



Citrus lemon leaf powder as a biosorbent for the removal of liquid phase toxic metals from textile effluent

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ABSTRACT

Citrus lemon leaf powder (CLLP) is used as a biosorbent for the removal of toxic metals from textile effluent in a batch process. The biosorbent of CLLP is cost-effective and holds excellent potential for the removal of toxic metals. The textile effluent is one of the major sources of toxic metals that contaminate the river and groundwater. The main objective of this research is to purify the textile effluent and to reduce the toxicity of cadmium [Cd(II)_(L)], lead [Pb(II)_(L)], nickel [Ni(II)_(L)], zinc [Zn(II)_(L)], and copper [Cu(II)_(L)]. Besides, it intrigues the effect of various factors/parameters like pH, dosage content, and contact time of metals. It is found that in 50 ml of effluent, 80%–90% of the toxic metals could be removed by 2.0 g of the citrus lemon leaves powder. The results obtained through experimental data are examined by the various isotherms like Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Harkins–Jura, and Jovanovic. The adsorption data fitted well to Langmuir isotherms. The regression coefficient value is greater than 0.9. The absorbed R_L of Langmuir isotherm for all cases is around 0–1, which is a favorable one. In the cases of adsorptions, the parameters such as 'n' falling in the range of 1–10 indicate favorable sorption. The results show that CLLP could be used as a low-cost biosorption process for the removal of metals from textile effluent.

Keywords: Lemon leaf; Toxic metals; Biosorption; Langmuir isotherm; Freundlich isotherm; Temkin isotherm; Dubinin–Radushkevich isotherm; Harkins–Jura isotherm; Jovanovic isotherm

1. Introduction

Textile industries play a significant role in the economic development of India. The textile industries utilize around 829.8 million m³ of groundwater and after various dyeing processes, it nearly discharges wastewater of around 637.3 million cubic meters to the ground. Due to the dyeing processes, the textile outlets have more toxic elements (heavy metals) like cadmium (Cd), chromium (Cr), copper

(Cu), lead (Pb), nickel (Ni), and zinc (Zn). The textile industries release wastewater in water and that affects the living organisms. The toxic metals pollute natural resources like river and groundwater and thus they are considered as environmental pollutants [1]. Hence textile industries are one of the primary sources of water pollution.

Industrial effluents extracted out of pigments and dyeing, leather, oil refining, sequencing of photographic films, etc., in textile industries discharge wastewater that are either

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partially treated or untreated to the ground. This results in water and soil pollution, as a significant amount of toxic metals are released continuously to the ground. Polluted natural resources cause various diseases to humans and even death in some cases. The activated carbon is the most commonly used sorbent, that should be regenerated and it is too expensive. Certain treatments like chemical precipitation [2], ion exchange, flotation [3], membrane separation [4], filtration, and electrochemical treatment could also be utilized to remove toxic metals and these treatments are desirable for significant scale methods to obtain a vast amount to exercise. Because most of the above methods of treatment, the percentage removal of toxic metals is low and the above methods require a large amount of area to set-up the treatment plant [5]. In recent years, many researchers have developed various novel materials as adsorbents from different plant resources, that could replace the activated carbon process as an effective and cheaper method. Therefore, the treatment of adsorbents is developed to treat wastewater from different contaminants and that prompts environmental engineers and scientists to remove pollutants at low cost [6,7].

The metal binding capacities of various biological adsorbents makes biosorption as an innovative technology in the segregation of toxic metals from wastewater. Low-cost, high efficiency, regeneration of biosorbents, and possible action of metal recovery are the significant advantages of biosorption over conventional treatment methods [8,9]. The biosorption process gives the best result in the removal of toxic metals with low-cost technology [10–12].

The most important task of the biosorption study is to select different kinds of biosorbent from readily available and economic biomaterials. Hence, several low-cost organic sorbents like teak leave powder [13,14], mansonia sawdust [15], pine bark (*Pinus brutia* Ten.) [16], mango leaf powder and rice husk [17], peat, banana pith, soybean, cotton hulls, peanut, shells, hazelnut shell, wool, orange peel, and compost [18–20] are suggested to remove toxic metals from contaminated water. Many biological materials for the uptake of toxic metals are available in nature, but biosorbents with a high level of metal-binding capacity are appropriate for a complete biosorption process. It is the fastest-growing process for the segregation of toxic metals by various other solvents, namely neem leaves, *Psidium* Guava leaves, rice husk, wood, straw, soybean hulls, tea waste, wheat bran, sawdust, peapod, etc., [21–24].

The biosorbents such as groundnut husk, tea leaves, tree bark, sawdust, neem leaves (*Azadirachta indica*) are successfully used for the removal of cadmium, zinc, copper, nickel, and chromium from aqueous solutions at higher concentrations [25–30]. In this methodology, the physico-chemical pathways uptake (parameters such pH, dosage content (DC), contact time (CT), temperature, and concentration) are used to remove toxic metals [31]. The removal of Pb is attained at pH 7, 100 rpm, and 90 min of contact time by using adsorbents such as chicken eggshell powder, banana peel powder, and pumpkin powder [32,33]. Agitation, speed, different contact time, and pH values are the various parameters intrigued by periwinkle shell carbon, commercial activated carbon [34], cement kiln dust and biochar-filters [35]. Thus, this work is aimed at analyzing the

biosorption behavior of citrus lemon leaf powder (CLLP) for the removal of toxic metals from the textile effluent.

2. Preparation and conservation of lemon leaf

2.1. Materials

Removal of toxic metals from a sedimentary solution is one of the most significant issues in many industries. The effective removal of toxic metals from textile wastewater is analyzed using citrus lemon leaves as powder content.

In ancient times, citrus lemon trees were found in the Northern part of India. These trees have the habit of fighting against dry season and poor soil. They are productively grown in Mediterranean climates. It is cultivated in Africa, in and around Europe and other countries also. The lemon belongs to the blooming plant family, *Rutaceae*. It is local to Asia. The characteristic of citrus lemon leaves is shown in Table 1.

To extract dust and impurities accumulated on the surface of the citrus lemon leaf (CLL), it is washed with running sterile water. The CLL is air-dried and then oven-dried at 80°C to constant mass. The dried leaves are pulverized and sieved to obtain particle sizes less than 300 µm. The dried biomass is preserved in airtight glass bottles to protect it from moisture.

2.2. Collection of textile wastewater sample

The textile effluent is collected from different places of Komarapalayam in Namakkal district. It is located between Salem and Bhavani (11.4433°N, 77.1138°E), Tamil Nadu, India. It is on the bank of river Bhavani, which is a branch of River Cauvery. Untreated or partially treated dye effluents are released directly into the river Bhavani. The collected samples were characterized randomly with the permissible limits according to IS: 10500 in Table 2. In most of the places, the quality of water is not found suitable for drinking activities and irrigation and due to high concentrations of parameters [36,37].

2.3. Experimental analysis

The biosorbent (CLLP) is used for the uptake of toxic metals viz., $Pb(II)_{(L)}$, $Zn(II)_{(L)}$, $Cd(II)_{(L)}$, $Ni(II)_{(L)}$ and $Cu(II)_{(L)}$ from the textile effluent. This textile effluent is analyzed under the three parameters, such as pH level of effluent, DC of biosorbents, and contact time.

Table 1
Characteristic of citrus lemon leaves

Moisture content	4.77%
Fixed oil	6%
Volatile oil	0.365%
Resin	3.15%
Tannin	8.50%
Bulk density	262 g/dm ³

Table 2
Characteristics of typical untreated textile wastewater

Sl. No.	Parameters	Textile wastewater	Desirable limits (IS: 10500)	Permissible limits	Method of test (IS: 3025)	Remarks
1	Potential of hydrogen (pH)	11.16	6.5 to 8.5	No relaxation	Part 11	<6.5 – acidity >8.5 – alkalinity
2	Specific conductivity (Milli Mho)	6.025	NA	–	–	–
3	Turbidity (NTU)	4.12	1	5	Part 10	–
4	Color (Hazen Units)	Reddish Violet	5	15	Part 4	Extended to 15 only, if toxic substances are not suspected in absence of alternate sources
5	Total solids (mg/L)	12,265.97	500	–	–	–
6	Total dissolved solids (mg/L)	12,242.70	500	2,000	Part 16	–
7	Total suspended solids (mg/L)	400	100	–	–	–
8	BOD ₅ (mg/L)	1,100	500	1,050	–	–
9	COD (mg/L)	3,800	250	3,200	–	–
10	Copper (Cu(II)) (mg/L)	3.65	0.05	1.5	Part 42	–
11	Zinc (Zn(II)) (mg/L)	6.65	5	15	Part 49	–
12	Nickel (Ni(II)) (mg/L)	2.23	0.02	No relaxation	Part 54	–
13	Lead (Pb(II)) (mg/L)	9.21	0.01	No relaxation	Part 47	–
14	Cadmium (Cd(II)) (mg/L)	1.02	0.003	No relaxation	Part 41	–

The test is accomplished in a batch mode for the measurement of adsorption capabilities. The conical glass flask of 250 ml is filled with 50 ml of the textile wastewater with an adsorbent at various dosages such as 0.5, 1.0, 1.5, 2.0, and 2.5 g. The initial pH of the textile effluent solution is changed with the working values (pH level of 1–11) by including either a few drops of 0.1 M HCl or 0.1 M NaOH aqueous solutions. The glass flask is shaken during a pre-determined period at room temperature with an orbital shaker for a while in 60, 120, 180, 240, and 300 min at 300 rpm. The adsorbent and solution are divided by filtration with Whatman filter paper No. 44, and it is kept in a little glass holder inside the refrigerator before analysis. The residual metal ion concentrations are determined by utilizing an atomic absorption spectrometer (AAS), model: AAS-201.

Fig. 1 shows the biosorption of toxic metals uptake to the potential of hydrogen. The pH level gradually increases with the increase in metal uptake and observes the optimum level of pH 4 and 5 at 2.0 g of biosorbent. The percentage of adsorption and equilibrium adsorption capacity (q_e mg/g) is evaluated using the following equations:

$$\% \text{ Adsorption} = \left(\frac{A_c - B_c}{A_c} \right) \times 100 \quad (1)$$

$$q_e = \left(\frac{V(A_c - B_c)}{W} \right) \quad (2)$$

where A_c (mg/L) is the initial dye concentration, B_c is the concentration at equilibrium time (t), V (l) is the volume of dye solutions, and W (g) is the weight of the adsorbent.

3. Results and discussions

3.1. Effect of pH

The biosorption of toxic metals from the textile effluent is mainly influenced by the pH of the solution. In this work, the extent of toxic metals biosorption was investigated from pH 1.0–11.0. The various amounts of CLLP (0.5–2.5 g) for toxic metals solution of concentration 50 mg/L are shown in Fig. 2. The extent of metals absorbed is low and negligible from the DC of 0.5–1.5 g. At a low pH level, the removal of metal ions is inhibited by the net positive charge on the sorbent and competition between metal and hydrogen ions in solution. The biosorption of Cd(II)_(L) and Ni(II)_(L) is maximum at pH 4.0 and Pb(II)_(L), Zn(II)_(L), and Cu(II)_(L) are observed maximum at pH 5.0 for CLLP (2.0 g). After increasing the pH from 5 to 11, the removal percentage slowly drops down (Fig. 2) by increasing the biosorbent from 2.0–2.5 g, and reaches equilibrium condition.

Through batch processing, the removal efficiency (RE) of Cd(II)_(L) is observed as 54.73% (pH 1) and it attains a maximum of 85.16% at pH 4.0. At pH 1, the minimum RE of Ni(II)_(L) is 61.02%, and 84.18% is the maximum RE at pH 4. Increasing the pH gradually reduces the RE. The sorption may be an opposition between metal ions and protons for biosorption sites. It is also affected by the pH. The Pb(II)_(L) metal ion gets slightly affected when there is a change in pH level. There is a slight increase in the RE of Pb(II)_(L) from 57.33% to 85.03%, with the rise in pH from 1 to 5. For a pH 1, the RE of Zn(II)_(L) is 70.34%. It increases pH from 1 to 2 and the RE is 75.05%. At pH 5, the RE of Zn(II)_(L) is achieved maximum (88.70%). The biosorption of Cu(II)_(L) ion is conducted through batch processing to remove the effluent at different pH levels. Cu(II)_(L) ion is effectively sorbed

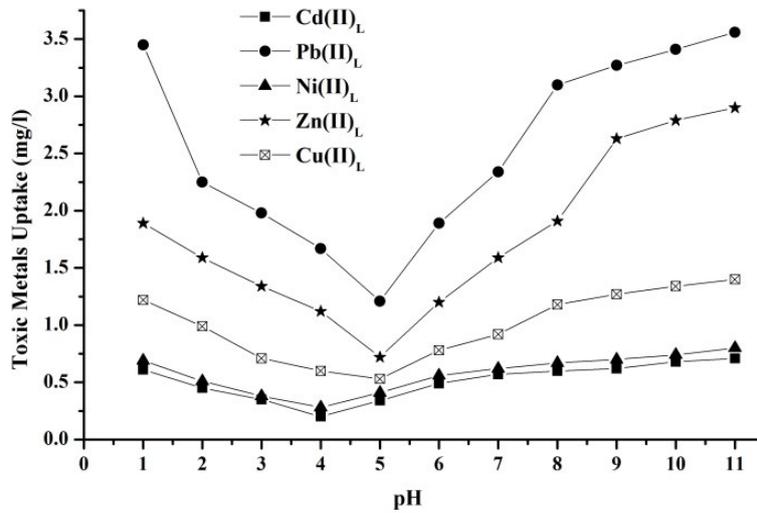


Fig. 1. pH vs. toxic metals uptake.

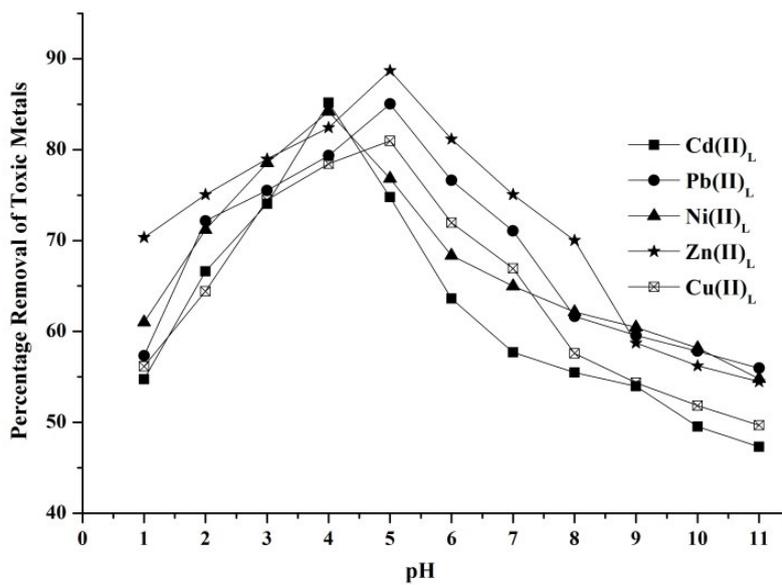


Fig. 1. DC vs. toxic metals uptake (pH 5).

in the pH level from 1 to 5. At pH 5, the maximum RE of Cu(II)_(L) is achieved (80.95%). When the pH level increases to more than 5, the biosorption dilutes. When the pH level is above optimum, the removal of metal ions is inhibited by the net negative charge on the sorbent and it results in the competition between metal and hydrogen ions in solution. It is found through this research that the biosorption of Cd(II)_(L) and Ni(II)_(L) is performed at pH 4. The toxic metals of Pb(II)_(L), Zn(II)_(L) and Cu(II)_(L) are observed at pH 5 for CLLP, respectively.

3.2. Effect of DC

The effect of DC of CLLP on the RE of toxic metals is analyzed with the varying dosage from 0.5 to 2.5 g, keeping all other parameters constant (pH and initial contact time

60 min). This batch biosorption is carried out on a shaker at 300 rpm and 30°C using a 100 ml conical glass flask containing 0.5 g of biosorbent and 50 ml of CLLP solutions of the desired pH. Figs. 3 and 4 show the biosorption of toxic metals uptake to DC. For pH levels of 1, 2, and 3, the biosorbent of toxic metals is low and negligible. For pH 4, the evacuation of liquid phase Cd(II)_(L) and Ni(II)_(L) ions increases sharply from 56.90% to 85.16% and from 60.40% to 84.18%, when the dosage raises from 0.5 to 2.0 g (Fig. 5). At pH 5, the removal of Pb(II)_(L), Zn(II)_(L) and Cu(II)_(L) are attained at 85.03%, 88.70%, and 80.95%, respectively at an increased dosage of 2.0 g (Fig. 6). The initial rapid increase is due to the increasing availability of binding sites and surface area, which makes the biosorption of the ions quite easy until it reaches equilibrium. RE attains the balance over 2.0 g of dosage.

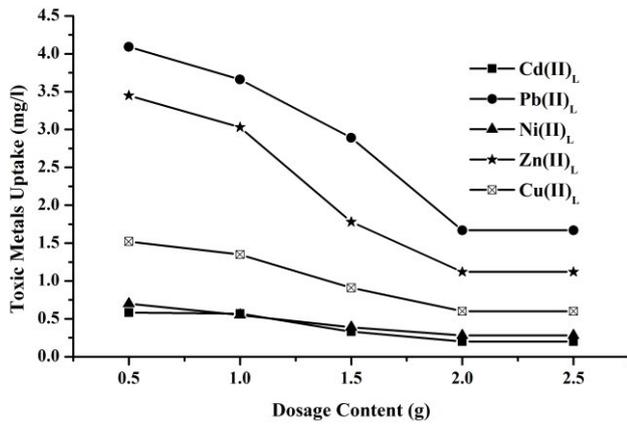


Fig. 3. DC vs. toxic metals uptake (pH 4).

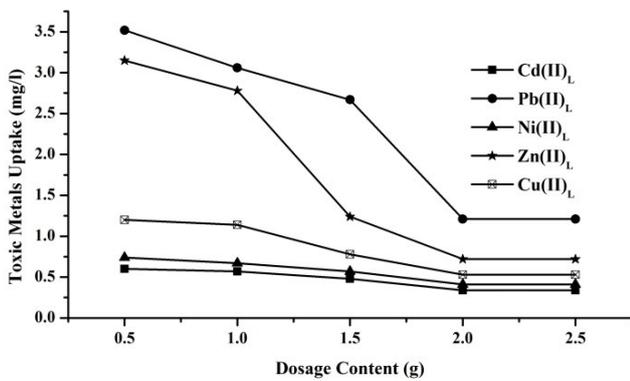


Fig. 4. DC vs. toxic metals uptake (pH 5).

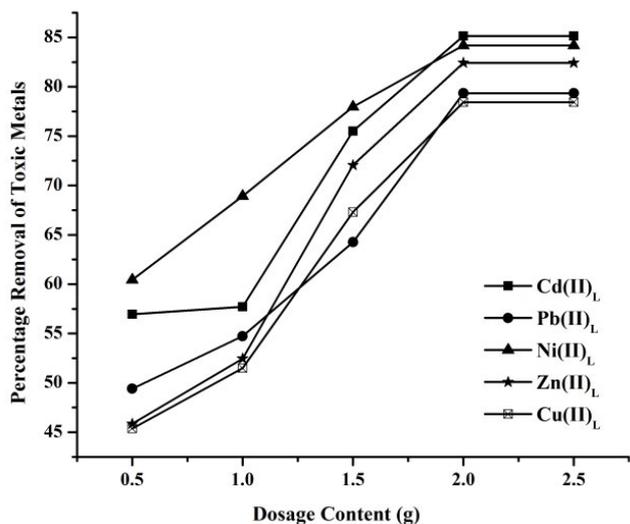


Fig. 5. DC vs. RE of toxic metals of pH 4.

3.3. Effect of contact time

The effect of CT is studied to find the time taken by this batch biosorption until it reaches the desired DC of 2.0 g and equilibrium condition for pH 4 and 5. Figs. 7 and 8 show

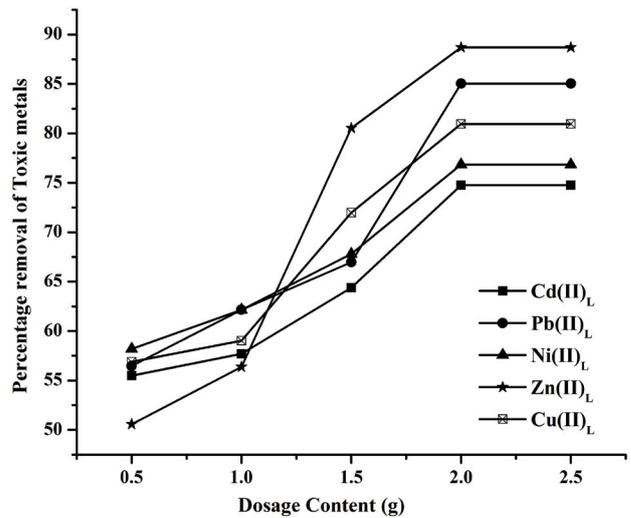


Fig. 6. DC vs. RE of toxic metals of pH 5.

the batch biosorption of toxic metals uptake to the contact time. Biosorption technology is used to remove metals with the help of a natural source of biosorbent, which depends on the interaction of functional groups in the effluent. The transfer of ion developments are based on biosorption, contact times are crucial parameters. Hence, the main focus is to study the biosorption process. The contact time increases the ability of biosorbents during the removal of toxic ions. The RE of toxic metals is measured in periodic contact time intervals (60 min) up to 300 min the dosage of 2.0 g with the pH 4 and 5. It is found appreciable comparing to other parameters.

The rate of biosorption is rapid in the initial stages because of the availability of an adequate surface area of the biosorbent. After the increase in contact time, more amount of toxic metals are adsorbed onto the surface of the biosorbent due to Van der Waal's force attraction and it decreases in the available surface area [38]. The result shows that the biosorption of toxic metals is low from pH 1–3. The rate of metal ions in RE is higher at the beginning owing to the larger surface area [39]. The maximum RE of Cd(II)_(L) and Ni(II)_(L) are attained as 89.61 and 88.70 at 180 min (Fig. 9). Besides, an increase of contact time and the biosorption reach the equilibrium conditions.

At pH 5, the rate of RE of Pb(II)_(L) and Zn(II)_(L) attains maximum (88.30% and 89.49%) at 180 min. Further, the increase in contact time makes the rate of evacuation reach the equilibrium condition (Fig. 10). It shows that the remaining empty sites on the biosorbent is occupied, which leads to repulsive forces between adsorbed toxic metals ions on the biosorbent and those in the aqueous phase [40,41]. The maximum RE of Cu(II)_(L) reaches 87.06% with the contact time of 240 min at 2.0 g of biosorbents at pH 5 (Fig. 10).

The biosorption of each metal ion is spontaneous and the order of spontaneity of the biosorption process is Cd(II)_(L) > Zn(II)_(L) > Ni(II)_(L) > Pb(II)_(L) > Cu(II)_(L). This shows that the biosorbent of CLLP holds excellent potential for the removal of toxic metals from the textile effluent.

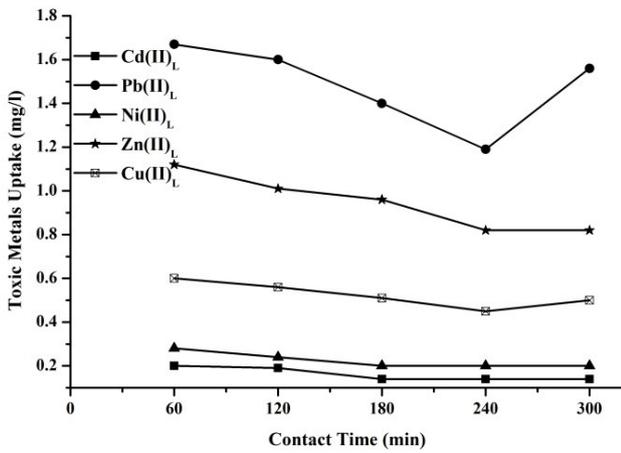


Fig. 7. CT vs. toxic metals uptake (pH 4).

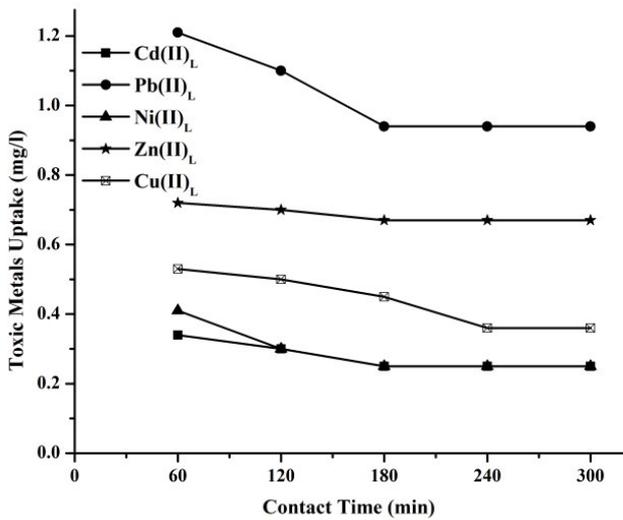


Fig. 8. CT vs. toxic metals uptake (pH 5).

4. Biosorption kinetics

The biosorption kinetics describes the extent of uptake of toxic metal using biosorbents. This rate controls the equilibrium time. The interactions appear to attain equilibrium rapidly after an hour of agitation. The mathematical models are carried out to describe the equilibrium behaviors of adsorbate uptake with well-known isotherms. The Dubinin–Radushkevich ($D-R_i$), Freundlich (F_i), Harkins–Jura ($H-J_i$), Jovanovic (J_i), Langmuir, Redlich–Peterson ($R-P_i$), and Temkin (T_i) isotherm are considered as independent models [42]. The characteristics of the isotherm model are tabulated in Table 3.

4.1. Langmuir isotherms

The assumption of the Langmuir adsorption [43,44] process is the monolayer of the adsorbent. It is formed at the outside surface of the adsorbent and no further adsorption occurs after that:

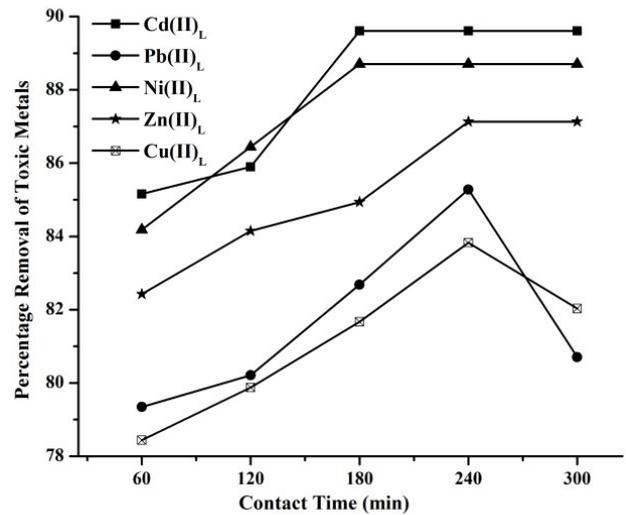


Fig. 9. CT vs. RE of toxic metals of pH 4 (2.0 g).

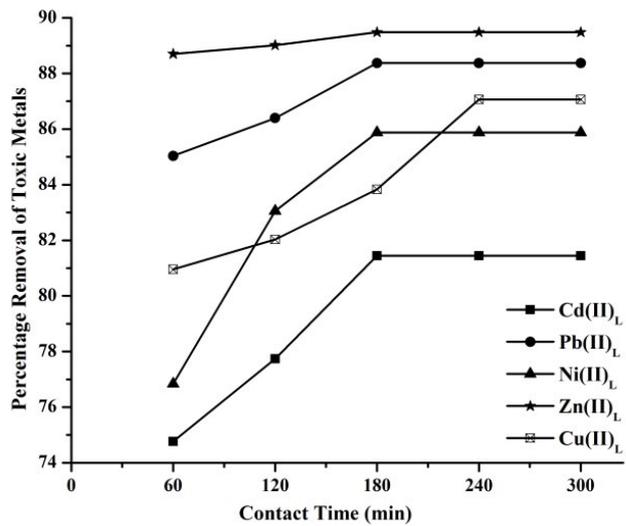


Fig. 10. CT vs. RE of toxic metals of pH 5 (2.0 g).

$$q_e = \left(\frac{x}{m} \right) = \left(\frac{q_{\max} K C_e}{1 + K C_e} \right) \quad (3)$$

$$\left(\frac{C_e}{q_e} \right) = \left[\left(\frac{C_e}{q_{\max}} \right) + \frac{1}{q_{\max}} K \right] \quad (4)$$

where x is the amount of ions adsorbed; m is the unit mass of adsorbent; ' q_e ' is the amount of metal ion adsorbed per unit mass of adsorbent.

Based on a dimensionless equilibrium parameter R_L , further study of the Langmuir equation could be performed.

The factor of separation is given by:

$$R_L = \left(\frac{1}{1 + K C_{\text{ref}}} \right) \quad (5)$$

where K and C_{ref} are the Langmuir constant and equilibrium liquid-phase concentrations of the solute, respectively. R_L represents the favorable adsorption, $0 < R_L < 1$, while $R_L > 1$ represents unfavorable adsorption, $R_L = 1$ is linear adsorption and $R_L = 0$ is irreversible.

The values of q_{max} and b are calculated from the slope and intercept of the linear plot (Fig. 11). The better R^2 value for Langmuir isotherm indicates the applicability of this model to the removal of toxic metals for CLLP. The regression analysis of the parameters for Langmuir isotherm shows that the maximum biosorption capacity per unit of biosorbent (q_{max}) and biosorption equilibrium constant (b) corresponds to the toxic metals. The obtained correlation coefficient (R^2) fits well for Langmuir isotherm indicates the applicability of this model as shown in Table 3. The dimensional separation parameter (R_L) indicates the isotherm form and predicts that the adsorption process is positive.

4.2. Freundlich isotherms

The Freundlich [45,46] introduced an empirical adsorption isotherm equation that could be applied for ranges between low concentrations and intermediate concentrations. The general form of isotherm is given as:

$$q_e = KC_e^{\frac{1}{n}} \tag{6}$$

The linear form:

$$\text{Log } q_e = \text{Log } K + \left(\frac{1}{n}\right) \text{Log } C_e \tag{7}$$

The Freundlich constants K_F and n are found from the slope and intercept of the linear plot figured in Fig. 12. The magnitude of the component ‘ n ’ gives a sign of the favorability of the adsorption procedure, and K_F is consistently identified with the adsorption capacity. The isotherm constants K_F calculated by this model and represented in

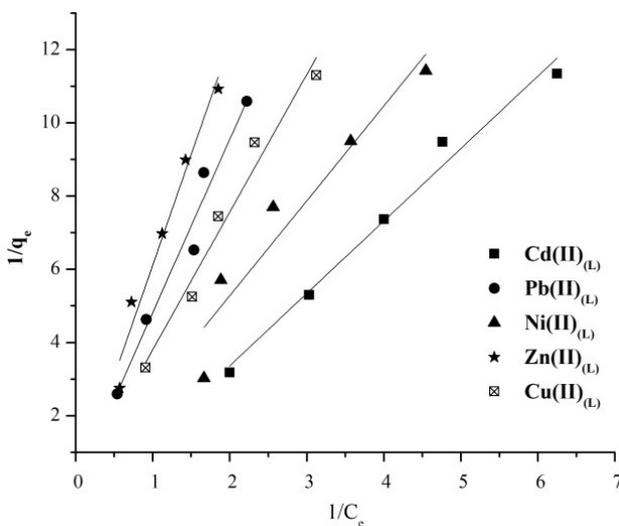


Fig. 11. Langmuir isotherm.

Table 3. According to this process, the value of ‘ n ’ is shown greater than unity which represents favorable biosorption.

4.3. Temkin isotherms

The Temkin isotherm is considered to be the reason for the effects of some indirect sorbate interactions on adsorption isotherms and it is suggested that it is because of these interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage [47].

The equation expressed as:

$$q_e = \left(\frac{RT}{b}\right) \ln AC_e \tag{8}$$

The linear equation as:

$$q_e = [B(\ln A) + B(\ln C_e)] \tag{9}$$

where $B = (RT/b)$ where B and A are the Temkin constant related to the heat of sorption (J/Mol) and isotherm constant

Table 3 Isotherm models

Isotherm parameters	Cd(II) _(L)	Pb(II) _(L)	Ni(II) _(L)	Zn(II) _(L)	Cu(II) _(L)
L_i					
R^2	0.984	0.970	0.915	0.970	0.971
R_L	0.969	0.882	0.943	0.944	0.976
q_{max} (mg/g)	23.810	12.820	11.364	17.857	31.250
b (L/mg)	0.023	0.016	0.033	0.010	0.008
F_i					
R^2	0.878	0.886	0.905	0.875	0.850
n	1.340	1.202	1.344	1.453	1.153
K_F (mg/g)	0.324	0.070	0.233	0.100	0.164
T_i					
R^2	0.648	0.665	0.705	0.804	0.690
B	0.114	0.077	0.194	0.045	0.109
K_T (L/mg)	2.789	1.195	1.830	1.356	1.257
$D-R_i$					
R^2	0.965	0.720	0.833	0.909	0.968
q_D (mg/g)	1.388	1.944	1.543	2.112	1.663
B	0.127	0.105	0.045	0.120	0.071
$H-J_i$					
R^2	0.938	0.828	0.873	0.951	0.911
A	3.240	4.277	4.274	3.931	3.920
B	1.851	1.570	1.870	1.714	1.755
J_i					
R^2	0.933	0.932	0.908	0.891	0.889
q_{max}	0.294	0.387	0.316	0.324	0.374
K_j	0.587	0.324	0.975	0.407	0.435

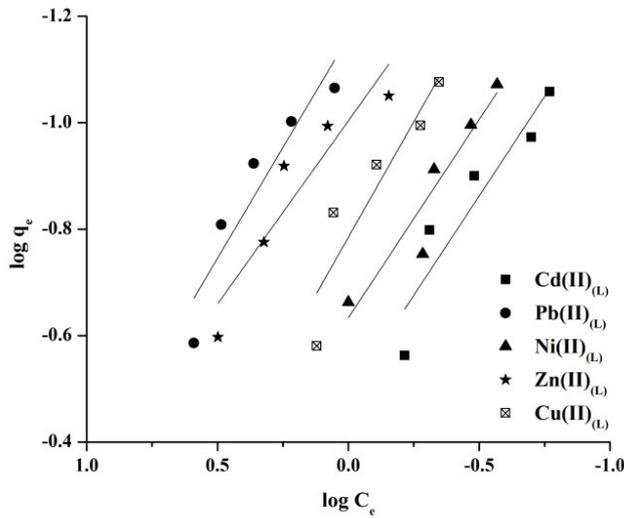


Fig. 12. Freundlich isotherm.

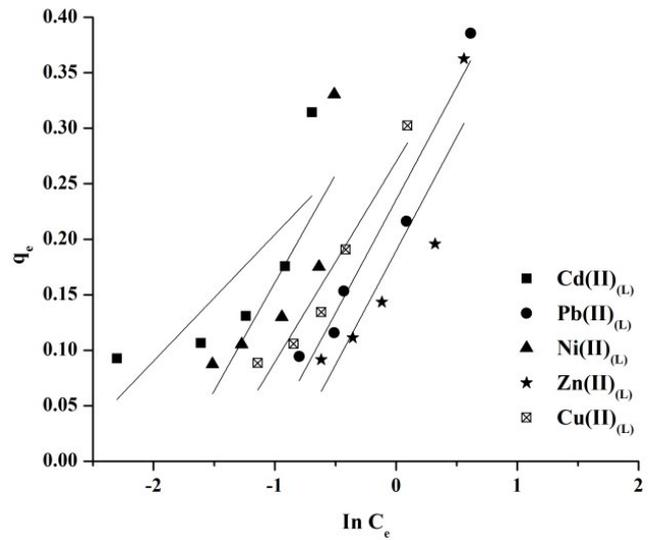


Fig. 13. Temkin isotherm.

(L/g), respectively, R is the gas constant (J/Mol K), and T is the absolute temperature (K).

The equilibrium data are observed and fitted to the isotherms (Fig. 13), hence the coefficient value of K_T (L/mg) and B for the toxic metals, whereas the coefficient of correlation (R^2) given in Table 3.

4.4. Dubinin–Radushkevich isotherms

To estimate the characteristic porosity of the biomass and the apparent energy of adsorption, the Dubinin–Radushkevich isotherm model [48,49] is selected. The following equation shows the model:

$$q_e = q_D \text{Exp} \left\{ -B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \right\} \quad (10)$$

The linear form of the equation as:

$$\ln q_e = \ln q_D - \left[2_{BD} RT \ln \left(1 + \frac{1}{C_e} \right) \right] \quad (11)$$

The apparent adsorption energy (E_D) of the Dubinin–Radushkevich isotherm model could be determined using the given relationship:

$$E_D = \sqrt{\frac{1}{2B_D}} \quad (12)$$

where B_D is the free energy of sorption per mole of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution, q_D is the Dubinin–Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface.

The equilibrium data are obtained and fitted to the isotherms (Fig. 14), related to the degree of sorbate sorption

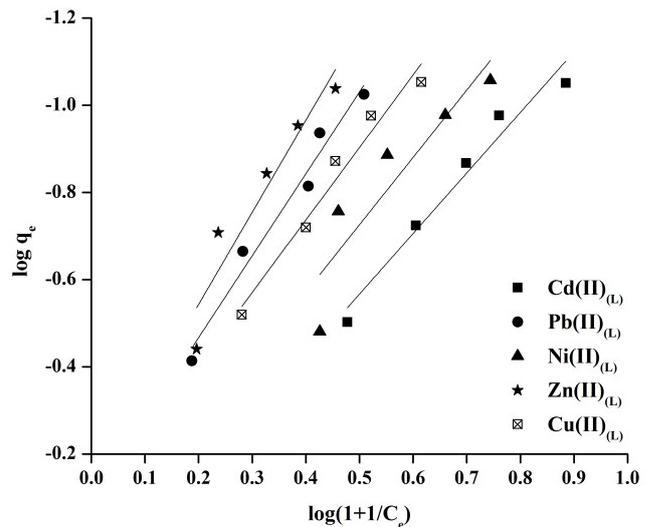


Fig. 14. Dubinin–Radushkevich isotherm.

by the sorbent surface value of q_D (mg/g) and B for the toxic metals, whereas the coefficient of correlation (R^2) is given in Table 3.

4.5. Harkins–Jura isotherms

Harkins–Jura adsorption isotherm multilayer adsorption that could be explained by a heterogeneous pore distribution [50,51].

$$\left(\frac{1}{q_e^2} \right) = \left[\left(\frac{B}{A} \right) + \left(\frac{1}{A} \right) \text{Log } C_e \right] \quad (13)$$

where B and A are the isotherm constants.

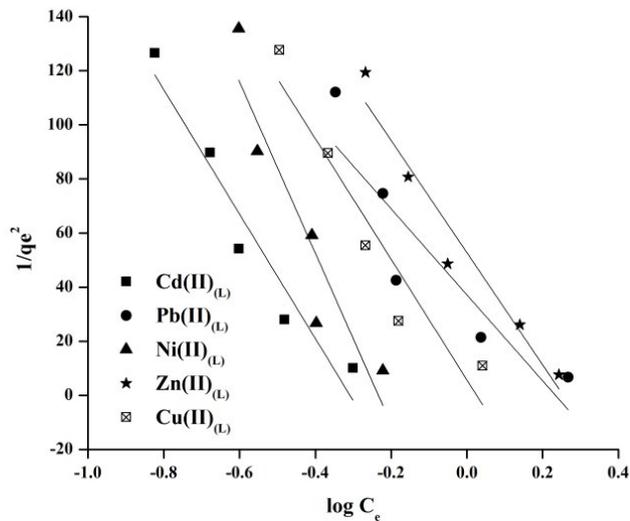


Fig. 15. Harkins–Jura isotherm.

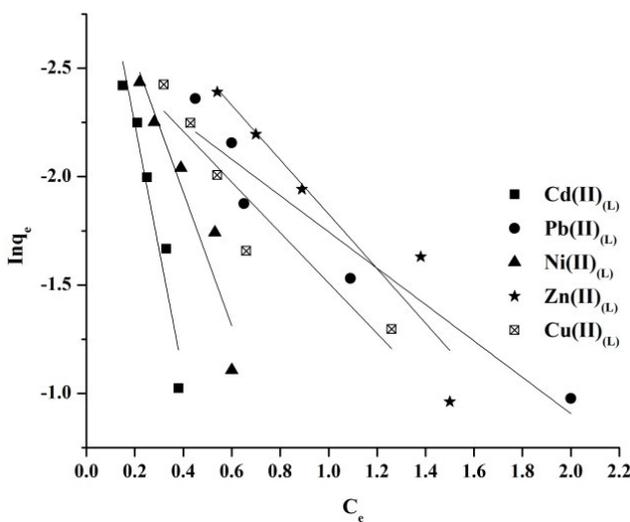


Fig. 16. Jovanovic isotherm.

The observed equilibrium data are fitted to the isotherms (Fig. 15), hence the isotherm constant value of A and B to the toxic metals, whereas the coefficient of correlation (R^2) is given in Table 3.

4.6. Jovanovic isotherms

The model of an adsorption surface considered by Jovanovic [52,53] is equivalent to the one found by Langmuir. A similar sort of estimation prompts the outcome that the Langmuir isotherm depicts monolayer adsorption of mobile hard circles. The linear type of the Jovanovic isotherm is expressed as follows:

$$\ln q_e = \left\{ \ln q_{\max} - [K_j \ln(C_e)] \right\} \quad (14)$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), q_{\max} is the maximum uptake of adsorbate obtained from the plot of $\ln q_e$ to the C_e , and K_j is the Jovanovic constant.

The equilibrium data are computed and fitted to the isotherms (Fig. 16), hence the coefficient value of K_j and q_{\max} to the toxic metals, whereas the coefficient of correlation (R^2) given in Table 3.

The test results are evaluated with various isotherms, the theoretical plots of each isotherm are applied to the exploratory sorption information of $\text{Cd(II)}_{(L)}$ particle on textile wastewater. Every one of the coefficients of assurance (R^2) of the non-straight strategy is near solidarity. For biosorption of each toxic metals, good fits are attained to the following adsorption isotherms namely, Langmuir isotherms > Dubinin–Radushkevich isotherms > Harkins–Jura isotherms > Jovanovic isotherms > Freundlich isotherm > Temkin isotherms based on its R^2 values as mention in Table 3.

5. Conclusion

CLLP is a naturally available adsorbent and it is used effectively for the removal of toxic metals from textile effluent. The biosorption experiments are analyzed in various levels of pH and desired DC (2.0 g) at the respected time intervals. The optimum results of Cd(II)_L and Ni(II)_L are removed at 89.61%, and 88.70%, respectively. It is observed at the time interval by 180 min in the level of pH 4. The removal of Pb(II)_L and Zn(II)_L are attained effectively (88.37% and 89.49%) at pH 5, and at the contact time of 180 min. The maximum removal of Cu(II) is 87.06% at pH 5, and the contact time is 240 min. The biosorption of each metal ion is spontaneous and the order of spontaneity of the biosorption process is $\text{Cd(II)}_{(L)} > \text{Zn(II)}_{(L)} > \text{Ni(II)}_{(L)} > \text{Pb(II)}_{(L)} > \text{Cu(II)}_{(L)}$. From these results, it is concluded that CLLP holds excellent potential for the removal of $\text{Cd(II)}_{(L)}$ from the textile effluent. The Langmuir isotherm for CLLP as biosorbent obtains the regression coefficient (R^2) of 0.984, followed by the Dubinin–Radushkevich (0.965), Harkin–Jura isotherm (0.938), Jovanovic isotherm (0.933), Freundlich isotherm (0.878) and the least value is obtained with the Temkin isotherm (0.648). From the above-obtained regression coefficients with isotherm models, the Langmuir isotherm model fits best for the equilibrium data of $\text{Cd(II)}_{(L)}$ metal ion. Comparing to the rest of the other isotherm, the R_L of Langmuir isotherm of all cases of adsorption is around 0 to 1 and this shows that adsorption operation is the favorable one.

References

- [1] A. Sharma, K.G. Bhattacharyya, *Azadirachta indica* (Neem) leaf powder as a biosorbent for removal of Cd(II) from aqueous medium, *J. Hazard. Mater.*, 125 (2005) 102–112.
- [2] J.O. Esalah, M.E. Weber, J.H. Vera, Removal of lead, cadmium and zinc from aqueous solutions by precipitation with sodium di-(*n*-octyl) phosphinate, *Can. J. Chem. Eng.*, 78 (2000) 948–954.
- [3] A.I. Zouboulis, K.A. Matis, B.G. Lanara, C. Loos-Neskovic, Removal of cadmium from dilute solutions by hydroxyapatite. II. Floatation studies, *Sep. Sci. Technol.*, 32 (1997) 755–1767.

- [4] L. Canet, M. Ilpide, P. Seta, Efficient facilitated transport of lead, cadmium, zinc and silver across a flat-sheet-supported liquid membrane mediated by lasalocid A, *Sep. Sci. Technol.*, 37 (2002) 1851–1860.
- [5] H. Eccles, Treatment of metal-contaminated wastes: why select a biological process?, *Trends Biotechnol.*, 17 (1999) 462–465.
- [6] Y.S. Ho, G. McKay, The sorption of lead(II) ions on peat, *Water Res.*, 33 (1999) 578–584.
- [7] S.E. Bailey, T.J. Olin, R.M. Bricks, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.*, 33 (1999) 2469–2479.
- [8] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, *Trends Biotechnol.*, 16 (1998) 291–300.
- [9] V.K. Gupta, P.J.M. Carrott, M.M.L.R. Carrott, Suhas, Low-cost adsorbents: growing approach to wastewater treatment—a review, *Crit. Rev. Env. Sci. Technol.*, 39 (2009) 783–784.
- [10] Y.S. Ho, J.C.Y. Ng, G. McKay, Removal of lead(II) from effluents by sorption on peat using second-order kinetics, *Sep. Sci. Technol.*, 36 (2001) 241–261.
- [11] C. Hall, D.S. Wales, M.A. Keane, Copper removal from aqueous systems: biosorption by *Pseudomonas syringae*, *Sep. Sci. Technol.*, 36 (2001) 223–240.
- [12] Y. Sağ, B. Akçael, T. Kutsal, Ternary biosorption equilibria of chromium(VI), copper(II), and cadmium(II) on *Rhizopus arrhizus*, *Sep. Sci. Technol.*, 37 (2002) 279–309.
- [13] R. Salim, M. Al-Subu, E. Dawod, Efficiency of removal of cadmium from aqueous solutions by plant leaves and the effects of interaction of combinations of leaves on their removal efficiency, *J. Environ. Manage.*, 87 (2008) 521–532.
- [14] P. King, P. Srinivas, Y. Prasanna Kumar, V.S.R.K. Prasad, Sorption of copper(II) ion from aqueous solution by *Tectona grandis* l.f. (teak leaves powder), *J. Hazard. Mater.*, 136 (2006) 560–566.
- [15] A.E. Ofomaja, Y.S. Ho, Effect of temperatures and pH on methyl violet biosorption by mansonia wood sawdust, *Bioresour. Technol.*, 99 (2008) 5411–5417.
- [16] A. Gundogdu, D. Ozdes, C. Duran, V.N. Bulut, M. Soylak, H.B. Senturk, Biosorption of Pb(II) ions from aqueous solution by pine bark (*Pinus brutia* Ten.), *Chem. Eng. J.*, 153 (2009) 62–69.
- [17] S. Kamsonlian, S. Suresh, V. Ramanaiah, C.B. Majumder, S. Chand, A. Kumar, Biosorptive behaviour of mango leaf powder and rice husk for arsenic(III) from aqueous solutions, *Int. J. Environ. Sci. Technol.*, 9 (2012) 565–578.
- [18] N. Feng, X. Guo, S. Liang, Y. Zhu, J. Liu, Biosorption of heavy metals from aqueous solutions by chemically modified orange peel, *J. Hazard. Mater.*, 185 (2011) 49–54.
- [19] N. Khalid, S. Ahmad, S.N. Kiani, J. Ahmed, Removal of mercury from aqueous solutions by adsorption to rice husks, *Sep. Sci. Technol.*, 34 (1999) 3139–3153.
- [20] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, *Bioresour. Technol.*, 99 (2007) 3935–3948.
- [21] H.K. Alluri, S.R. Ronda, V.S. Settalluri, J.S. Bondili, V. Suryanarayana, P. Venkateshwar, Biosorption: an eco-friendly alternative for heavy metal removal, *Afr. J. Biotechnol.*, 6 (2007) 2924–2931.
- [22] M. Karthikeyan, B. Asha, Biosorption of aqueous nickel(II) by *Psidium guajava* leaves from textile wastewater, *Int. J. Creat. Res. Thoughts*, 6 (2018) 447–453.
- [23] K. Vijayaraghavan, Y.S. Yun, Bacterial biosorbents and biosorption, *Biotechnol. Adv.*, 26 (2008) 266–291.
- [24] J. Wang, C. Chen, Biosorbents for heavy metals removal and their future, *Biotechnol. Adv.*, 27 (2009) 195–226.
- [25] F.E. Okeimen, E.U. Okunia, D.E. Ogbeifun, Sorption of cadmium and lead ions on modified groundnut (*Arachis hypogea*) husks, *J. Chem. Technol. Biotechnol.*, 51 (1991) 97–103.
- [26] K. Periasamy, K. Srinivasan, P.K. Murugan, Studies on chromium (VI) removal by activated groundnut husk carbon, *Indian J. Environ. Health*, 33 (1991) 433–439.
- [27] T.W. Tee, A.R.M. Khan, Removal of lead, cadmium and zinc by waste tea leaves, *Environ. Technol. Lett.*, 9 (1988) 1223–1232.
- [28] A.M. Deshkar, S.D. Dara, Sorption of mercury by tectona grandis bark, *Asian Environ.*, 10 (1988) 3–11.
- [29] P.S. Bryant, J.N. Petersen, J.M. Lee, T.M. Brouns, Sorption of heavy metals by untreated red fir sawdust, *Appl. Biochem. Biotechnol.*, 34 (1992) 777–788.
- [30] M. Karthikeyan, B. Asha, Feasibility study on using low-cost adsorbents for the removal of Cd(II) from textile wastewater, *Int. J. Sci. Adv. Res. Technol.*, 3 (2017) 437–441.
- [31] E. Fourest, J.C. Roux, Heavy metal biosorption by fungal mycelial by-products: mechanism and influence of pH, *Appl. Microbiol. Biotechnol.*, 37 (1992) 399–403.
- [32] M. Kanyal, A.A. Bhatt, Removal of heavy metals from water (Cu and Pb) using household waste as an adsorbent, *J. Biorem. Biodegrad.*, 6 (2015) 1–6.
- [33] M. Karthikeyan, B. Asha, Adsorption of toxic metals from fabric dye effluent by utilize *Azadirachta indica* foliages, *Int. J. Print. Packag. Allied Sci.*, 4 (2016) 257–267.
- [34] M.A.O. Badmus, T.O.K. Audu, B.U. Anyata, Removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells, *Turk. J. Eng. Environ. Sci.*, 31 (2007) 251–263.
- [35] X.S. Wang, F. Liu, H.J. Lu, P. Zhang, H.Y. Zhou, Adsorption kinetics of Cd (II) from aqueous solution by magnetite, *Desal. Water Treat.*, 36 (2011) 203–209.
- [36] M. Lenin Sundar, M.K. Saseetharan, Ground water quality in Coimbatore, Tamil Nadu along Noyyal River, *J. Environ. Sci. Eng.*, 50 (2008) 187–190.
- [37] M. Lenin Sundar, M.K. Saseetharan, Assessment of groundwater quality of Noyyal river basin, Tamil Nadu, India, *Ecol. Environ. Conserv.*, 12 (2006) 643–648.
- [38] D.S.N.R. Varma, C. Srinivas, C. Nagamani, T. PremSagar, M. Rajsekhar, Studies on biosorption of Cadmium on *Psidium guajava* leaves powder using statistical experimental design, *J. Chem. Pharm. Res.*, 25 (2010) 29–44.
- [39] P. Senthil Kumar, K. Kirthika, Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto Bael tree leaf powder, *J. Eng. Sci. Technol.*, 4 (2009) 351–363.
- [40] L.P. Lingamdinne, J.R. Koduru, R.K. Jyothi, Y.Y. Chang, J.K. Yang, Factors affect on bioremediation of Co(II) and Pb(II) onto *Lonicera japonica* flowers powder, *Desal. Water Treat.*, 57 (2016) 13066–13080.
- [41] Y. He, P. Wu, W. Xiao, G. Li, J. Yi, Y. He, C. Chen, P. Ding, Y. Duan, Efficient removal of Pb(II) from aqueous solution by a novel ion imprinted magnetic biosorbent: adsorption kinetics and mechanisms, *PLoS One*, 14 (2019) 1–17.
- [42] M. Karthikeyan, B. Asha, D. Selva Kumar, The diminution of toxic ions by using *Mangifera indica* foliages as adsorbent from textile effluent, *Int. J. Adv. Sci. Res. Eng.*, 3 (2017) 32–40.
- [43] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.*, 38 (1916) 2221–2295.
- [44] B.B. Mathew, J. Monisha, V.G. Biju, K.N. Beeregowda, Role of bioadsorbents in reducing toxic metals, *J. Toxicol.*, (2016) 1–13, doi: 10.1155/2016/4369604.
- [45] H. Freundlich, Ueber die adsorption in loesungen, *Z. Phys. Chem.*, 57 (1906) 387–470.
- [46] X. Li, Y. Li, Adsorptive removal of dyes from aqueous solution by KMnO₄-modified rice husk and rice straw, *J. Chem.*, 2019 (2019) 1–9, doi: 10.1155/2019/8359491.
- [47] M.J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, *Acta Phys. Chim. URSS*, 12 (1940) 217–225.
- [48] M.M. Dubinin, L.V. Radushkevich, The equation of the characteristic curve of activated charcoal, *Proceedings of the Academy of Sciences, Physical Chemistry Section*, 55 (1947) 331–333.
- [49] H.K. Boparai, M. Joseph, D.M.O. Carroll, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, *J. Hazard. Mater.*, 186 (2011) 458–465.
- [50] W.D. Harkins, E.J. Jura, The decrease of free surface energy as a basis for the development of equations for adsorption

- isotherms; and the existence of two condensed phases in films on solids, *J. Chem. Phys.*, 12 (1944) 112–113.
- [51] N. Ayawei, A.T. Ekubo, D. Wankasi, E.D. Dikio, Adsorption of congo red by Ni/Al-CO₃: equilibrium, thermodynamic and kinetic studies, *Orient. J. Chem.*, 31 (2015) 1307–1318.
- [52] D.S. Jovanovic, Physical adsorption of gases I: isotherms for monolayer and multilayer adsorption, *Colloid. Polym. Sci.*, 235 (1969) 1203–1213.
- [53] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, *Chem. Eng. J.*, 156 (2010) 2–10.