Batchwise Biosorption of Sn^{2+} Ions by using Chemically Treated Banana Peel

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ABSTRACT

Biosorption has attracted attention as a cost-effective means for the treatment of metal-bearing wastewater. While using novel biosorbents, optimization of operating conditions becomes more important for the efficiency of the process. In this study, a novel biosorbent i.e banana peel were used for biosorption of Sn^{2+} from aqueous media. The effect of various parameters, such as, contacts time of solution with biosorbent, temperature, pH, biosorbent dose and agitation speed were studied. A comparative study of modification of biosorbent using acid and base was also performed. It has been found that acid treated banana peel has greater biosorption capacity as compared to untreated and base treated peel. Langmuir and Freundlich isotherms were also employed to evaluate maximum biosorption capacity of untreated and chemically treated banana peel for Sn^{2+}. This research work is of great significance with respect to practical wastewater treatment by biosorption.

Key words: Biosorption, Sn^{2+}, Banana peel, Langmuir and Freundlich isotherms.

INTRODUCTION

Industrial effluents are usually loaded with heavy metals which are harmful for humans and other forms of life. Their toxic nature has a severe environmental impact on ecosystems. This has resulted in the enforcement of stringent laws for the maximum permissible limits of their discharge into open landscapes and water bodies[1]. Heavy metals are dangerous as they bioaccumulate. Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost (metabolized or excreted).

Thus, longer the biological half-life of the substance, the greater is the risk of chronic poisoning, even if environmental levels of the toxins are very low[2]. Tin, which goes by Sn on the periodic table, is a trace mineral that very little research has been done on[3]. In fact, scientists are still not absolutely sure that tin is essential or non essential for human beings, a claim which has some merit as tin is not an essential mineral for many animals[4].

Tins as single atoms or molecules are not very toxic to any kind of organism, the toxic form is the organic form. Organic tin components can

maintain in the environment for long periods of time. They are very persistent and not fairly biodegradable. Microorganisms have a great deal of trouble breaking down organic tin compounds that have accumulated on water soils for many years. The concentrations of organic tins still rise due to this.

Organic tins can spread through the water systems when adsorbed on sludge particles. They are known to cause a great deal of harm to aquatic ecosystems, as they are very toxic to fungi, algae and phytoplankton. Phytoplankton is a very important link in the aquatic ecosystem, as it provides other water organisms with oxygen. It is also an important part of the aquatic food chain[5].

There are many different types of organic tin that can vary greatly in toxicity. Tributyltins are the most toxic tin components to fish and fungi, whereas trifenyltin is much more toxic to phytoplankton. Organic tins are known to disturb growth, reproduction, enzymatic systems and feeding patterns of aquatic organisms. The exposure mainly takes place in the top layer of the water, as that is where organic tin compounds accumulate[6].

Tin is mainly applied in various organic substances. The organic tin bonds are the most dangerous forms of tin for humans. Despite the dangers they are applied in a great number of industries, such as the paint industry and the plastic industry, and in agriculture through pesticides. The number of applications of organic tin substances is still increasing, despite the fact that we know the consequences of tin poisoning.

The effects of organic tin substances can vary. They depend upon the kind of substance that is present and the organism that is exposed to it. Triethyltin is the most dangerous organic tin substance for humans. It has relatively short hydrogen bonds. When hydrogen bonds grow longer a tin substance will be less dangerous to human health. Humans can absorb tin bonds through food and breathing and through the skin[7-9]

Biosorption is emerging as an effective and benign methodology for removal of heavy metals[10-15]. Recently a lot of research work has been carried out by different investigators for the elimination of various heavy metals from solutions using raw and modified biosorbents which are economically feasible such as agricultural wastes like sunflower stalks[16], Eucalyptus bark[17], Maize bran[18], Casurina leaves[19], leaf mould[20], Moss peat[21], green algae[22], coconut waste[23], rubber wood[24], waste tea, rice straw, tree leaves, peanut and walnut[25]. New economical, easily available and highly effective biosorbents are still demanded and work is in progress in this regard.

In this piece of research work, banana peels (*Musa sapientum*) were utilized as a biosorbent for removal of Sn (II) from aqueous media. There are different uses for banana peels in daily life which include polishing silverware, leather shoes, and the leaves of house plants but now scientists have added purification of drinking water contaminated with potentially toxic metals[26]. The purpose of present study is to evaluate the efficiency of untreated and chemically treated banana peels as biosorbent for Sn (II) and to establish two parameter equations – (Langmuir and Freundlich isotherms) for modeling the biosorption data. Biosorption capacity of biosorbents and biosorption intensity of the adsorbate on biosorbent surface were determined by Langmuir and Freundlich isotherms, respectively. For examining the structural changes due to chemical treatment, untreated and chemically treated biosorbents were characterized by FT-IR.

EXPERIMENTAL

Chemicals
All chemicals employed during this research work of AnalaR grade and were used as such. $K_2Cr_2O_7$ (Merck), HCl (Merck, 11.6M), NaOH (Merck, Mol. Wt = 40g/mol) were utilized. Double distilled water was used for preparing all types of solutions and dilutions where required.

Instrumentation
Balance ER-120A (AND), Electric grinder (Ken Wood), pH meter (HANNA pH 211), Flame Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst 100) using air-acetylene flame.

Standard Solutions
1.896 g of $SnCl_2$ was taken in 1000 mL

measuring flask and dissolved in double distilled water, making volume up to the mark. This was 1000 ppm Stock's solution of Sn (II). Standard solutions of required concentrations were prepared by successive dilution of the stock solution.

Preparation of biosorbents

The banana peel were collected from the Chowkit fuit market Kuala Lumpur.. After washing the leaves with distilled water, these were air dried for three to four days, followed by oven drying at 60 $^{\circ}$C for two hours. Then they were ground to 60 mesh (ASTM) particle size. This was the sample of the untreated biosorbent (U.T.B). Acid treated biosorbent (A.T.B) was prepared by dipping 100 g of dried leaves powder into one liter of 0.1 M HCl solution for 24 hours. Then after filtering, it was dried again in oven at 60 $^{\circ}$C for two hours. Similarly base treated biosorbent (B.T.B) was prepared by using 0.001M NaOH instead of acid. Higher concentration of NaOH like 0.1 M and 0.01 M were not used for treatment, because in that case leaves powder partially dissolved and paste was formed which cannot be filtered out. The surface of untreated and chemically treated biosorbents was characterized by Fourier Transforms Infrared Spectrophotometer (Perkin Elmer Spectrum R XI).

Biosorption Experiments

The biosorption studies were carried out at 25 ± 1 °C. pH of the solution was adjusted to different values according to the requirement, with 0.1 M HCl and 0.1 M NaOH. A known amount of different biosorbents were added to samples separately and allowed sufficient time for biosorption equilibrium. The mixtures were then filtered and metal ion concentrations were determined in the filtrate using flame atomic absorption spectrophotometer working at resonance wavelength 357.9 nm for tin.

The effects of various parameters on the rate of biosorption process were investigated by varying contact time, t (5-50 min), biosorbent amount (0.3-3.0 g) , initial pH of the solution (1-10), agitation speed (25-200 rpm) and temperature (10-80 °C). The solution volume (V) was kept constant (50 mL). The metal ion biosorption (% age) at any instant of time was determined by using the following equation:

$$\% \ age \ Biosorption \ = \frac{C_o - C_e}{C_o} \times 100 \quad ...(1)$$

Where C_o and C_e are the initial and final concentrations of Sn (II) solutions respectively. To increase the accuracy of the data, each experiment was repeated three times and average values were taken[2, 9, 28].

Study of adsorption isotherm

50 mL of six solutions with concentrations 30, 40, 50, 60, 70 and 80 ppm were prepared by proper dilution of Stock's solution of Sn (II). The optimized conditions of pH, biosorbent dose, agitation speed, temperature and contact time were adopted according to the sample of biosorbent used for studying adsorption isotherms. At the end, suspensions were filtered off and filtrates were analyzed for remaining Sn (II) concentration by using flame atomic absorption spectrophotometer.

Data evaluation

Langmuir isotherm was plotted by using its standard straight-line equation (Eq. 2):

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad ...(2)$$

The value of q is calculated with this formula:

$$q = \frac{(C_o - C_e)V}{m} \quad ...(3)$$

Freundlich isotherm was plotted by applying its standard straight-line equation (Eq. 4):

$$\log q = \log K_F + \frac{1}{n}\log C_e \quad ...(4)$$

Where 'q' (mg g^{-1}) is the amount of metal ion adsorbed, 'C_e'(ppm) is final concentration of metal ion in solution. 'q_m' (mg g^{-1}) and b (L g^{-1}) are Langmuir isotherm parameters which were calculated from the slope and intercept values of

the linear plot of '1/q' versus '1/ C_e'. Whereas 'V' (L) is the volume of Sn (II) solution, 'm' (g) is the mass of biosorbent used. 'K_F' and '1/n' are Freundlich isotherm parameters. 'K_F' can be determined from intercept value and '1/n' can be determined from the slope of the linear graph of 'log q' versus 'log C_e'[2, 9, 28].

RESULTS AND DISCUSSION

FT-IR Characterization

  The first step was the characterization of *Alstonia scholaris* leaves to confirm the presence of groups like -OH, -CO, -CHO, N-H, -CONH, -C=C- and -COOH that can be used for bonding with Sn (II) during biosorption and evaluation of the structural changes occurring as a result of chemical treatment. For this purpose, the biosorbents were characterized by FT-IR and the resulting characteristic vibration frequencies are mentioned in Table 1.

  In case of untreated biosorbent, the characteristic absorption bands of N-H, -OH, -CHO, -CO, and -NCO groups are present in its spectrum. The intensities of these peaks enhanced after chemical treatment of biosorbent. Vibrational peaks between 2000 and 2300 cm^{-1} in the spectra of untreated and chemically treated biosorbents wereassigned to -NCS, -NCO, or -CN. After biosorption, the organic components of leaves were digested partially, which appeared as aromatic components peaks in their spectra. Peaks were shifted toward lower wave number after biosorption process, which indicated that these functional groups were involved in coordinating with Sn (II) during biosorption. Region below 1000 cm^{-1} cannot be used to represent any particular functional group as it corresponds to the complex interacting vibration (fingerprint region)[27].

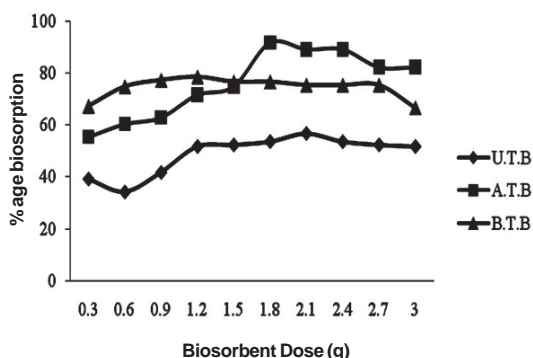**Table 1: Characteristic FTIR band absorption frequencies of biosorbent**

Bond frequencies cm^{-1}	U.T.B		A.T.B		B.T.B	
	Before biosorption	**After biosorption**	**Before biosorption**	**After biosorption**	**Before biosorption**	**After biosorption**
ν (N-H)	3291 (m), 1612 (m)	3354.4 (w), 1613.4 (m)	3372.8 (m), 1620.9 (m), 1521.4 (s)	3246.9 (w), 1621.9 (w), 1557.7 (w), 1539.7 (w)	3290.7 (w), 1613.1 (s)	3648.3 (w), 3325.7 (w), 1616.1 (m), 1540 (w)
ν (C-H) of -CHO	2917 (w)	2918.7 (m), 2849.4 (w)	2916.2 (m)	2921.9 (m), 2849.6 (w)	2917.7 (w), 2849.9 (w)	2921.5 (s), 2849.0 (w)
ν(O-H)	1023 (m)	-	1320.7 (w)	-	-	-
ν (-NCS), (-NCO) or (–CN)	2354.3 (w)	2357.4 (m), 2099.7 (w)	2361.7 (w)	2362 (m)	2357.4 (m), 2334 (w)	2362.1 (m)
ν (C=C) of aromatic ring	-	1447.9 (m)	-	1456.2 (w)	-	1455.9 (w)
ν(C-H) of aromatic ring	-	-	887.9 (w), 827.8 (s), 756 (w)	-	-	-
ν (C=O)	1241.6 (s)	-	1683.7 (m), 1158.8 (w)	1240.5 (w)	1238 (w)	1683.4 (s), 1240 (w)
ν (C-N)	1023 (m)	1031.6 (s)	1249.4 (m), 1009.3 (s)	1031.8 (s)	1025.2 (s)	1032.1 (s)

Where s= strong, m= medium and w= weak signal in FT-IR spectrum

U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent.

Effect of biosorbent dose

        Biosorbent dose variation effect was studied for the batch biosorption of Sn (II). The results are presented in Fig. 1. It was observed that the biosorption % age increased as the biosorbent dose increases. This proves that banana peel can be used for biosorption of Sn (II). The maximum biosorption values were obtained when the biosorbent dose was 2.1, 1.8 and 1.2 g using untreated (U.T.B), acid treated (A.T.B) and base treated biosorbent (B.T.B), respectively. This increase in biosorption with small biosorbent dose in case of chemically treated biosorbent was due to the availability of more adsorption sites. The maximum biosorption % age for acid treated biosorbent (A.T.B) was 91.71. While it is 78.58 % using base treated biosorbent (B.T.B) and 56.7 % in case of untreated biosorbent (U.T.B). These results showed that acid treatment of biosorbent improved the efficiency of banana peel to remove Sn (II).

chemically treated biosorbent was due to the availability of more adsorption sites which bounds Sn (II) quickly. The maximum biosorption % age for acid treated biosorbent was 87.33 %. But for base treated biosorbent it was 79.82 % while for untreated biosorbent it was 47.38 % only. The results showed that acid treatment improved the efficiency of banana peel to remove Sn (II) from aqueous medium. This biosorption characteristic indicated a rapid uptake of the adsorbate. The rate of biosorption decreased to a constant value with increase in contact time due to complete coverage of active site available for binding of metal ions to the surface of biosorbent[2, 9, 12].

Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent.

**Fig. 2: Effect of contact time
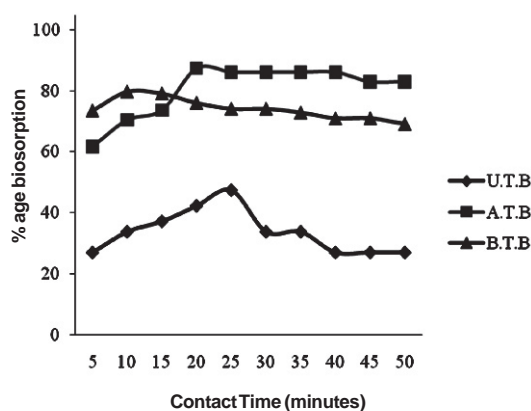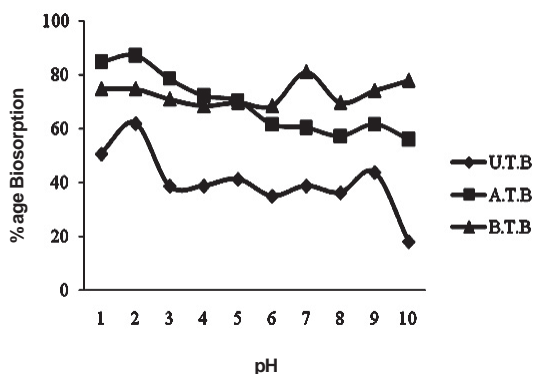on % age biosorption of Sn (II)**

Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent.

**Fig. 1: Effect of biosorbent dose
on % age biosorption of Sn (II)**

Effect of contact time

        The effect of various contact intervals between biosorbent and Sn (II) solution on biosorption was evaluated. The results are given in Fig. 2. The maximum biosorption values were obtained when the contact time was 25, 20 and 10 minutes using untreated, acid treated and base treated biosorbent respectively. This increase in biosorption with less contact time in case of

Effect of pH

        The pH of the aqueous solution is very crucial in controlling the biosorption process. The results are shown in Fig. 3. The maximum biosorption values were obtained when the pH was 2.0 using untreated and acid treated biosorbent, while pH 7.0, using base treated biosorbent (B.T.B). The maximum biosorption % age for acid treated biosorbent was 87.33. It was 81.08 % using base treated biosorbent and 62.08 % in case of untreated biosorbent (U.T.B). The results showed that chemically modified banana peel can remove Sn (II) more effectively in severe conditions. The increase in biosorption efficiency due to chemical

treatment was due to the development of more functional groups in biosorbent which can chelate more Sn (II) from solution and resulted in increased percentage biosorption
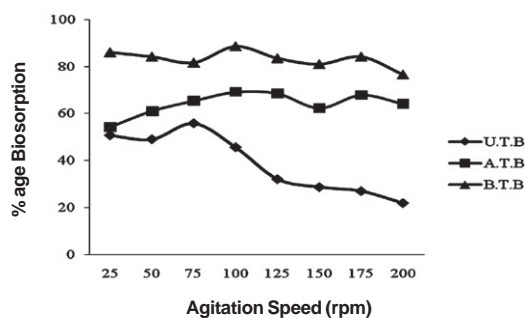

Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent.

Fig. 3: Effect of pH on % age biosorption of Sn (II)

Effect of agitation speed

        The effect of variation in the agitation speed on the biosorption efficiency of banana peel for removing Sn (II) from aqueous media was studied. The results are presented in Fig. 4. It was observed that biosorption yield increased with decrease in agitation rate. The maximum biosorption values were obtained when the agitation speed was 75 rpm using untreated biosorbent and 100 rpm using acid treated or base treated biosorbents. The maximum biosorption % age was 88.58, by using base treated biosorbent (B.T.B). It was 69.20 % when acid treated biosorbent (A.T.B) was employed and only 55.88 % using untreated biosorbent. By increasing the speed further, there was no further increase in biosorption. This is because all the binding sites have been consumed for chelating Sn (II) from the solution and no binding sites were available for further biosorption. An increasing agitation rate may reduce the film boundary layer, surrounding the biosorbent particles, thus increasing the external film diffusion rate and the uptake rate[2, 9, 28]. The results indicated that acid treatment enhanced the efficiency of banana peel to remove Sn (II).
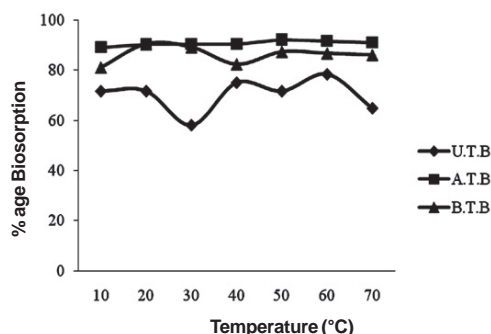

Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent.

Fig. 4: Effect of agitation speed on % age biosorption of Sn (II)

Effect of temperature

        Temperature is a very critical factor for biosorption processes. The % age biosorption was studied at various temperatures ranging 10-80°C. The results are shown in Fig. 5. The maximum biosorption values were obtained when the temperature was 60, 50 and 20°C employing untreated, acid treated and base treated biosorbents respectively. The maximum biosorption % age for acid treated biosorbent was 92.33. While using base treated biosorbent, it was 90.46 % and 78.40 % using untreated biosorbent. These results also pointed out that acid treatment improved the efficiency of banana peel to remove Sn (II). It was observed that the % age biosorption decreased at higher temperatures. The decrease in biosorption occurred on account of the fact that at high temperature, the molecules move with greater speed and less time of interaction was available for adsorbate with biosorbent material[2,9].

Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent.

Fig. 5: Effect of temperature on % age biosorption of Sn (II)

Langmuir isotherm

The Langmuir isotherms for untreated and chemically treated biosorbents are shown in Figs. 6-8 and the corresponding parameters are given in Table 2. 'q_m' value was 1.448, 6.878 and 3.824 mg g^{-1} for untreated, acid treated and base treated biosorbents respectively. 'b' is an adsorption equilibrium constant related to apparent energy of biosorption. It is related to the affinity of the binding sites, which allows to make a comparison of the affinity of the biomass towards the metal ions. Its value for Sn (II) was 0.041, 0.032 and 0.015 L g^{-1} for untreated, acid treated and base treated biosorbents correspondingly. The correlation coefficients values R^2 shows that adsorption

isotherms model well fitted to the experimental data or not. *R^2* (correlation coefficient) value close to one clearly indicated that Langmuir isotherm model holds well to explain biosorption of Sn (II) on banana peel.

These results revealed the active sites are distributed in homogeneous manner on the biosorbent surface, since it is the basic assumption of Langmuir isotherm that the surface of adsorbent is homogeneous and adsorption is mono layer rather than in multi layer fashion. The increasing values of 'b' for the metal ions showed the increase in the biosorption will occur with increasing temperature[2, 9, 12].
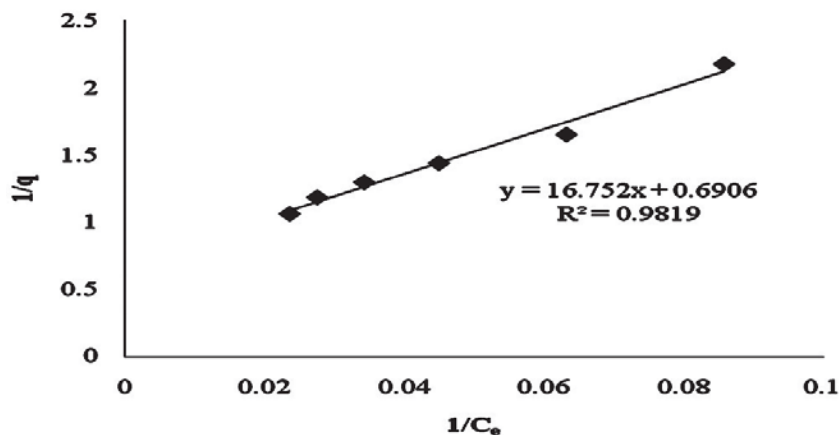

y = 16.752x + 0.6906
R² = 0.9819

Fig. 6: Langmuir isotherm for biosorption of Sn (II) on untreated banana peel
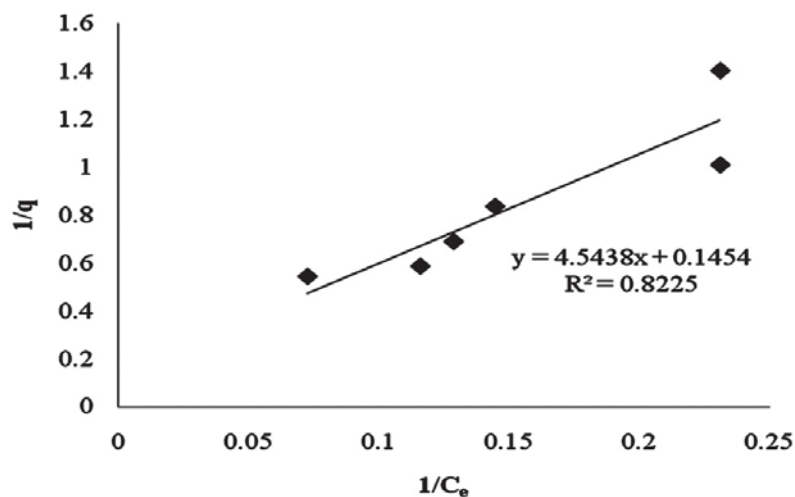

y = 4.5438x + 0.1454
R² = 0.8225

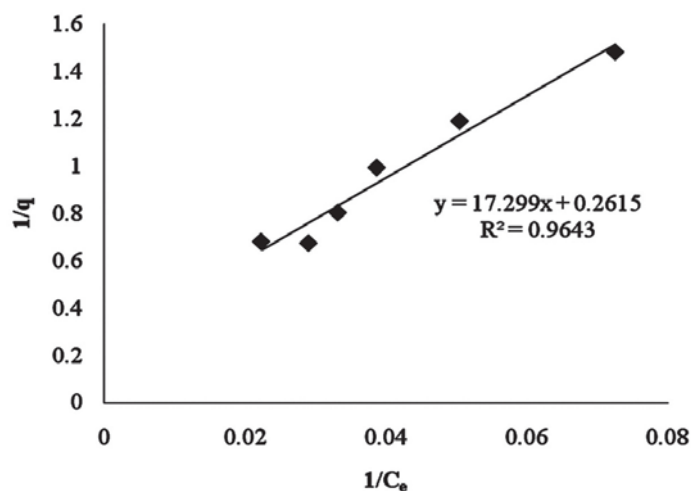**Fig. 7: Langmuir isotherm for biosorption of Sn (II) on acid treated banana peel**

Fig. 8: Langmuir isotherm for biosorption of Sn (II) on base treated banana peel

Freundlich isotherm

The Freundlich isotherms for untreated and chemically modified biosorbents were shown in Figs. 9-11 and the corresponding parameters are given in Table 2. 'K_F' is the binding constant related to adsorption capacity. Its value was 5.643×10^{-5}, 0.295 and 0.096 for untreated, acid treated and base treated biosorbents respectively. '$1/n$' is an empirical factor related with adsorption intensity. It varies with heterogeneity of the adsorbent. Its value for Sn (II) was in that order; 2.652, 0.741 and 0.738 for untreated, acid treated and base treated biosorbents. The higher K_F value means greater biosorption intensity. The values of 1/n, less than one is a sign of significant biosorption taking place at lower concentration of adsorbate[2, 9, 12]. From this, it can be concluded that chemically treated banana peel can be applied for waste water treatment for effective removal of Sn (II) even at lower concentration.
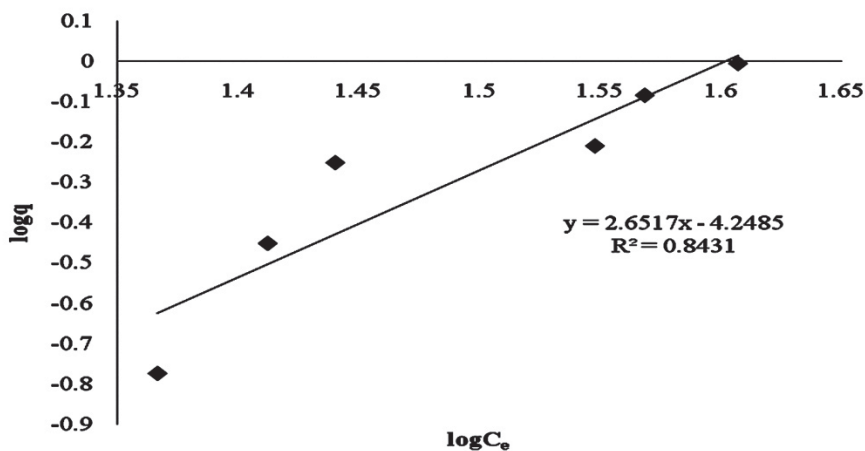

Fig. 9: Freundlich isotherm for biosorption of Sn (II) on simple untreated banana peel
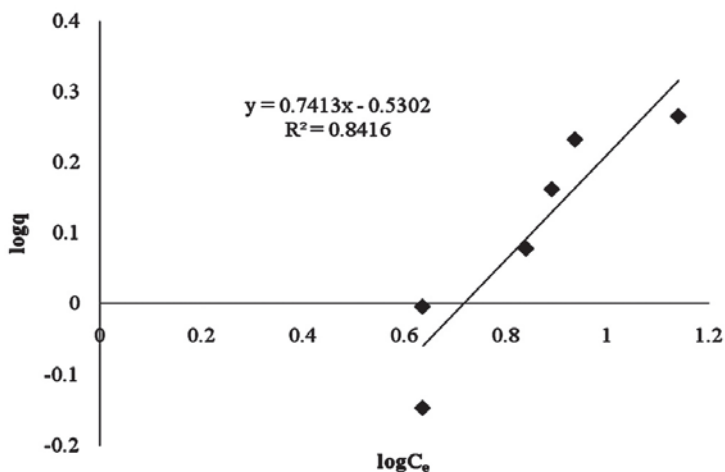
$$y = 0.7413x - 0.5302$$
$$R^2 = 0.8416$$

Fig. 10: Freundlich isotherm for biosorption of Sn (II) on acid treated banana peel

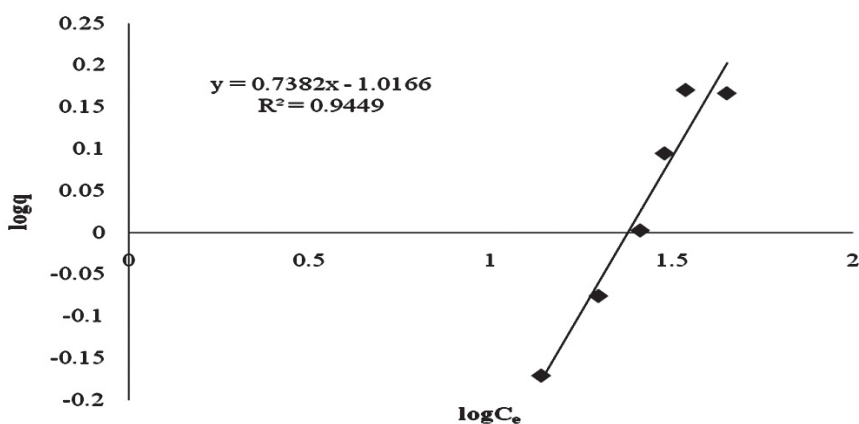$$y = 0.7382x - 1.0166$$
$$R^2 = 0.9449$$

Fig. 11: Freundlich isotherm for biosorption of Sn (II) on base treated banana peel

The value of R^2 (correlation coefficient) indicates that adsorption isotherm model well fitted to the experimental data or not. The correlation coefficients obtained from the linear plots of Freundlich equation (R^2 = close to 1) fitted better than Langmuir equation in case of acid treated biosorbent (Table 2). This describes that the equilibrium data better fit to the Freundlich isotherm model. It refers to multi layer physical biosorption of all the metals ions on the acid treated biosorbent.

Table 2: Isotherm parameters for biosorption of Sn (II) on banana peel.

Biosorbent	Langmuir Isotherm Parameters			Freundlich Isotherm Parameters		
	R^2	q_m(mg g^{-1})	b(L g^{-1})	R^2	K_F	1/n
U.T.B	0.9819	1.448	0.041	0.8431	5.643×10^{-5}	2.652
A.T.B	0.8225	6.878	0.032	0.8416	0.295	0.741
B.T.B	0.9643	3.824	0.015	0.9449	0.096	0.738

Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent

CONCLUSION

It is safely concluded from this research work that banana peel are a proficient biosorbent for the removal of Sn (II) from aqueous media. By applying chemical treatment, its capability can be further enhanced. Especially the acid treatment of biosorbent increased its efficiency a lot. Optimum conditions for removing Sn (II) using acid treated biosorbent were: 0.2 g of biosorbent, 0°C temperature, 15 minutes contact time, 300 rpm stirring speed and 2.0 pH. q_m value was 15.06 which pointed out that acid treated banana peel leaves can efficiently be utilized for Sn (II) removal from wastewater using the optimized operational conditions. The observed trend of biosorption for banana peel after chemical treatment was decreased in the order, acid treated > Base treated biosorbent > Untreated.

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