to form a conductive layer around the non-metallic sample and to prevent accumulation of electron beams. Prior to analysis, the samples were mounted on a metallic stub with a conductive carbon tape. Micrograph of the samples were obtained after irradiation with 20 kV beam of electrons under a vacuum.

2.3. Validation of Analytical Methods

Calibration standards of 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 5.0 mg/L, 7.0 mg/L and 10 mg/L were prepared from a stock solution of lead(II) ion (1000 mg/L) supplied by Merck (pty), Ltd., Johannesburg, South Africa. A linear calibration curve was obtained with correlation coefficient of 0.998. Instrumental detection limit (IDL) and Method detection limit (MDL) of 0.52 µg/L and 0.30 µg/L were determined for lead(II) ion using the US EPA method 200.9 [30]. Recovery studies were also performed by spiking an aqueous solution of Pb with known concentration of lead(II) ion and 98% recovery was obtained.

2.4. Preparation of Solution

Analytical grade reagents were used. A stock solution of 1000 mg/L of lead(II) ion was supplied by Merck (pty, Ltd), Modderfontein, South Africa. Hydrochloric acid (32%) and sodium hydroxide were purchased from Sigma Aldrich, Johannesburg, South Africa. Working concentrations were obtained by serial dilution from the stock solution. The pH of the solutions was adjusted to the desired value using 0.1 M HCl and 0.1 M NaOH.

2.5. Batch Adsorption Studies

One gram of powdered leaves of DEP was used for the adsorption of lead(II) ion onto the surface of mucilaginous leaves of DEP using a Stuart reciprocal mechanical shaker with the speed of 250 rpm at 298 K. The effect of adsorbent dosage was investigated by varying the initial mass of the adsorbent between 0.01–2.0 g. The optimum dosage obtained was used for subsequent processes. Similarly, the effects of pH, initial lead(II) ion concentration and equilibration time were varied between 2–12 and 1–50 mg/L and 5–120 min, respectively. The percentage removal of lead(II) ion from aqueous solution was estimated by using Equation (1):

$$\%R = \frac{(C_o - C_e)100}{C_o} \tag{1}$$

where C_o and C_e are the initial and equilibrium lead(II) ion concentrations, respectively.

The amount of metal adsorbed by the adsorbent was calculated using Equation (2):

$$q_e = \frac{(C_o - C_e)V}{W} \tag{2}$$

where q_e is the amount of metal adsorbed in mg/g, V is the volume of the aqueous solution in litre and W is the weight of the adsorbent used in grams.

2.6. Desorption Studies

One gram of adsorbent was introduced into a 100 mL Teflon container containing 10.7 mg/L lead(II) ion. After equilibration for 60 min, the adsorbent was recovered. Residual Pb on the surface of the used adsorbent was removed by washing it three times with ultra-pure water. De-ionized water, 0.1 M NaOH and 0.1 M HCl were tested as potential desorbing agents. Forty milliliters of the desorbing agents were introduced into a 100 mL Teflon container containing the recovered adsorbent and equilibrated for

60 min at a speed of 250 rpm and T = 298 K. The aqueous solutions after equilibration were centrifuged and the supernatant were analysed to determine the concentration of lead(II) ion after desorption.

3. Results and Discussion

3.1. Infra-Red Spectroscopy Results

The results from the Fourier transform infra-red showed a broad peak at 3355 cm^{-1} with a high transmittance frequency, which can be attributed to either –OH or –NH groups [1,16]. As shown in Figure 1, the band observed at 2924 cm^{-1} is possibly due to C–H stretching vibrations of saturated aliphatic compounds as reported by Khambathy *et al.* [31] while the band at 1644 cm^{-1} can be attributed to –NH bending vibration of primary amines [31,32]. A small peak was observed at 1429 cm^{-1} and corresponds to v(C–C) stretching vibrations of aromatic rings [16].

The peaks observed at 1248 cm^{-1} and 1043 cm^{-1} corresponds to the C–O stretch of alcohols, carboxylic acids, esters or ethers [16]. The absorption band at 611 cm^{-1} can be due to the presence of an alkyl halide. Barone *et al.* [33] also confirmed that mucilage extracted from *Diceriocaryum* species contains carboxyl functional group. The presence of acidic functional groups is responsible for its adsorptive property [33]. Bhatti *et al.* [34] and Gilbert *et al.* [35] stated clearly from their studies of natural plant materials that the biochemical characteristics of acidic functional groups are responsible for their metal ion uptake.
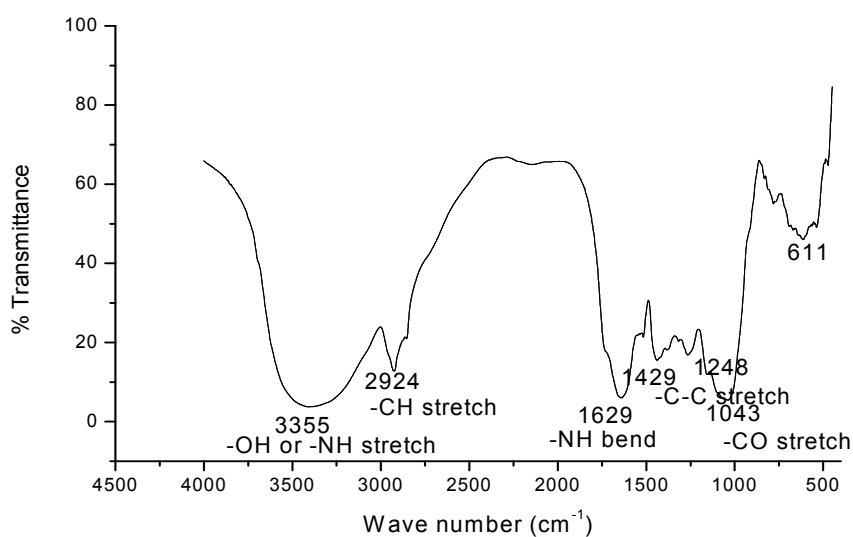

Figure 1. Infra-red spectra of the mucilaginous leaves of *Diceriocaryum eriocarpum* plant (DEP).

3.2. Morphology and Textural Examination of the Adsorbent

Morphological studies of the adsorbent showed a fluffy and highly porous and rough microstructure (Figure 2) containing some voids and cracks which is suitable for the adsorption of Pb [29]. The chemical composition of the adsorbent is presented in Table 1.

Table 1. Analysis of mucilaginous leaves of DEP.

Component	% Composition	Component	% Composition
Na_2O	1.17	K_2O	11.7
MgO	6.93	CaO	23.9
Al_2O_3	6.15	TiO_2	1.33
SiO_2	23.6	MnO	0.778
P_2O_5	2.42	Fe_2O_3	12.8
SO_3	5.68	SrO	1.24
Cl	1.09	BaO	0.521
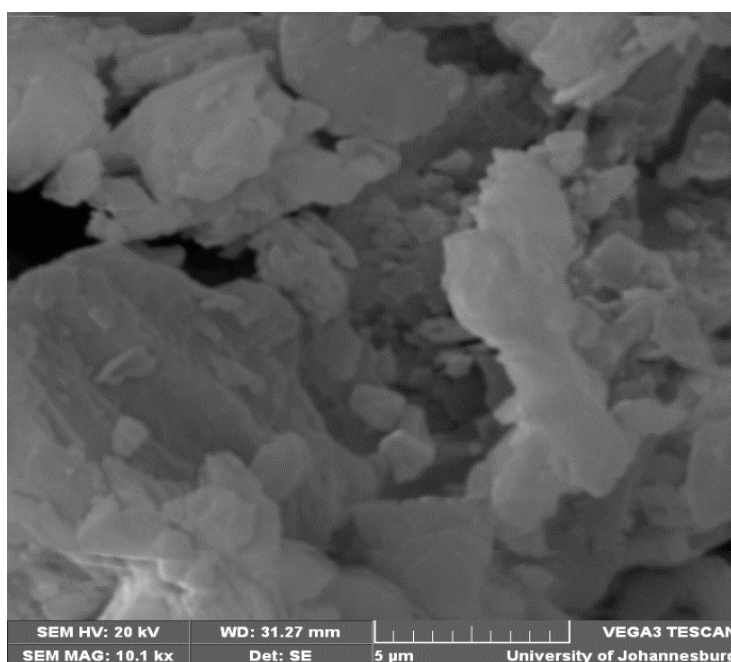
Figure 2. Scanning electron microscope micrograph of mucilaginous leaves of DEP.

The Brunaeur-Emmett Teller (BET) surface area of the adsorbent was 1.8517 m^2/g (Table 2). This is comparable to 1.88 m^2/g reported by Mousavi *et al.* [29] for waste rubber ash used for the removal of lead ions from aqueous solutions. The average pore diameter of DEP was within the range of $20 < d < 500 \times 10^{-8}$ cm and the adsorbent was classified as a mesoporous material [36,37].

Similarly, Rodrigues *et al.* [38] and Zvinowanda *et al.* [28] reported BET surface areas of 1.083 m^2/g and 2.52 m^2/g for activated carbon from macademia nuts used for phenol removal and maize tassels for heavy metal removal from polluted waters, respectively although adsorbents with higher surface areas have been widely reported in literature [15,39–41].

Table 2. Brunaeur-Emmett-Teller characteristics of mucilaginous leaves of DEP.

Physical Parameters	Result Obtained
BET surface area (m^2/g)	1.8517
Micropore surface area (m^2/g)	1.6061
Total pore volume (cm^3/g)	0.008244
Micropore volume (cm^3/g)	0.008055
Average pore diameter (A^o or 10^{-8} cm)	163.104

3.3. Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of lead(II) ion was determined by varying the adsorbent dosage from 0.05–2.0 g. The percentage removal of lead(II) ion by the adsorbent increased sharply from 31.31% at adsorbent dosage of 0.05 g to 94.68% at 1.0 g but decreased slightly to 94.40% when 2.0 g was used. The initial rapid increase observed could be due to the increased availability of binding sites and surface area which makes the adsorption of the ions quite easy until equilibrium was reached [10]. The subsequent decrease in the removal efficiency could be due to aggregation or overlapping of the adsorption site. These findings agree with other results reported in the literature [12,15,16,38].

3.4. Effect of Contact Time

Figure 3 shows the effect of contact time on the adsorption of lead(II) ion onto mucilaginous leaves of DEP. There was a rapid uptake of lead(II) ion with a removal efficiency of 97% within five minutes of equilibration. The rapid uptake was due to fast transfer of the metal ion onto the empty adsorption sites on the surface of the adsorbent [16,42]. Afterwards, there was a slow additional uptake of the metal ion from 5 min up to 60 min of equilibration, accounting for 98.36% Pb removal. There was no significant increase in the removal of lead(II) ion after 60 min indicating that equilibrium condition has been reached. This shows that the remaining empty sites on the adsorbent has been occupied leading to repulsive forces between adsorbed lead(II) ion on the adsorbent and those in the aqueous phase [37].
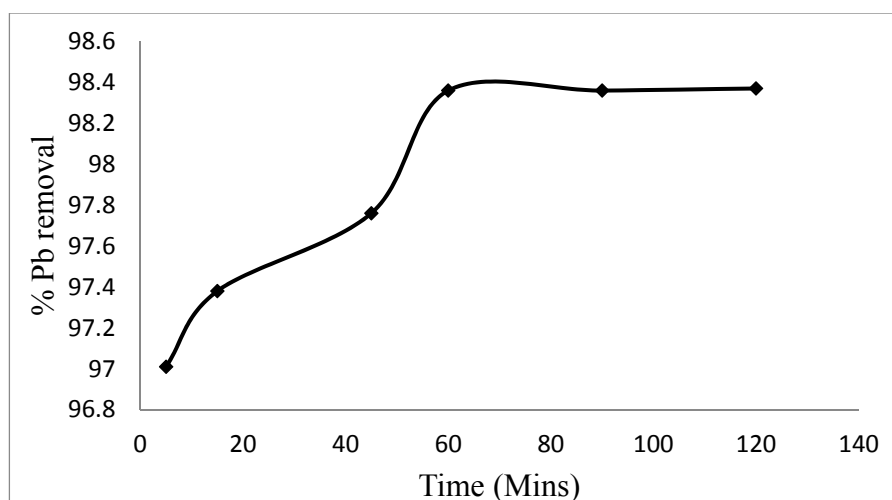

Figure 3. Variation of percent lead(II) ion removal with contact time (initial concentration = 10.7 mg/L, T = 298 K, pH = 4, shaking speed = 250 rpm, adsorbent dosage = 1.0 g).

3.5. Effect of pH

The competition between metal ions and protons for sorption sites is also affected by the pH of the solution [43]. Lead(II) ion removal was slightly affected by changes in the pH of the solution. There was a slight increase in metal uptake from 98.22%–98.88% as pH values changed from 2 to 4. This was accompanied by a slight decrease after pH 4 (98.69%). There was a relatively constant percentage

removal from pH 6–10 (98.69%–98.74%). However, a decrease in removal efficiency was observed at pH value of 12 (96.26%). A similar trend in pH has been reported by Abdus-Salem and Itiola [44].

3.6. Adsorption Isotherms

Experimental data for the adsorbed metal against initial concentration were fitted into the Langmuir and Freundlich adsorption isotherms. The Langmuir model assumes that the adsorption of an ideal gas on an ideal surface occurs only at fixed number of sites and each site can only hold one adsorbent molecule (monolayer) [1]. It also assumes that all available sites are equivalent and there is no interaction between adsorbed molecules on adjacent sites [1]. The linearised equation for Langmiur model is represented by Equation (3).

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{bq_{max}}\right)\frac{1}{C_e} \tag{3}$$

where Ce is the equilibrium concentration of the metal ion (mg/L), q_e is the quantity of Pb(II) ion adsorbed at equilibrium (mg/g), q_{max} is the maximum amount adsorbed (mg/g) and b is the adsorption constant (L/mg).

The plot of $1/q_e$ against $1/C_e$ gave a straight line with a regression coefficient of 0.9661 (Figure 4) indicating that the adsorption conforms to Langmuir model. The maximum concentration of lead(II) ion adsorbed and the adsorption capacity was calculated from the slope and intercept of the plot and are shown in Table 3. The conformity of the adsorption process to Langmuir model was determined using Equation (4):

$$R_L = \frac{1}{(1 + bC_O)} \tag{4}$$

where R_L is the separation factor, C_o is the initial metal concentration (mg/L) and b is the Langmuir constant (L/mg). $R_L > 1$ indicates an unfavourable monolayer adsorption process, $R_L = 1$ linear, $0 < R_L < 1$ favourable and $R_L = 0$ irreversible [15,45]. The result obtained from this study has an R_L value between zero and one, indicating a favourable adsorption process. This implies that chemisorption process duly explains the adsorption of lead(II) onto mucilaginous leaves of DEP.

Table 3. Langmuir and Freundlich constant for lead(II) ion sorption onto mucilaginous leaves of DEP.

Adsorption Isotherm	Parameter	Value
Langmuir	q_{max} (mg/g)	41.49
	b	0.02
	R^2	0.9661
	R_L	0.82
Freundlich	K_f	0.860
	n	0.909
	R^2	0.9547

The plot area shows data points with the fitted line labeled:

y = 1.1844x + 0.0241
R² = 0.9661

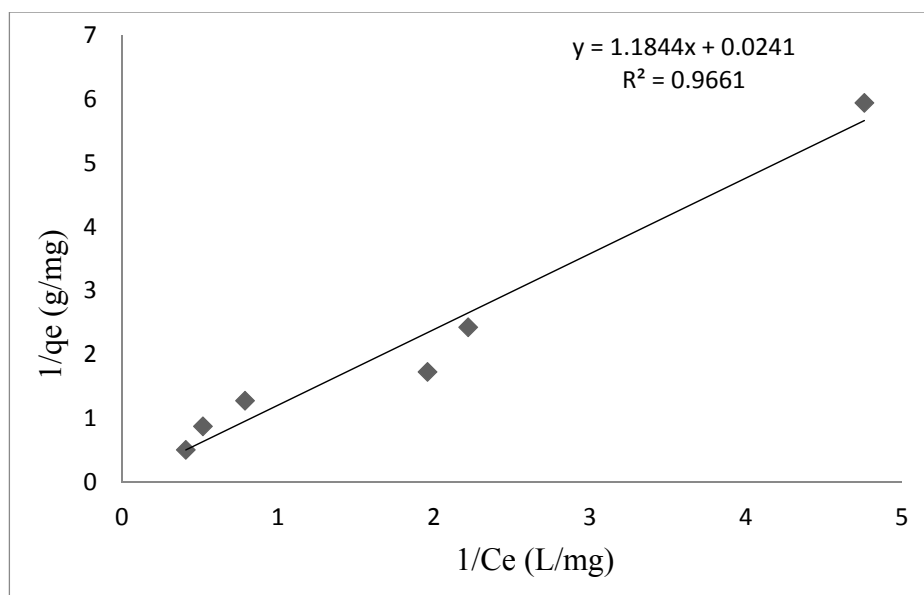Axes: y-axis "1/qe (g/mg)" ranging 0 to 7; x-axis "1/Ce (L/mg)" ranging 0 to 5.

Figure 4. Langmuir plot for lead(II) ion adsorption onto mucilaginous leaves of DEP.

The Freundlich isotherm model describes a multi-site adsorption for heterogeneous surfaces and can be represented by Equation (5);

$$q_e = K_f C_e^{\frac{1}{n}} \tag{5}$$

where K_f is the adsorption capacity (L/mg) and $1/n$ is the intensity of the adsorption showing the heterogeneity of the adsorbent site and the energy of distribution [46]. Equation (6) was obtained by taking the logarithm of Equation (5):

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{6}$$

A plot of $\log q_e$ against $\log C_e$ gave a linear graph with a regression coefficient of 0.9547 (Figure 5), indicating that the adsorption also fits into Freundlich model. From the linearised coefficients obtained from both models, the Langmuir model best described the adsorption process than the Freundlich model. This suggests a chemisorption process rather than a physisorption process. The constants obtained for the Langmuir and Freundlich plot is presented in Table 3.

A maximum adsorption capacity of 41.9 mg/g was obtained in this study for the adsorption of lead(II) ion. Comparison of the adsorption efficiency of DEP and other plant materials is presented in Table 4. The use of mucilaginous leaves of DEP is therefore a potential candidate for the removal of lead(II) in water and wastewater.
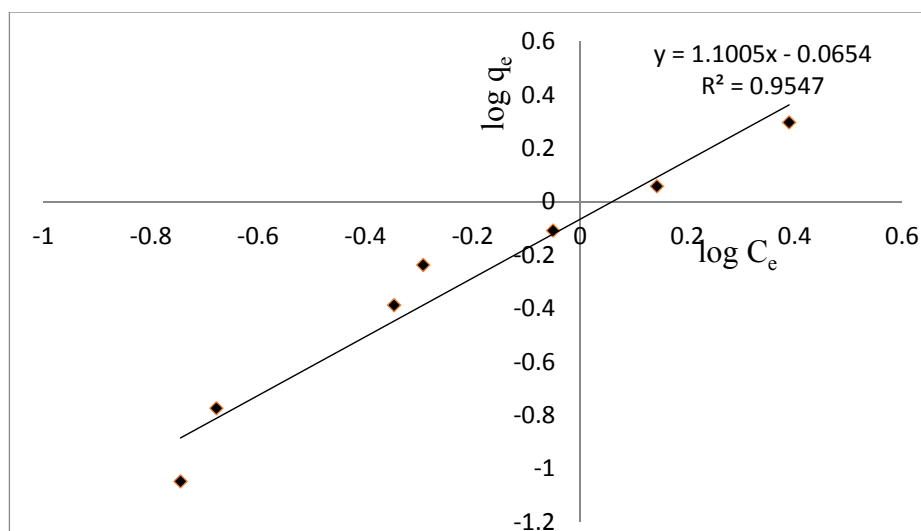
Figure 5. Freundlich plot for lead(II) ion adsorption onto mucilaginous leaves of DEP.

Table 4. Comparison of the maximum adsorption capacity of lead(II) ion by various adsorbents from plant origin.

Adsorbent	Maximum Adsorption Capacity (mg/g)	References
Activated carbon (AC) *Phaseolus aureus* hulls	21.80	[47]
Natural maize tassels	1.7	[16]
Acid treated maize tassels	37.31	[15]
Hazelnut shell	28.18	[48]
Saw dust of *Pinus Sylvestris*	22.22	[49]
Nitric acid treated peanut shell AC	35.5	[50]
Peels of banana	5.71	[51]
Tea waste	65	[52]
Mucilaginous leaves of DEP	41.49	This study

3.7. Adsorption Reaction Based Models

The mechanism adsorption reactions are usually carried out using adsorption reaction models and adsorption diffusion models [53]. Both models are used to understand the kinetics of the reaction.

The linearised equations for the pseudo first and pseudo second order kinetics are presented in Equations (7) and (8), respectively.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303}\right) \tag{7}$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e} \tag{8}$$

where q_e and q_t are the amounts of lead(II) ion adsorbed at equilibrium and at a given time t; k_1 and k_2 are the rate constants of pseudo first and pseudo second order models. The pseudo first order kinetic model was used to treat the experimental data obtained by plotting $\log(q_e - q_t)$ *vs.* equilibration time (Figure 6). A linearity coefficient of 0.7454 was obtained. Similarly, a linear graph ($R^2 = 1.00$) was

obtained by plotting t/qt values against time t (Figure 7). The pseudo second order best describes the kinetics of the adsorption process and this agrees with other results reported in the literature [39,54]. The result obtained from the kinetic plot favors chemisorption mechanistic pathway rather than physisorption.
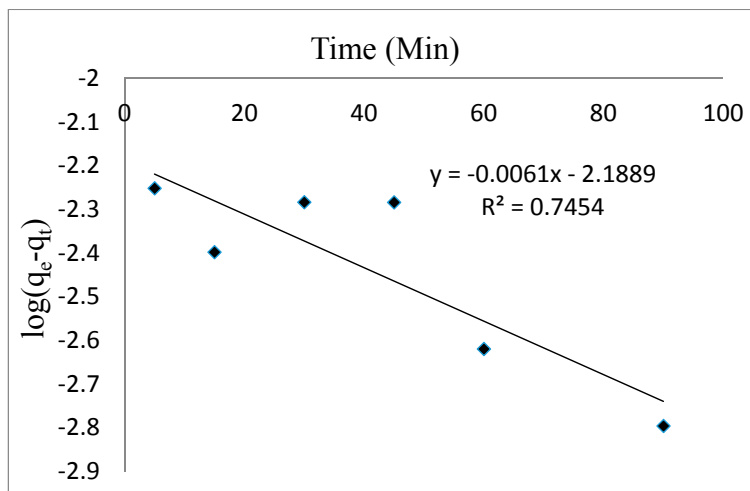

Figure 6. Pseudo first order kinetics for lead(II) ion adsorption onto mucilaginous leaves of DEP.
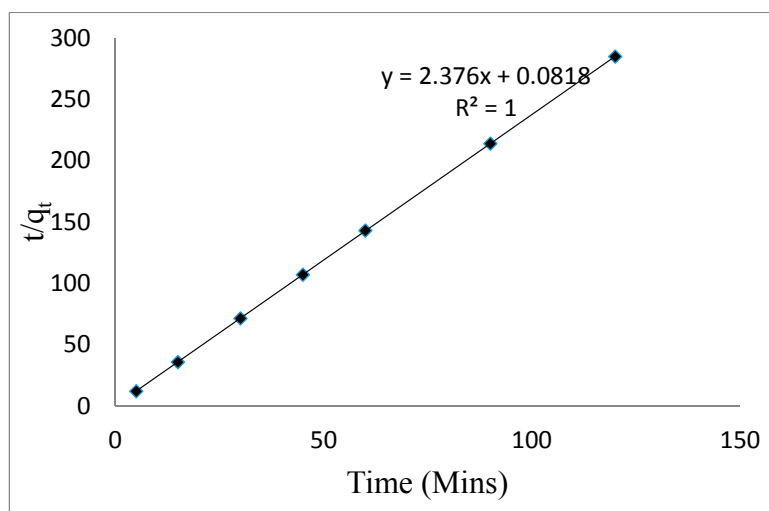

Figure 7. Pseudo second order kinetics for lead(II) ion adsorption mucilaginous leaves of DEP.

3.8. Mechanism Based Model

Weber-Morris mechanistic model in Equation 9 [55] was used to ascertain whether intra-particle diffusion or film diffusion (external diffusion) is the rate-controlling step.

$$q_t = k_d \sqrt{t} + I \tag{9}$$

where k_d is the intra-particle diffusion rate constant (mg/g min$^{-0.5}$) and I (mg/g) is a constant describing the thickness of the boundary layer.

A linear plot of q_t *versus* $t^{0.5}$ passing through the origin will suggest intra-particle diffusion as the sole rate-determining step [56]. However, if a linear plot was obtained that is not passing through the origin, it means the adsorption process is controlled by more than one mechanism. In this study, a linear plot was obtained that did not pass through the origin (Figure 8), suggesting that the mechanism of the reaction is multi-linear and the rate-limiting reaction is controlled both through film diffusion and intra-particle diffusion.
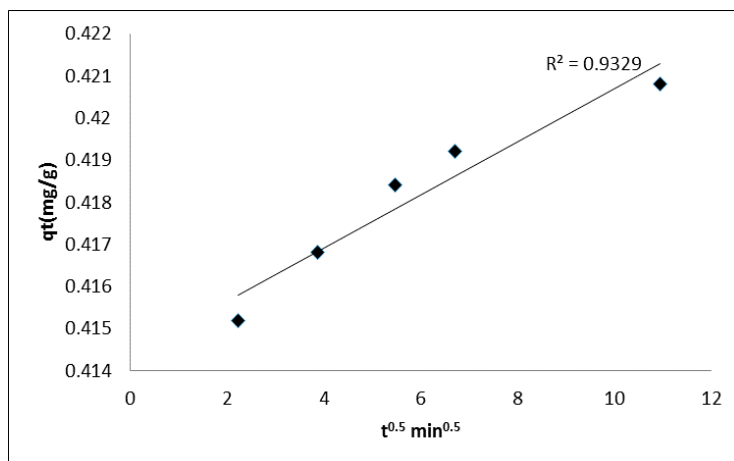

Figure 8. Intra-particle diffusion model plot for lead(II) ion adsorption onto mucilaginous leaves of DEP.

3.9. Treatment of Real Wastewater Samples

One gram of the adsorbent was used to treat spiked wastewater samples with pH of 7.8 and 8.34 collected from the effluent of Siloam waste stabilization ponds in Vhembe District of South Africa with lead(II) ion concentrations of 10 mg/L and 12 mg/L, respectively. The adsorbent showed percentage removal efficiencies of 95.8 and 96.4%, respectively. The results obtained were comparable to those of the simulated aqueous samples with removal efficiencies in the range of 95%–98.9% in the batch adsorption studies.

3.10. Desorption Studies

This study was carried out to assess the most suitable desorbing agent for eluting adsorbed lead(II) ion from the surface of mucilaginous DEP. The effects of de-ionized water, 0.1 M NaOH and 0.1 M HCl solutions were tested for their ability to remove the adsorbed lead(II) ion from the surface of the adsorbent. HCl was a better desorbing agent and was able to recover 50% of lead(II) ion adsorbed to the surface of the adsorbent. NaOH and de-ionized water showed desorption efficiencies of 18% and 2%, respectively. Desorption is beneficial for the separation and enrichment of lead(II) ion as well as the regeneration of the adsorbent [54].

4. Conclusions

The adsorption ability of powdered mucilaginous leaves from DEP has been investigated and found effective for the removal of lead(II) ion from wastewater. Acidic functional groups present on the surface

of the adsorbent is believed to be responsible for the removal of lead(II) ion from aqueous media. The Langmuir isotherm model gave a better description of the adsorption process than the Freundlich isotherm model. Pseudo-second order kinetics best described the kinetics of the reaction while 0.1 M HCl was a better desorbing agent than 0.1 M NaOH and de-ionized water.

Acknowledgments

Author Contributions

Joshua N. Edokpayi prepared the samples and performed analyses. John. O. Odiyo, Titus A. M. Msagati and Elizabeth O. Popoola contributed immensely to the writing and discussion of the final manuscript. All authors approved the final manuscript for publication.

Conflicts of Interest

The authors declare no conflict of interest.

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