Biosorption Performance of Apple Pomace from Different Geographical Locations For Pb²⁺ Ions Removal

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Abstract—Lead ions are one of the most prevalent heavy metals in South Africa wastewater and have been linked to many health-related problems in humans which include damage to the reproductive and renal systems as well as cancer. This research is focused on the removal of Pb^{2+} ions from wastewater using apple pomace collected from Belgium and South Africa as adsorbents. The biosorbents were characterized before and after adsorption to determine the functional groups present, using Fourier Transform Infrared Spectroscopy (FT-IR). The Isotherm and kinetic studies were conducted in pH range of 5-6, with initial concentration of 1-100 mg/L, and adsorbent dosage of 0.5 g. The isotherm studies showed that Freundlich isotherm was the best fit for the adsorption experimental data obtained from South Africa pomace with a strong correlation coefficient ($R^2 = 0.9563$), signifying a multilayer adsorption, while Belgium apple pomace adsorption data fitted the Elovich model (R^2 = 0.74958), corresponding to multilayer adsorption as well. For the Kinetic study, pseudo-secondorder model fitted the experimental data for both samples. The adsorption mechanism was suggested to be chemisorption process. Maximum removal efficiencies of Belgium and South Africa apple pomaces were 99.97% and 54.45%, respectively. This study has shown that apple pomace can be used as an efficient biosorbent to remove Pb^{2+} ions from wastewater.

*Keywords***—**Apple pomace, biosorption, characterization, isotherm, kinetic

I. INTRODUCTION

The massive industrialization and urbanization in this modern age has led to the discharge of wastewater containing heavy metals and other contaminants into the natural water systems [1-3]. The industries generating wastewater containing these metal ions include the tanneries, metal plating, mining, painting, battery industry, paper industries, printing and photographic industries, pesticides and fertilizer industries, and car radiator manufacturing [1, 4, 5]. The different heavy metal ions found in wastewater depending on the nature of the industry include Pb²⁺, Cd²⁺, Ni⁺, Fe²⁺, Cr³⁺/Cr⁶⁺, Zn²⁺, Cu²⁺ and $Co²⁺$, among others. These heavy metals have high solubility in water and therefore they are easily absorbed by living organisms [6]. Of all these heavy metal ions, the most prevalent heavy metal contaminants found in South African wastewater are the lead ions [1, 7]. Lead poisoning in humans has got very adverse effects on the skeletal organs, liver, brain, heart,

kidneys, and nervous system [8-10]. Symptoms of lead poisoning include headache, loss of memory, decrease in intellectual capacity, and dullness among others [11-13]. Lead ions are also a possible carcinogenic substance in humans in accordance with the International Agency for Research on Cancer (IARC). The acceptable discharge limit of Lead ions in wastewater as per the stipulation by the Environmental Protection Agency (EPA) and World Health Organization (WHO) is 0.015 mg/L and 0.01 mg/L respectively [1, 11] Hence, there is a great need to find cheap and effective ways to eliminate heavy metals from the wastewater since the conventional methods like chemical oxidation, electrostatic precipitation, coagulation, flocculation etc., are expensive and leave out a lot of sludge behind, giving rise to secondary pollution [14]. However there have been many findings reported by various researchers pointing out that adsorption is a better technique since it is flexible to design, efficient, cheap and generates minimal sludge compared to conventional methods. Therefore, this research focuses on biosorption, which is the remediation of wastewater using agricultural waste as adsorbents, specifically apple pomace. Several million tons of apple pomace are generated annually globally by apple juice processing industries, but there are problems regarding its handling and disposal resulting in environmental pollution [15--17]. Currently, the apple pomace is disposed of from the production facilities into landfills so that it decomposes naturally, but this has a negative future effect as it will produce methane gas upon its decomposition which will be released into the atmosphere thereby contributing to global warming [16]. However, the apple pomace has been found to contain various functional groups which include phenolic groups, carbonyl and carboxylic groups, and this makes it highly suitable for the adsorption of heavy metals [16, 18, 19]. The research seeks to find economic and highly efficient ways to remove lead ions from wastewater which will be an opportunity to economically dispose of the waste apple pomace from the apple processing industries by utilizing it as an efficient adsorbent for the removal of lead ions in water. The use of apple pomace as a biosorbent can reduce the adsorbent cost by almost 10 times, making the water treatment process more economically efficient [20, 21].The main aim of this study was to characterize and evaluate the performance of the apple pomace from the two 41st CAPE TOWN Intermediate the method of the method internal Engine Conference on Chemical and Engine Conference on Top 2² Long Cape Cape Town (CCBE) and Engine Cape Cape Town (CCBE) and Engine Cape Cape Town (CCBE) an

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different geographical areas for the removal of Pb^{2+} ions in wastewater. The objectives were to characterize the apple pomaces before and after adsorption using Fourier transform infrared spectroscopy (FT-IR) to determine the functional groups present and to conduct the isotherm and kinetic studies for the adsorption process.

II.MATERIALS AND METHODS

A.Adsorbent preparation

Two different apple pomace samples were used in this study, the first apple pomace was collected from Materne Company, located in Namur, Belgium whilst the second sample of apple pomace was collected from Associated Fruit Processors (Pty) Ltd located in Cape Town, South Africa. Both samples were dried in an oven at 60° C for 24 hours. Afterwards the apple pomace samples were ground using a laboratory grinder (Retsch GmbH 5657 Haan West-Germany) and finally sieved to achieve particle sizes ranging from 55µm to 600 µm on a sieve shaker equipment. The samples were characterized using FT-IR (Cary 630, Agilent, USA) before and after adsorption.

B.Preparation of adsorbate stock solution

1000 mg/L of the Pb^{2+} ions solution was prepared by dissolving 1.598g of lead nitrate $[Pb(NO₃)₂]$ in deionized water in a 1000 ml volumetric flask filled to the mark. The solution was thoroughly mixed to ensure that all the lead nitrate dissolves completely.

C.Isotherm Study

Isotherm experiments were conducted to characterize adsorption at equilibrium and to gain insight into the mechanism of adsorption. Adsorption equilibrium provides information needed for better understanding of adsorption process, which is critical for the overall improvement of adsorption mechanism pathways and help in the effective design of adsorption systems [22]. 100 ml of different concentrations ranging from 10–100 mg/L of the lead nitrate solution were prepared from the stock solution through serial dilutions and put in 10 separate clearly labelled 250 ml conical flasks. The pH of each solution was measured using a digital pH meter (SensoDirect 150) and recorded. 0.5g of adsorbent (150 μ m) was added to each beaker. The solution was then mixed thoroughly on a linear shaker (Orbital shaker 262) for 2 hours at a speed of 180 rpm at room temperature. Afterwards the solution was firstly filtered using a Whatman filter paper followed by syringe filters $(0.45 \mu m)$. The filter residue (spent biosorbent) was dried in a conventional oven (Scientific 221) for 24 h at 60° C, and sent for FT-IR analysis. The filtrate sample was analyzed using micro-plasma atomic emission spectrophotometer (MY 18379001, Agilent, USA) to determine quantity of Pb^{2+} ions adsorbed. The experiments were conducted in duplicates. Langmuir, Elovich and Freundlich Isotherm models were used to analyze and validate the experimental data. 41.24. The Microsofte of Conference of the Conference of the Conference on the Conference on the Chemical and Environmental Engine and The Conference of the Conference on Conference on the Conference of the Conference of

Freundlich Isotherm model

Freundlich Isotherm model is given by the equation below and is based on the assumption that adsorption mechanism is monolayer and adsorption surface is not uniform [1]. It also assumes that the adsorption energy is not uniform on the surface of the adsorbent.

$$
q_e = K_f C_e^{\frac{1}{n}}
$$
 (1)

Where: K_f and n are constants, q_e is the equilibrium adsorption capacity (mg/g), C_e is the final metal ions concentration at equilibrium (mg/L).

Langmuir Isotherm Model

Langmuir isotherm model is given by the equation (2) below and it is based on the assumption that the surface of the adsorbent is smooth and uniform, and lateral interactions between adsorbed sites are negligible [1]. It also assumes that there is uniform adsorption energy on all the adsorption sites regardless of what will be adsorbed in neighbouring sites [1]. The Langmuir isotherm model was the first adsorption isotherm to be developed theoretically and all other models developed preceded from the Langmuir model [1, 23].

$$
Q_e = \frac{Q \max b \ C_e}{1 + b C_e} \tag{2}
$$

Where: Q_{max} is the maximum adsorption capacity of the metal ion in mg/g); b is the Langmuir constant (L/mg), q_e is the equilibrium adsorption capacity (mg/g) and C_e is the final metal ions concentration at equilibrium (mg/L)

Elovich Isotherm Model

This model is given by the equation (3) below. It is derived from a kinetic principle which assumes that adsorption sites increase exponentially with adsorption, implying a multilayer adsorption phenomenon.

$$
\frac{q_e}{q_m} = K_e C_e \frac{q_e}{q_m} \tag{3}
$$

Where q_e is the equilibrium adsorption capacity, q_m is maximum adsorption capacity, K_e is the Elovich constant, C_e is the equilibrium concentration. Elovich maximum adsorption capacity and Elovich constant are calculated from the slope and intercept of the plot of $\ln \frac{q_e}{c_e}$ versus q_e

D.Kinetic Study

This study is used to explain the rate of adsorption with time. Three 100 mg/L solutions of lead nitrate were prepared from the stock solution through serial dilutions and put into three separate 1000 ml beakers labeled A, B and C. The beakers were arranged on a jar test equipment (VELP JLT6) and 1g of adsorbent was added into each solution in the beaker. The solution was thoroughly mixed for 24 h at a speed of 180 rpm at room temperature. Samples were drawn from each beaker at different time intervals, starting from 5 min up to 24 h. Experimental kinetic data was validated using pseudo-firstorder and pseudo-second-order kinetic models.

Pseudo-first-order model

$$
\ln(q_e - q_t) = \ln q_e - k_1 t
$$
\n
$$
Pseudo-second-order model
$$
\n(4)

$$
\frac{\mathbf{t}}{\mathbf{q_t}} = \frac{1}{\mathbf{k}_2 \mathbf{q_e}^2} + \frac{\mathbf{t}}{\mathbf{q_e}}\tag{5}
$$

Where: q_e and q_t are the amount (mg/g) adsorbed at equilibrium and at time (t) respectively, t is time (h), k_1 is the pseudo-first-order reaction rate constant (h) , k_2 the pseudosecond-order reaction rate constant (g mg⁻¹h⁻¹

E. Removal Effeciency

The removal efficiency for both samples of the adsorbent was calculated using the equation below [1, 24]

Percentage removal (
$$
\%
$$
) = $\frac{C_i - C_f}{C_i} \times 100$ (6)

Biosorption capacity per gram of the biosorbent q (mg/g) was calculated using the equation below

$$
q = \frac{(C_i - C_f) \cdot V}{m} \tag{7}
$$

Where C_i is the initial metal concentration in the solution (mg/L), C_f is the final concentration of the solution (mg/L), V is the volume of the solution (ml), and m is the mass of sorbent (g).

III. RESULTS AND DISCUSSION

A.FT-IR spectroscopy analysis

The FTIR spectra of both apple pomace samples before and after adsorption were measured between 398 and 4000 cm $^{-1}$ to identify the functional groups that are present on the surface of the adsorbent as indicated in Figures 1 and 2. The FT-IR Spectra showed significant number of peaks which signifies the adsorptive nature of the biosorbent. The shapes and bands show similarities for both samples of apple pomaces before and after adsorption, suggesting the presence of common functional groups in both samples. The peaks were observed at 3410.2, 2919.8, 2850.7, 1733.9, 1645.3, 1455.7, 1375, 1160.6, 1053.7, and 570.4 cm-1 . The broad band at the region of the 3000–3500 $cm⁻¹$ noticed in all samples indicate the presence of $(-OH)$ groups. The peaks at 2850.7 to 2919.8 cm⁻¹ represent the $-C-$ H stretching of aliphatic carbon chain. The peaks at 1733.9, 1645.3, 1455.7, cm−1 showed the presence of the –C=O of ester, carbonyl (–CO) and –C–O–C– group of ether respectively. In almost all the peaks, there are changes in the transmittance after adsorption which indicated that interactions occurred between metal ions, and the functional groups present in the apple pomace 41st CAP TOWN 1 of Conference on Chemical Research of Conference on Environmental Engineering Cape (2) and Conference on the Conference of CCBEE-24) Nov. 21-22, 2024 Cape Town (CPB) and Engineering Cape Cape Town (CPB) an

 Fig. 1: FT-IR spectra before and after adsorption for Belgium apple pomace

 Fig. 2: FT-IR Spectra before and after Adsorption for South Africa apple pomace

IV. KINETIC STUDY RESULTS

The adsorption of Pb^{2+} ions occurred rapidly in the first 5 min for the South Africa apple pomace as evidenced in the plot of removal efficiency (%) against time (Figure 3), after which removal rate decreased considerably until an equilibrium was reached at 5 h. The reduction in removal efficiency indicates that the active site of adsorbent was close to saturation. The equilibrium was reached within 5 h and after that no considerable adsorption of Pb^{2+} ions took place. For apple pomace from Belgium, the percentage removal efficiency reached 99% within the first 5 min and almost 100% as the time progressed (Figure 4). The equilibrium was reached within the first 15 min, and beyond that time no considerable change took place, this is because all the adsorption sites on the surface of the biosorbent were saturated. Adsorption of the apple pomace sample from Belgium reached equilibrium faster than the sample from South Africa.

Fig. 3: Percentage removal with time for South Africa apple pomace

Fig. 4: Percentage removal with time for Belgium apple pomace

The pseudo-first order and pseudo-second-order models were fitted to the experimental data of both biosorbent samples, and the plots are shown in the Figures 5, 6, 7 and 8. The data obtained from the apple pomace sample from South Africa showed a weak negative correlation for the Pseudo-first-order model with a correlation coefficient of $R^2 = 0.5966$ (Figure 5), while the correlation coefficient for the Pseudo-second-order model was $R^2=0.989$ (Figure 6). This suggests that the adsorption of lead ions on apple pomace sample from South Africa is not influenced by the Vander Waals forces and other interactions between the molecules, but it is mainly dominated by chemisorption. For the apple pomace sample from Belgium, the correlation coefficient (R^2) for the pseudo-first-order model was found to be 0.169 (Figure 7) while the correlation coefficient($R²$) for the Pseudo-second-order model was 0.999 (Figure 8). Maximum removal efficiencies of Belgium and South Africa apple pomaces were 99,97% and 54,45% respectively, as shown in Figure 3 and Figure 4. 441 SCAPE TOWN Intermental Conference on "Chemical Biological" (CCBE) and Conference of Conference of Conference on the Conference of Con

 Fig. 5: Pseudo-first-order model Plot for South Africa apple pomace

 Fig. 6: Pseudo-second-order model Plot for South Africa apple pomace

 Fig. 7: Pseudo-first-order model plot for Belgium apple pomace

 Fig. 8: Pseudo-second-order model plot for Belgium apple pomace

V. ISOTHERM STUDY

The isotherm studies were conducted by varying the initial adsorbate concentrations whilst keeping all other parameters constant. Freundlich isotherm best fitted the adsorption data obtained from South Africa pomace with a strong positive correlation coefficient (R^2 = 0.9563; 9.79 mg/g) as shown in Figure 9, signifying a multilayer adsorption, while Figure 13 shows that Belgium apple pomace adsorption data best fitted the Elovich model ($R^2 = 0.7496$; q=19.99 mg/g) depicting a multilayer adsorption. The adsorption capacity increased with increasing initial adsorbate concentration for both samples. For apple pomace from South Africa, at 10 mg/L of the adsorbate, the removal was 1,036 mg/g and as the concentration increased to 100 mg/L of adsorbate, the adsorption capacity was 9.78 mg/g which was the maximum. The capacity for the apple pomace from Belgium at 10 mg/L of adsorbate concentration, was found to be 1.975 mg/g whilst the maximum capacity of 19.99 mg/g was recorded at 100 mg/L concentration. from South Africa pomace with a strong positive

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 Fig. 9: Freundlich isotherm plot for South Africa apple pomace

Fig. 10: Langmuir isotherm for South Africa apple pomace

Fig. 11: Elovich model for South Africa apple pomace

Fig. 12: Freundlich isotherm for Belgium apple pomace

Fig. 13: Langmuir model plot for Belgium apple pomace

Fig. 14: Elovich model plot for Belgium apple pomace

VI. CONCLUSION

From the experiments done and findings of both isotherm and kinetic studies, it was shown that apple pomace has a great potential of application in the adsorption of Pb²⁺. Maximum removal efficiencies of Belgium and South Africa apple pomaces were 99.97% and 54.45% respectively. The isotherm studies showed that Freundlich isotherm was the best fit for the adsorption data obtained from South Africa pomace with a strong positive correlation coefficient ($R^2 = 0.9563$; $q_e = 9.78$) mg/g), signifying a multilayer adsorption, while Belgium apple pomace adsorption data fitted the Elovich model (\mathbb{R}^2 = $0.7496; q_e=19.99 \text{mg/g}$, corresponding to multilayer adsorption as well. Multilayer adsorption occurs when the surface of adsorbent is not uniform and with the aid of Van Der Waals forces, hence it was concluded that the surface of the apple pomace is not uniform. For the Kinetic study, pseudo-secondorder model fitted the experimental data for both samples with a strong positive correlation coefficient of close to 1. Considering the FT-IR analysis results, isotherm and kinetic results, the adsorption mechanism was suggested to be both chemisorption and physisorption process, with the chemosorption being the predominant mechanism. It was also 41st CAPE TOWN Intermentation of the conference on the conf

noticed that the performance of apple pomace or biosorbents at large, can vary depending on its source, processing conditions and region. It was also observed that different apple pomaces from different sources contain almost similar and equal functional groups as evidenced by the peaks occurring at same positions.

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