BIOSORPTION OF AQUEOUS NICKEL(II) BY PSIDIUM GUAJAVA LEAVES FROM TEXTILE WASTEWATER

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Abstract: The aim of this research work is to remove Nickel (II) ion from textile industrial effluent through biosorption using the biomaterial from Psidium Guajava leaf powder as a biosorbant. The experimental study was investigated with respect to different adsorbent doses, contact time and pH. The dosage of biosorbent is 2 gram/L. The maximum percentage (77.97%) removal efficiency of Ni(II) ion was attained at pH level of 6.00 with the dosage level of 1.0g of Psidium Guajava leaf powder. The intensity values of adsorption processes are in the range of 1 to 10 indicated that biosorbent material from Psidium guajava are very valuable as Nickel adsorbent in the textile wastewater. The suitability of the adsorbent was tested by fitting the adsorbent data with Langmuir and Freundlich isotherms.

Index Term: Psidium guajava, Heavy metals, Biosorbents, Langmuir Isotherm Isotherms, Freundlich Isotherms.

Introduction

The textile industries are one among the industries which are important in the economic growth of India. They utilized the underground water around 829.80 million cubic meters and discharge wastewater to the ground nearly 637.30 million cubic meters. The textile wastewater is rated as the most polluting among all industrial sectors considering both volume and composition of effluent (Vanndevivera *et al*., 1998). Textile dyeing process cycle involves de-sizing, scouring, bleaching, washing, dyeing, fixing, washing, finishing and drying of thread. Out of these processes, bleaching and dying process generate large quantities of wastewater. The textile wastewater containing heavy metals from industrial activities could contribute to harmful effect of the environment. Heavy metals, such as chromium, Nickel, copper, lead, cadmium, etc, are dangerous environmental pollutants. One of the major problems concerning heavy metal pollution is that it persists indefinitely in soil.

The ground water is polluted through discharging of large amount of wastewater to the ground surface, after various chemical treatment processes are found to have more toxic effect due to the presence of chemicals. Disposal of dyes in precious water resources must be avoided, however, and for that various treatment technologies are in use [Upadhye GC and Yamgar RS(2016) ; Suresh S., 2016]. The textile industry contributed about 2.2% of the total value of industrial in our country. Heavy metals are present in different hyper of industrial effluent being responsible for environmental pollution. There has been increasing concern over the unknown accumulation of heavy metals such as Cadmium, Lead and Nickel in the food chain and persistence in nature.

Various methods are adopted to remove heavy metals from water including chemical, biological, physical treatments. However these methods are quite expensive and difficult. Hence there is need of easy and cost effective method to remove heavy metals including iron from water. Agricultural bi-products such as hazelnut hull (Ali Sheibani et al. 2012), duckweed (Jameel .M. Dhabab 2011), pomegranate peel carbon (Masoud Rohani et al. 2013), moringa oleifera i.e. drum sticks (Desai B. et al. 2013), rice husk ash (Sathy Chandrasekhar 2006), banana and orange peels (G. Annadurai et al. 2002) and coconut shell charcoal (K.S. Beenakumari 2009) were tested to remove heavy metals from aqueous solutions. Adsorption has been a technique of interest . Large number of experiments have been performed Recently, kinetic studies on removal of phenol in aqueous solution have been reported by Latharsee .S (2015). Studies have shown that heavy metals can be removed using certain plant materials Khan. N. A et.al (2004), Innocent OBOH, Emmanuel ALUYOR, and Thomas AUDU Leonardo Biomaterial (2009) ; Tangjuank, N et al., (2009).

Adsorption techniques have become popular for wastewater treatment due to their efficiency in the removal of pollutants that are to be removed by biological methods. Materials locally available such as natural raw materials, agricultural wastes and industrial wastes in many instances are relatively inexpensive, abundant in supply, have good mechanical properties and eventually enhance of their adsorption capabilities (Puganeshwary Palaniandy et al 2016).

Study area

For the study of this effective biosorption on textile effluent, different samples from different places were collected from Komarapalayam Town. The Komarapalayam town is located between Salem and Bhavani (11.4433ºN, 77.1138ºE). It is on the bank of Bhavani which is a branch of Cauvery. Untreated or partially treated dye effluents are directly released into the river Bhavani (**Fig. a**).
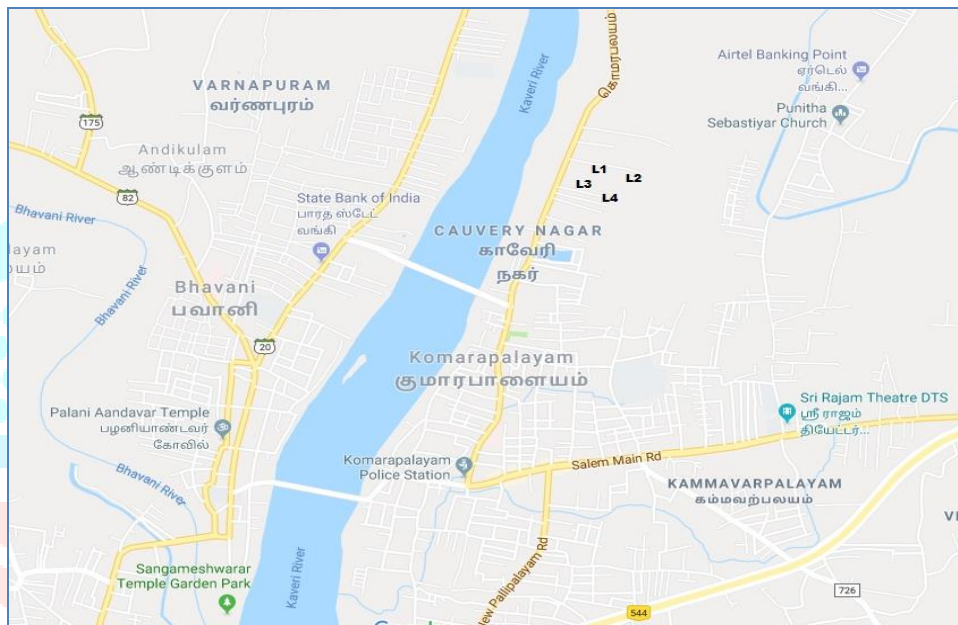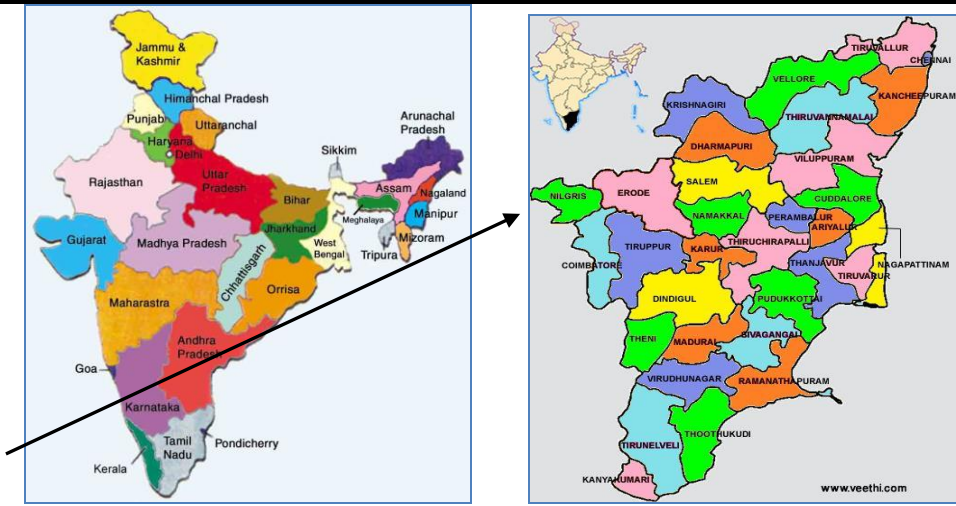
Fig. a. Map showing Tirupur location and textile dye effluent collection sites

Materials and Methods

Psidium guajava leaves as Biosorbant

The Psidium guajava tree is in the family Meliaceae is native to the Indian sub-continent, and its leaves and seeds have been used traditionally to treat a number of human being ills and also as a household pesticide. The tree is known as an air purifier and different parts of the tree such as leaves, bark and seeds have been reported to possess a variety of medicinal and germicidal properties. It is a genus of about 133 genera and more than 3800 species of tropical shrubs. A small tree about 10m height with spreading branches and thrives on all kinds of soils. It is one of the most gregarious fruit trees and also known as "poor man's apple". It contains 8.50%, 6% fixed oil, Tannin, 4.77% Moisture Content, Resin 3.15%, 0.365% volatile oil and $262g/dm^3$ Bulk density. Figure 1 is the raw Psidium guajava leaves and Figure 2 is the dry sorbent.

Fig.1. Fresh GLP Leaves   **Fig.2. Dry GLP Leaves**

Preparation of Biosorbent

The Mature Psidium guajava leaves were thoroughly washed with distilled water three to four times to remove dust and other impurities and were allowed to dry first at room temperature in a shade and then in an oven at 60°C till the leaves became crisp that could be crushed into a fine powder in a mechanical grinder and then screened. Dried Psidium guajava leaves powder were keeping in plastic containers stored in humidifier for further use. These fine powders were used as a biosorbent.

Biosorption Study

A known quantity of biomass is taken and added with the industrial waste and the mixture is placed over the mechanical shaker. The sample were taken out at a specific duration of time and centrifuged at 1000 rpm for 15 min. the supernatant liquid was separated and the low residual heavy metals are analyzed by Atomic adsorption spectrophotometer.

Results and Discussion

Effect of pH on percentage removal efficiency of Cd(II) metal ion

The effect of variation in pH level of the textile effluent in the removal of Cd(II) ion by varying the dosage of PGFP from 0.5 to 2.5g (keeping the contact time of 60 minutes constant) was analysed. From pH level 1 to 3, the amount of metals biosorbed was low and negligible. Increasing the dosage of biosorbent at higher pH, the percentage removal efficiency was also high. At low pH level, there is a preferential biosorption by protons with respect to the toxic metals on the active sites of the biosorbent. For pH values from 1 to 11 and the dosage content of AIFP from 0.5g to 2.5g was carried out. The effect of pH on the biosorption of Cd(II) metal ion by PGFP showed that the biosorption process, in pH levels from 1 to 6 was better. By increasing the pH level from 7 to 11 the percentage removal efficiency of Cd(II) was dropped down slowly (**Fig. 3**).
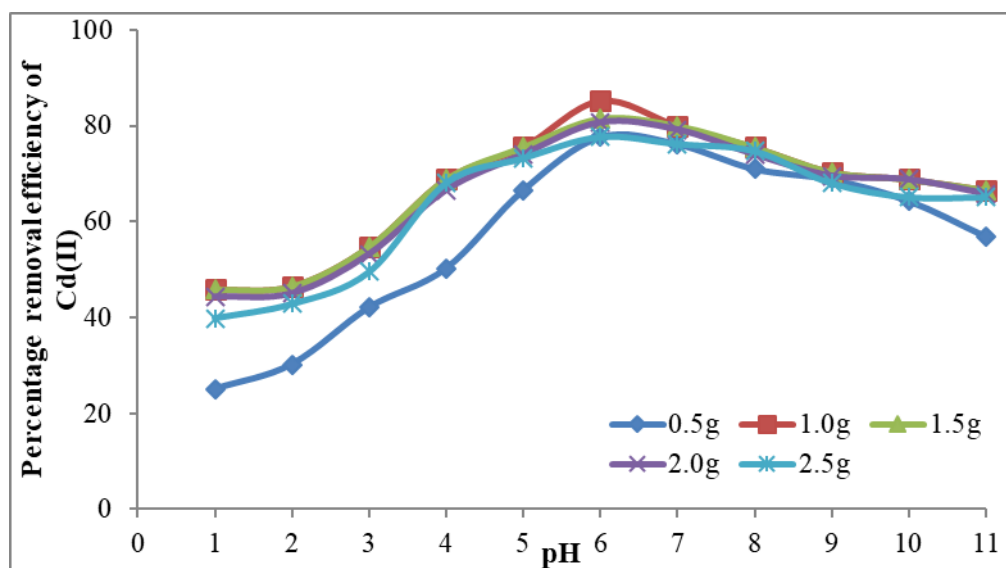
Fig. 3. pH Vs Percentage removal efficiency of Cd(II) metal ion by PGFP

For pH 1 the percentage removal efficiency of Cd(II) ion was 25.05 at 0.5g of biosorbents. For the same dosage of biosorbent with the pH value of 6, the maximum percentage removal efficiency was attained and it was 77.74. For the same dosage (0.5g) with increasing pH, the removal efficiency started decreasing. The removal of Cd(II) at lower pH was slow, due to competition between Hydrogen and Cd(II) ion in the biosorption sites. When increasing the biosorbent dosage (1.0g), the maximum percentage removal efficiency of Cd(II) ion was attained and it was 85.16 at pH value 6. By increasing the biosorbent dosage from 1.0 to 1.5g, the percentage removal efficiency of Cd(II) ion reduced to 81.45. By further increasing, the dosage of biosorbent from 1.5 to 2.5g the percentage removal efficiency of Cd(II) ion reduced and it was minimum (77.74) at pH level 6.

Effect of pH on percentage removal efficiency of Ni(II) metal ions

Analytical studies were conducted to identify the percentage removal efficiency of Ni(II) ion in various pH levels of effluent and by varying dosage of PGFP from 0.5g to 2.5g (keeping the contact time of 60 minutes constant). The experiment was conducted to remove Ni(II) ion from textile effluent at different pH levels of effluent. The results indicated that the strong force of interaction between the metal ion and PGFP biosorbent that either H^+ or OH^- ions could influence the biosorption capacity.

For 0.5g of biosorbents and pH level of 1, the minimum and maximum percentage removal efficiency of Ni(II) was 30.51 and 70.06 at pH level of 6. For pH level of 6 with the dosage level of PGFP (1.0g) the percentage removal efficiency of Ni(II) ion was maximum and it was 77.97. At pH level of 6 and biosorbents dosage of PGFP (1.5g) the percentage removal efficiency of Ni(II) was same (77.97). For the same pH level of effluent with further increasing the dosage level of PGFP from 1.5g to 2.5g the removal percentage was decreased and attained the equilibrium (**Fig. 4).**
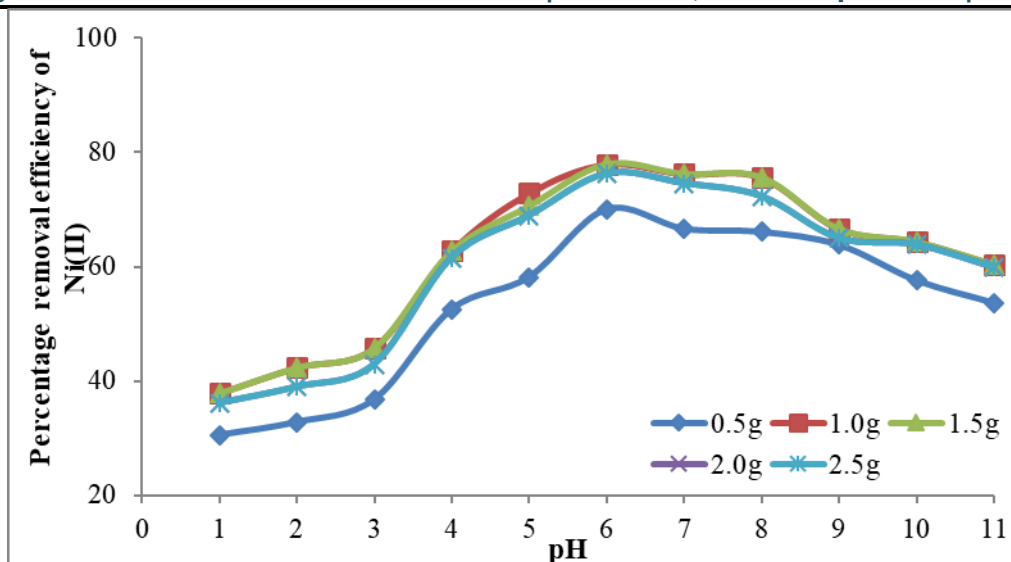
Fig. 4 pH Vs Percentage removal efficiency of Ni(II) metal ion by PGFP

Role of dosage content in the percentage removal efficiency of toxic metals

For dosage of 0.5g of biosorbent the percentage removal efficiency of toxic metals vary with respect to different level of pH of the effluent. In the beginning the experiment with PGFP dosage was analysed from the range pH 1 to 11. From pH 1 to 5 the toxic metals adsorbed were low and negligible. The effect of dosage content on the biosorption of Cd(II) ion was determined by varying the biosorbent dosage from 0.5g to 2.5g, keeping contact time of 60 minutes as constant with varying the pH level . The percentage removal efficiency of Cd(II) ion increased sharply from 77.74 at dosage of 0.5g to 85.16 at dosage of 1.0g, but decreased slightly to 81.45 at 1.5g of biosorbent. The initial rapid increase is due to the increased availability of binding sites and surface area which makes the biosorption of the ions quite easy until equilibrium reached (Fatima, T., et al., 2013). The reduction of percentage removal efficiency of Cd(II) ion is due to aggregation or overlapping of the sorption site at pH level of 7(Fig .5.).

The percentage removal efficiency of Ni(II) ion was studied for the varying dosage of PGFP. 0.5g of PGFP with the pH level of 6 the percentage removal efficiency of Ni(II) ion was 70.06. When the dosage of PGFP was 1.0g at same pH level the percentage removal efficiency of Ni(II) was 77.97 and it was maximum. By further increasing dosage content from 1.0g to 1.5g and at the same pH level, the percentage removal efficiency of Ni(II) was also same. After increasing dosage of biosorbent from 1.5g to 2.0g at the pH level of 6, the percentage removal efficiency of Ni(II) decreased to 76.27 and attained the equilibrium. For the same dosage level of PGFP and for pH level to 7 of the effluent the percentage removal efficiency decreased and attained the equilibrium(Fig.5).

Variation of percentage removal efficiency of Cd(II) ion

The variation of contact time in the percentage removal efficiency of Cd(II) ion by using PGFP was analysed. The rate of biosorption was rapid in the initial stages because of the adequate surface area of the biosorbent was available. After increased contact time, more amount of Cd(II) got absorbed onto the surface of the biosorbent due to Vander Waal's force attraction and results were decreased in the available surface area (Ch. Srinivas et al., 2010).

At pH level of 6 and dosage of PGFP 1.0g for the contact time 60 minutes, the percentage removal efficiency of Cd(II) ion was 85.16. As the contact time was increased to 240 minutes the percentage removal efficiency of Cd(II) ion was maximum and it was 89.61 with 1.0g of biosorbent and pH level of 6 (**Refer Fig. 3**). For 300 minutes with pH level of 6 and dosage content of PGFP 1.0g, the percentage removal efficiency was constant (89.61). By further increasing the pH level and dosage content did not show significant change in the equilibrium concentration, i.e., the biosorption phase reached equilibrium conditions.

Variation of percentage removal efficiency of Ni(II) ion

Biosorption of Ni(II) ion was measured at given contact time from 60 to 300 minutes. The characteristic curve showed that the rate of percentage removal efficiency of Ni(II) was higher at the beginning. This was due to larger surface area of the leaves being available at beginning for the biosorption of Ni(II) ions (Senthil Kumar and Kirthika, 2009). The initial percentage removal efficiency of Ni(II) ion was 77.97 in 60 minutes for 1.0g of PGFP and pH level of 6. The maximum percentage removal efficiency of Ni(II) ion was 89.83 in 180 minutes for the same dosage content and pH level. By further increase of contact time; the biosorption had reached the equilibrium conditions. When increased of pH level from 6 to 7, the degree of Ni(II) ion removal also decreased. This was due to the decreased of number of vacant sites on the surface of PGFP (**Fig. 4**).

Adsorption Isotherm on Psidium Guajava Foliages Powder

Langmuir Isotherm

An adsorption isotherm was characterized by certain constants; the result shows the surface properties and affinity of the biosorbent.. The linearised Langmuir obtained at room temperature were shown in **Figures 5.** and biosorption coefficients computed from these figures by using the equations Eq. 1 , 2 and 3.

$$q_e = \left(\frac{x}{m}\right) \qquad\qquad\qquad\qquad \text{(Eq. 1)}$$

Hence, $$q_e = \left(\frac{q_{max}\,KC_e}{1+KC_e}\right) \qquad\qquad \text{(Eq .2)}$$

$$\left(\frac{1}{q_e}\right) = \left(\frac{1}{q_{max}}\right) + \left(\frac{1}{q_{max}\,K}\right)\left(\frac{1}{C_e}\right) \qquad \text{(Eq. 3)}$$

Where
x = Amount of ions adsorbed (g),
m = Unit mass of adsorbent (g),
C_e = Equilibrium metal concentration (mg/l)
q_e = Amount of metal ion adsorbed per unit mass of adsorbent.
q_{max} = Maximum monolayer coverage, capacity (mg/g)
K = Langmuir Isotherm Constant (l/mg)

The plot of $1/C_e$ with respect to the $1/q_e$ showed that biosorption of Langmuir isotherm model was shown in **Figure 5.** The R_L value obtained indicates the type of isotherm to be favourable ($0<R_L<1$), linear ($R_L=1$) and unfavourable ($R_L>1$). The effect of the dimensionless separation factor was observed to be favorable conditions.
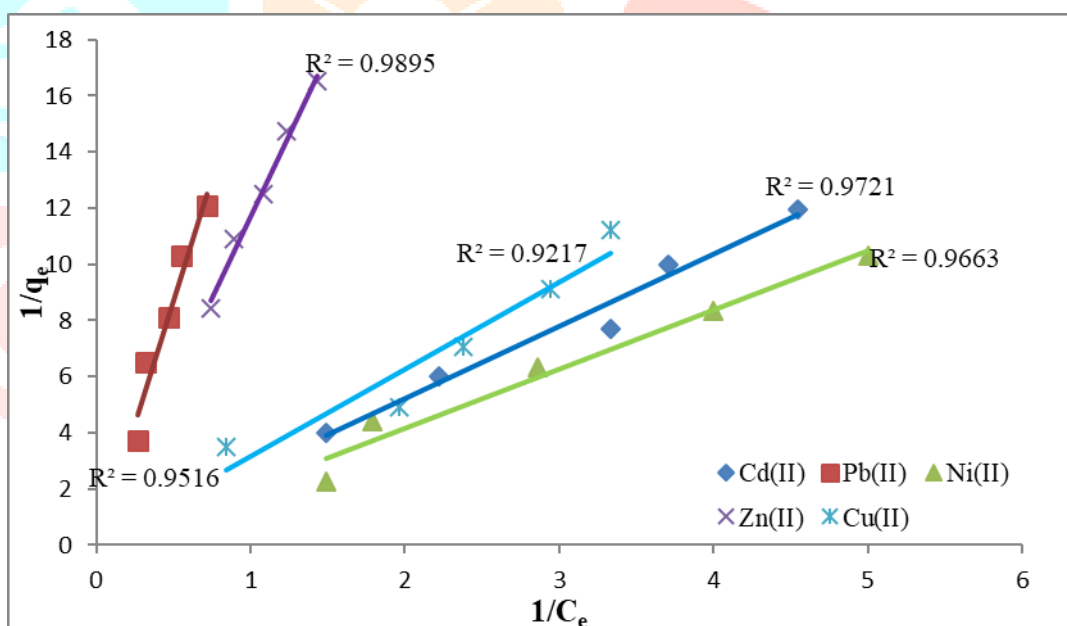
Figure 5.Linearised Langmuir isotherms for the adsorption of toxic metals by PGFP

Langmuir Isotherm

The plot of $\log C_e$ with respect to the $\log q_e$ showed that biosorption follow Freundlich isotherm model was fitted with experimental data to compute the value of 'K$_F$' and 'n' by using the equation **(Eq. 3),** whereas the co-efficient of correlation (R^2) were represented in **Fig .6.**

For Freundlich equation,

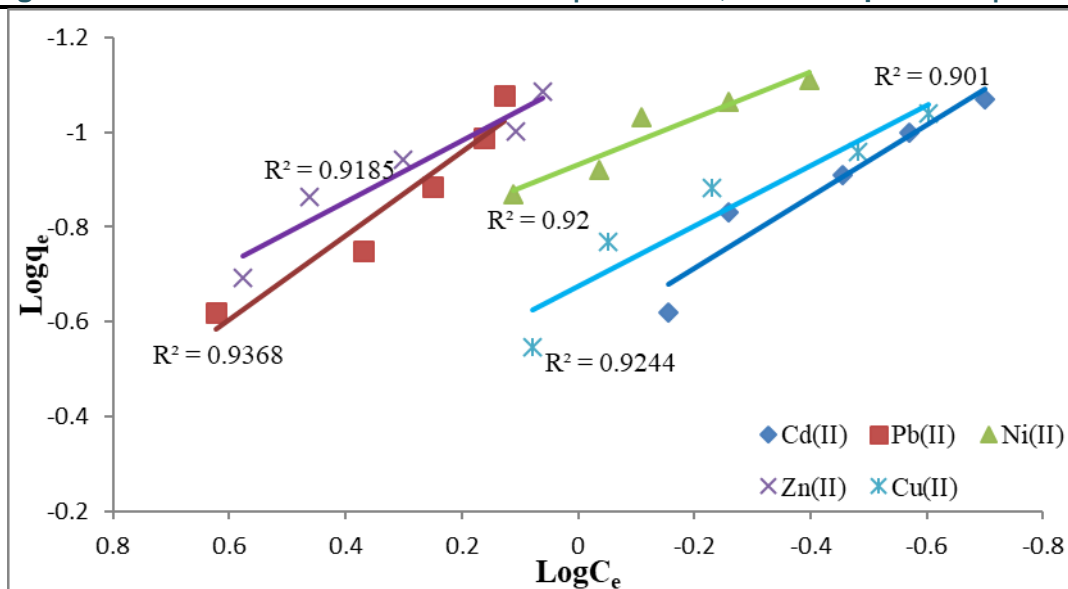$$q_e = K_F C_e^{\,1/n} \qquad\qquad\qquad\qquad \text{(Eq. 4.)}$$

$$\text{Log } q_e = \text{Log } K_F + \left(\frac{1}{n}\right)\text{Log } C_e \qquad\qquad \text{(Eq. 5.)}$$

Where

K_F = Adsorption equilibrium constant
1/n = Heterogeneity factor, which is related to the capacity and intensity of the adsorption
C_e = Equilibrium concentration (l/mg).

Figure 6.Linearised Freundlich isotherms for the Adsorption of Toxic Metals by PGFP

The regression analysis of the parameters of Temkin Isotherm equations **(Eq. 6** and **7)** are represented in **Figure 7.** The observed equilibrium data were fitted to the isotherms, hence the coefficient value of K_T and B with respect to the toxic metals, whereas the co-efficient of correlation (R^2) was given in **Table 5.2**.

The Temkin model is linearly represented as an equation (Eq. 6) and generally applied in the following form:

$$q_e = B \ln A + B \ln C_e \qquad \text{(Eq. 6)}$$
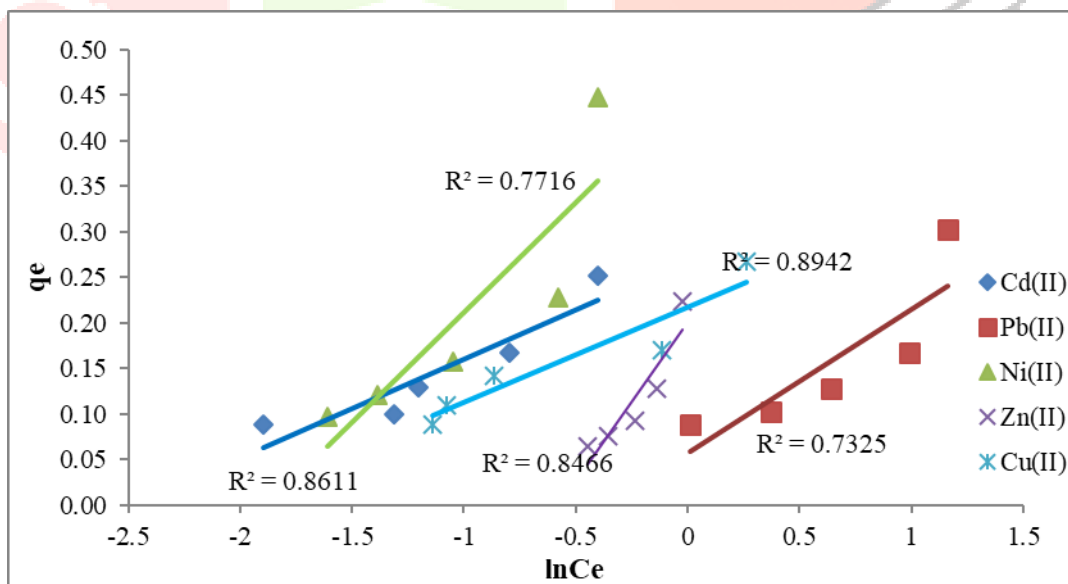$$b = RT/B \qquad \text{(Eq. 7)}$$

Where

A = Temkin isotherm constant (L/g)
B = Heat of sorption (J/mol)
R = Gas constant (J/mol/k)
b = Temkin isotherm constant linked to the energy parameter, B
T = Absolute temperature in Kelvin

Figure 7. Linearised Temkin isotherms for the adsorption of toxic metals by PGFP

Conclusions

In the present study, Biosorption experiments for the removal of Cd(II) and Ni(II) ions from aqueous solutions have been carried out using dried Guava leaf powder as low cost and natural available adsorbents. It was found that the biosorption was rapid and increased by the decrease in biosorbent average particle size. The optimum biosorption was achieved at pH 6.0 for Cd(II) and Ni(II) respectively. The maximum percentage removal of heavy metals about Cd(II) and Ni(II) were attained optimum efficiency at 1.0g which is 89.61% at 240 minutes and 89.83% at 180 minutes in the adsorption. The adsorption isotherm data was satisfactory explained by Langmuir and Freundlich isotherm models. The Freundlich isotherm had been well fitted the biosorption of Pb with chemically modified Guava leaf powder.

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