Assessment of the Performance of SDS-Impregnated Brewery Waste as Suitable Adsorbent for the Removal of Pb and Cd from Water

Elvis Fosso-Kankeu*, Meiklejohn Leamy, Enoch Akinpelu and Frans Waanders

Abstract— **Due to increasing populations and an ever-changing climate, limited water resources are South Africa's burden. Clean water is important for all living organisms' health and environmental sustainability. To achieve efficient and cost-effective ways of removing heavy metals from water, the development of different water treatment technologies are important. This study evaluates the performance of organic waste in the form of brewery waste as suitable adsorbent for removing Pb and Cd from water. Raw brewery waste was treated with sodium dodecyl sulphate (SDS) to investigate whether pre-treatment of raw organic waste can possibly enhance the removal rate of metals. Characterization of the adsorbents was done by FTIR analyses. Pseudo-first-order and pseudo-second-order kinetic models were utilized as well as the Langmuir and Freundlich isotherm models to determine the adsorption rate and affinity of the adsorbents. Other factors influencing the adsorption process that was investigated include the effects of adsorbent dosage, contact time, initial metal ions concentration and temperature. The untreated brewery waste removed 68.17% Pb(II) and 56.28% Cd(II) which increased to 95.30% Pb(II) and 83.29% Cd(II) when treated with SDS. Treatment of brewery waste can be used to enhance the adsorption capacity. Thermodynamic parameter evaluation indicated that the adsorption process was endothermic in nature and thermodynamically favourable in the case of treated brewery waste. Treated brewery waste can therefore be used for efficient Pb and Cd removal from water.**

***Keywords*—**Adsorption of cadmium and lead, Organic waste, Brewery waste, Langmuir isotherm, Freundlich isotherm and Adsorption kinetics

I. INTRODUCTION

Heavy metals have the tendency to accumulate in ecosystems and are a serious threat to the health of living organisms. Most heavy metals are toxic even at very low concentrations and have the ability to enter the food chain and accumulate, subsequently causing damage to living organisms [1]. The main pollution source of heavy metals is industrial effluents such as waste solutions from the electroplating industry and mining operations [2, 3-14]. Toxic metals have the ability to disrupt enzyme functions and structures by replacing co-factors or binding with protein and thiol groups [1]. Plant habitats become limited due to the toxicity of heavy metal contaminated soils, resulting in ecological and nutritional problems [15;16]. It is therefore of great importance to remove these heavy metals from the water to provide humans with safe water for consumption and to ensure environmental safety.

The conventional procedures applied for heavy metal treatment include chemical precipitation, ion exchange, reverse osmosis, chemical oxidation or reduction, membrane filtration, electro-dialysis and solvent extraction [17,18]. However, several disadvantages are associated with these methods [19]. A summary of the conventional methods' limitations are as follows: high costs required, formation of contaminated sludge that requires special treatment, complicated operation and maintenance, requiring large quantities of chemical reagents and ineffective removal of heavy metals especially in wastewater polluted with trace amounts of heavy metals [20;21;22;23;24]. Therefore, these conventional treatment methods cannot be considered as sustainable processes [25]. And are considered as short-term solutions for heavy metal contaminated water treatment. In this study, the adsorption process is considered as an alternative method for heavy metal removal by using organic waste as potential effective low-cost adsorbents. Recently, agricultural and industrial wastes have been researched and considered as potential heavy metal adsorbents [25]. Industrial activities generate large quantities of solid waste materials and by-products, of which only some of them can be reused while the rest are sent for disposal in landfills [26;27]. Therefore, the need to reuse and recycle these industrial waste materials to reduce the amount of waste. The

Manuscript received October 03, 2018.

E. Fosso-Kankeu is with the Water Pollution Monitoring and Remediation Initiatives Research Group and the School of Chemical and Minerals Engineering at the North-West University, Potchefstroom, South Africa.

Meiklejohn Leamy is with the Water Pollution Monitoring and Remediation Initiatives Research Group and the School of Chemical and Minerals Engineering at the North-West University, Potchefstroom, South Africa.

Enoch Akinpelu is with the Water Pollution Monitoring and Remediation Initiatives Research Group and the School of Chemical and Minerals Engineering at the North-West University, Potchefstroom, South Africa.

F.B. Waanders is with the Water Pollution Monitoring and Remediation Initiatives Research Group and the School of Chemical and Minerals Engineering at the North-West University, Potchefstroom, South Africa..

https://doi.org/10.17758/EARES4.EAP1118244

most attractive aspect of utilizing industrial wastes is that they usually are provided free of charge or at low costs [27]. Hence the use in this study of organic waste in the form of brewery waste as potential low-cost adsorbent for the removal of heavy metals from polluted waters. The utilization of this abundantly available raw material as adsorbent can potentially reduce heavy metals from polluted waters and in the process creates an outlet for this waste material. The heavy metals of interest for this study are lead, Pb(II), and cadmium, Cd(II), ions. Chemical pre-treatment of industrial wastes can enhance the adsorption capacity by extracting soluble organic compounds [28]. In this study brewery waste will be pre-treated with sodium dodecyl sulphate (SDS) to enhance its adsorption capacity.

II. EXPERIMENTAL

A. *Preparation of Adsorbents*

Sorghum brewery waste was obtained from Tlokwe Brewery, Potchefstroom, South Africa. The collected waste was thoroughly washed with deionised water to remove brewers' residues and oven dried at 60 ℃. The dry mass was then pulverised and screened to pass 250μm. This product was subsequently referred to as "Bree untreated" for simplification of further discussions and will serve as the untreated (raw) brewery waste adsorbent during the adsorption experiments. The raw brewery waste was chemically treated with sodium dodecyl sulphate (SDS). This chemical treatment was done by adding 20 grams of the Bree untreated to 500 mL of deionized water to a solution containing 10 grams per litre SDS. The mixture was kept in suspension for 24 h at 60℃ and 150 rpm by using a temperature-controlled shaker. The mixture was centrifuged and the solid was dried at 60℃. This product was subsequently referred to as "Bree treated" for simplification of further discussions and will serve as the treated brewery waste adsorbent during the adsorption experiments.

B. *Characterization of Adsorbents*

Fourier transform infrared spectroscopy (FTIR) analyses were performed to evaluate the functional groups present on the surface of the adsorbents which are responsible for Pb(II) and Cd(II) ions removal. A Perkin-Elmer Spectrum 100 spectrometer (USA) was utilized with the potassium bromide pellet method in the spectral range of 4000 cm^{-1} to 400 cm^{-1} with a 4 cm^{-1} resolution.

C. *Adsorption Studies*

To determine the equilibrium concentration of each metal solution, a ICP Expert II Software for 720 Series ICP-OES was used. The following parameters were kept constant while the effect of adsorbent dosage (1-4 g/L), initial metal concentration (20-150 mg/L) and contact time (10-150 min) were determined: rotation speed of 160 rpm, temperature of 25℃ and solution volume of 0.05 L. The effect of temperature was investigated at 25, 35, 45 and 55℃ for 60 minutes at a shaking speed of 160 rpm and solution concentration of 100 mg/L Pb(II) and Cd(II) ions.

D. *Isotherm and Kinetic models*

The relationship between metal uptake and initial metal concentration, at a fixed adsorbent dosage and temperature, is illustrated by adsorption isotherms [29]. The Langmuir isotherm model assumes monolayer adsorption for single solutes [30]. The linearized form of the Langmuir isotherm is given by:

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

A linear plot of $\frac{C_e}{q_e}$ versus C_e was considered to determine the adsorption equilibrium constant (K_L) and the maximum adsorption capacity (q_{max}).
The Freundlich isotherm is applied for heterogeneous adsorption and considers the interaction between adsorbed molecules [31;32]. The linearized form of the Freundlich equation is as follows:

$$ln(q_e) = \ln(K_F) + \left(\frac{1}{n}\right)\ln(C_e) \tag{3}$$

A plot of $ln(q_e)$ versus $\ln(C_e)$, was considered to determine the Freundlich isotherm constants (n and K_F). In the two given isotherm models, C_e is the metal in solution's equilibrium concentration ($\frac{mg}{L}$), q_e is the adsorption capacity of the adsorbent at equilibrium ($\frac{mg}{g}$), C_i is the initial metal ion concentration, q_{max} is the maximum amount of metal ion adsorbed per dry weight of adsorbent ($\frac{mg}{g}$), K_L is the Langmuir equilibrium adsorption constant related to the maximum adsorption capacity and bonding energy, K_F is the Freundlich isotherm constant and is related to the bonding energy, n is an empirical constant which is an indication of deviation or not from linearity.

Pseudo-first-order and Pseudo-second-order kinetic models are used to aid in determining the adsorption rate. The pseudo-first order expression's integrated form is [33]:

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1}{2.303}(t) \tag{4}$$

The pseudo-first order rate constant (k_1) can be determined by plotting $\ln(q_e - q_t)$ versus t. The linearized form of the pseudo-second order equation is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{1}{q_e}(t) \tag{5}$$

The values of q_e and k_2 are determined by plotting $\frac{t}{qt}$ versus t. In the given kinetic models, q_e is the equilibrium adsorption capacity ($\frac{mg}{g}$), q_t is the adsorption capacity at time t ($\frac{mg}{g}$), k_1 is the pseudo-first order adsorption rate constant ($\frac{1}{min}$) and k_2 is the pseudo-second order rate constant.

III. RESULTS & DISCUSSION

A. *FTIR analyses*

The FTIR spectrums of the Bree untreated and Bree treated are illustrated in Figures 1 and 2 respectively. The FTIR spectrum of the Bree untreated and treated showed broad peaks at 3286.72 and 3292.99 cm^{-1} respectively which indicates the O-H stretching vibrations of hemicellulose, cellulose, lignin and pectin which are known to be present in brewery waste [34]. The stretching vibrations of OH takes place within a broad range of frequencies, which represent the existence of free hydroxyl groups and bonded OH bands of carboxylic acids [35]. The bands at 2923.32 cm^{-1} of Bree untreated and 2921.94 cm^{-1} of Bree treated are indicative of the stretching vibrations of -CH_3 [36]. While the bands at 2857.00 cm^{-1} of Bree untreated and 2855.52 cm^{-1} of Bree treated corresponds to the stretching vibrations of -CH_2 [36]. The strong peaks at around 1642.85 and 1648.87 cm^{-1} of the Bree untreated and treated respectively could be assigned to the C=C stretch vibration from the alkenes group. The respective peaks between the spectral range of 1350 and 1550 cm^{-1} of both the Bree untreated and Bree treated FTIR analyses indicate the presence of C-C stretching of aromatic ring. Within this range there are also peaks corresponding to the bending vibrations of C-H of alkanes. The definite peak at 1220.28 cm^{-1} (Figure 2), formed after surface impregnation of the raw brewery waste with SDS, corresponds to stretching vibrations of S-O [37]. The S-O bonds are present in sodium dodecyl sulphate (SDS) and it is therefore expected that SDS-treated brewery waste will contain this functional group. The strong peaks observed at 1007.67 cm^{-1} and 1006.62 cm^{-1} of Bree untreated and Bree treated respectively are indicative of C-O stretching vibrations of alcohols.

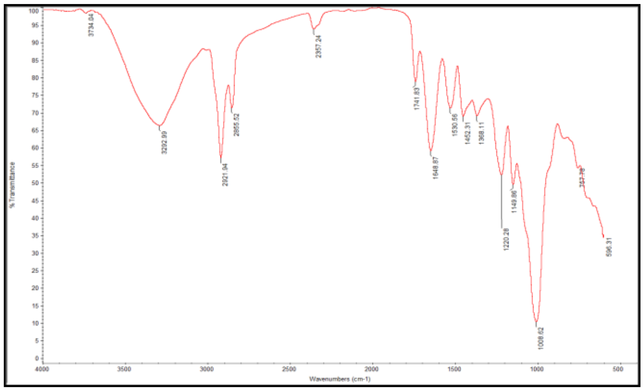

Fig 1: FTIR spectra of Bree untreated

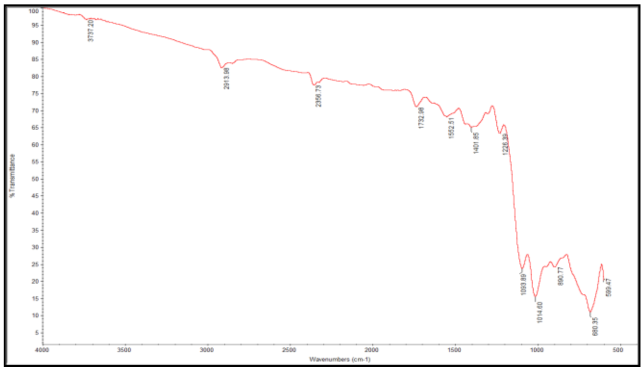

Fig 2: FTIR spectra of Bree treated

B. *Adsorption study*

1) *Effect of adsorbent dosage*

The dosage of Bree untreated and Bree treated was varied over the range of 1-4 g/l as shown in Figures 4 and 5. An increase in removal efficiency and decrease in adsorption capacity was observed for both Bree untreated and Bree treated. This increase in the removal efficiency of metal ions as the adsorbent dose increase is attributed to the availability of more and more surface area and binding sites for metal ions interaction and uptake [38]. The adsorption capacity reduces as the dose of adsorbent increases due to a lower ratio of adsorbate to binding site where the ions are distributed onto larger amount of biomass binding sites [39]. The removal efficiency of both adsorbents started to reach a maximum at 4 g/L due to the saturation of the adsorbents' binding sites at higher dosages. The pre-treatment of the raw brewery waste with SDS enhanced the removal percentage of both Pb(II) and Cd(II). The adsorbents also showed better removal efficiencies for Pb(II) than Cd(II).

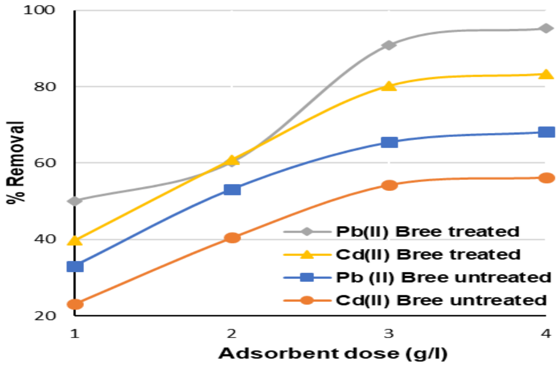

Fig 4: Effect of adsorbent dose on removal efficiency

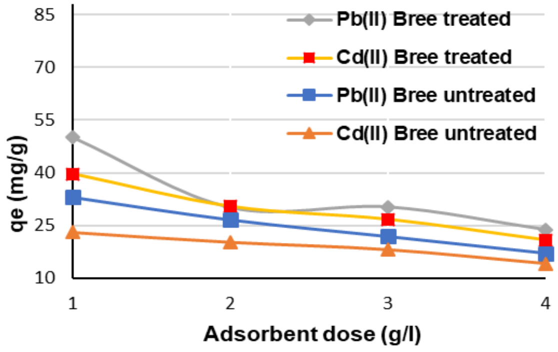

Fig 5: Effect of adsorbent dose on the adsorption capacity (mg/g)

2) *Effect of contact time*

Both Bree untreated and Bree treated experienced similar behaviour with increasing contact time as illustrated in Figure 6. The adsorption of Pb(II) and Cd(II) showed an increasing trend up to a contact time of 50 minutes, after which the adsorption only exhibited a steady increase due to the saturation of the adsorbents. After 120 minutes, equilibrium of the removal efficiencies was reached for both adsorbents.

https://doi.org/10.17758/EARES4.EAP1118244

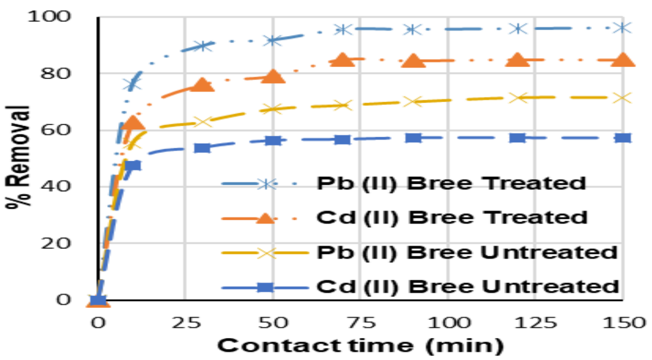

Fig 6: Effect of contact time on removal efficiency

3) *Effect of initial metal concentration*

The removal efficiency of Pb(II) and Cd(II) decreased with an increase in metal concentration as shown in Figure 8. This behaviour can be attributed to the fact that at lower metal concentrations in the solution, majority of ions will interact with the high available binding sites whereas at higher concentrations, saturation of binding sites occurs resulting in more ions left unabsorbed in the solution [39]. A continuous increase in metal uptake capacity (mg/g) was experienced as the metal concentration increased as illustrated in Figure 7. This increase in adsorption capacity illustrates the effectiveness of the adsorbents to remove the metal ions.

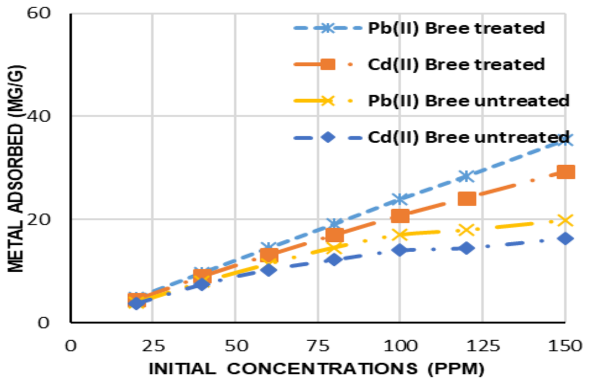

Fig 7: Effect of initial concentration on removal efficiency

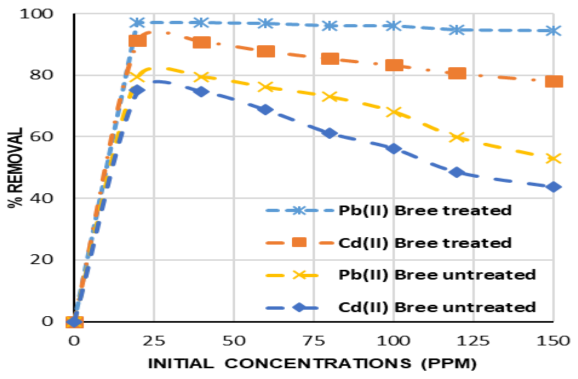

Fig 8: Effect of initial concentration on the adsorption capacity (mg/g)

4) *Isotherm and Kinetic model results*

The Langmuir and Freundlich isotherms were utilized in order to better understand the mechanism of adsorption of Pb(II) and Cd(II). The Langmuir and Freundlich parameters were obtained by plotting $\frac{C_e}{q_e}$ versus C_e and $ln(q_e)$ versus $\ln(C_e)$, the results are shown in Tables 1 to 4. From the coefficient of determination (R^2) values it can be concluded that overall the Langmuir isotherm model illustrated the best fit of the adsorption of both Pb(II) and Cd(II) onto Bree untreated while the Freundlich isotherm model better fits the adsorption of Pb(II) and Cd(II) onto Bree treated.

TABLE I: LANGMUIR ISOTHERM CONSTANTS FOR LEAD REMOVAL

Lead Removal	**Langmuir isotherm**		
Adsorbent	q_{max} **(mg/g)**	**K_L(l/mg)**	R^2
Bree untreated	25.25	0.06	0.9905
Bree treated	58.82	0.16	0.9700

TABLE II: LANGMUIR ISOTHERM CONSTANTS FOR CADMIUM REMOVAL

Cadmium Removal	**Langmuir isotherm**		
Adsorbent	q_{max} **(mg/g)**	**K_L(l/mg)**	R^2
Bree untreated	19.76	0.05	0.9945
Bree treated	40.49	0.07	0.9822

TABLE III: FREUNDLICH ISOTHERM CONSTANTS FOR LEAD ADSORPTION

Lead Removal	**Freundlich isotherm**		
Adsorbent	**n**	K_F **(mg/g)**	R^2
Bree untreated	1.82	2.29	0.9211
Bree treated	1.41	8.25	0.9825

TABLE IV: FREUNDLICH ISOTHERM CONSTANTS FOR CADMIUM ADSORPTION

Cadmium Removal	**Freundlich isotherm**		
Adsorbent	**n**	K_F **(mg/g)**	R^2
Bree untreated	2.05	2.11	0.9272
Bree treated	1.72	3.48	0.9848

A kinetic study was performed to predict the removal rate of lead and cadmium and to determine the capacity of the adsorbents. The values of the kinetic parameters are illustrated in Tables 5 and 6. The constants of the pseudo-first-order model were not determined due to the very weak fit of this model to the adsorption behaviour of both lead and cadmium as illustrated by Figures 9 and 10. The good fit of the pseudo-second-order model to the adsorption behaviour of both lead and cadmium are illustrated in Figure 11. This good fit and the obtained values of R^2 for both adsorbents and metals, indicate that the pseudo-second-order model is suitable for the prediction of the adsorption behaviour. The calculated adsorption capacities of the pseudo-second-order model are very close to the experimental obtained ones as depicted in Tables 5 and 6. This implies that Pb(II) and Cd(II) removal occurs through a chemisorption mechanism [40, 49]

TABLE V: PSEUDO- SECOND-ORDER KINETIC MODEL PARAMETERS FOR LEAD ADSORPTION

	Pseudo-second-order kinetics			
Adsorbent	q_e(exp) (mg/g)	q_e(cal) (mg/g)	k_2 (g/mg.min)	R^2
Bree untreated	17.88	18.38	0.01	0.9997
Bree treated	24.08	24.57	0.01	0.9999

TABLE VI: PSEUDO-SECOND-ORDER KINETIC MODEL PARAMETERS FOR CADMIUM ADSORPTION

	Pseudo-second-order kinetics			
Adsorbent	q_e(exp) (mg/g)	q_e(cal) (mg/g)	k_2 (g/mg.min)	R^2
Bree untreated	14.28	14.47	0.04	0.9999
Bree treated	21.27	21.93	0.01	0.9995

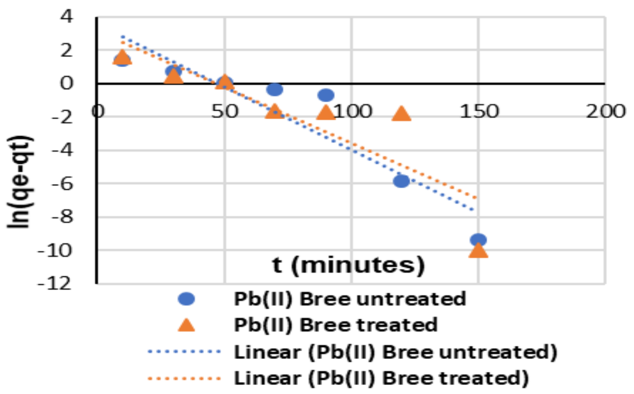

Fig 9: Validation of Pseudo-first-order model for lead adsorption

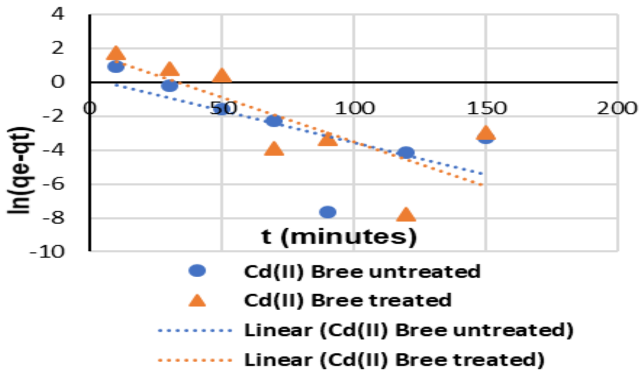

Fig 10: Validation of Pseudo-first-order model for cadmium adsorption

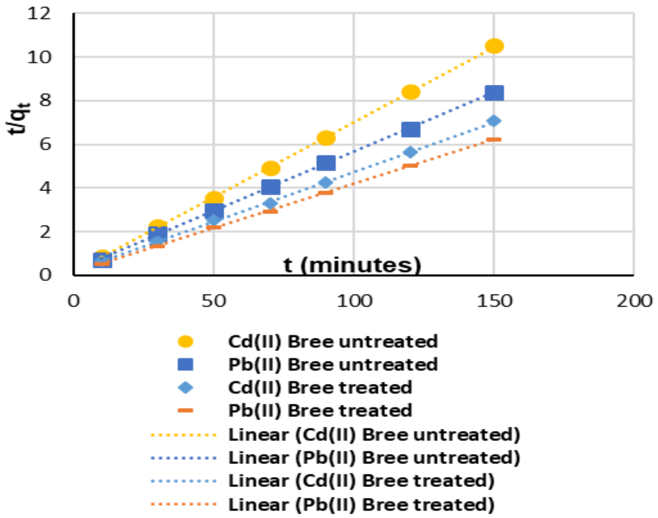

Fig 11: Validation of Pseudo-second-order model

5) *Thermodynamic study*

The effect of temperature at 25, 35, 45 and 55 ℃ was determined on the adsorption of Pb and Cd by raw and treated brewery waste. It was found that the adsorption of both metals increased with an increase in temperature. The following equation was used to calculate the thermodynamic parameters such as Gibbs free energy (ΔG°, kJ/mol), change in enthalpy (ΔH°, kJ/mol) and change in entropy (ΔS°, J/mol.K):

$$\ln K_a = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (6)$$

with K_a(q_e/C_e) as the equilibrium constant, T as the temperature (K) of the solution and R as the universal gas constant (8.314×10^{-3} kJ/mol,K). A plot of $\ln K_a$ versus 1/T resulted in obtaining of the $\Delta H^0$and ΔS^0 values. The obtained values are shown in Tables 7 and 8. The negative values of ΔG^0obtained for the adsorption performance of Bree treated, indicate the presence of spontaneous adsorption and the positive values of ΔH^0 corresponds to an endothermic nature of the adsorption process [50;51]. The positive values of ΔG^0 obtained for adsorption of both metal ions with Bree untreated are due to the relatively low removal efficiency experienced with Bree untreated as adsorbent and the adsorption is thus not spontaneous.

TABLE VII: THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF LEAD

Lead removal adsorbent	Ka	Temperature (K)	ΔG (kJ/mol)	DS (J/mol.K)	DH (kJ/mol)
Bree untreated	0.54	298.15	1.55	45.93	15.13
	0.73	308.15	0.82		
	0.85	318.15	0.44		
	0.94	328.15	0.16		
Bree treated	5.07	298.15	-4,03	25.44	3.55
	5.39	308.15	-4,31		
	5.55	318.15	-4,53		
	5.81	328.15	-4,8		

TABLE VIII: THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF CADMIUM

Lead removal adsorbent	Ka	Temperature (K)	ΔG (kJ/mol)	DS (J/mol.K)	DH (kJ/mol)
Bree untreated	0.32	298.15	2.81	64.37	21.81
	0.51	308.15	1.71		
	0.63	318.15	1.21		
	0.73	328.15	0.87		
Bree treated	1.25	298.15	-0,55	38.74	10.99
	1.46	308.15	-0,97		
	1.65	318.15	-1,32		
	1.88	328.15	-1,72		

IV. CONCLUSION

In this study, the performance of organic waste (brewery waste) was investigated on the removal of Pb and Cd from water. It was demonstrated throughout this study that brewery waste modification with SDS treatment enhanced the performance of raw brewery waste as adsorbent for both Pb and Cd removal. It can be concluded that the high removal efficiencies of treated brewery waste can validate the additional costs of pre-treatment with SDS. This study also showed that both raw and treated brewery waste have higher removal capabilities for Pb than Cd. From this it can be concluded that the affinity of brewery waste for Pb(II) are greater than that of Cd(II).

An increase in initial metals concentration in the solution increased the amount of Pb(II) and Cd(II) adsorbed onto the adsorbents which was observed as a continuous increase in adsorption capacity. The batch studies revealed that the Freundlich isotherm model explains the adsorption of Pb(II) and Cd(II) onto treated brewery waste, while the Langmuir Isotherm model describes the adsorption of both metals onto raw brewery waste. Thus, the adsorption of metals on the treated brewery waste occurs on several layers, while in the case of untreated brewery waste it occurs only on one layer. The pseudo-second-order model was the suitable model to predict the adsorption capacity of the adsorbents and confirmed the higher performance of treated brewery waste versus untreated brewery waste.

The adsorption process was found to be endothermic of nature, confirming a chemisorption mechanism. The adsorption onto raw brewery waste was not spontaneous in contrast to the spontaneous adsorption of the metals onto treated brewery waste, which further amplifies the importance of pre-treatment with SDS.

From the obtained results, it can be concluded that low-cost and abundantly available organic waste, brewery waste, adsorbents can be used to remove Pb and Cd effectively.

ACKNOWLEDGMENT

M. Leamy thanks Prof. E. Fosso-Kaneu for the guidance and support, he is a wonderful person and excellent study leader.

REFERENCES

[1] Ayangbenro, A.S. & Babalola, O.O. 2017. A New Strategy for Heavy Metal Polluted Environments: A Review of Microbial Biosorbents. *International Journal of Environmental Research and Public Health*, 14(1):94. https://doi.org/10.3390/ijerph14010094

[2] Volesky, B. & Naja, G. 2007. Biosorption technology: starting up an enterprise. *International Journal of Technology Transfer and Commercialisation*, 6(2-4):196-211. https://doi.org/10.1504/IJTTC.2007.017806

[3] E. Fosso-Kankeu, A. Mulaba-Bafubiandi, B.B. Mamba, T.G. Barnard, Indigenous microorganism strains as bio-extractants of Ca, Fe and Mg from metallurgical and mine drainages. The Southern African Institute of Mining and Metallurgy, Hydrometallurgy Conference 2009. Symposium Series S54, pp 93-100, 2009.

[4] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, B.B. Mamba, L. Marjanovic, and T.G. Barnard, Optimising the removal by b subtilis and b bacterium of metals found around mining areas: evaluation of the effect of physical and physiological parameters. In: Water Institute of Southern Africa & International Mine Water Association: Proceedings, International Mine Water Conference. International Mine Water Association Conference, Pretoria 2009. ISBN: 978-0-9802623-5-3. 2009.

[5] E. Fosso-Kankeu, A. Mulaba-Bafubiandi, B.B. Mamba, T.G. Barnard, Mitigation of Ca, Fe, and Mg loads in surface waters around mining areas using indigenous microorganism strains. Journal of Physics and Chemistry of the Earth, Vol. 34, pp. 825-829, 2009. https://doi.org/10.1016/j.pce.2009.07.005

[6] E. Fosso-Kankeu, A. Mulaba-Bafubiandi, B.B. Mamba, L. Marjanovic, T.G. Barnard, A comprehensive study of physical and physiological parameters that affect biosorption of metal pollutants from aqueous solutions. Journal of Physics and Chemistry of the Earth, Vol. 35, pp. 672-678, 2010. https://doi.org/10.1016/j.pce.2010.07.008

[7] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, G. Tlou and L. Piater, The next step in the bioremediation of heavy metal polluted water: Development of suitable microbial-sorbent. International Mine Water Conference, October 2012 Bunbury-Australia (**Award Winning Paper**). Editors, McCullogh, Lund and Wyse. ISBN: 978-0-7298-0707-4. Pp. 593-599, 2012.

[8] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, T.G. Barnard, Effective desorption of metals from loaded biomass using response surface methodology based on Box-Behnken design. International Mine Water Conference, October 2012 Bunbury-Australia. Editors, McCullogh, Lund and Wyse. ISBN: 978-0-7298-0707-4. Pp586-592, 2012.

[9] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, T.G. Barnard, P. Campana, Indirect implication of bacterial proteins in the biouptake of metals from aqueous solution. – In: Brown, A.; Figueroa, L. & Wolkersdorfer, Ch.: Reliable Mine Water Technology (Vol II). – p. 843 – 849; ISBN: 978-0-615-79385-6-Volume 2, Denver, Colorado, USA (Publication Printers). 2013.

[10] E. Fosso-Kankeu, L. Simelane, Kinetic study of methylene blue removal by Gram-negative and Gram-positive bacteria. International Multi-conference on Education, Law, Environment and Metallurgical Engineering (IMELEME' 2013); 27-28 November 2013, Johannesburg-South Africa. **(Award Winning Paper)**. Editors: Sandhu S and Muzenda E. ISBN: 978-93-82242-50-5. 2013.

[11] E. Fosso-Kankeu, F. Waanders, Metal Ions Adsorption Affinity of Clay Materials from the North West Province of South Africa. An Interdisciplinary Response to Mine Water Challenges. International Mine Water Conference, August 2014 Xuzhou China. Editors, Sui, Sun & Wang (Eds). 2014 China University of Mining andTechnology Press, Xuzhou, ISBN: 978-7-5646-2437-8. Pp374-378. 2014.

[12] F. Waanders, M. Nel, E. Fosso-Kankeu, Adsorption potential of bentonite clay and attapulgite applied for the desalination of sea water. 6th International Conference on Green Technology, Renewable Energy and Environmental Engineering (ICGTREEE'2014). 27-28 November 2014, Cape Town-South Africa. Editors: Muzenda E. and Sandhu S. ISBN: 978-93-84468-08-8. Pp 275-279. 2014.

[13] E. Fosso-Kankeu, F. Waanders, M. Reitz, Selective adsorption of heavy and light metals by natural zeolites. 6th International Conference on Green Technology, Renewable Energy and Environmental Engineering (ICGTREEE'2014). 27-28 November 2014, Cape Town-South Africa.

(**Award Winning Paper**). Editors: Muzenda E. and Sandhu S. ISBN: 978-93-84468-08-8. Pp 271-274. 2014.

[14] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, Implication of plants and microbial metalloproteins in the bioremediation of polluted waters. Journal of Physics and Chemistry of the Earth. Vol. 67-69, 242-252, 2014. https://doi.org/10.1016/j.pce.2013.09.018

[15] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, Challenges in the escalation of metal-biosorbing processes for water treatment: applied and commercialized technologies. African Journal of Biotechnology. Vol. 13, no. 17, pp. 1756-1771, 2014. https://doi.org/10.5897/AJB2013.13311

[16] Abdul-Wahab, S. & Marikar, F. 2012. The environmental impact of gold mines: pollution by heavy metals. *Open Engineering*, 2(2):304-313. https://doi.org/10.2478/s13531-011-0052-3

[17] Mani, D. & Kumar, C. 2014. Biotechnological advances in bioremediation of heavy metals contaminated ecosystems: an overview with special reference to phytoremediation. *International Journal of Environmental Science and Technology*, 11(3):843-872. https://doi.org/10.1007/s13762-013-0299-8

[18] Ozdes, D., Gundogdu, A., Kemer, B., Duran, C., Senturk, H.B. & Soylak, M. 2009. Removal of Pb (II) ions from aqueous solution by a waste mud from copper mine industry: equilibrium, kinetic and thermodynamic study. *Journal of hazardous materials*, 166(2-3):1480-1487. https://doi.org/10.1016/j.jhazmat.2008.12.073

[19] Sekhula, K.S. 2010. CADMIUM AND COPPER BIOSORPTION BY A BACTERIAL STRAIN ISOLATED FROM SOUTH AFRICAN ANTIMONY MINE. *UNIVERSITY OF LIMPOPO*.

[20] Volesky, B. 2001. Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy*, 59(2-3):203-216. https://doi.org/10.1016/S0304-386X(00)00160-2

[21] Kitagawa, T., Nishikawa, Y., Frankenfeld, J. & Li, N. 1977. Wastewater treatment by liquid membrane process. *Environmental Science & Technology*, 11(6):602-605. https://doi.org/10.1021/es60129a008

[22] Gupta, R., Ahuja, P., Khan, S., Saxena, R. & Mohapatra, H. 2000. Microbial biosorbents: meeting challenges of heavy metal pollution in aqueous solutions. *Current science*:967-973.

[23] Johnson, D.B. & Hallberg, K.B. 2005. Acid mine drainage remediation options: a review. *Science of the total environment*, 338(1-2):3-14. https://doi.org/10.1016/j.scitotenv.2004.09.002

[24] Ramla, B. & Sheridan, C. 2015. The potential utilisation of indigenous South African grasses for acid mine drainage remediation. *Water SA*, 41(2):247-252. https://doi.org/10.4314/wsa.v41i2.10

[25] Mashangwa, T.D. 2016. An investigation into the efficacy of eggshells as a low-cost adsorbent for the removal of potentially toxic inorganic elements from aqueous solutions.

[26] Amer, H.A.T. 2016. Removal of lead from industrial wastewater using a low-cost waste material.

[27] Ahmaruzzaman, M. 2011. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in colloid and interface science*, 166(1-2):36-59. https://doi.org/10.1016/j.cis.2011.04.005

[28] Bonilla-Petriciolet, A., Mendoza-Castillo, D.I. & Reynel-Ávila, H.E. 2017. Adsorption processes for water treatment and purification: Springer. https://doi.org/10.1007/978-3-319-58136-1

[29] Aliyah, N.A. 2012. Adsorption of lead using rice husk. UMP.

[30] Hossain, M.A. 2013. Development of novel biosorbents in removing heavy metals from aqueous solution.

[31] Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical society*, 40(9):1361-1403. *https://doi.org/10.1021/ja02242a004*

[32] Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y.-H., Indraswati, N. & Ismadji, S. 2009. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *Journal of hazardous materials*, 162(2-3):616-645. https://doi.org/10.1016/j.jhazmat.2008.06.042

[33] Unagolla, J. & Adikary, S. 2015. Adsorption of cadmium and lead heavy metals by chitosan biopolymer: A study on equilibrium isotherms and kinetics. (*In*. Moratuwa Engineering Research Conference (MERCon), 2015 organised by: IEEE. p. 234-239).

[34] Sekhula, K.S. 2010. CADMIUM AND COPPER BIOSORPTION BY A BACTERIAL STRAIN ISOLATED FROM SOUTH AFRICAN ANTIMONY MINE. *UNIVERSITY OF LIMPOPO*.

[35] Feng, N., Guo, X. & Liang, S. 2009. Adsorption study of copper (II) by chemically modified orange peel. *Journal of Hazardous Materials*, 164(2-3):1286-1292. https://doi.org/10.1016/j.jhazmat.2008.09.096

[36] Namasivayam, C. & Kavitha, D. 2006. IR, XRD and SEM studies on the mechanism of adsorption of dyes and phenols by coir pith carbon from aqueous phase. *Microchemical Journal*, 82(1):43-48. https://doi.org/10.1016/j.microc.2005.07.002

[37] Cheraghi, E., Ameri, E. & Moheb, A. 2015. Adsorption of cadmium ions from aqueous solutions using sesame as a low-cost biosorbent: kinetics and equilibrium studies. *International journal of environmental science and technology*, 12(8):2579-2592. https://doi.org/10.1007/s13762-015-0812-3

[38] Viana, R.B., Da Silva, A.B. & Pimentel, A.S. 2012. Adsorption of sodium dodecyl sulfate on Ge substrate: the effect of a low-polarity solvent. *International journal of molecular sciences*, 13(7):7980-7993. https://doi.org/10.3390/ijms13077980

[39] Prabha, R. & Udayashankara, T. 2014. Removal of heavy metal from synthetic wastewater using Rice husk and Groundnut shell as adsorbents. *J. Environ. Sci. Tox & Fo. Techno*, 8:7.

[40] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, B.B. Mamba and T.G. Barnard, Prediction of metal-adsorption behaviour in the remediation of water contamination using indigenous microorganisms. Journal of Environmental Management. Vol. 92, no. 10, pp. 2786-2793, 2011. https://doi.org/10.1016/j.jenvman.2011.06.025

[41] H. Mittal, E. Fosso-Kankeu, Shivani B. Mishra, Ajay K. Mishra, Biosorption potential of Gum ghatti-g-poly (acrylic acid) and susceptibility to biodegradation by B. subtilis. International Journal of Biological Macromolecules. Vol. 62, pp. 370-378, 2013. https://doi.org/10.1016/j.ijbiomac.2013.09.023

[42] E. Fosso-Kankeu, H. Mittal, S.B. Mishra, A.K. Mishra, Gum ghatti and acrylic acid based biodegradable hydrogels for the effective adsorption of cationic dyes. Journal of Industrial and Engineering Chemistry. Vol. 22, pp. 171-178, 2015. https://doi.org/10.1016/j.jiec.2014.07.007

[43] E. Fosso-Kankeu, H. Mittal, F. Waanders, I.O. Ntwampe, S.S. Ray, Preparation and characterization of gum karaya hydrogel nanocomposite flocculant for metal ions removal from mine effluents. International Journal of Environmental Science and Technology. Vol. 13, pp. 711-724, 2016. https://doi.org/10.1007/s13762-015-0915-x

[44] E. Fosso-Kankeu, F. Waanders, E. Maloy, Copolymerization of ethyl acrylate onto guar gum for the adsorption of Mg(II) and Ca(II) ions. Desalination and Water Treatment. doi: 10.1080/19443994.2016.1165147: pp. 1-10, 2016.

[45] E. Fosso-Kankeu, F. Waanders, C.L. Fourie, Adsorption of Congo Red by surfactant-impregnated bentonite clay. Desalination and Water Treatment. doi: 10.1080/19443994.2016.1177599: pp. 1-9, 2016.

[46] E. Fosso-Kankeu, A.F. Mulaba-Bafubiandi, L.A. Piater, M.G. Tlou, Cloning of the cnr operon into a strain of Bacillaceae bacterium for the development of a suitable biosorbent. World Journal of Microbiology and Biotechnology. DOI 10.1007/s11274-016-2069-5. 2016.

[47] E. Fosso-Kankeu, H. Mittal, F. Waanders, S.S. Ray, Thermodynamic properties and adsorption behaviour of hydrogel nanocomposites for cadmium removal from mine effluents. Journal of Industrial and Engineering Chemistry. Vol. 48, pp. 151-161, 2017. https://doi.org/10.1016/j.jiec.2016.12.033

[48] E. Fosso-Kankeu, F.B. Waanders, F.W. Steyn, Removal of Cr(VI) and Zn(II) from an aqueous solution using an organic-inorganic composite of bentonite-biochar-hematite. Desalination and Water Treatment. Vol. 59, pp. 144-153, 2017.

[49] E. Fosso-Kankeu, 2018. Synthesized af-PFCl and GG-g-P(AN)/TEOS hydrogel composite used in hybridized technique applied for AMD treatment. Journal of Physics and Chemistry of the Earth. 2018.

[50] Abdelghani, N. T., & Elchaghaby, G. A. (2014). biosorption for metal ions removal from aqueous solutions: a review of resent studis, Journal of Latest Research in Science and Technology 3(1), 24–42.

[51] Y. Onal, C. Akmilbasar, D. Eren, C. Sariciozdemir, T. Depci, Adsorption kinetics of malachite green onto activated carbon prepared from Tunc¸bilek lignite, J. Hazard. Mater. 128 (2006) 150–157. https://doi.org/10.1016/j.jhazmat.2005.07.055

[52] A.D. Hiwarkar, V.C. Srivastava, I.D. Mall, Comparative studies on adsorptive removal of indole by granular activated carbon and bagasse fly ash, Environ. Progr. Sustain. Energy 34(2) (2015) 492–503. https://doi.org/10.1002/ep.12025