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Isotherm Studies of the Biosorption of Pb (II) and Cu (II) Using Chicken Feather

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Authors' contributions

This work was carried out in collaboration between all authors. Author SAO designed the study, performed the statistical analysis. Authors AWF and AHD wrote the protocol and wrote the first draft of the manuscript. Authors SAO and AH managed the analyses of the study. Author SAO managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

This study was carried out to examine the adsorption isotherm (Langmuir, Freundlich, Temkin, and Dubinin Radushkevich adsorption isotherm) of Pb(II) and Cu(II) in order to determine the maximum adsorption capacity of chicken feather, CF. Equilibrium sorption of Pb(II) and Cu(II) using homogeneously sized Chicken Feather (CF) was carried out and the physico-chemical properties of the feathers were determined. Results revealed that the maximum biosorption capacity of Pb(II) and Cu(II) by the chicken feather from Langmuir isotherm model were 79.36 and 61.92 mg/g respectively. Separation factor R_L were 0.195 and 0.018 indicating a favourable adsorption process. Mean free energy (E) from Dubinin Radushkevich isotherm model were 1.291 and 0.102 KJ/mol for Pb(II) and Cu(II) respectively, indicating a physical adsorption process. Negative standard Gibbs free energy (ΔG) obtained indicated that the Pb(II) biosorption process was spontaneous and thermodynamically feasible.

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1. INTRODUCTION

The presence of heavy metals in the ambient environment, particularly the water bodies cannot be over emphasized. The presence of these heavy metals in the environment is of concern all over the world because they are toxic, persistent, non-biodegradable with bioaccumulation potential [1]. Heavy metal contamination of the environment occur majorly through effluents generated from various anthropogenic activities such as extractive activities, metal plating, metal finishing, tanning/dyeing, battery production processes, pigments/paints production etc [2]. In recent years, a large number of studies have indicated that rivers especially in urban areas are seriously contaminated by heavy metals [3-5]. Prolonged consumption of lead and copper contaminated water will be of health risk overtime [6]. Lead and copper are toxic heavy metals which are common contaminants in aquatic environments. Lead can exist in organic and inorganic forms. Both forms have been identified to be poisonous with the former being more poisonous [7]. The removal of Pb(II) from wastewater has become imperative globally as a result of it toxicity on living beings [8–11]. Lead value above 0.1 mg/l can lead to nervous irritability, mental retardation, brain damage and can also inhibit haem synthesis. Short term exposure to copper can lead to gastrointestinal distress, while long term exposure can cause liver and kidney damage. The permissible limit for lead according to World Health Organization (WHO) guidelines for drinking water is 0.01 mg/l, whereas less than 0.015 mg/l is adopted by the United States Environmental Protection Agency (USEPA) [12]. The permissible limit for lead in effluent discharge into inland surface water is 0.1 mg/L [13].

Metals enter into the food web through leaching from waste dumpsites and metal bearing soil/water. The concentration of the metals increase at every level of food chain and are transferred onto the next higher level through a process known as bioaccumulation or bio-magnification [14] which causes several ailments and abnormal health conditions in humans and other living organisms [15]. Anthropogenic activities are the major sources of pollution in all environments [16]. Thus, heavy metals removal from industrial effluents is of prime importance [17]. Some of the conventional methods for metals removal from industrial effluents include chemical precipitation, membrane filtration, adsorption, ion exchange, cementation, biological operations, coagulation/flocculation, sedimentation, electrochemical processes, and solvent extraction. However, some of these techniques may show technical and/or economical disadvantages such as high cost, high energy demand, high sensitivity to operational conditions, sludge generation [12] and low removal efficiency at high metal concentrations [18]. Natural adsorbents are widely used for the removal of metals from wastewater due to their eco friendly nature and high uptake capacity [19-20]. With increasing environmental awareness and stringent government policies, it is imperative to develop new eco friendly ways to clean up contaminants using low-cost methods and materials [21].

In this study, CF was cut into homogeneous sizes, then used to adsorb Pb(II) and Cu(II) from aqueous solution followed by Isotherm modelling of the adsorption data.

2. MATERIALS AND METHODS

Adsorbate preparation was done by preparing 1000 mg/l stock solution of Pb(II) and Cu(II) which were further diluted to the desired concentration for each experiment. 0.1 M NaOH and 0.1 M HNO_3 were used for pH adjustment.

Chicken feathers (CF) were obtained from a public slaughter point in Gwagwalada area council of the FCT. The CF were cut into smaller sizes which were used in the biosorption experiments.

2.1 Physico-chemical Characterization of Chicken Feather

The CF was characterized by determining the following parameters: pH, moisture content, loss of mass on ignition and bulk density using standard procedures:

2.1.1 Determination of moisture content

5 g of CF was weighed into a dried pre-washed crucible and placed in an oven at a constant temperature of 105°C. After some time, the sample was removed and transferred quickly into a desiccator. The sample was reweighed after cooling. This procedure was repeated several times until a constant weight was obtained.

Moisture content was calculated from the difference in mass obtained [22].

$$\frac{W_2 - W_3}{W_2 - W_1} X\ 100$$

W_1 = Weight of empty crucible
W_2 = Weight of crucible + sample before heating
W_3 = Weight of crucible + sample after heating

2.1.2 Determination of loss on ignition

Loss of mass on ignition was done using 10 g CF. The CF was ashed in a furnace at a temperature of 600℃. The ashed CF was removed from the furnace after 2 hours and cooled in a desiccator. The ash obtained was weighed and loss of mass on ignition was calculated using the formula below.

$$\frac{W_2 - W_3}{W_2 - W_1} X\ 100$$

W_1 = Weight of empty crucible
W_2 = Weight of crucible + sample before ashing
W_3 = Weight of crucible + sample after ashing

2.1.3 Determination of pH

pH of CF was determined by boiling 1 g of CF in a beaker containing 100 cm^3 of distilled water for 5 minutes. The mixture was then diluted to 200 cm^3 with distilled water and allowed to cool at room temperature. The pH was then determined using a pH meter [23].

2.1.4 Determination of bulk density

Archimedes's principle was used in bulk density determination. A glass cylinder was washed, dried and the CF packed into it, leveled and weighed. The weight of CF used was obtained by subtracting the weight of empty cylinder from the weight of packed cylinder while the volume of the cylinder was obtained by filling it to the brim with distilled water and bulk density was calculated using [23].

$$\frac{W_2 - W_1}{V}$$

W_1 = Weight of empty cylinder
W_2 = Weight of cylinder after packing with CF
V = Volume of cylinder

2.2 Biosorption Experiment

Isotherm studies were carried out at 25±1℃, varying the initial metal concentration using single metal Pb(II) and Cu(II) aqueous solution. 50 cm^3 of aqueous solution at pH 4.0 was stirred using a magnetic stirrer at 250 rpm with 0.05 g of CF. After stirring, the mixture was filtered and the filtrate analyzed for metal ions concentration using AAS. The data were fitted into the following isotherms: Langmuir Freudlich, Temkin and Dubinin-Raduskevich isotherm model.

Q in mg/g is the metal uptake which is equivalent to the amount of metal adsorbed per unit mass of sorbent was calculated using the equation:

$$\frac{(C_i - C_f)\ X\ V}{W}$$

The percentage biosorption (%) was calculated using the equation:

$$\frac{(C_i - C_f)}{C_i} X\ 100$$

C_i = Initial concentration of metal in aqueous solution (mg/l)
C_f = Final concentration of metal (mg/l)
V = Volume of solution (L)
W = Weight of CF used (g)

3. RESULTS AND DISCUSSION

The results for physico-chemical analysis of CF is given in Table 1 below:

Table 1. Physico-chemical analysis of CF [24]

Properties	CF
pH	8.10
Moisture Content (%)	8.54
Loss on Ignition (%)	85.97
Bulk Density (g/cm^3)	0.037

FTIR analysis was carried out in order to determine the functional groups on the surface of CF which may be responsible for Pb(II) and Cu(II) sorption process. The spectra of CF before and after the sorption process were similar, showing that the major functional groups on CF did not change significantly during the metal sorption process, which can be an indication of the possible reuse of CF. From the FTIR spectra obtained, the potential metal binding groups include hydroxyl, carboxyl, amino and sulphur containing functional groups.

3.1 Langmuir Isotherm Model

The Langmuir isotherm model is based on the following assumptions:

- The surface of the sorbent posses a finite number of sites which are energetically uniform.
- The amount of sorbate adsorb has no effect on the rate of adsorption because there is no interactions among adsorbed species.
- A monolayer is formed when the sorbent surface becomes saturated.

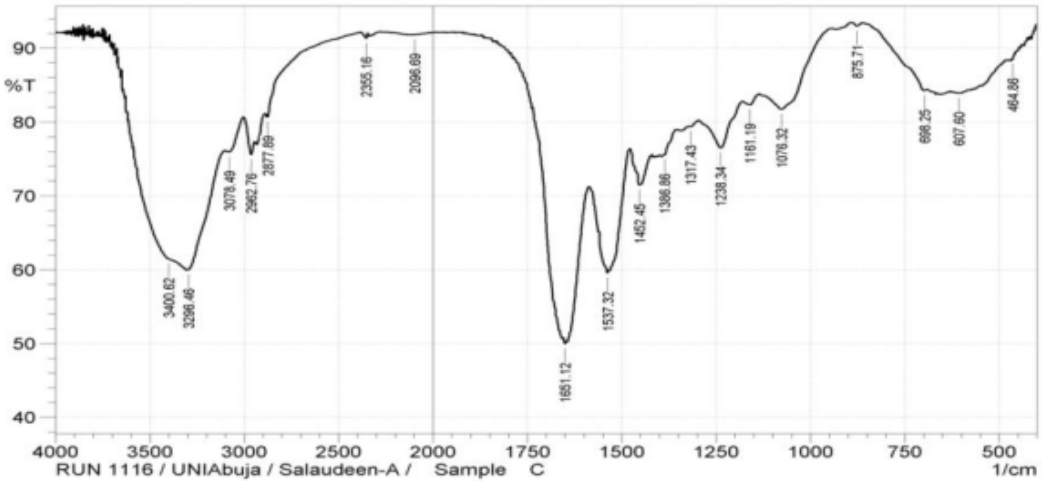

Fig. 1. Full scan spectra of virgin CF [24]

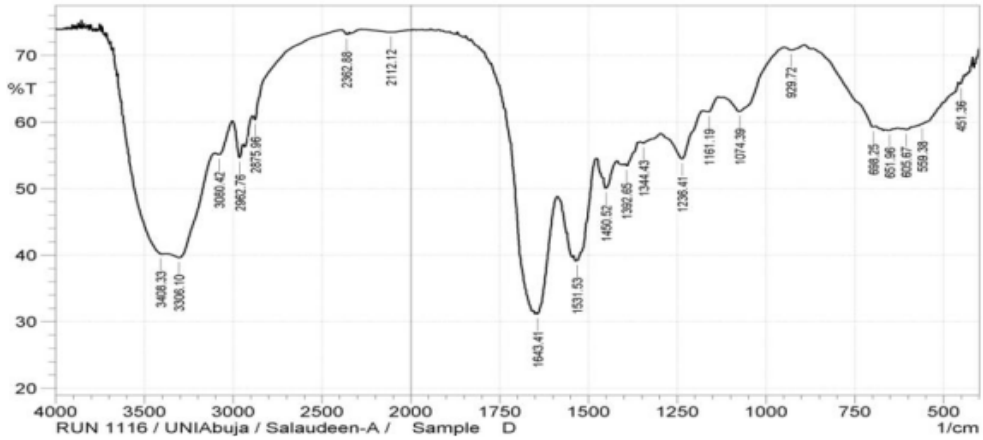

Fig. 2. Full scan spectra of metal loaded CF [24]

Table 2. FTIR spectra bands and assignments of CF [24]

Assignments	Wave numbers (cm^{-1})
N-H stretch	3296.46
Methyl C-H asym/sym. Stretch	2962.76/2877.89
Amide I, 80% C=O stretch and 20% N-H bend	1651.12
Amide II, 60% N-H bend and 40% C-N stretch	1537.32
Amide III, 40% C-N stretch, 30% N-H bend and O=C=N bend	1238.34
Sulphonate S-O asym. Stretch	1161.19
Sulphonate S-O sym. Stretch	1032.11
Cystine dioxide (R-SO_2-S-R)	1238.34
Cystine monoxide (R-SO-S-R)	1076.32
Cystine	1176.62 – 1031.95

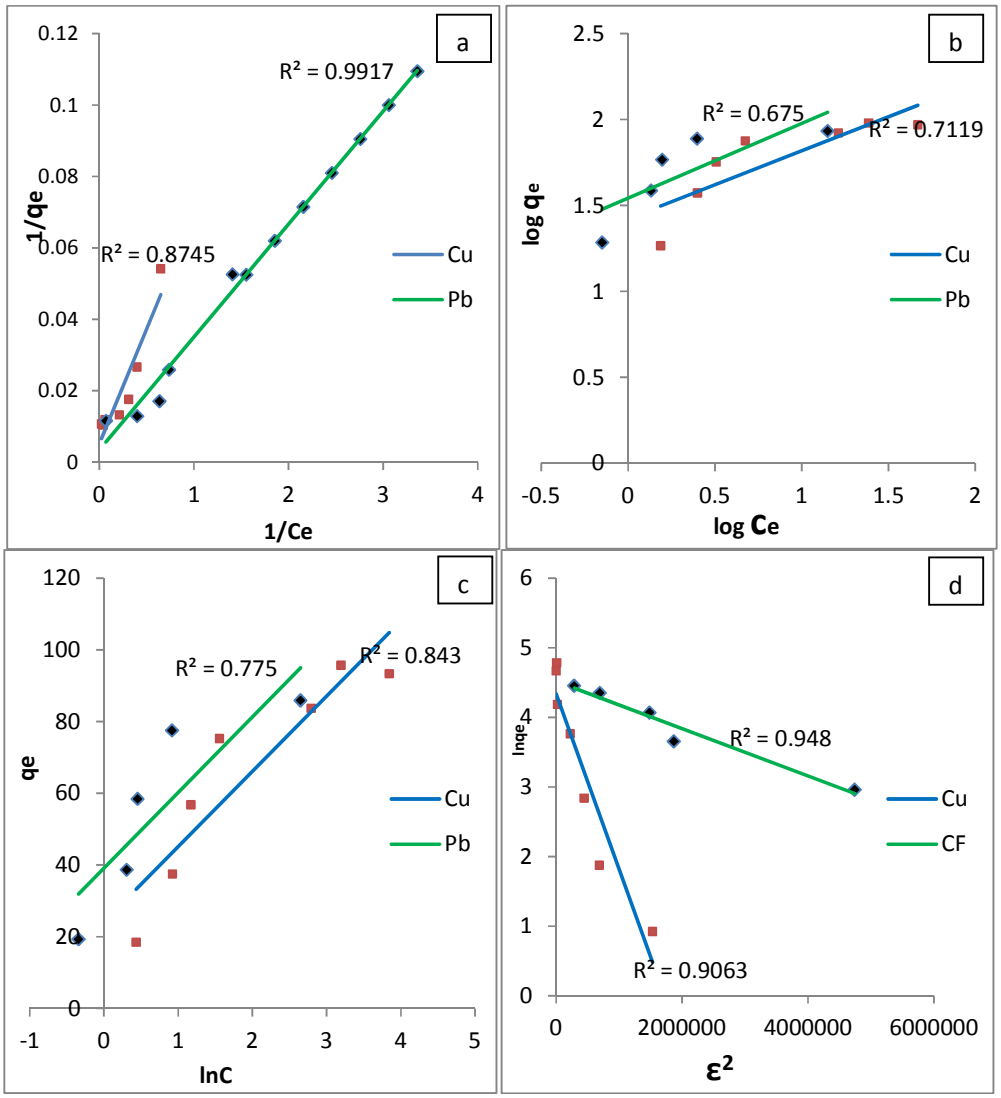

Fig. 3. (a) Langmuir, (b) Freundlich, (c) Temkin and (d) D-R isotherm plots for the biosorption of Pb(II) and Cu (II) by CF

Langmuir equation is represented as [25].

$$q_e = \frac{Q_{max} b C_e}{1 + bC_e}$$

Where

Ce = equilibrium concentration of adsorbate (mg/L),
qe = amount of metal adsorbed per unit mass of adsorbent at equilibrium (mg/g),
Qmax = maximum uptake capacity (mg/g) and
b = Langmuir isotherm constant (L/mg).

Langmuir equation can be linearized as:

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}.bC_e}$$

Qmax and b can be obtained from the plot of 1/qe versus Ce.

An important feature of Langmuir isotherm equation is a dimensionless constant known as separation factor or equilibrium parameter, R_L which is expressed as:

$$R_L = \frac{1}{1 + (1 + bC_o)}$$

Co = initial concentration (mg/l) and
b = Langmuir constant (L/mg).

R_L value indicates the adsorption nature to be either unfavourable if R_L>1, linear if R_L =1, favourable if 0< R_L<1 and irreversible if R_L=0.

From this research work, R_L values (the separation factor) were 0.195 for Pb(II) and 0.018 for Cu(II) indicating that the equilibrium sorption was favourable, the maximum monolayer capacity (Qmax) from Langmuir Isotherm model were determined to be 79.36 and 61.92 mg/g for Pb(II) and Cu(II) respectively, *b* values (Langmuir isotherm constant) were 0.0625 L/mg for Pb(II) and 0.0781 L/mg for Cu(II), and the R^2 values were 0.991 and 0.874 for Pb(II) and Cu(II) respectively proving that the sorption data fitted well to Langmuir Isotherm model for Pb(II) only.

3.2 Freundlich Isotherm Model

The Freundlich equation is based on adsorption on heterogeneous surface [26] and can be expressed as:

$$q_e = K_F . C_e^{1/n}$$

where

K_F = adsorption capacity and
n = adsorption intensity
the linearized form of the equation is given as:

$$\log qe = \log K_F + 1/n \log Ce$$

The slope and intercept gives the values of 1/n and logK_F.

Values of n between 1-10 or 1/n < 0 indicate a favourable adsorption. Value of n indicates the degree of non-linearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1 then adsorption is a chemical process; if n>1, then adsorption is a physical process.

From the Freundlich plot, a correlation coefficients of 0.675 and 0.711 were obtained for Pb(II) and Cu(II) respectively, which are less than those obtained for the Langmuir, Temkin and Dubinin Radushkevich models.

Table 3. Isotherm constants for the adsorption of Pb(II) ion unto CF

Langmuir isotherm				**Freundlich isotherm**			
qmax(mg/g)	b(L/mg)	R_L	R^2	1/n	n	K_F(mg/g)	R^2
79.36	0.0625	0.195	0.991	0.433	2.309	4.674	0.675
Temkin isotherm				**Dubinin Radushkevich isotherm**			
A_T (L/mg)	b_T	B (J/mol)	R^2	Q_S (mg/g)	K_D (mol^2/KJ^2)	E (kj/Mol)	R^2
6.4180	117.60	21.07	0.775	91.286	3 X 10^{-7}	1.291	0.948

Table 4. Isotherm constants for the adsorption of Cu (II) ion unto CF

Langmuir isotherm				**Freundlich isotherm**			
Qmax(mg/g)	b(L/mg)	R_L	R^2	1/n	n	K_F(mg/g)	R^2
61.92	0.0781	0.018	0.874	0.395	2.532	4.145	0.711
Temkin isotherm				**Dubinin Radushkevich isotherm**			
A_T (L/mg)	b_T	B (J/mol)	R^2	Q_S (mg/g)	K_D (mol^2/KJ^2)	E (Kj/Mol)	R^2
1.1527	118.20	20.96	0.843	82.675	5 X 10^{-5}	0.102	0.906

Table 5. Gibbs free energy from Langmuir constant for Pb(II)

Sorbent	**b(L/mg)**	**b(L/mmol)**	**ΔG^O (Kj/Mol)**
CF	0.0625	12.95	-33.40

Table 6. Gibbs free energy from Langmuir constant Cu(II)

Sorbent	**b(L/mg)**	**b(L/mmol)**	**ΔG^O (Kj/Mol)**
CF	0.0781	4.96	-31.03

3.3 Temkin Isotherm Model

This model contains a factor that explicitly considers adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies [27].

Temkin constants can be derived from the slope and intercept of the plot. The model is given by the following equations:

$$q_e = \frac{RT}{b} \ln (A_T C_e)$$

$$q_e = \frac{RT}{b_T} lnA_T + \left(\frac{RT}{b}\right) lnC_e$$

$$B = \frac{RT}{b_T}$$

$$q_e = B\ln A_T + B\ln C_e$$

A_T =Temkin isotherm equilibrium binding constant (L/g), b_T = Temkin isotherm constant, R= universal gas constant (8.314J/mol/K), T= Temperature at 298K, and B = Constant related to heat of sorption (J/mol).

From the plot, A_T = 6.4180 L/mg and 1.1527 L/mg, B which indicates the amount of heat of adsorption was 21.07 J/mol and 20.96 J/mol for Pb(II) and Cu(II) respectively corresponding to physiosorption mechanism.

3.4 Dubinin Radushkevich Isotherm Model

The Dubinin-Radushkevich isotherm model is an empirical model where adsorption process is assumed to follow a pore filling mechanism. It is generally applied to express the adsorption process which occurs on both homogeneous and heterogeneous surfaces. The non-linear expression of Dubinin-Radushkevich isotherm model can be illustrated as:

$$q_e = q_s \exp (-K_{DR}\mathcal{E}^2)$$

Which can be linearized into:

$$lnq_e = \ln(q_s) - (K_{DR}\mathcal{E}^2)$$

q_s and K_{DR} can be obtained from the plot of lnq_e versus ε^2,

$$\mathcal{E} = RTln(1 + \frac{1}{C_e})$$

where

qs = theoritical adsorption capacity (mg/g)
K_{DR} = Dubinin-Radushkevich constant related to mean free energy of adsorption (mol^2/kJ^2)
R = the gas constant (J/mol K)
T = the absolute temperature (K) and
ε = Polanyi potential

The values of q_s computed for Pb(II)/CF and Cu(II)/CF from Dubnin-Radushkevich model were 91.286 mg/g and 82.675 mg/g respectively, mean free energy, E = 1.291 KJ/mol indicating a physiosorption process with an R^2 value of 0.948.

The Gibbs free energies (ΔG^o) were -33.40 and -31.03 kJ/mol at 25℃ for Pb(II) and Cu(II) sorption onto CF respectively indicating a spontaneous and feasible process.

4. CONCLUSION

In this study, the feasibility of CF as a biosorbent for Pb(II) and Cu(II) removal from aqueous solutions was carried out. The results obtained revealed that CF could be used for the removal of Pb(II) and Cu(II) ions from aqueous solution. Equilibrium adsorption studies showed that Pb(II) and Cu(II) sorption followed the trend: Langmuir > Dubinin Radushkevich > Temkin > Freundlich model with Langmuir model having a better fit for the adsorption process of Pb(II) and Dubinin Radushkevich model having a better fit for Cu(II) adsorption process due to higher correlation coefficients. It could therefore be concluded that the adsorption of Pb(II) onto CF followed a monolayer process. FTIR analysis confirmed the presence of carboxyl, hydroxyl, amino and sulphur containing functional groups on CF, with no substantial variation in the spectra obtained before and after adsorption indicating possible re use of CF. Finally, It could be concluded that CF is an active and potential biosorbent for Pb(II) and Cu(II) removal from aqueous solution.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Jain M, Garg VK, Kadirvelu K. Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomass. Journal of Environmental Management. 2010;91(4): 949–957.
2. Argun ME, Dursun S, Ozdemir C, Karatas M. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. Journal of Hazardous Materials. 2007;141(1): 77–85.
3. Dipak P. Research on heavy metal pollution of river Ganga: A review. Ann. Agrar. Sci. 2017;15:278–286.
4. Islamabad MS, Ahmed MK, Raknuzzaman M, Mamun MHA, Islam MK. Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country. Ecol. Indic. 2015;48: 282–291.
5. Xie XJ, Wang FY, Wang GJ, Mei RW, Wang CZ. Study on Heavy Metal Pollution in Surface Water in China. Envron. Sci. Manag. 2017;42:31–34.
6. Salaudeen AO, Adeloju E, Abdulkareem A. Concentrations of heavy metals in water, sediment and fish parts from Asa River, Ilorin, Kwara state. Imperial Journal of Interdisciplinary Research. 2016;2(4):142-150.
7. Krishna KR, Phillip L. Bioremediation of Cr (VI) in contaminated soils. Journal of Hazardous Materials. 2005;121:109–117.
8. Zhao DD, Yu Y, Chen P. Treatment of lead contaminated water by a PVDF membrane that is modified by zirconium, phosphate and PVA. Water Res. 2016;101:564–573.
9. Vergili I, Gönder ZB, Kaya Y, Gürda˘g G, Çavus S. Sorption of Pb (II) from battery industry wastewater using a weak acid cation exchange resin. Process Saf. Environ. Prot. 2017;107:498–507.
10. Milind MN, Santosh KD. Lead resistant bacteria: Lead resistance mechanisms, their applications in lead bioremediation and biomonitoring. Ecotox. Environ. Saf. 2013;98:1–7.
11. Abreham TB, Abaynesh YG, Ramato AT, Dawit N, Efrem C, Lidietta G. Removal of emerging micropollutants by activated sludge process and membrane bioreactors and the effects of micropollutants on membrane fouling: A review. J. Environ. Chem. Eng. 2017;5:2395–2414.
12. Volesky B. Detoxification of metal-bearing effluents: biosorption for the next century. Hydrometallurgy. 2001;59(2-3): 203–216.
13. TERI Energy Data Directory & Yearbook, Tata Energy Research Institute, New Delhi, India, 2005-2006.
14. Paknikar KM, Pethkar AV, Puranik. Bioremediation of metalliferous Wastes and products using Inactivated Microbial Biomass. Indian J. Biotechnol. 2003;2: 426-443.
15. Godwin HA. The biological chemistry of lead, Current Opinion in Chemical Biology. 2001;5:223-227.
16. Salaudeen AO. Physico chemical analysis of water from Asa River, Ilorin, Nigeria. Imperial Journal of Interdisciplinary Research. 2016;2(3):119-126.
17. Capponi F, Sartori M, Souza ML. Modified column flotation of adsorbing iron hydroxide colloidal precipitates. Mineral Process. 2006;79:167-73.
18. Taghi Ganji M, Khosravi M, Rakhshaee R. International Journal of Environmental Science & Technology. 2005;4:265-271.
19. Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG, Gupta VK. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. Ecotoxicol. Environ. Saf. 2018;148: 702–712.
20. Mohammad KU. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chem. Eng. J. 2017;308:438–462.
21. Chandra Sekhar K, Kamalaa CT, Chary NS, Sastry ARK, Nageswara Rao T, Vairamani M. Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass. Journal of Hazard Matter. 2004;108:111.
22. Abdel-Halim ES, Abou-Okeli A, Hashem A. Adsorption of Cr(VI) oxy-anions onto modified wood pulp. Polymer-Plastics Technology and Engineering. 2006;45:71-76.
23. Toshiguki S, Yukata K. Pyrolysis of Plant, Animal and Human Wastes; Physical and Chemical Characterization of the Pyrolytic Product; Bioresource Technology. 2003; 90(3):241-247.

24. Olawale SA, Funke AW, Dede AH, Hajara Y. Biosorption of Pb (II) and Cu (II) from Aqueous Solution Using Chicken Feathers: Thermodynamics and Mass Balance Studies. 2018;1(3):1-9.
25. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 1918;40: 1362-1403.
26. Freundlich HMF. Over the adsorption in solution. J. Phys. Chem. 1906;57:385-471.
27. Dada AO, Olalekan AP, Olatunya AM, Dada O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry. 2012;3(1): 38-45.

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