IJSAR, 4(8), 2017; 83-92

International Journal of Sciences & Applied Research

www.ijsar.in

Waste biomass as biosorbent for lead removal from aqueous solutions

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Abstract

Water contamination with heavy metals due to industrial activities generates serious environmental problems because of their high toxicity and non-biodegradability.

Various waste materials for biosorptive removal of heavy metal ions from aqueous solutions: olive leaves, almond shell residues, hazelnut shell, coconut husk, coffee ground, tea leaves, groundnut husk were selected because of a low cost and a higher biosorption capacity.

The effective removal of Pb^{2+} from aqueous solutions using low-cost biosorbents: carrot residue and green tea waste was studied. These waste materials were selected because of a low cost and the availability of functional groups such as carbonyl, hydroxyl, carboxylic etc. due to high cellulose, hemicellulose or lignin content, which favours biosorption of heavy metal ions.

The equilibrium data were described by typical Freundlich, Langmuir and Temkin adsorption models for each heavy metal - adsorbent system. The adorption equilibrium exhibited better fit to Langmuir model within the concentration range studied for carrot residue and the adsorption of Pb^{2+} by green tea waste showed a slightly better fit with the Freundlich model compared to Langmuir and Temkin.

This study revealed that carrot residue and green tea waste can be used as inexpensive, excellent biosorbent for the removal of Pb^{2+} from aqueous solutions.

Keywords: Adsorption, removal, heavy metals, biosorbent

Introduction

Different forms of water pollution have occurred as a result of the development of industrial activities. The contamination of water systems by toxic heavy metals through the discharge of industrial wastewater is a world wide environmental problem. Heavy metals are non-biodegrable and toxic to all forms of life, including humans. Fossil fuel combustion, mining operations, dyes and pigments, metallurgical industries, batteries and pesticides are known as main sources of lead and copper pollution. [1]

Among the important natural metal sources of pollution, forest fires, volcanic activity and continent weathering can be mentioned. [2]

Heavy metal toxicity can result in damage or reduced central nervous function and damage to blood composition, lungs, kidneys, liver and other vital organs. [3]

The tolerance limit for discharge of lead into drinking water is 0.05 mg/L and in land surface waters is 0.1 mg/L. An excess of lead ions inhibit the biosynthesis of heme, causing damage both to the kidney and liver. This metal can remain immobilized for years in human body and is very difficult to detect its metabolic disorder.[4]

Various methods such as precipitation, electrochemical process, oxidation/ reduction, ion exchange, have been used to reduce and reclaim heavy metals from wastewater; however, these methods are expensive and can cause secondary pollution problems. [1-3]

Over the last few years number of investigations has been conducted to test the low cost adsorbents for heavy metal ion removal. Waste biomass, industrial waste, and mineral waste have been investigated and biomass has shown better adsorption properties. [3]Various bio-adsorbents have attracted considerable interest in the recent years. [1-4]

Adsorption methods are considered suitable for heavy metals removal, due to their utility and low cost, especially when the adsorbent is inexpensive and readily available. The utilization of numerous waste biomass sources is increasingly becoming a vital concern because these wastes represent unused resources and in many cases present serious disposal problems. [3]

Waste agricultural materials may constitute an important source of adsorbents for metals: shells of wheat, rice, orange peels, litchi pericarp, pomegranate peel, sunflower leaf, olive stones, coconut husk, palm pressed fibers, corn cob, hazelnut shell and almond shell. [2] The use of waste biomass eliminates the problem of toxicity and the economics aspects of culture maintenance or nutrient supply. [1-4]

The biosorption efficiency by using waste biomass depend on physical and surface properties of adsorbent, operating conditions and metal ion properties. Therefore, the specific effect of adsorbent properties and operating conditions depends on the waste biomass-metal ion system. [5]

The kinetics and maximum adsorption capacity vary with the type of sorbent, as well as the metal ions. Different waste materials as alternative sorbents for activated carbon have received considerable attention.[6]

Biosorption takes place in a heterogeneous system, which involves solid biosorbent and liquid phase (solution) with dissolved species. [2,6]

The mechanism of biosorption is rather complex and involves many different processes: chemisorption, complexation, ion-exchange, chelation, and physical adsorption. As an example, in the case of ligno-cellulosis biosorbents, the functional groups of which are mostly presented by carboxyl, carbonyl and hydroxyl groups, predominant biosorption mechanisms are ion-exchange, complexation and chelation.[7,8]

Natural materials that are available in large quantities or certain waste products from agricultural or industrial operations may have potential as inexpensive sorbents.[7-11]

Large amounts of waste which has no commercial value are produced, for example carrot residues and green tea waste, which may have potential as inexpensive sorbents. Carrot residue and tea waste were investigated in our previous study as low cost non-conventional adsorbents for the sorption of cadmium ions from the contaminated water under various experimental conditions. [5]

For the present work, the adsorption of lead ions onto *green tea waste and carrot residue* from aqueous solutions was studied, to enable comparison with alternative commonly available absorbents.

Several equilibrium models were used to describe the adsorption process: Langmuir, Freundlich and Temkin isotherm models.

Adsorption isotherms are important to describe the adsorption mechanism of a solute on adsorbent surface.

Isotherm adjustable variables and coefficients of determination (R^2) were computed from linearized equations of these isotherm models.

The results of the current study would help in developing effective and environmentally friendly technique for the removal of lead from contaminated water systems and also in optimizing the design of a specific adsorption process.

Materials and methods

1. Instrumentation

A Varian AA 240 FS type atomic absorption spectrometer with an air-acetylene flame and a hollow cathode lamp for Pb was used for metal ion analysis. The absorbance of the samples was read in triplicate.

A research-grade CyberScan PCD 6500 touchscreen meter with a combined glass electrode was used for *p*H measurement. Final *p*H of the sorbate–sorbent adsorption system was measured at sorption equilibrium.

2. Preparation of stock solution and standards

All the chemicals and reagents used in our study were of analytical reagent grade and used without further refinement.

For preparation of 1000 mg/L stock solution of Pb^{2+}, 1.5960 g of $Pb(NO_3)_2$ were dissolved in one liter volumetric flask and final volumes were made up to the mark with deionised water. The standard solutions of lead were prepared before use by the appropriate dilution of the stock solutions.

3. Preparation of the adsorbent supports

Waste materials that are available in large quantities: carrot residues (CR) and green tea waste (GTW) were used as adsorbents for the removal of lead from synthetic wastewater. These materials were selected because of a low cost and the availability of functional groups such as phenolic and carboxylic, due to high cellulose, hemicellulose, or lignin content, which exist in caffein either the cellulosic matrix or in the materials associated with cellulose such as hemicellulose, lignin and favours biosorption of heavy metal ions.

These natural polymers have been reported having metal binding capacity.[12-15]

The main objective of this work was to evaluate the biosorption capacity of carrot residues (CR) and green tea waste (TW) for the effective removal of Pb^{2+} from aqueous solutions by varying solution initial Pb^{2+} concentration, *p*H and biosorbent dose.

Preparation of biosorbents was performed as in our previous study. [5]

4. Carrot residue (CR)

Carrot residue is a the fibrous by-product of carrot milling operation and it can be obtained from a carrot-juice processing plant in a large quantity. This material was washed with distilled water to remove the surface adhered particles or other soluble impurities, then it was oven dried for 24 h, at 80°C. The biosorbent was ground and sieved, to get homogenous particle sized material. In order to eliminate soluble components such as tannin, resins reducing sugars, coloring substances, the residue was washed with 0.1 M HCl and distilled deionized water, until a constant *p*H was achieved.

The lignified plant cell wall is a composite material in which cellulose, hemicelluloses and lignin are in tight association.[12]

Carrot residue has potential adsorption capacity because of some functional groups in its structure: carboxyl or phenolic hydroxyl groups. (fig.1)

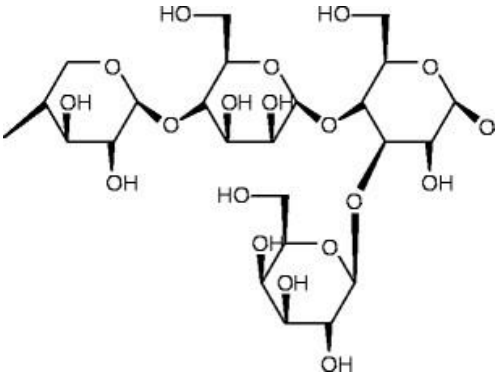

Figure 1: Hemicellulose structure [13].

5. Green tea waste (GTW)

Tea waste is available in cafetarias and the tea factories. Soluble and coloured compounds, surface impurities from green tea waste were removed by washing with boiling distilled water. This was repeated until the water was colourless. The tea residues were then washed with distilled water and dried in oven for 12h at 105°C. The dried tea waste was ground and sieved through a 9-mesh sieve (2-mm mesh). The fine powder was stored in sealed polythene bags and it was used for the sorption studies. Tea waste used for this study was not treated chemically or thermally.

The major catechins of green tea are (−)-epicatechin (EC), (−)-epicatechin-3-gallate (ECG), (−)-epigallocatechin (EGC) and (−)-epigallocatechin-3-gallate (EGCG) [14]. As shown in Fig..., catechins are polyphenolic compounds with diphenyl propane skeleton. [14] This structure may explain the potential adsorption capacity of green tea waste.

6. Synthetic wastewater preparation

Synthetic wastewater solutions were prepared by dissolving analytical grade $Pb(NO_3)_2$ in distilled water, to obtain 1000 mg of Pb^{2+}/L stock solutions.

Each metal solution was diluted to the required concentration (20, 40, 60 and 80 mg/L) for our experiments.

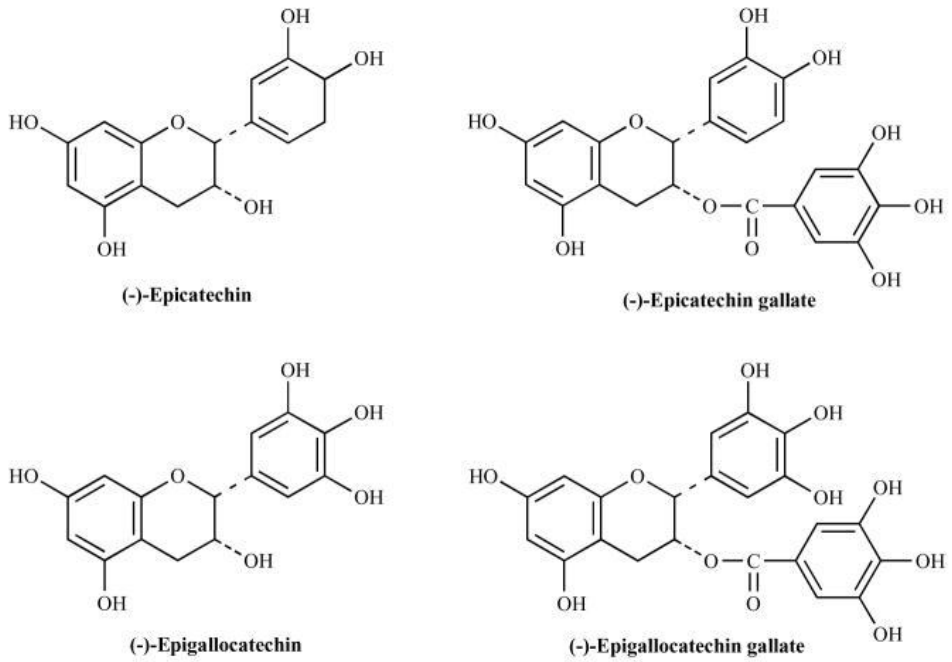

Figure 2: Chemical structures of catechins [14].

Series of experiments were carried out at room temperature i.e. 25 °C, to determine the effect of adsorbent dose, initial metal ion concentration and *p*H value.

The necessary adsorbent weight was introduced in a 250 ml conical flask containing 100 ml of 20-80 mg/L test solutions of Pb^{2+}.

The contents of each flask were filtered through Whatman 42 blue band filter paper and the filtrate was analyzed for Pb^{2+} concentration using atomic absorption spectrophotometry. A Varian AA 240 FS type atomic absorption spectrometer with an air-acetylene flame and a hollow cathode lamp for Pb was used for metal ion analysis. The absorbance of the samples was read in triplicate.

Effect of initial solution *p*H on adsorption was determined by adding 0.1 M HCl or 0.1 M NaOH.

A *p*H-meter CYBERSCAN PCD 6500 with a combined glass electrode was used for *p*H measurement. Final *p*H of the sorbate–sorbent adsorption system was measured at sorption equilibrium.

7. Equilibrium studies

The adsorption equilibrium data is important to optimize the parameters of an adsorption system and to provide physicochemical information, to explain the mechanism of adsorption. The sorption capacity of an adsorbent can also be described by equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of an adsorbent support. [16]

The adsorption capacity q_e (mg/g) after equilibrium - the amount of lead adsorbed at equilibrium per unit mass of the adsorbent material is calculated by using the following equation: [16,17]

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (1)$$

where C_0 (mg/L) is the initial concentration of heavy metal ion, C_e (mg/L) is the final (residual) metalic ion concentration, V is the volume of the solution (L) and W is the mass of the dry adsorbent material (g).

Adsorption equilibrium data is very important to optimize the parameters of an adsorption system. [16, 17]

In this study, Langmuir, Freundlich and Temkin isotherm models are selected to fit the experimental data.

The Freundlich model can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer sorption. The Freundlich model is described as follow (Freundlich, 1906): [16, 17]

$$q = K_F \cdot C^{1/n} \quad \text{(2) original form;}$$

$$lgq = lgK_F + \frac{1}{n} lgc \quad \text{(3) linearized form}$$

where K_F (mg g^{-1}) and n (value between 0 and 1) are Freundlich equilibrium constants; 1/n is an empirical parameter relating the adsorption intensity, which varies with the heterogeneity of the material.

The Langmuir model describes the adsorption process and adsorption capacity of the metal ions based on the physical hypothesis. This model assumes that adsorption occurs at specific homogeneous sites on the adsorbent and is used in many monolayer adsorption processes. It was determined in accordance with the following equations (Langmuir, 1918): [16, 17]

$$q = \frac{q_m \cdot K_L \cdot C}{1 + K_L C} \quad \text{(4) original form;}$$

$$\frac{c}{q} = \frac{1}{K_L q_m} + \frac{c}{q_m} \quad \text{(5) linearized form}$$

where q (mg g^{-1}) is the maximum amount of metal ions adsorbed per specific amount of adsorbent, when all binding sites are occupied; C_{eq} (mg L^{-1} or mmol L^{-1}) is the equilibrium concentration; q_m (mg g^{-1}) is the amount of metal ions required to form a monolayer; K_L is the Langmuir equilibrium

constant related to the energy of sorption (L mg^{-1} or L $mmol^{-1}$).
For determination of the Langmuir parameters, C/q can be plotted versus C_{eq}.

The Temkin (Aharoni and Ungarish, 1977) isotherm has generally been applied in the following form: [18]

$$q = \frac{RT}{b} \ln (K_T . C_e) \quad (6) \text{ original form}$$

$$q = \frac{RT}{b_T} lnK_T + \frac{RT}{b_T} lnC \quad (7) \text{ linearized form}$$

where K_T (L mg^{-1}) and b_T (KJ/mole) are Temkin isotherm constants.

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage, due to adsorbent–adsorbate interactions [1, 18]

Results

1. Effects of experimental parameters on heavy metal biosorption

1.1. Effect of the initial concentration

The initial concentration is one of the parameters which have a pronounced effect on the removal of adsorbate species from aqueous solution. (Fig.3)
The influence of the initial metal concentration on the adsorption capacity of *GTW and CR* was studied for concentration in the range 20–80mg/L, at *p*H = 6.5, at room temperature and contact time 24h, as shown in Fig. 3.

The results shown in Fig. 3 indicate that the percentage removal of metal ions initially increases and a further increase in concentration will decrease the percentage removal, indicating that the metal uptake is dependent on the initial concentration of metal ions in solution. At higher concentration values, the available sites for adsorption are already saturated. [15]

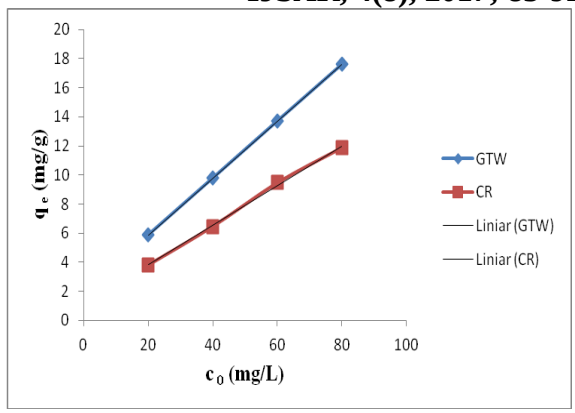

Figure 3: Effect of initial concentration of Pb^{2+} on the adsorbent materials (GTW and CR).

1.2. Effect of biosorbent amount on adsorption

In order to investigate the effect of sorbent dose on the amount of Pb^{+2} sorbed per gram of sorbent (i.e. q_e,, $mg \cdot g^{-1}$), experiments were conducted at initial Pb^{+2} concentration of 60 mg/L, with varying amounts of sorbent: from 0.10 to 1.00 g, at room temperature.
The effect of adsorbent amount on metal ion biosorption is presented in Fig.4.

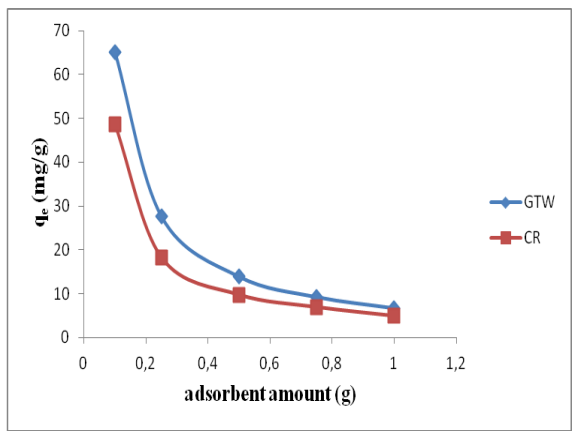

Figure 4: Effect of adsorbent dose on the adsorption of Pb^{2+} using different materials (GTW and CR).

The results, as depicted in Fig. 4, clearly indicate that for a sorbent dose of 10 mg Pb^{+2} uptake was around 70.0 $mg \cdot g^{-1}$ for GTW and around 50 $mg \cdot g^{-1}$ for CR and

continued to decrease with further increase in sorbent dose.

This may be attributed to the fact that increase in sorbent dose occurs in a greater proportion relative to a corresponding enhancement in Pb^{+2} uptake. This finally results in a decrease in the amount of Pb^{+2} sorbed per gram of sorbent. [5,20]

1.3. Effect of pH

The adsorption mechanism is highly influenced by the *p*H value of the metal aqueous solution, as it affects the surface charge of adsorbent, the degree of ionization and the species of adsorbate. [15]

The equilibrium estabilished in solution between metal ions and the sorbent may be described as following[19]:

$$\mathbf{M^{n+} + BH_n \rightleftharpoons BM + n\,H^+} \quad (8)$$

where M represents the metal, *n* represents its charge and B the active sorption sites of the adsorbent. [19]

The effect of *p*H on Pb^{+2} removal was studied by performing equilibrium adsorption experiments at different *p*H values (3, 6 and 9). The adsorbent dosage was 0.5 g, in 100mL and 60 mg/L Pb^{+2} solutions; all other variables such as adsorbent amount, contact time and temperature were kept constant.

A little sorption capacity was observed at the initial *p*H=3. The low metal sorption at this *p*H may be explained on the basis of active sites protonation, resulting in H^+ and Pb^{2+}competition to occupy the binding sites. [5,15]

The best *p*H value for the removal of Pb^{+2} was found to be 6, using GTW and CR as adsorbent materials. (fig.5) The optimum adsorption results at *p*H value 6 could be also attributed to the cellulose component of the substrates, where site binding adsorption might be occurring.

A slightly decrease in Pb^{2+} ion removal capacity at *p*H >6.0 may be caused by hydrolysis accompanying by precipitation of metal hydroxide. This effect weakens electrostatic interactions and decreases adsorption. At a *p*H higher than the presented optimal values, several hydroxyl low-soluble species may be formed, such as: $Pb(OH)^+$, $Pb(OH)_2$. [5, 18]

From the point of view of an industrial application, this may provide an important advantage, since working at extreme *p*H would be avoided.[5]

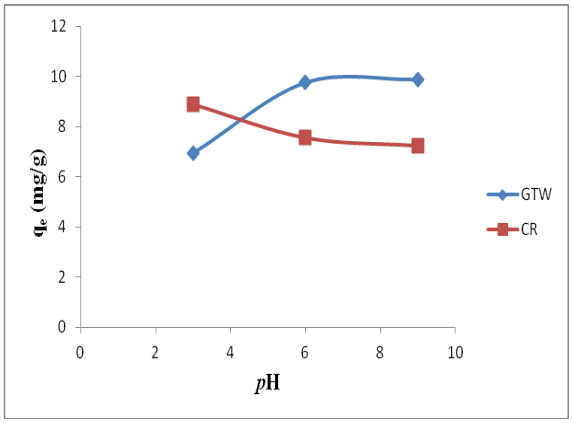

Figure 5: Effect of *p*H on the adsorption of Pb^{2+} using different materials (GTW and CR).

Discussion

Adsorption isotherm study

The equilibrium data were used to determine the maximum capacities of the adsorbents in this experiment. The linearized Langmuir, Freundlich and Temkin isotherms of Pb^{2+} are presented in Fig. 6–8.

The isotherms provide an estimate of the adsorption capacity and also important information about applicability of a potential adsorbent for the adsorption of a pollutant.

The adsorption intensities and adsorption capacities (q_m) were determined from the intercept and slope data, respectively, for each adsorbent support.

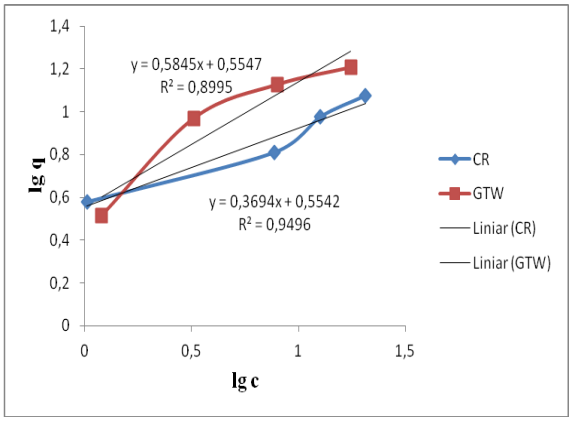

Figure 6: Freundlich isotherms plot for Pb^{2+}adsorption onto different types of adsorbents (GTW and CR).

The values of the biosorption capacity q_{max} and Langmuir constant K_L were calculated by linear regression. (table 1) The values of Freundlich parameters were calculated from the slope and intercept of the linear plot of lg q against lg C.

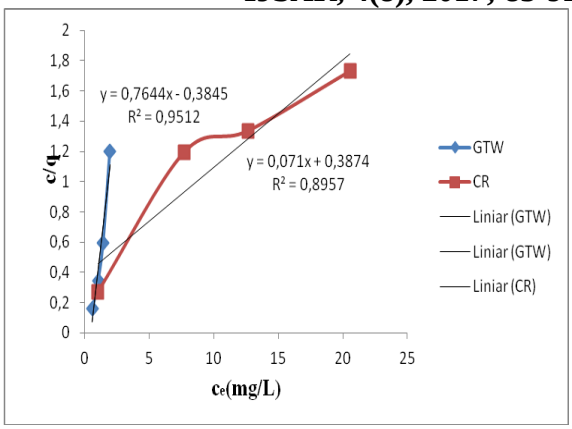

Figure 7: Langmuir isotherms plot for Pb^{2+}adsorption onto different types of adsorbents (GTW and CR).

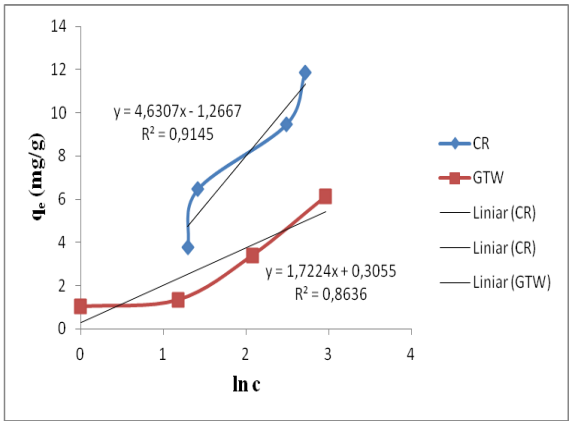

Figure 8: Temkin isotherms plot for Pb^{2+}adsorption onto different types of adsorbents (GTW and CR).

Table 1: Parameters of Freundlich, Langmuir and Temkin adsorption isotherm models for lead removal.

Sorbent	Langmuir Model	Freundlich Model	Temkin Model
Carrot residue (CR)	R^2=0,8957 q_m=14,164mg/g K_L=0,811L/mg ΔG=0,514KJ/Kmol	R^2=0,9496 K_F=1,4468mg/g n=1,80	R^2=0,9145 K_T=1,354L/g b_T=0,49KJ/mol
Green tea waste (GTW)	R^2=0,9512 q_m=12,61mg/g K_L= 1,988 L/mg ΔG=0,1656 KJ/Kmol	R^2=0,8995 K_F=1,247mg/g n=1,243	R^2=0,8636 K_T=1,688L/g b_T= 0,14143KJ/mol

A comparison of the three isotherms reveals that the correlation coefficient for the Freundlich model was the highest and showed better fits for carrot residue (CR). Langmuir isotherm provided a better fit for the other adsorbent, green tea waste (GTW).
The equilibrium data which fitted Langmuir isotherm, with high coefficients suggest that the adsorption process followed monolayer sorption in this case.
The essential charactersitics of Langmuir isotherm can also be expressed in terms of a dimensionless constant, separation factor R_L, that is given as [20]:

$$R_L = \frac{1}{1+b \cdot C} \qquad (9)$$

where C_0 is the initial concentration of sorbate (mg/L), and b (L/mg) is the Langmuir constant.

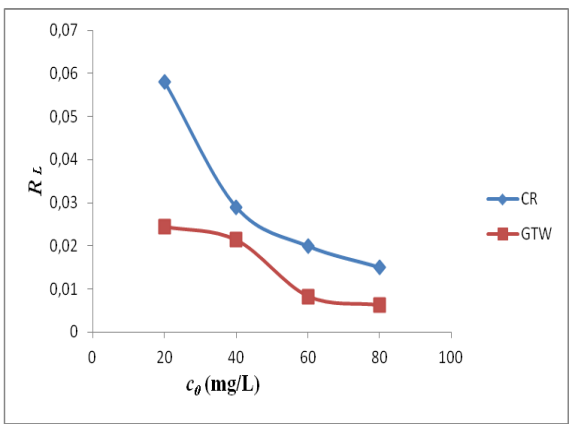

Figure 9: Variation of R_L with initial concentration C_0 (mg/L).

The R_L values were calculated using the equilibrium sorption data obtained at 25 ºC and variation of R_L with initial concentration C are shown in Fig. 9. The value of R_L indicates the shape of the isotherm to be either unfavourable (R_L >1), linear (R_L =1), favourable ($0 < R_L < 1$) or irreversible (R_L = 0).[20] R_L values between 0 and 1 indicate favourable adsorption. It can be observed that R_L values are in the range of 0.0580 to 0.0151 for CR and 0.0245 to 0.0062 for GTW, respectively, thus indicating that although adsorption is favourable at 25 ºC.
In addition, at higher initial Pb^{2+} concentrations it is almost irreversible for both adsorbents.
Table 1 shows a slightely increase of the adsorption capacities of the carrot residue, comparing to available experimental data of the green tea waste adsorbent.
The results presented in table 1 reveal that the value of 'n' Freundlich parameter was greater than 1, which indicates that the adsorption of lead on investigated materials (CR and GTW) was favourable and suggested also the adsorption of the metal ion on the biosorbents. For a good adsorbent the value of 'n' Freundlich parameter is usually between 1 and 10.
The Temkin parameter b_T (KJ/mol) related to heat of sorption, is less than 8 for all adsorbents, that indicate weak interaction between metal and sorbent. [5,18]The process, as indicated by b_T parameter, can be expressed as physiosorption.

Conclusion

In this study, we have selected two low cost, environmental friendly waste materials such as *carrot residues (CR) and green tea waste (GTW).*
From the experimental data it can be concluded that *carrot residues (CR) and green tea waste (GTW)* have considerable biosorption capacity. These waste materials are available in abundant, nonhazardous agro material and they can be used as effective materials for treatment of wastewater stream containinglead ions.
The adsorption of metal ions (Pb^{2+}) was dependent on the following experimental conditions: *p*H, initial concentration and adsorbent amount.
The results of the research reveal that lead ions were adsorbed onto the surface of the adsorbents, suggesting that these are capable of removing Pb^{2+} from aqueous solution and

that they can therefore be employed in wastewater purification systems.

The equilibrium sorption data were applied to various sorption isotherm models, and the order of fitness was: Langmuir > Freundlich >Temkin for carrot residue and Freundlich > Langmuir >Temkin for green tea waste.

A comparison of the three isotherms reveals that the correlation coefficient for the Freundlich model was the highest and showed better fits for carrot residue (CR). Langmuir isotherm provided a better fit for the other adsorbent, green tea waste (GTW).

The values of $\Delta G<+10$ KJ/mol suggested the feasibility of the present adsorption process and the spontaneous nature of the adsorption of Pb^{2+} onto GTW and CR.

Due to their low cost and a good uptake capacity, the two solid wastes studied in this work (carrot residue and green tea waste) are promising biosorbent materials. Because tea consumption is worldwide and tea wastes can easily be acquired, it is speculated that tea waste has a high potential for practical applications in treating wastewater. Carrot residue is also an environmentally friendly, biodegradable, low cost and potential biosorbent for the removal of heavy metals.

Non-hazardous waste materials, low-cost and environment friendly, as carrot residues (CR) and green tea waste (GTW) used successfully for removal of Pb (II) from aqueous solutions can also be used for industrial wastewater treatment, to overcome water pollution problems.

References

1. Bozbas¸S., Boz, Y., 2016, Process Safety and Environmental Protection, 103, 144–152.
2. Ben-Ali, S., Jaouali,I., Souissi-Najar,S., Abdelmottaleb Ouederni Journal of Cleaner Production, 2017, 142, 3809-3821.
3. Amarasinghe, B.M., Williams, R.A., Chemical Engineering Journal, 2007, 132, 299–309.
4. Ata,S., Hamid Wattoo,F., Rukh Sidra, L., Sarwar Wattoo, M., Tirmizi,S.A., Din,I., Mohsin,I., Turk J Biochem, 2012, 37 (3) 272–279.
5. Bondarev, A., Pantea, O., Mihai,S., Calin, C., Gheorghe,C.G., 2016, Rev.Chim., 67 (4), 728-733.
6. Tarek, G. A., Ecological Engineering, 2014, 71, 466–473.
7. Mitic-Stojanovic, D., Zarubica, A., Purenovic,M., Bojic,D., Andjelkovic,T., Bojic,A., 2011,Water SA, 37 (3), 303-312.
8. Poojari, A., Maind S., Bhalerao,S.A., 2015, Int.J.Curr.Microbiol.App.Sci, 4 (4), 653-671.
9. Pushpendra, K. S., Sohail, A., Chandra, N. T., International Refereed Journal of Engineering and Science (IRJES), 2013, 2319-1821, 2 (8), 18-27.
10. Mahajan,G., Sud, D., 2014, Pol. J. Chem. Tech., 16 (4), 6-13.
11. Rajvinder, K., Joginder, S., Rajshree, K., Amjad, A., 2012, Universal Journal of Environmental Research and Technology, 2 (4), 325-335.
12. Puls, J., 1997, Macromolecular Symp., 120 (1), 183–196.
13. Kaith Hemant, B. S., Mittal Rajeev, J., Susheel, K., 2011, Cellulose Fibers: Bio- and Nano-Polymer Composites, 1, 425-451.
14. Velayutham, P., Babu, A., Liu, D., 2008, Curr Med Chem. 15(18), 1840–1850.
15. Shrestha, B., Homagai, P.L., Pokhrel, M.R., Ghimire, K.N., 2012, J. Nepal Chem. Soc., 30, 123-129.