

Research Article

Biosorption of toxic metals from leachate using *Pleurotus pulmonarius*

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Abstract

The biosorption of Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} by *Pleurotus pulmonarius* from municipal open solid waste leachate was investigated to evaluate its effectiveness for removing toxic metals. The composite leachate samples were analyzed for some physicochemical parameters. The results were obtained as colour, smell, pH, total solids, total volatile solids, suspended solids, total dissolved solids, COD, BOD_5 , COD/ BOD_5 ratio are light brown, Malodorous, 7.79 ± 0.02 , 5993 ± 33.0 mg/L, 228 ± 8.5 mg/L, 887 ± 6.5 mg/L, 12168 ± 22.1 mg/L, 868 ± 0.12 mg O_2 /L, 373 ± 0.002 mg O_2 /L and 0.43, respectively while the toxic metals in the leachate were determined using AAS and their concentrations (mg/g) for Pb, Ni, Co, Cr and Cd were 0.461 ± 0.0010 , 0.0845 ± 0.0004 , 0.2045 ± 0.0009 , 0.5211 ± 0.0011 and 0.1565 ± 0.0010 respectively. The biosorbent was modified and its physico-chemical properties were determined by measuring the bulk density (356.33 kg/m³), surface area (27.75 m²/g), total pore volume (0.0213 cm³/g) and pore size (1.187 nm), pH (7.32), point of zero charge pH_{pzc} (6.40). The SEM analysis showed some cylindrical pores of various sizes on the surface of the biosorbent. The FTIR spectroscopic analysis showed the following functional groups were on its surfaces O-H, N-H, C-H, C=N, N=N, C=C, H-O-H, C=O, C-CH₃, S-O, -NH₂ and C-O. Proximate analysis of biosorbent showed that crude protein content was ($15.75 \pm 0.04\%$), moisture content ($2.65 \pm 0.01\%$), crude lipid ($10.35 \pm 0.06\%$), ash content ($7.32 \pm 0.01\%$), crude fibre (6.60 ± 0.0 %) and carbohydrate ($57.33 \pm 0.02\%$). The effect of contact time, initial toxic metal ion, pH, biosorbent dosage, temperature were carried out in batches mode. The experimental data were tested with eight experimental models. The thermodynamic experiments were also conducted. The results from the biosorption studies proved that the biosorbent can be an effective, alternative low-cost biosorbent for the removal of toxic metal ions from leachate.

Keywords: Biosorption; Leachate; Toxic metals; Biosorbent.

Introduction

The continuous increase in the use of toxic metals over the years has inevitably resulted in an increased flux of metallic substances in aquatic environment. Toxic metals are those metallic elements that have a relatively high density and are toxic or poisonous even at low concentration. Toxic metals in general, applies to the group of metals and metalloids with atomic density greater than 4 g/cm³, or 5 times or more, greater than water [1]. Toxic metals include Pb, Cd, Ni, Co, Fe, Zn, Cr, As, Ag and the Pt group elements. Toxic metals are largely found naturally in dispersed form in rock formations. Industrialization and urbanization have increased the anthropogenic contribution of toxic metals in biosphere [2]. Some of the toxic metal such as Cd, Hg and As are strongly

poisonous to metal-sensitive enzymes, resulting in growth inhibition and death of organisms [3]. Toxic metal pollution can originate from natural and anthropogenic sources. Activities such as mining, smelting operation, industrial effluent and agriculture (fertilizer and pesticide), waste, domestic effluents, agricultural runoff/fungicides, acid rain, solid waste leachates etc have all contributed to some extent to the toxic metal loads in the water bodies [4, 5].

Makurdi is the capital of Benue State, Nigeria which is currently experiencing the problem of municipal waste management, principally as a result of unplanned development, rural-urban migration and natural increase within the city [6].

Generally in Makurdi metropolis, municipal open solid waste (MOSW) is disposed of in open areas without taking proper precautions or operational controls. Therefore, municipal open solid waste generates leachate which is one of the major environmental problems of water treatment plants [7]. The municipal authorities in Benue State, Benue State Environmental Sanitation Agency (BENSESA) subsequently convey those solid wastes to a common open dumping ground at the outskirts or within the town. Despite the attempts at waste avoidance, reduction, reuse and recovery, open dumpsites are still the principal focus for ultimate disposal of residual wastes and incineration residues world-wide. The placement and compaction of municipal wastes in open site facilitates the development of facultative and anaerobic conditions that promotes biological decomposition of open dump solid wastes. Hence, leachates of diverse composition are produced, depending on site construction and operational practices, age of the open dump solid waste, climatic and hydrogeological conditions and surface water ingress into the solid waste. Leachates from these open solid waste dumps migrate vertically and laterally into the environment by direct discharge into River Benue serving many communities around and far away from the open dump sites. The open-dump solid waste leachates containing pollutants are introduced into the ecosystems without treatment. This has resulted in the release of obnoxious gases and toxic metals into the environment [8].

The realization of the polluting effects of open solid waste leachates on the environment has prompted a number of studies. These include studies on domestic wastes, leachate quality, as well as underground water quality. For treatment however, neutralisation, chemical treatment, gravel filtration, waste stabilisation pond and constructed wetlands, among other strategies are been investigated in order to develop a cost effective and sustainable method of treatment of toxic metals from leachates at the open dump site [9].

One of the most serious threats today is the toxic metal pollution that occurs in the aquatic systems. Most of the pollutants present in leachate possess a significant threat to both environment and public health as they contain

xenobiotics and toxic metals which are non-biodegradable and persistent. The need for economical and effective methods for removing or reducing toxic metals from wastewater such as leachates has therefore resulted in the search for other materials that may be useful in reducing the levels of toxic metals in the leachate. Existing conventional technologies such as ion exchange resin, solvent extraction, electrolytic and precipitation processes, electro dialysis, membrane technology, granular activated carbon to reverse osmosis are used for toxic metal removal from wastewaters are costly [10]. These processes are however, not economically feasible for small scale industries prevalent in developing economies due to large capital investment. Since most of these conventional technologies are neither effective nor economical, especially when used for the reduction of toxic metal ions to low concentrations, new separation methods are required to reduce toxic metal concentrations to environmentally acceptable levels at affordable cost [11].

Biosorption processes has emerged as promising eco-friendly technology for the removal and recovery of metal ions from aqueous solutions in water pollution control [12]. The major advantages of biosorption over conventional treatment methods include low operating cost, no production of secondary compounds, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, regeneration of biosorbent, possibility of metal recovery, environmentally friendly etc.

The use of biological materials as a biosorbent for the removal of toxic metal ions has been reported by Eneji [13]. Biosorption of toxic metals using biosorbents have been reported by Pandey [14]. Studies have shown that macrofungus was represented as a good potential material for remediation of wastewaters containing toxic metal ions. But there are no reports on the use of dry *Pleurotus pulmonarius* as a potential biosorbent for the removal of toxic metals from leachate. The use of *Pleurotus pulmonarius* as a biosorbent is considered to be ideal for the purpose of evaluation as biosorption of toxic metals ions [15]. The aim of the study was to investigate the biosorption potential of using dry *Pleurotus pulmonarius* as a biosorbent

for the removal of Cr^{6+} , Cd^{2+} , Ni^{2+} , Co^{2+} and Pb^{2+} from leachate in Makurdi municipal open solid waste.

Materials and methods

Materials

The materials used in this study include reagents/chemicals that were supplied by May and Baker Limited Dagenham England which were of analytical grade and used without further purification. These include $\text{Pb}(\text{NO}_3)_2$, CoCl_2 , NiSO_4 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$. The reagents used are; Concentrated H_2SO_4 , CuSO_4 , KMnO_4 , sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), Manganese sulphate, alkali-iodide, $\text{Na}_2\text{S}_2\text{O}_3$, NaOH , HCl and NaCl . Distilled-deionized water was used for their preparation and dilution of all solutions. Others are dry *Pleurotus pulmonarius* biosorbent, leachate etc. The apparatus used were volumetric flasks, evaporating dish, thermostat water bath, filter paper, beakers, conical flasks, sieve, mortar and pestle. The instruments used were oven, Fourier Transform Infrared (FTIR) spectrophotometer, digital JENWAY pH meter (Model 3310), digital weighing balance, thermometer, Atomic Absorption Spectrophotometer etc. All the glassware used in the present study are Borosil grade. They were cleaned by soaking them in a detergent solution first and then in nitric acid (10%) for 48 h. These were then rinsed with distilled water prior to use.

Methods

Preparation of biosorbate Solutions

Distilled-deionized water was used for their preparation of biosorbate Solutions and dilution of all solutions using dilution principles.

Chromium solution

Exactly 2.0 g of $\text{K}_2\text{Cr}_2\text{O}_7$ was weighed and dissolved in 100 cm^3 distilled water in a beaker and the solution was transferred to 1000 cm^3 volumetric flask and finally making up to the mark with a concentration of 1000 mg/L. The solution was homogenized and kept for use.

Lead solution

Exactly 2.3 g of anhydrous $\text{Pb}(\text{NO}_3)_2$ was weighed and dissolved in 100 cm^3 distilled water in a beaker and the solution was transferred to 1000 cm^3 volumetric flask and finally making up

to the mark with a concentration of 1000 mg/L. The solution was homogenized and kept for use.

Cadmium solution

Exactly 2.1 g of crystallized $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was weighed and dissolved in 100 cm^3 distilled water in a beaker and the solution was transferred to 1000 cm^3 volumetric flask and finally making up to the mark with a concentration of 1000 mg/L. The solution was homogenized and kept for use.

Nickel solution

Exactly 1.05 g of anhydrous NiSO_4 was weighed and dissolved in 100 cm^3 distilled water in a beaker and the solution was transferred to 1000 cm^3 volumetric flask and finally making up to the mark with a concentration of 1000 mg/L. The solution was homogenized and kept for use.

Colbalt solution

Exactly 1.2 g of anhydrous CoCl_2 was weighed and dissolved in 100 cm^3 distilled water in a beaker and the solution was transferred to 1000 cm^3 volumetric flask and finally making up to the mark with a concentration of 1000 mg/L. The solution was homogenized and kept for use.

Spiking of biosorbate Solutions with Leachate

Chromium solution spiked with leachate

A mixture of Chromium Cr(VI) solution and leachate were prepared by transferring 100 cm^3 of 1000 mg/L of $\text{K}_2\text{Cr}_2\text{O}_7$ solution into a 1000 cm^3 volumetric flask containing 900 cm^3 of leachate. Then homogenized and kept for use.

Lead solution spiked with leachate

A mixture of $\text{Pb}(\text{NO}_3)_2$ solution and leachate were prepared by transferring 100 cm^3 of 1000 mg/L of $\text{Pb}(\text{NO}_3)_2$ solution into a 1000 cm^3 volumetric flask containing 900 cm^3 of leachate. Then homogenized and kept for use.

Cadmium solution spiked with leachate

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution and leachate were prepared by transferring 100 cm^3 of 1000 mg/L of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution into a 1000 cm^3 volumetric flask containing 900 cm^3 of leachate. Then homogenized and kept for use.

Nickel solution spiked with leachate

A mixture of NiSO_4 solution and leachate were prepared by transferring 100 cm^3 of 1000 mg/L of NiSO_4 solution into a 1000 cm^3 volumetric flask

containing 900 cm³ of leachate. Then homogenized and kept for use.

Colbalt solution spiked with leachate

A mixture of CoCl₂ solution and leachate were prepared by transferring 100 cm³ of 1000 mg/L of CoCl₂ solution into a 1000 cm³ volumetric flask containing 900 cm³ of leachate. Then homogenized and kept for use.

Preparation and Characterization of biosorbent

The biosorbent was sun-air dried for three consecutive days, pounded into tiny pieces, sieved through a mesh of particle size >0.4 mm, stored in air tight glass container and was used throughout the study as a biosorbent [16]. The biosorbent was characterized using standard methods. The bulk density was determined by methods adopted from Agnew and Leonard [17], pH was adopted from AWWA [18], The point of zero charge was determined using the pH drift method, Scanning electron microscope was determined by methods adopted from Boldizar [19]. The FTIR spectra were recorded using the transmittance method, the toxic metals were determined using AAS, the proximate composition of the biosorbent was determined by Standard Official Methods of Analysis of the AOAC [20]. The moisture content, Total ash content, Crude fibre, crude protein content was determined by method 14:004, method 14:006, method 14:020, Microkjeldahl method and the total fat content was determined using Soxhlet extraction for 4 h starting with methanol and ethanol, respectively. The total percentage carbohydrate content was determined by the difference method as reported by Onyeike [21]. Biosorption parameters were conducted using batch experiments.

Statistical Analysis

The biosorption capacity was calculated using the mass balance as shown equation (1):

$$qe = C_0 - C_{eq} / M \times V \quad (1)$$

Percentage (%) biosorption was used for the estimation of biosorption efficiency.

Calculation of percentage efficiency of biosorbent = initial concentration (C₀) – final concentration (C_e) / initial concentration (C₀) x100.

where *qe* is the biosorption capacity i.e. the amount of toxic metal ion sorbed onto unit

amount of *Pleurotus pulmonarius* biosorbent (mg /g); C₀ and C_{eq} are the concentrations (mg/L) of Pb²⁺, Cr⁶⁺, Co²⁺, Ni²⁺, and Cd²⁺ in the initial leachate and concentration after biosorption respectively; c_t is the concentration at time t, V is the volume of the synthetic leachate and M is the weight of the biosorbent [22].

Error Analysis

Errors were analysed on all the measurements in the experiments done in triplicate. The arithmetic averages of the results were considered in data analysis using analysis of variance (ANOVA).

Results and discussions

Scanning Electron Microscope (SEM) analysis

SEM analysis gives the surface morphology of a biosorbent. The SEM micrographs of virgin biosorbent with a magnification of 1500x was presented in Fig. 1. However, the micrograph is different from the SEM of coal fly ash which is spherical with irregular shaped particles reported by Agay [23]. Mahmooda [24] investigated the SEM of dried dead *Aspergillus flavus* biomass and reported an irregular shape with different tiny pores on its surfaces. Boldizar [19] examined the morphological structure of biomass, SEM micrographs of *A. bisporus* taken before and after Cd (II) and Zn (II) biosorption the SEM micrograph of unloaded biosorbent indicates a smooth regular spherical structure of the macrofungus surface but after metal loading, some deformation and appearance of cavities onto the macrofungus surface were observed but the spherical form remains unmodified after metal loading. It is clear from the micrograph obtained from this study that the biosorbent has sufficient numbers of cylindrical pores of various lengths on the surface where the toxic metal ions may undergo interactions, be trapped and adsorbed easily.

Determination of proximate composition of the biosorbent

Moisture content

The moisture content (2.65±0.01 %) of *Pleurotus pulmonarius* obtained in this study (Table 1) was lower than 17.35± 0.83 % reported by Okwulehie [25]. Findings by Cheung [26] also revealed that the moisture contents are in the range of (1.4-44.0 %) in some edible mushrooms commonly used as food and

medicine. Taye [27] harvested *Pleurotus ostreatus* from *Alstonia congensis* had a moisture content of 21.06%, which was not significantly different from that of *P. florida* harvested from *A. congensis* (19.40%). The moisture content was at maximum at the immature stage irrespective of the substrate, and

decreased during further development of the mushroom [28]. The low moisture content of the mushrooms obtained in this work ($2.65 \pm 0.01\%$) is an indication that the fresh mushroom can be kept for a long time, as low water activity may not enhance microbial growth easily.

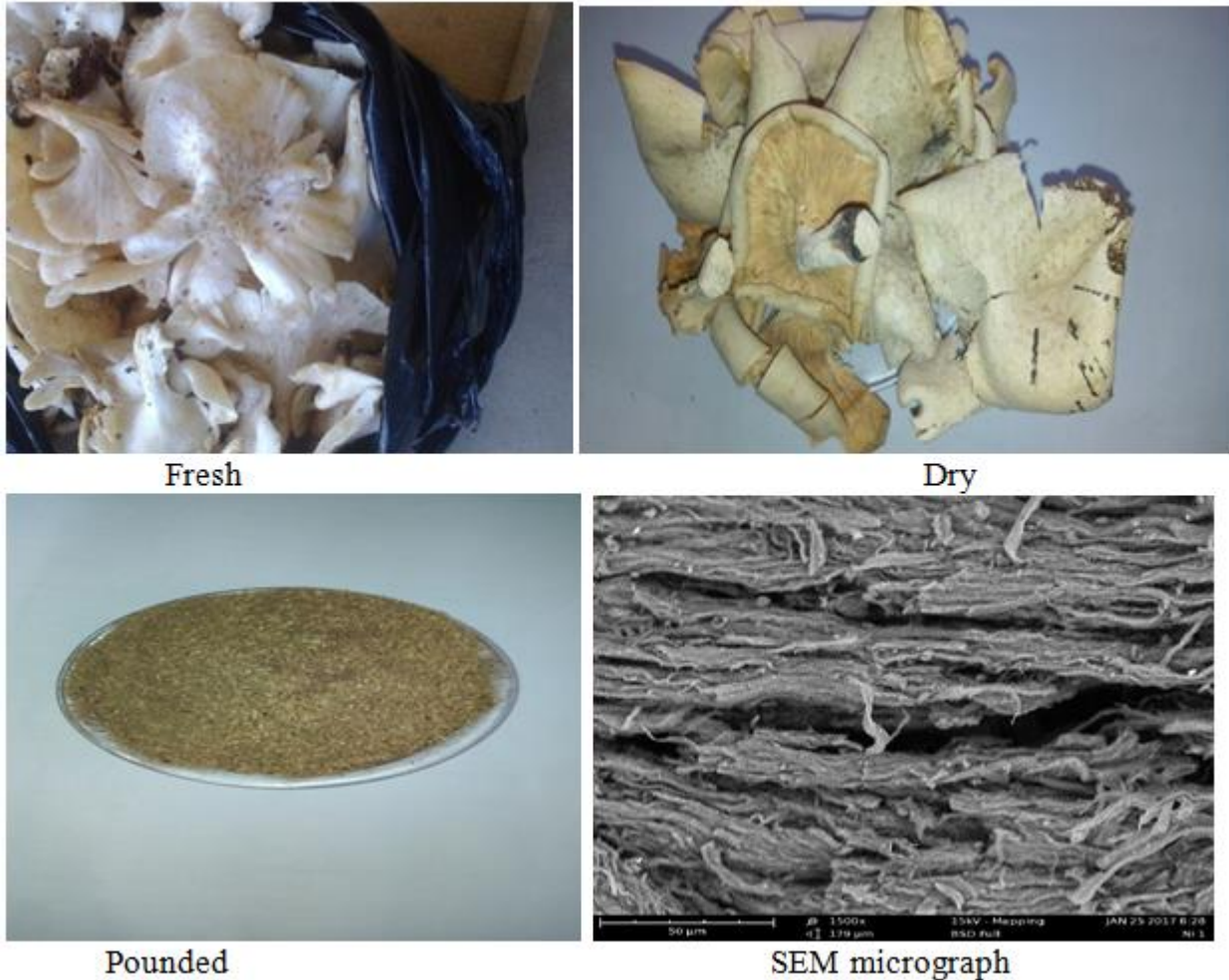


Fig. 1. Picture of fresh, dry, pounded and SEM micrograph of modified Biosorbent

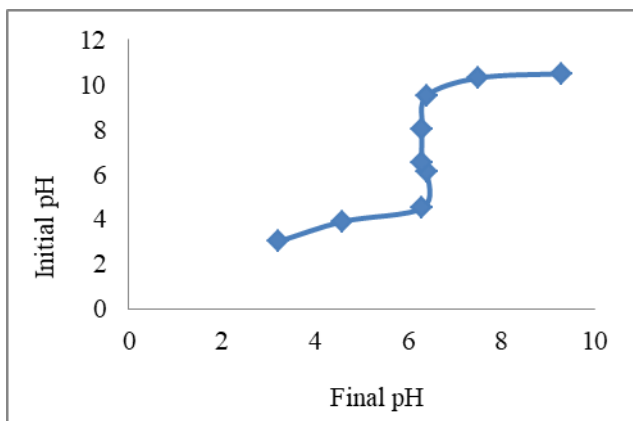


Fig. 2. The point of zero charge

Ash content

The mean ash content of *Pleurotus pulmonarius* $7.32 \pm 0.01\%$ obtained in this work was similar to the values presented by Adejumo [29], when

they worked with several species of *Pleurotus* grown in commercial substrate, obtained variation of 5.65 and 7.95 % of ash content. The value found were also lower than the ash content presented by Ibe [30], with $25.78 \pm 4.28\%$ which occur more in young fruiting bodies of *Volvariella volvacea*. The ash content showed an opposite trend, occurring more in matured fruit-bodies and less in young fruit-bodies irrespective of the substrate. The result is in variance with that of Kalmis [31], where young fruit-bodies contained ash content (5.35 %) which was more than the ash content (3.71 %) of matured ones.

Crude lipid

The fats content of *Pleurotus pulmonarius* was $10.35 \pm 0.06\%$ higher than the fat contents of cultivated *P. pulmonarius*, *P. florida* and *P.*

ostreatus which are in the range of 1.84 - 3.56 %, 1.04 - 3.96 % and 1.29 - 3.23 %, respectively reported by Taye [27] was similar to the results of Okwulehie [25] where they found out that fats was 2.31 % for *P. ostreatus* and 2.34 % for *P. pulmonarius*. The finding by Valverde [32] also revealed low fat contents in some edible mushrooms in the range of 1.0–4.3 % of dry weight. The low fat content of the mushroom shows that it has lower caloric food great for a diet that does not allow cholesterol and could be good for people with cardiac problems. The low value of fat content obtained in this study is in line with the report of Okhuoya and Okogbo [33] who maintained that mushrooms generally contain low-oil and fat, and because of the low content of oil and fat in mushrooms, they are recommended as good supplements for patients with cardiac problems.

Table 1. Proximate analysis of the biosorbent

Parameter	Mean values (%)
Moisture content	2.65±0.01
Ash content	7.20±0.01
Crude lipid	10.35±0.06
Crude protein	15.75±0.04
Crude fibre	6.60±0.01
Carbohydrate	57.33±0.02

Crude protein

The mean protein content obtained from this study was 15.75±0.04 % lower than the protein content reported by Adejumo [29, 25] of 23.63, 32.31 and 27.17±0.12 %, respectively. However, Okwulehie [25] presented the protein content of the biosorbent of 7.06± 0.10%. Protein content of the both fungi was high side with *P. pulmonarius* and *Pleurotus ostreatus* having the highest at 28.20±0.03 and 27.28 ± 0.02 %, respectively. The average protein content as recorded above falls in line with involving *Agaricus bisporus*, *Lentinula edodes* and *Pleurotus ostreatus* where protein content showed varying result but was averaged at 24%. Crude protein was found more in *Pleurotus ostreatus* (27.23%) than in *P. djom* (24.83%) [34]. Similarly, the protein content of four Nigeria mushrooms, *Auricularia auriculia*, *Pleurotus squarrosulus* *P. tuber-regium* and *Russula spp* ranged from 15 - 24.96 g/100g on dry matter basis was presented by Stamets [35]. *Pleurotus* and *Cortinarius* species are good

source of protein especially for vegetarian because this edible mushroom contains some essential amino acid for human intakes [36]. The digestibility of edible mushroom *Pleurotus* species proteins is as same as that of plants (90%) and comparable with meat (99%). According to Patil [37], the protein content stated as a percentage of a dry weight in mushrooms in general in range between 10 and 40 %, and varied extensively among and within the species. However, the average of protein content of *Pleurotus* is most common between 20 and 25%. The high protein contents of the *P. pulmonarius* fruit bodies cultivated on the various logs confirms the assertion by several workers that mushroom protein is intermediate between that of animals and vegetables, but superior to most other foods, including milk and contains all the nine essential amino acids required by man [38]. The low value of protein content obtain from this study may be as a result of the stages of maturation, availability of nitrogen content in the medium and the harvest location [39].

Crude fibre

The fibre content (6.60±0.01%) was similar with the values reported by Peter and Tolulope [16], Adejumo [29] and Okwulehie [25] of 6.8±0.07 %, (8.16, 5.97 %) and 7.71 ± 0.11%, respectively but lower than the percentages presented by Ibe [30] who worked with several *Pleurotus* species and obtained large variations in fibre content in their studies (13.64±0.59 % and 20.37±0.22 %.), respectively. The nutritional value of fibres of mushrooms is different. Major sources of fibre are cellulose and other un-digestible cell wall polymers. Although fibre is un-digestible, it has substantial nutritional role in human physiological processes [40].

Carbohydrate Content

The carbohydrate content was 57.33±0.02% which is consistence with the value (55.68±1.00) reported by FAMILONI [41] on some wild edible mushrooms. The value obtained in this study is higher than those reported by Colak [39], of 18.00±0.44% when he studied the nutrition from some mushrooms. Carbohydrates contribute around 50-60% of mushroom dry weight basis, which consists of various compounds: sugars (monosaccharides, disaccharide and oligosaccharides) and directly associated in synthesis process of polysaccharides (glycans)

[42]. Carbohydrates are mainly deposit in *P. ostreatus* as polysaccharides are represented by glycogen, indigestible fibre (cellulose, dietary fibres, chitin, α and β glucans) and other hemicelluloses (mannans, xylans and galactans) [43].

Physico-chemical Parameters of the Dry Biosorbent

pH

The pH of the dry biosorbent in water shown on Table 2 was 7.32 ± 0.05 which show that the biosorbent in water is slightly basic. At this pH, the biosorbent surface becomes more negative and the positively charged toxic metal ions undergo interactions due to electrostatic attraction. The pH of the biosorbent in this study is lower than the pH reported by Madu and Lajide, [44] of 8.90 obtained from activated Carbon derived from melon seed husk. However, the value is within the range of those reported for activated carbon which specifies a pH of 6-8 [45].

pH of Point of zero charge (pH pzc)

The pH of point of zero charge determination of biosorbent is important in elucidating biosorption mechanism. Biosorption of cations is favour at $\text{pH} > \text{pH}_{\text{PZC}}$, while anion biosorption is favoured at $\text{pH} < \text{pH}_{\text{PZC}}$. The plot of change in solution pH (ΔpH) versus initial pH (pH_i) showed that with increasing initial solution pH (Fig. 2), the pH change became more negative and the zero value of ΔpH was reached at pH_i value of 6.40, which is considered as the pH_{PZC} of the biosorbent. The obtained value is lower than the 5.0 for bagasse reported by Modak and Natarjan, [46] and similar to 6.91 of mansonia wood saw dust reported by Augustine and Yuh-Shan [47]. At pH 6.40, the charge of the biosorbent will be zero and above this pH, it will be negatively charged. So the increase in biosorption capacity of the biosorbent with increasing pH in the present study can be attributed to increase in electrostatic attractions between toxic metal ions and biosorbent [48]. The pH of the dry biosorbent in water was 7.32 ± 0.05 which is greater than pH_{pzc} of 6.40 indicate that the biosorption of cations is favoured.

Ash content

Ash content is the residue that remains when carbonaceous portion is burnt off and is considered as the impurity. It is an indication of the quality of the biosorbent and should be in the range of 2-10 % [49]. Good quality biosorbent should have low ash content [50]. Its high value indicates that the inherent carbon in the starting material is high [51]. The ash content of 7.4 ± 0.03 % was obtained in this work as shown in Table 2. The value is higher than the value (3.45 %) presented by Chang [52] on some mushrooms cultivation, nutritional value, medicinal effect, and environmental impact. The percentage ash content obtained in this work falls within the accepted range indicating that it is a quality biosorbent.

Table 2. Mean Values of Physico-Chemical Parameters of the Biosorbent

Parameter	Values
pH	7.30 ± 0.05
pH pzc	6.40 ± 0.07
Ash content (%)	7.4 ± 0.03
Moisture content (%)	2.65 ± 0.02
Bulk density (kg/m^3)	356.33 ± 1.0
Total pore volume (cm^3/g)	0.021 ± 0.001
Surface area (m^2/g)	27.748 ± 5.0
Total pore size (nm)	1.187 ± 0.002

Moisture Content

Moisture content suggests extensive porosity in the structure of the biosorbents. The moisture content of the biosorbent was $2.65 \pm 0.02\%$. The value obtained in this investigation is lower than the value reported by Das, [53] of 4.91% when he carried out a study on the diversity and conservation of wild mushrooms in Sikkim with special reference to Barsey Rhododendron Sanctuary. Okoro and Achuba, [54] reported values of the moisture content of some wild edible mushrooms in the range of 3.54-4.32 %. The result shows that, the moisture content of the biosorbent may have high biosorptive capacity because of its low value. Sugunadevi [55] observed that if the moisture content of the biosorbent is high, its adsorptive capacity will be reduced.

Bulk density

Bulk density is an important parameter of the biosorbent as it is a measure of the amount of adsorbate the biosorbent can hold per unit volume. It is a useful property that gives an idea of the volume activity of the biosorbent and depends on the starting raw material. A bulk density of $356.33 \pm 12 \text{ kg/m}^3$ was recorded in this work (Table 2) which is higher than minimum requirements of 250 kg/m^3 for the application in the removal of pollutants from waste water [18]. However, it is lower than the bulk density (784.34 kg/m^3) presented by Abbas [1] of activated sludge. Guoying [56] reported the bulk density of mushroom powder of 0.455 ± 0.009 , 0.475 ± 0.007 and $0.437 \pm 0.005 \text{ mg/L}$ for control without physical modification, superfine grinding and high pressure processing powders of *A. chaxingu* respectively. Antima [57] reported a bulk density of 0.869 g/ml for De-oiled mustard cake. Madu and Olajide, [44] reported the value for bulk density 0.54 for activated carbon 540°C lower than the one obtained from this work. The value of the bulk density obtained in this study shows that the biosorbent can be used for the removal of toxic metals from the leachate.

Surface area

The surface area is a parameter used to characterize the biosorbent. It is a measure of the micro-porosity created during physical modification and is responsible for pore sizes of the biosorbent. Biosorbent with high surface area and pore sizes perform better in the removal of micro-contaminants. The result shows that the biosorbent had a surface area, pore size and total pore volume of $27.748 \text{ m}^2/\text{g}$ as presented in Table 2 was less than those for activated carbon from *Vilellera paradoxo* shell presented by Cao [58] and Abbas [1] of 13.42 and $6.999 \text{ m}^2/\text{g}$, respectively. Mahmooda [24] investigated dried dead *Aspergillus flavus* biomass particle size and presented the particle size of dead *Aspergillus flavus* biosorbent which varies between $1 \mu\text{m}$ to $10 \mu\text{m}$. Also the pore volume of $0.021 \text{ Cm}^3/\text{g}$ shown by the biosorbent is comparable to that of other biosorbents reported by Bohli [59]. The value of the surface area and pore volume obtained for the biosorbent shows that it can be used for the removal of toxic metal ions from leachate.

FTIR Spectra for the Biosorbent

The FTIR measurement of virgin and spent biosorbent loaded with Pb^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} and Cr^{6+} respectively are shown in Fig. 3. These spectra were recorded in order to get information about the interactions between toxic metal ions and binding sites. The spectrums of the biosorbent are as evidenced by the presence of a large number of peaks. The broad peaks obtained at 3276 cm^{-1} in Fig. 3 indicate the presence of O-H (hydrogen bonded) and N-H stretching groups which may be due to the presence of proteins, alcohols, carbohydrates and nucleic acids on the surfaces of the biosorbent. The sharp peak at 2918 cm^{-1} represents the biosorption arising due to C-H stretching. A weak peak at 2310.9 cm^{-1} is attributed to P-H. Peaks in the range of 2169.3 - 1871 cm^{-1} are due to C=N, N=N, and C=C. The sharp peak at 1367.9 cm^{-1} is due to C-CH₃ and S-O stretching which are more or less identical to that reported in the literature [60]. The peak on 1640.0 cm^{-1} is attributed to C=O and H-O-H bending mode show the presence of lattice water or hydrated water in the biosorbent. Strong biosorption due to asymmetrical C-O bond stretching in ethers occurs in the 1025.0 cm^{-1} [61, 62]. The FTIR spectrum of the virgin biosorbent shows that there may be the present of the following functional groups on the surface of the bosorbent include: N-H and O-H (3276 cm^{-1}), S-O (1367.9 cm^{-1}) and P-H (2310.9 cm^{-1}), C=N, N=N, and C=C (2169.3 - 1871 cm^{-1}).

FTIR Spectra for *Pleurotus Pulmonarius* sorbent (pps) of Virgin and Spent Biosorption by Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} and Cr^{2+} biosorption are shown in Table 3. The intensity of the peaks for toxic metal after biosorped by biomass was either minimized or shifted slightly. It can be seen that the stretching vibration of -OH and -NH groups shifted from 3276 cm^{-1} to 3287 cm^{-1} , 3280.1 cm^{-1} , 3280.1 cm^{-1} and 3280.1 cm^{-1} for Co^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+} respectively except for Cr^{2+} where there was no change in the wave number possible due to low affinity to the biosorbent. These results revealed that there was a chemical interaction between Co^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+} and the hydroxyl and amine groups occurred on the biomass surface which does not occur with the Cr^{2+} . Abbas [1] presented the FTIR spectrum of activated sludge absorber before and after cations biosorption, which showed that there was a substantial decrease in

the wave number and biosorption intensity of carboxylic acid, amide, and amine groups at 3411.84, 2929.81, 1652.88, 1570, and 1450 cm^{-1} . The presence of the peak at 1640.0 cm^{-1} shows

C=O stretching before biosorption of the biosorbent shifted to 1636.3 cm^{-1} for all the toxic metals after biosorption was also reported by Eneji [13] on activated carbon from water lily.

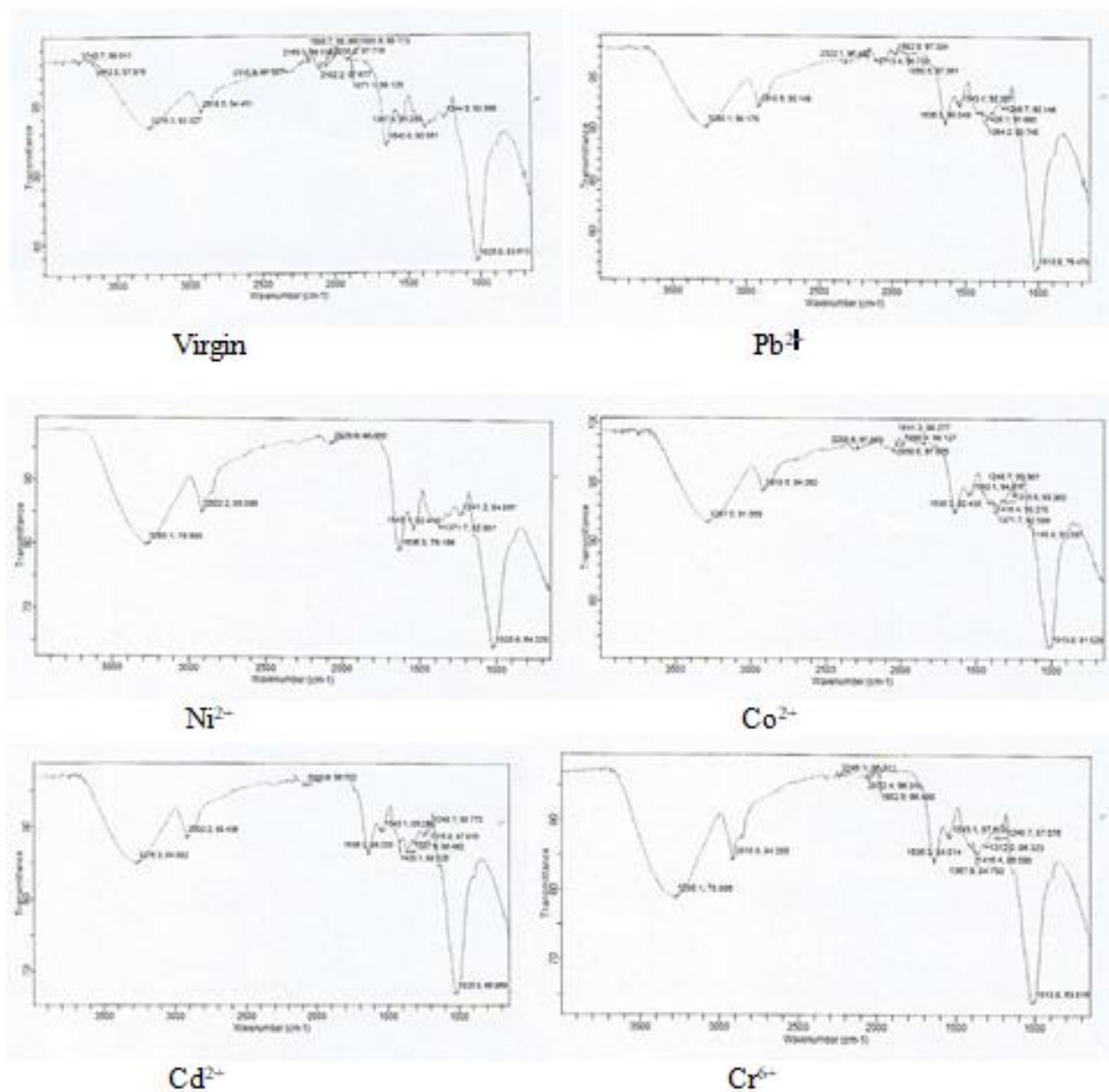


Fig. 3. FTIR Spectrum of virgin, Spent Pb^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} and Cr^{6+}

The decrease in the wave number of the peak is characteristic for the C=O and C=N groups from carboxylic acids revealed that the interaction with carbonyl functional group are present between biosorbent and toxic metals. These results indicated that the free carboxyl groups changed into carboxylate which occur during the reactions of the toxic metal ions and carboxyl groups of the biosorbents. No changes in frequency were observed in the C-H, - NH_2 , - CH_3 , S-O, C-O and P-H groups of the biosorbent after the toxic metal biosorption indicating that there was no interaction of the toxic metal ions with those functional groups on the surface of the biosorbent. Therefore it can be concluded

that the functional groups which could bind the metal ions are of type -OH, -NH, C=N, C=O and C=C.

Biosorption experiments

The effect of contact time

The studies on effect of time are significant since the data can be used for determining the time required to reach equilibrium and to evaluate the maximum biosorption capacity. In general, biosorption increases with the increase in contact time until the equilibrium is reached. The longer the time the more complete the biosorption will be. Fig. 4 shows the effect of contact time on the removal of Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} . The

biosorption of all toxic metal ions in this study slowly increased as a function of time up to 36 minutes at initial concentration of 7 mg/L and kept rapidly increasing until equilibrium is established forming a plateau. The results showed that the toxic metal uptake increase with

increase contact time and the biosorption capacity are 3.01 mg/g (95.19 %) for Cd^{2+} , 3.5 mg/g (98.47 %) for Pb^{2+} , 3.5 mg/g (92.14 %) for Ni^{2+} and 3.5 mg/g (96.41 %) for Co^{2+} and 4.0 mg/g (97.93) for Cr^{6+} .

Table 3. FTIR Spectra for *Pleurotus Pulmonarius* sorbent (pps) of Virgin and Spent Biosorption by Toxic Metals

Vibrational assignment/functional groups	Observed wave number (cm^{-1})					
	Virgin ppb	Spent pps with Co^{2+}	Spent pps with Ni^{2+}	Spent pps with Cd^{2+}	Spent pps with Cr^{6+}	Spent pps with Pb^{2+}
O-H, N-H	3276.3	3287.5	3280.1	3280.1	3276.3	3280.1
C-H	2918.5	2918.5	2922.2	2918.5	2922.2	2918.5
P-H	2310.9	2288.6	-	2240.1	-	2322.2
C=N, N=N	2050.0	2050.0	2079.9	2072.4	2033.0	2113.4
C=C, H-O-H, C=O	1640.0	1636.3	1636.3	1636.3	1636.3	1636.3
C- CH_3 , S-O	1367.9	1543.1	1543.1	1543.1	1543.1	1543.1
- NH_2	1244.9	1248.7	1241.2	1248.7	1248.7	1248.7
C-O	1025.0	1013.8	1025.0	1013.8	1025.0	1013.8

Biosorption of all the studied toxic metal ions occurred at the 160 minutes, therefore remaining almost constant up to 180 minutes. The constant value at equilibrium stage is due to the vacant spaces been gradually filled by toxic metals ions and after some time, there is no available space for toxic metal ions binding to the cell wall surface. As a result, a repulsive force occurred. The result revealed that biosorption of toxic metal ions occurred in two stages of the process where the initial rapid uptake due to surface biosorption to the cell walls and subsequent slow uptake due to membrane transport into the cytoplasm of the cells. Based on these results, the contact time was fixed at 3 h to ensure the reaction equilibrium can be reached. The relatively slow rate and irreversible nature of the biosorption as well as the order of the magnitude of the heat biosorption value suggested that the biosorption was of a chemical type. It was found that the biosorption of toxic metals ions in leachate is in the order of $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Cr}^{6+} > \text{Pb}^{2+}$. The degree of toxic metal ion removal from single, multiple system and wastewaters usually is different and it is influenced by several factors.

This was expected due to the complex composition of the leachate which influenced the biosorption efficiency [12]. Jinzhou [63] studied the contact time for biosorption of lead (II) in aqueous solution by spent mushroom *Tricholoma lobayense*, It is clear that during the first 20 minutes, the biosorption rate is fast, and the biosorbent even adsorbs about 87% of the total biosorbed lead ions instantly after mixing with the lead(II) solution. Then, the rate becomes much slower and gradually reaches equilibrium in 2 h.

Effect of Initial Concentration

The initial concentration of the toxic metal ions has a remarkable influence on the biosorption process and provides an important driving force to overcome the mass transfer resistance of all of the molecules between the aqueous and solid phase. As generally expected, due to the higher availability of toxic metal ions, increasing the Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} concentration with a given unsaturated and constant mass of biosorbent would increase the biosorption capacity (ions biosorbed per unit weight of biosorbent, q, mg/g), but decrease the percentage

of the toxic metal ions biosorbed. This variation trend was found in this experiment. As Fig. 4 shows, when the initial concentration of the toxic metal ions in this experiment increased from 10 to 70 mg/L, the biosorption capacity of the biosorbent gradually increased from 0.1 to 4.90, 0.49-4.09, 0.49-3.40, 0.99-3.10 and 0.49-3.92 mg/g for Cr^{2+} , Co^{2+} , Pb^{2+} , Cd^{2+} and Ni^{2+} , respectively. The biosorption capacity of the biosorbent increase rapidly due to the higher toxic metal concentration means a greater driving force for mass transfer from the aqueous solution to the solid biosorbent. While the removal percentage (Fig. 4) decreased from 95.57 % to 93.05 %, 97.50 to 95.14 %, 95.55 % to 93.00 %, 97.55 to 94.40 % and 97.55 to 94.16 % for Cd^{2+} , Pb^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} , respectively. It indicates that removal is highly concentration dependent at higher concentrations. This can be explained by the fact that the biosorbent has a limited number of active sites that become saturated above a certain concentration. At low Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} concentrations, the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the active functional groups on the surface of the biosorbent and be removed from the solution. However, with increased Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} concentrations, the number of active biosorption sites is not enough to accommodate the Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} . Boldizsar [19] reported the influence of initial Cd(II) and Zn(II) ions concentration on *Agaricus bisporus* macrofungus that the biosorption capacities for Cd(II) increase from 1.00 mg/g biomass for the initial of 50 mg/L to 3.49 mg/g biomass for the initial of 235 mg/L. In case of Zn(II) adsorption capacities increase from 0.89 mg/g for the initial of 60 mg/L to 2.39 mg/g for the initial 245 mg/L.

Effect of pH

The effect of pH on Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} biosorption was investigated at 301 K with 7 mg/L solution of the toxic metals and 100 mg of the biosorbent. The solution pH has a great influence on the biosorption process, which can determine the surface charge of the biosorbent, the degree of ionization and speciation of the biosorbate. The effects of pH on the biosorption of toxic metal ions on the biosorbent are shown in Fig. 4. The removal efficiencies increased remarkably with increasing pH. The maximum

removal efficiency at pH 9 for Pb^{2+} , Cd^{2+} , Cr^{6+} and Ni^{2+} and their percentage removal was 50.72 %, 56.78 %, 60.49 % and 65.97 %, respectively while maximum removal efficiency of Co^{2+} was at pH 6 with 73.37 % removal efficiency. The analysis result indicated that the affinity of heavy metals ions towards the biosorbent at pH 3–9 followed the order of $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cr}^{6+} > \text{Cd}^{2+} > \text{Pb}^{2+}$. At low pH 3-6 for Co^{2+} and Ni^{2+} the removal efficiencies dropped by 23.78% and 23.06% at pH7 respectively. The removal efficiencies increases with increase in the pH 8-9 while Cr^{6+} , Cd^{2+} and Pb^{2+} removal efficiencies increased remarkably with increasing pH 3-9. This decrease may be attributed to the surface of the biosorbent surrounded by H^+ ions at pH 7 which prevented the metal ions from approaching the biosorptive sites of the biosorbent. According to the results by Suseem and Mary [64] chromium has the more biosorption efficiency at pH 3.0 and then decreases gradually and the percentage removal of chromium was 21.5 % for *P.eous* at pH 3.0, the percentage removal was lower than the value obtained from this study. However, with increasing pH value, the competitive biosorption of H^+ ions decreased and the biosorbent surface became more negatively charged. Thus, the positively charged metal ions can be readily biosorbed onto the negatively charged sites of the biosorbent. Devlina [65] reported the Percent removal of silver was noted to be maximum at pH 6.0 for all the biosorbents (33.95%) in case of *P.platypus* followed by *C.indica* (27.3%) and *V. volvacea* (17.25%) and maximum removal percentage of zinc was found to be 44.9 %, 39.9% and 28.3% for *P.platypus*, *Calocybe indica* and *Vovariella volvacea* at pH 5.0.

Effect of biosorbent dosage

Biosorbent dosage determines the sorbent-sorbate equilibrium of the system and the number of binding sites. The number of available sites and exchangeable ions for biosorption depends upon the amount of biosorbent in the biosorption process. In case of Pb^{2+} , Cd^{2+} , Cr^{6+} and Ni^{2+} the amount sorbed rapidly increases with increasing concentration of the biosorbent up to a dosage of 140 mg of biosorbent (Fig. 4). The increase in the uptake can be attributed to the increased number of biosorption sites, surface area and exchangeable ions available for biosorption [66]. Except Co^{2+} which the amount sorbed increases

rapidly with increasing concentration of biosorbent up to 120 mg and decreases with a dosage of 140 mg. Its biosorption capacity dropped from 60.31 mg/g to 51.23 mg/g with increasing dosage from 60-140 mg for Co^{2+} . At dosage value beyond the optimum value, toxic metal uptakes were found to decrease. This could be probably due to the clumping of the biosorbent thereby decreasing the surface area [67, 68]. Maximum percent removal of Pb^{2+} , Cr^{6+} , Ni^{2+} , Co^{2+} and Cd^{2+} was found to be 46.24%, 55.09%, 66.94%, 52.53% and 59.49%, respectively for biosorbent dosage of 140 mg was lower than the values reported by Suseem and Mary [64] where the maximum percentage of removal of lead, chromium and nickel was 94.4%, 28.6% and 33.8%, respectively for *P. eous* at biosorbent dosage of 0.2 g. The test biomass showed significant affinity for Ni^{2+} and Pb^{2+} . The affinity ranking based on the percentage biosorption on a dosage of 140 mg was established as $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cr}^{6+} > \text{Co}^{2+} > \text{Pb}^{2+}$.

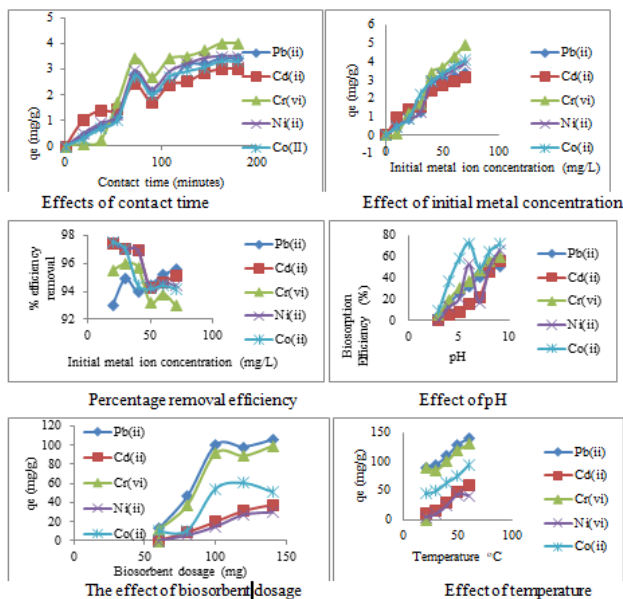


Fig. 4. The effects of biosorption parameters

Effect of temperature

Temperature is one of the most important controlling parameter in biosorption. It affects the biosorption rate by altering molecular interactions and solubility of biosorbate [69]. The effect of temperature was investigated in the temperature range of 20–60 $^{\circ}\text{C}$ as shown in Fig. 4. It was observed that the removal of all the toxic metals (Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+}) increased from 29.96 to 34.96 mg/g by increasing the temperature from 20 to 60 $^{\circ}\text{C}$. This increase in biosorption is mainly due to

increase in number of biosorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the biosorbent [70]. This phenomenon also leads to an increment in the availability of active surface sites, increased porosity and in the total pore volume of the biosorbent [71, 72].

Kinetic Biosorption Model Parameters

The Pseudo First-Order Equation

To analyze the biosorption kinetics of the toxic metal ions, the linear equation of pseudo-first-order, pseudo-second-order models were applied [73].

$$\text{Pseudo-first-order: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\text{Pseudo-second-order: } t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad (2)$$

where, q_e and q_t refer to the amount of metal ions adsorbed (mg/g) at equilibrium and at any time t (min), respectively and k_1 (1/min), k_2 (g/mg min) are the equilibrium rate constants of pseudo-first order and pseudo-second order models, respectively. Table 4 presented the pseudo-first order and pseudo-second-order rate constants and R^2 values for toxic metal ions biosorption on the biosorbent. The correlation coefficients obtained when the pseudo-first order kinetic model (Figure 4) was applied to metal ions biosorption was less than 0.9 so does not fit the experimental data. Based on this remark it can be concluded that the biosorption process cannot be classified as pseudo-first order.

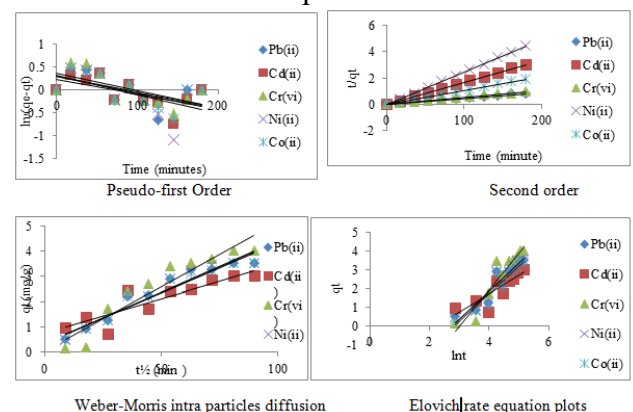


Fig. 5. Pseudo-first Order, second order, Weber-Morris intra particles diffusion and Elovich rate equation plots

Pseudo second-Order Lagergren Equation

When pseudo-second-order kinetic model was applied for the considered biosorption process, Table 4 and Fig. 5, correlation coefficients was greater than 0.9 which was higher than those obtained with pseudo-first order plot obtained for Pb^{2+} , Cd^{2+} , Cr^{6+} , and Ni^{2+} . Therefore it was

concluded that all the metal ions sorbed on the biosorbent which obeyed the pseudo-second-order kinetic model, suggesting that the process took place as chemisorptions. This is similar with the research carried out and reported by Cossich [74] where the adsorption kinetics didn't fit the pseudo first order model well with R^2 less

than 0.810 at the given concentration range of 20-70 mg/L. In contrast, the biosorption kinetics obeyed pseudo-second order model very well with R^2 close to 1.0. It has been observed that, most toxic metal ions biosorption kinetics fits pseudo second-order model [1, 12,75].

Table 4. Kinetic Biosorption Model Parameters

Isotherm model	Parameters	Toxic metal ions				
		Pb ²⁺	Cd ²⁺	Cr ⁶⁺	Ni ²⁺	Co ²⁺
Pseudo-first-order	Qe expt (mg/g)	225.63	59.30.	188.90	41.01	94.03
	Qe cal mg/g	1.96	1.66	2.35	2.06	1.92
	K ₁ (gmg ⁻¹ min ⁻¹)	1.91x10 ⁻³	3.12x10 ⁻³	2.34x10 ⁻³	1.96x10 ⁻³	2.02x10 ⁻³
	R ²	0.314	0.344	0.418	0.297	0.323
Pseudo-Second-order	Qe cal (mg/g)	225.63	62.50	200.00	41.67	100.00
	H	1.00	55.56	333.33	24.39	142.35
	K ₂ (gmg ⁻¹ min ⁻¹)	1.6 x10 ⁻⁵	1.4 x10 ⁻²	8.3 x10 ⁻³	1.4 x10 ⁻²	1.4 x10 ⁻²
	R ²	1.000	0.999	0.999	0.999	0.999
Elovich Equation	β (g/mg)	1.26	1.25	0.89	1.28	2.31
	α (mg/g/min)	3.12	4.49	3.3x10 ⁻⁷	1.88	29.42
	R ²	0.902	0.902	0.901	0.901	0.901
Weber	I	0.541	0.131	0.753	0.070	-1.049
Morris intra particles	K _d (mg/g.s ^{1/2})	0.059	0.052	0.049	0.056	0.125
	R ²	0.848	0.806	0.801	0.851	0.848

Intra-particle Diffusion Rate equation

The kinetic results were analyzed by the Weber and Morris [76] Intra-particle diffusion model is expressed as

$$qt = K_{id} t^{1/2} + I \quad (3)$$

where, I is the intercept and K_{id} is the intra-particle diffusion rate constant. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater is the contribution of the surface sorption in the rate controlling step. The K_{id} value was higher at the higher concentrations. Intra-particle diffusion is the sole rate-limiting step if the plot of qt vs $t^{1/2}$ is linear and passes through the origin. In fact, the linear plots at each concentration did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption. This indicated the existence of some boundary layer effect and further showed that Intra-particle diffusion was not the only the rate limiting step.

Apart from outer surface biosorption, there is also the possibility of intra particle diffusion from the outer surface into the pores of the materials [14]. The adsorption mechanism of a sorbate onto the biosorbent follows three steps viz: film diffusion, pore diffusion and intra particle transport [77]. There is however, the possibility of pore diffusion being the rate-

limiting step in the batch process being high, the sorption rate parameters which controls the batch process for most of the contact time is the intraparticle diffusion [78].

The Weber and Morris intra-particle diffusion model was then applied to analyze the kinetic data to explain the mechanism of diffusion as expressed in equation (VII)

$$qt = K_{id} t^{1/2} + I \quad (4)$$

where I is the intercept and reflect the boundary layer effect. K_{id} is the intra-particle diffusion rate constant. These constants were determined from the plot of qt vs $t^{1/2}$ (Fig. 5) and the values of Intra-particle diffusion parameters are given in Table 4. The value of I was higher in Cr⁶⁺ > Pb²⁺ > Cd²⁺ > Ni²⁺ > Co²⁺ implying a greater contribution of the surface biosorption in the rate controlling step. Intra-particle diffusion is the sole rate controlling step if the plot of qt vs $t^{1/2}$ is linear and passes through the origin. Where there is a deviation from linearity, then other surface phenomena are involve. The regression values for all the toxic metals were both less than unity. The linear plots for all the toxic metals did not pass through the origin. This deviation from origin is due to differences in the rate of mass transfer in the initial and final stages of the biosorption [79]. This also means that the rate limiting step was not only intra-particle diffusion but also other surface phenomena on the biosorption process.

Also, the high values of R^2 obtained for the toxic metal ions indicated that Morris-Weber model was suitable for describing the diffusion rate of the toxic metal ions onto the biosorbent. Whereas, low K_d value and I values were greater than zero except Co^{2+} that has I values less than 1 (Table 4), showed that the mode of transport was affected by more than one process [80]. Similar results were reported for the removal of heavy metals from aqueous solution using activated carbon from neem seed and husk [81].

The Elovich Rate Equation

The Elovich equation is given by:

$$dq_t/dt = \alpha \exp(-\beta q_t) \quad (5)$$

According to Badmus [82] the linearized form is given as [83] as eq. (6).

$$qt = [1/\beta] [\ln(\alpha\beta) + \text{Lnt}] \quad (6)$$

where β (g/mg) and α (mg/g/min) are the Elovich constants corresponding to the extent of surface coverage and rate of sorption at zero coverage. Plots of q_t versus Lnt for the Cd^{2+} , Co^{2+} , Cr^{6+} , Ni^{2+} , Co^{2+} and Pb^{2+} systems are shown in Fig. 5 and constants were determined from the linear plot. The R^2 value for Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} has R^2 greater than 0.900 (Table 4). The R^2 value greater than 0.9 was also reported by Abuh [84] when they carried out a study on the kinetic rate equations application on the removal of copper (ii) and zinc(II) by unmodified lignocellulosic fibrous layer of palm tree trunk-single component system studies. It can be concluded that the Elovich equation has a good fit to the experimental data for all the toxic metals. However, Co^{2+} had a highest extent of surface coverage 2.31 g/mg while Cr^{2+} has the least surface coverage of 0.89 g/mg.

Biosorption Isotherms

The capacity of biosorption isotherm provides a panorama of the course taken by the system under study in a concise form, indicating how efficiently an adsorbent will adsorb and allows an estimate of the economic viability of the adsorbents commercial applications for the specified solute. Biosorption isotherms usually describe the equilibrium relation between sorbent and sorbate. They give the equilibrium relationship between the quantity of metal sorbed and that remaining in aqueous solution at a fixed temperature. By plotting solid phase concentration against liquid phase concentration, it is possible to predict the equilibrium isotherm.

The isotherm thus yields certain constants whose values express the surface properties and affinity of the sorbent.

The biosorption isotherm profiles provide information regarding the nature and the intensity of a particular adsorbate-biosorbent system. The isotherms for Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} were somewhat s-shaped Fig. 6 indicating a high affinity rate of toxic metal ions towards the biosorbent. This suggest that hydration of the metal ions was less preferred compared to sorption onto the biosorbent which resulted in the preferred sorption [1].

It is important to determine the most appropriate correlation for equilibrium biosorption isotherm, to optimize the design of a sorption system. The Freundlich, Langmuir, Temkin, Hurkins-Jura, Halsay, Redlich-Peterson, Dubinin-Radushkevich and Jovanovich isotherm models were used to analyze the biosorption equilibrium. Experimental isotherm data were obtained at biosorption time of 180 min at different temperatures.

Isotherm constants for the toxic metal ions biosorption onto the biosorbent

The biosorption isotherms plots in this study are presented in Fig. 6 while the calculated parameters for the toxic metal ions onto the biosorbent are shown in Table 5.

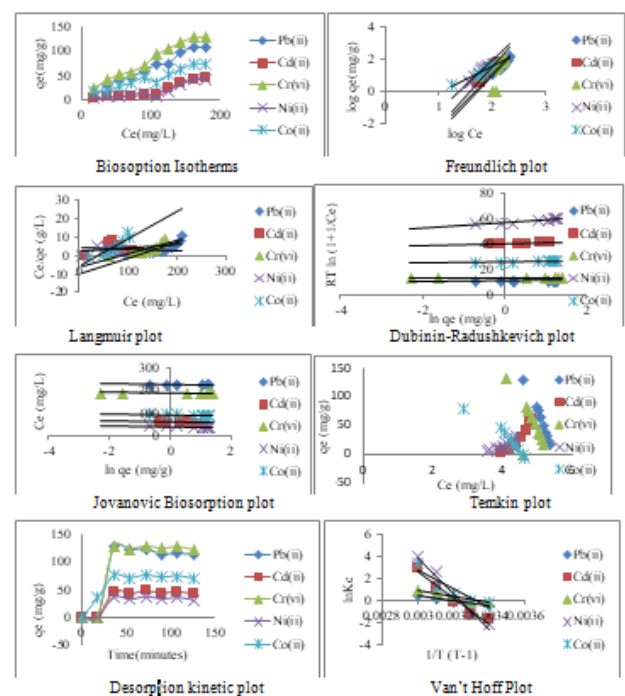


Fig. 6. Isotherms, desorption and Van't Hoff plot

Table 5. Isotherm constants for the toxic metal ions biosorption onto the biosorbent

Isotherm model	Parameter	Metal ions				
		Pb ²⁺	Cd ²⁺	Cr ⁶⁺	Ni ²⁺	Co ²⁺
Langmuir	q _m (mg/g)	9.96	9.02	5.81	0.115	8.642
	K _L (g/mg)	0.08	0.04	0.06	0.124	0.204
	R ²	0.701	0.024	0.716	0.056	0.723
Freundlich	K _F (L/g)	0.85	0.46	0.73	0.52	1.73
	1/n _F	0.41	0.45	0.58	0.41	0.42
	R ²	0.938	0.966	0.947	0.948	0.909
Dubinin	B _D (mol ⁻¹ /KJ ²)	0.089	0.023	0.0036	0.016	0.037
Radushkevich	Q _D (mol/g)	1.192	2.892	1.074	9.125	1.552
	E (KJ/mol)	2.37	4.66	11.79	5.59	3.680
	R ²	0.969	0.933	0.900	0.948	0.949
Jovanovic	K _J (L/g)	1.009	1.034	1.010	1.055	1.023
	q _{max} (mg/g)	0.204	0.273	0.348	0.195	0.199
	R ²	0.941	0.958	0.911	0.954	0.955
Temkin	K _T (L/g)	0.797	0.750	0.777	0.678	0.767
	B _T (J/mol)	3.855	15.940	5.961	4.330	14.043
	R ²	0.983	0.906	0.971	0.906	0.929

Freundlich biosorption isotherm

The Freundlich biosorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the biosorption sites are distributed exponentially with respect to heat of biosorption. The biosorption isotherm is expressed by the equation (7).

$$q_e = k_F C_e^{1/n} \quad (7)$$

Linearized Freundlich equation (8).

$$\ln q_e = \ln K_F + 1/n_F \ln C_e \quad (8)$$

where q_e is the amount of metal ions or dyes adsorbed at equilibrium (mg/g) and C_e is the concentration of metal ions in the aqueous phase at equilibrium (mg/L). K_F (L/g) and $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity respectively. The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ Vs $\ln C_e$ plot. The Freundlich exponent, n_F , should have values in the range of 1 and 10 (i.e., $1/n_F < 1$) to be considered as favourable biosorption [85].

The values of Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ versus $\ln C_e$ plot, as shown in Fig. 6, and the model parameters are shown in Table 5. The magnitude of K_F ranged from 0.46-1.78. This values showed that Co^{2+} had the highest K_F (1.78) while Ni^{2+} have the least biosorbed. The Freundlich exponent, n_F , should

have values $1/n_F < 1$ to be considered as favourable biosorption [86]. However, the $1/n_F$ value was in the range of 0.41-0.58. The $1/n_F$ values obtained in this study was less than 1 indicating that Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} , and Co^{2+} are favourably biosorbed by the biosorbent. The Freundlich isotherm showed a good fit to the experimental data as indicated by R^2 greater than 0.900 for the toxic metals ions studied which agrees with the findings of Abbas [1] for binary, ternary and quaternary systems and the Langmuir model seems to give the best fitting for the experimental data with R^2 greater than 0.9. Antima [57] reported both Langmuir and Freundlich isotherm model produced values of R^2 0.99 and 0.98, respectively. The Freundlich isotherm R^2 in this study showed a good fit to the experimental data.

Langmuir biosorption isotherm

The Langmuir biosorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm in a linear form can be represented as $C_e/q_e = 1/q_m K_L + C_e/q_m$ (9) where, q_e is the amount of toxic metal ions biosorbed at equilibrium (mg/g), C_e is the concentration of toxic metal ions in the aqueous phase at equilibrium (mg/L), q_m is the maximum toxic metal ions uptake (mg/g) and K_L is the Langmuir constant related to adsorption capacity and the energy of biosorption (g/mg).

A linear plot of C_e/q_e Vs C_e was employed to determine the value of q_m and K_L . The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreased with an increase in the temperature. A high K_L value indicates a high biosorption affinity. Weber and Chakraborti. [87] expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation:

$$R_L = 1/1 + K_L C_o \quad (10)$$

where, C_o is the initial metal ions concentration (mg/L). Four scenarios can be distinguished: The sorption isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, the isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor (R_L) for metal ions removal were calculated at different concentrations and temperatures. A linear plot of C_e/q_e versus C_e was employed to determine the value of q_m and K_L , as shown in Fig. 6 and the data so obtained were also presented in Table 5. A low K_L value indicates a low biosorption affinity. The monolayer saturation capacity, q_m , is shown to be 9.963, 9.022, 5.813, 0.119 and 8.642 mg/g for Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} , and Co^{2+} respectively..

Weber and Chakraborti, [87] expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation (11)

$$R_L = 1/1 + K_L C_o \quad (11)$$

where C_o is the initial toxic metal concentration (mg/L).

Four scenarios can be distinguished:

- (1). The biosorption isotherm is unfavorable when $K_L > 1$.
- (2). the isotherm is linear when $K_L = 1$.
- (3). the isotherm is favorable when $0 < K_L < 1$
- (4). the isotherm is irreversible when $K_L = 0$.

The values of dimensionless separation factor (K_L) for toxic metal ions removal by the biosorbent were calculated and shown in Table 4. This indicated that, the values of R_L for all the toxic metals biosorption on the biosorbent were less than 1 and greater than zero, indicating favorable biosorption. The Langmuir isotherm does not show a good fit to the biosorption data for all the toxic metal ions under investigation since the R^2 are less than 0.8. The fact that the

Langmuir isotherm does not fits the experimental data may be due to heterogeneous distribution of active sites on the biosorbent surface. Abbas [1] presented R^2 value of less than 0.8 for a single solute system showing that it does not fit for Pb^{2+} , Hg^{2+} , Cr^{3+} and As^{5+} which agrees with the value obtained in this work.

Dubinin-Radushkevich biosorption isotherm

The Dubinin-Radushkevich biosorption isotherm as described by Dunnick [88] is assumed that the characteristic of the sorption curve is related to the porosity of the biosorbent. The linear form of the isotherm can be expressed as follows

$$\ln q = \ln Q_D - B_D [RT \ln(1 + 1/Ce)]^2 \quad (12)$$

where Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol^2/kJ^2). A plot of $\ln q$ Vs $RT \ln(1 + 1/Ce)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept.

A plot of $\ln q_e$ versus $RT \ln(1 + 1/Ce)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept, as shown in Fig. 6. The B_D ranged from 0.0036-0.089 $\text{mol}^{-1}/\text{kJ}^2$, Q_D values are in the range of 1.074-9.125 mol/g and R^2 ranged from 0.728-0.949 and the RMSE values in the range of 0.314-0.698. The mean energy of biosorption, E (kJ/mol) was calculated by the following equation (13).

$$E = 1/\sqrt{2B_D} \quad (13)$$

The calculated Dubinin-Radushkevich constants and mean free energy for biosorption are shown in Table 5. The E values obtained from this work ranged from 2.37-11.79 KJ/mol. The mean biosorption energy (E) was highest for (11.79 KJ/mol) Cr^{6+} while Pb^{2+} has the least E with a value of 2.37 KJ/mol indicating that energy was involved in the biosorption processes. The values in this work are similar to those presented by Conrad and Hansen [89] of Q_D (7.59 mg/g), B_D ($2 \times 10^{-8} \text{ mol}^{-1}/\text{kJ}^2$), E (5.00 KJ.mol^{-1}) and R^2 (0.987). Boldizsar [19] reported the R^2 of 0.746 heavy metals removal using *Agaricus bisporus* macrofungus which is lower than the R^2 value obtained for the toxic metal ions in this work with R^2 greater than 0.9 indicating that the isotherm model fitted into the experimental data. Abdel [90] presented Radushkevich constants and mean free energy of q_s value of 70.579 mg/g, the mean free energy, $E = 0.7 \text{ KJ/mol}$ indicating a physisorption process and the $R^2 =$

0.79 lower than the values obtained from this work.

Jovanovic biosorption isotherm

A biosorption surface assumption, considered in Jovanovic isotherm model corresponds to another approximation for monolayer localized biosorption without lateral interactions. This model is similar to that of Langmuir model, except that the allowance is made in the former for the surface binding vibrations of a biosorbed species.

The Jovanovich model leads to the following relationship [91].

The Jovanovic model leads to the following relationship:

$$q_e = q_{max}(1 - e^{-K_J C_e}) \quad (14)$$

The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln q_{max} - K_J C_e \quad (15)$$

where K_J (L/g) is a parameter, q_{max} (mg/g) is the maximum toxic metals uptake. The q_{max} is obtained from a plot of $\ln q_e$ and C_e .

The q_{max} is obtained from a plot of $\ln q_e$ and C_e , as shown in Fig. 6. Their related parameters are displayed in Table 5. The K_J ranged from 1.009 - 1.055 L/g, Q_{max} values were in the range of 0.195-0.348 mg/g and R^2 values are greater than 0.9 indicating that the R^2 values were found to have a good fit with the experimental data for removal of toxic metals from the leachate. Samarghandi [92] reported K_g ranged from - 0.017- 0.030 L/g, Q_{max} values were in the range of 1.048-1.155 mg/g and R^2 values are in the range of 0.868-0.925 from the study of two parameter isotherms of methyl orange sorption by pinecone derived activated carbon. K_J ranged from 0.003-0.014 L/g, Q_{max} values were in the range of 17.8 - 26.1 mg/g were reported by Barakat [93] when carrying out an investigation into the new trends in removing heavy metals from industrial wastewater. K_J ranged from 0.06 - 0.49 l/g, q_{max} values were in the range of 54.6 - 65.0 mg/g presented by Marimuthu [94] in pollution abatement by activated nano materials derived from natural plants and minerals.

Temkin biosorption isotherm

The Temkin adsorption isotherm assumes that the heat of biosorption decreases linearly with the sorption coverage due to biosorbent-adsorbate interactions The Temkin isotherm equation is given as

$$q_e = RT/\ln(K_T C_e) \quad (16)$$

The linearized form of the above equation is:

$$q_e = B_1 + \ln K_T - B_1 \ln C_e \quad (17)$$

where $B_1 = RT/b$; R is the universal constant (8.314 KJ/mol.K) and T is the absolute temperature (K). A plot of q_e Vs $\ln C_e$ enables the determination of isotherm constants K_T and bT from the slope and intercept.

The biosorption energy in the Temkin model, bT , is positive for toxic metal ions biosorption from the aqueous solution, which indicates that the favorable biosorption. The experimental equilibrium curve is close to that predicted by Temkin model.

A plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_T and bT from the slope and intercept, as shown in Fig. 6. Temkin-isotherm is based on the assumption that the heat of biosorption decreases linearly with the increase of coverage of biosorbent. From the Temkin plot, K_T were in the range of 0.678 - 0.777 L/g, B_T have values ranging from 3.855-15.94 J/mol and R^2 values were greater than 0.9 with RMSE values in the range of 0.299-1.28 as shown in Table 5. The values obtained from this work are an indication that the process involved was physical and heat of biosorption decreases linearly with the increase of coverage of biosorbent. Dada [91] reported Temkin constants of $K_T = 1.075$ L/g, $B_T = 25.34$ J/mol and the $R^2 = 0.62$ lower than the value obtained from this work. Also, Matthew [95] reported Temkin constants of K_T (1.66 L/mg), B_T (1.71) and R^2 of 0.971. Abbas [1] displayed similar constants in the range of K_T (0.5310 - 8.5310) L/g, B_T have values ranging from 133.38 - 1841.1 J/mol and R^2 values in the range of 0.9214 - 0.985. It can be concluded that based on R^2 value of 0.99 the equilibrium data were fitted to Freundlich, pseudo-second-order, Temkin, Dublin-Radushkavich and Jarunovic isotherm models.

Desorption kinetics

Desorption is a phenomenon, whereby the biosorbed metal ion is released from the surface of the biosorbent. Desorption studies help in elucidating the mechanism of metal ion removal and recovery from metal-loaded biosorbent and also for the regeneration and recycling of spent biosorbents, which in turn may reduce operational cost and protect the environment. Exploitation of biosorption technology for removal of toxic metals depends on the efficiency of regeneration of biosorbents after

metal ion desorption. The biosorbent needs to be regenerated for multiple reuse cycles using non-destructive recovery by mild desorbing agents. The process of desorption should result in high concentration of metal ion effluent, undiminished metal ion uptake on reuse and least physical /chemical damage to the biosorbent. The effect of double distilled water as desorbent was studied. The desorption of each toxic metal ions was carried out from each of biosorbent, which had been used in the biosorption of toxic metal ions with the same concentration of each toxic metal in this study [96]. As shown in Fig. 6, the desorption of toxic metals was very fast for Co^{2+} while Pb^{2+} , Cd^{2+} , Cr^{2+} and Ni^{2+} were initially slow and the equilibrium could be reached after 36 minutes while the rest were desorbed within the next 144 minutes. Cr^{6+} and Pb^{2+} have a similar desorption kinetic with its difference on the 72 minute with the desorbed amount of 129.37 mg/g and 123.90 mg/g respectively. Desorption of all the toxic metal ions from biosorbent was almost complete within the 54 minutes beyond which the amount of toxic metal ions desorbed came to a steady value. The percentage desorption for Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} were 56.89%, 79.22%, 67.80%, 88.41% and 80.35%, respectively. Pb^{2+} and Cr^{6+} were more readily desorbed and the percentage desorption was above 56.26% (128.90 mg/g) and 67.06% (129.30 mg/g), respectively. The desorption ranking based on the percent desorbed in this study are Pb^{2+} and $\text{Cr}^{6+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$. The desorption studies results indicated the biosorbent can be regenerated, recycled and have high reusability. Also, double distilled water can be used as a desorbent. Claudia and Mariana [97] reported using 0.05 M HNO_3 as an eluent for *polyporus squamosus* loaded with copper ions and obtain recovery efficiency of 84.89%. It has been found that 0.1 M HCl is effective in desorption of heavy metals [98]. The reuse of dead fungal biomass can be done for 4-5 cycles of biosorption and desorption without significant loss in biosorption capacity [24]. Wei *et al.*, [99] studied the desorption of perfluorooctane sulfonate and perfluorooctanoate on polyacrylonitrile fiber derived activated carbon fiber sand reported that desorption was not effective for the PFOS-adsorbed PACFs using distilled water, the percent regenerated was less than 5% for 48 h but when the mixture of

ethanol and distilled water was used as the regeneration solution, it was found that the regeneration rate increased with the increase of ethanol concentration. The regeneration of percent of pure ethanol and 50 % ethanol at 25°C after 24h were 87.29% and 85.01%, respectively. This show good reusability in sorption-desorption cycle studies however, desorption studies with doubly distilled water revealed that the regeneration of biosorbent was not satisfactory, which confirm the chemisorptive nature of biosorption.

Thermodynamic studies

In order to study the feasibility of the biosorption process, the thermodynamic parameters such as changes in standard Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy change, (ΔS°) were investigated using the equations (18-20)

$$\Delta G^\circ = -RT \ln K_{ad} \quad (18)$$

$$K_c = C_{Ae}/C_e \quad (19)$$

$$\Delta G^\circ = -\Delta S^\circ(T) + \Delta H^\circ \quad (20)$$

where, C_e is the equilibrium concentration in solution in mg/L and C_{Ae} is the equilibrium concentration on the sorbent in mg/L and K_c is the equilibrium constant. The Gibbs free energy (ΔG°) for the biosorption of toxic metal ions onto *Pleurotus pulmonarius* biosorbent at all temperatures was obtained from Equation 20. The values of ΔH° and ΔS° were calculated from the slope and intercept of the plot $\log K_c$ against $1/T$. where R is the universal gas constant (8.314 J/mol.K) and T is the absolute temperature (K).

The plot of the effect of temperature for the biosorption of toxic metals ions using biosorbent is presented in figure 4 while the plot of Van't Hoff and the calculated thermodynamic parameters for the biosorption of toxic metal ions onto the biosorbent are presented in Figure 6 and Table 6.

Temperature is an important parameter to be studied in order to determine the thermodynamic parameter (enthalpy change ΔH° , Gibbs free energy change ΔG° and Entropy change ΔS° of the system). The removal of Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} by biosorbent at different temperatures ranging from 393-333K was evaluated in a batch system. Experimental results from Van't Hoff Plot were used to calculate thermodynamic parameters for biosorption of toxic metals onto the biosorbent and are presented in Figure 5 and Table 6.

Table 6. Thermodynamic Parameter of Biosorption of toxic metal Ions onto the biosorbent

	T(°K)	ΔG°	ΔH°	ΔS°	R ²	E (%)
Pb ²⁺	293	+1047				39.38
	303	+857				41.53
	313	+208	-2380	7.59	0.972	47.93
	323	-698				56.39
	333	-1274				61.24
Cd ²⁺	293	+4166				15.36
	303	+2998				23.34
	313	+364	-11790	37.96	0.962	46.59
	323	-333				77.49
	333	-8223				95.14
Cr ⁶⁺	293	+292				47.02
	303	+50				49.57
	313	-755	-2980	9.912	0.965	57.17
	323	-1934				69.23
	333	-2740				72.99
Ni ²⁺	293	+5237				10.44
	303	+3225				21.10
	313	-468	-14740	47.82	0.844	54.51
	323	-10580				98.09
	333	-7226				93.15
Co ²⁺	293	+438				45.48
	303	-50				50.62
	313	-1691	-8440	28.04	0.844	65.60
	323	-333				77.59
	333	-9496				96.87

The Gibb's free energy at 293 K, 303 K, 313 K, 323 K and 333 K ranged from -9496-5237, the change in enthalpy ranged from -11790- (-8440) while the entropy change are in the range of 7.59-47.82 and the percentage efficient removal of the toxic metal ions from the leachate ranged from 10.44-98.09 %. The negative values of change in Gibbs free energy indicated that the biosorption process was feasible and spontaneous at higher temperatures [100]. The negative values of enthalpy change (ΔH°) confirmed the biosorption process to be exothermic. The positive values of entropy change (ΔS°) for all the toxic metal ions showed that there was randomness at the solute-solution which increases with each toxic metal ion retention in the biosorption process. The values obtained for the study is similar to the one presented by Shirahkumar [101] when they calculated and found that ΔG° was negative and showed spontaneous nature of biosorption process, ΔH° was positive and showed endothermic nature of biosorption process, ΔS° was positive and showed the increasing randomness at solid/liquid interface during the

adsorption of copper by *prosopis juliflora* leaf powder. The values demonstrate a spontaneous and favorable biosorption process. Cossich [74] found that the value of the change in entropy, $\Delta S^\circ = 104.84 \text{ J mol}^{-1}\text{K}^{-1}$, and the change in enthalpy, $\Delta H^\circ = 19.88 \text{ kJ mol}^{-1}$ and concluded that the positive value of change in entropy for the biosorption of the Pb (II) show that the sorption process is highly disordered. The positive values of ΔS° obtained implies that there was an increase in the number of steps involved in the biosorption of Pb(II) by elephant grass. Similarly, the enthalpy change was positive, indicative of endothermic process.

Proposed biosorption mechanism

The biosorption process involves a solid phase (biosorbent) and a liquid phase containing solution of metal ions in the leachate. The metal ions are attracted and bound to the biomass by a complex process that comprises of a number of mechanisms such as electrostatic interaction on the surface of the biosorbent, ion-exchange, surface precipitation, complexation, chelation and entrapment in capillaries and spaces of

polysaccharide network, due to the concentration causing diffusion through the cell wall and membrane. Particularly, it is due to the presence of certain functional groups, such as amine, carboxyl, hydroxyl, phosphate, sulfhydryl etc., on the cell wall of the biomass [102].

Desorption of Toxic Metals from Biosorbent

Desorption is a phenomenon, whereby the biosorbed metal ion is released from the surface of the biosorbent. Desorption studies help in elucidating the mechanism of metal ion removal and recovery from metal-loaded biosorbent and also for the regeneration and recycling of spent biosorbents, which in turn may reduce operational cost and protect the environment. Exploitation of biosorption technology for removal of toxic metals depends on the efficiency of regeneration of biosorbents after metal ion desorption. The biosorbent needs to be regenerated for multiple reuse cycles using non destructive recovery by mild desorbing agents. The process of desorption should result in high concentration of metal ion effluent, undiminished metal ion uptake on reuse and least physical /chemical damage to the biosorbent.

The effect of deionised distilled water as desorbent was studied. The desorption of each toxic metal ions was carried out from each of biosorbent, which had been used in the biosorption of toxic metal ions with the same concentration of each toxic metal in this study. The recovery percentage is obtained from equation 21 [95]. As shown in desorption kinetic plot Figure 5, the desorption of toxic metals was very fast for Co^{2+} while Pb^{2+} , Cd^{2+} , Cr^{2+} and Ni^{2+} were initially slow and the equilibrium could be reached after 36 mins while the rest were desorbed within the next 144 mins. Cr^{6+} and Pb^{2+} have a similar desorption kinetic with its difference on the 72 mins with the desorbed amount of 129.37mg/g and 123.90mg/g respectively. Desorption of all the toxic metal ions from biosorbent was almost complete within the 54 mins beyond which the amount of toxic metal ions desorbed came to a steady value. The percentage desorption for Pb^{2+} , Cd^{2+} , Cr^{6+} , Ni^{2+} and Co^{2+} were 56.89 %, 79.22 %, 67.80 %, 88.41 % and 80.35 %, respectively. Pb^{2+} and Cr^{6+} were more readily desorbed and the percentage desorption was above 56.26% (128.90 mg/g) and 67.06 % (129.30 mg/g), respectively. The desorption ranking based on

the percent desorbed in this study are Pb^{2+} and $\text{Cr}^{6+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$. The desorption studies results indicated the biosorbent can be regenerated, recycled and have high reusability. Also, double distilled water can be used as a desorbent. Claudia and Mariana [96] reported using 0.05 M HNO_3 as an eluent for *polyporus squamosus* loaded with copper ions and obtain recovery efficiency of 84.89 %. It has been found that 0.1 M HCl is effective in desorption of heavy metals [99]. The reuse of dead fungal biomass can be done for 4-5 cycles of biosorption and desorption without significant loss in biosorption capacity [24]. Wei [99] studied the desorption of perfluorooctane sulfonate and perfluorooctanoate (PFOS) on polyacrylonitrile fiber (PACFs) derived activated carbon fiber sand reported that desorption was not effective for the PFOS-adsorbed PACFs using distilled water, the percent regenerated was less than 5% for 48h but when the mixture of ethanol and distilled water was used as the regeneration solution, it was found that the regeneration rate increased with the increase of ethanol concentration. The regeneration of percent of pure ethanol and 50 % ethanol at 25°C after 24 h were 87.29% and 85.01%, respectively. This show good reusability in sorption-desorption cycle studies however, desorption studies with doubly distilled water revealed that the regeneration of biosorbent was not satisfactory, which confirm the chemisorptive nature of biosorption.

Conclusions

The work reported in this thesis was the investigation of the potential of using dry *Pleurotus pulmonarius* as a biosorbent for the removal of Cr^{6+} , Cd^{2+} , Ni^{2+} , Co^{2+} and Pb^{2+} from Makurdi municipal open solid waste leachate. Prior to the biosorption processes, the preparation and characterization of the dry *Pleurotus pulmonarius* were carried out. The functional groups found on the surface of the biosorbent which could bind the toxic metal ions were $-\text{OH}$, $-\text{NH}$, $\text{C}=\text{N}$, $\text{C}=\text{O}$ and $\text{C}=\text{C}$ which showed that the dry biosorbent has the potential to be used as a biosorbent. The biosorption kinetics was modeled by pseudo-second-order, Freundlich, Temkin, Dublin-Radushkevich, and Jovanovic models. Desorption studies shows the reusability of the biosorbent. The study confirms the efficiency of using dry *Pleurotus*

pulmonarius as a biosorbent for the removal of Pb, Cr, Cd, Co and Ni ions from leachate. I recommend that NESREA and state environmental and sanitation agencies should partner to upgrade the Nigeria metropolis refuse dump site into well engineered sanitary landfill to protect groundwater and surface water from contamination.

Conflict of interest

Authors declared no conflict of interests.

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