
BIOSORPTION OF MERCURY (II) IN AQUEOUS SOLUTION USING DRY PODS OF *PROSOPIS SPICIGERA*

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Abstract: Biosorption is a promising alternative method to treat industrial effluents, mainly due to the low cost and high metal binding capacity. In the present study biosorption of Mercury was done using pods of *Prosopis spicigera* by varying the parameters like pH, adsorbent dose, contact time, metal ion concentration and size variation. Maximum percent Mercury uptake was 94.09 with such optimum conditions as pH-6.0, adsorbent dosage 2.0 g/L, contact time 60 min, metal ion concentration 200 mgL⁻¹ with particle size 100 µm. The process was evaluated using Langmuir and Freundlich models, but Freundlich model fitted with experimental data. Kinetic studies performed using pseudo first order and pseudo second order equations showed that pseudo second order kinetics followed the biosorption process.

Keywords: Mercury, *P. spicigera*, SEM, Langmuir and Freundlich, Kinetic models, biosorption.

Introduction: The random release of heavy metals into the environment by various industrial activities damaged living organisms, and their accumulation throughout the food chain led to serious ecological and health problems (Rapsomanikis *et al.*, 1991). Mercury is one of the most dangerous and pervasive contaminants (Carlos Green- Ruiz, 2006) among the heavy metals in any form introduced to the natural environment from different sources and it gets converted to methyl mercury chloride by aquatic living organisms, which accumulates in the tissues of fishes and birds (Garcia, *et al.*, 1994). Mercury is released from anthropogenic activities which include agriculture, battery production, fossil fuel burning, mining, metallurgical processes, paint and chlor-alkali industries and wood pulping (Boening, 2000). Mercury has very high tendency of binding to proteins and main effects are neurological and renal disturbances as well as impairment of pulmonary function (Manohar *et al.*, 2002). Among these, Minamata disease which came to be known due to mercury poisoning is the result of eating contaminated fish

(P.A.D' Itri, 1977).

Investigations have been carried out for the removal of mercury by various processes such as chemical oxidation or reduction, chemical precipitation, evaporation and ion exchange. But these exhibit several disadvantages such as high cost, incomplete removal, low selectivity, high energy consumption, and generation of toxic slurries that are difficult to eliminate (Celaya *et al.*, 2000). Hence biosorption technique using waste or dead biomass has proven to be quite effective for the removal of metal ions which is not only low cost but environmentally friendly. Biosorption is passive adsorption of metal ions onto the surface of adsorbent, termed as biosorbent, is different from metabolically active process, the bioaccumulation. Biochemical structure or composition of cell wall of biomass is responsible for the quantity of heavy metal ions being attached on to the surface of the biomass (Velasquez & Dussan, 2009).

In the present study dried pods of *Prosopis spicigera* was used for the removal of Mercury (II) in the aqueous solution. The pod is straight, edible, smooth, 10 to 15 cm long, 0.6 cm thick which grows in dry and arid regions. Different parameters such as pH, contact time, adsorbent dose, particle size and initial metal ion concentration were studied and optimized for the maximum biosorption of Mercury. The biosorption kinetics and equilibrium isotherms were also investigated.

Materials and methods:

Preparation of Biosorbent: *Prosopis spicigera* belongs to Family *Fabaceae* whose pods were collected from Mysore district, Karnataka, India. The collected biosorbent was washed thoroughly with distilled water several times to remove the impurities. Then the pods were sun dried for several days, ground and sieved to get 100 μm to 400 μm sizes. The fine powder of these sizes were used as a biosorbent, and were kept in air tight plastic jars until used for further experiments.

Preparation of Metal ion solution: Mercury stock solution (1000 mgL^{-1}) was prepared by dissolving 1.353 g of Mercuric chloride (HgCl_2) in 1000 ml of deionized distilled water.

Characterization of Biosorbent: The scanning electron micrograph was used to reveal the surface texture and morphology of the biosorbent by using ZEISS, EVO/LS 15-15-41, smart SEM version 5.05.

A Fourier Transform Infrared (FTIR) spectrum of unloaded and metal bound *A. cookii* samples were recorded by dissolving the biosorbent with paraffin solution to obtain the spectrum using Jasco FT / IR- 4100 in wave

number range of 400-4000 cm^{-1} . The scanning electron micrograph was used to reveal the surface texture and morphology of the biosorbent by using ZEISS, EVO/LS 15-15-41, smart SEM version 5.05.

Batch Experiments: Biosorption studies were carried out by batch method with varying experimental parameters such as pH 2.0-7.0, contact time 5-120 min, metal ion concentration 25- 300 mgL^{-1} adsorbent dose 0.5-4.0 g and particle size variation 100- 400 μm . Each batch experiment was carried out by taking 2 g of the biosorbent with 20 ml of 1000 mgL^{-1} in an Erlenmeyer flask. The resulting solution was stirred in a rotary shaker at 180 rpm with time intervals of 5- 120 min. Afterwards the solution was centrifuged for 20 min at 6000 rpm. The resulting solution was decanted and unadsorbed metal ions were measured by AAS method. Each experiment was carried out in triplicates and the mean values were calculated.

The percent removal of Mercury was calculated for each run using the following formula.

$$R = (C_o - C_f) \times 100 / C_o \quad (1)$$

Where, C_o and C_f are the initial and residual concentrations of Mercury, respectively in solution in mg/L .

The adsorbed metal is based on the soluble metal concentration before and after the batch experiment. The percent removal can be calculated as:

$$q_e (\text{mg/g}) = V (C_o - C_e) / m \quad (2)$$

Where, C_o is the initial concentration (mg/l) and C_e is the equilibrium metal concentration (mg/l), V is the volume of metal solution (L) and m is the mass of the biosorbent.

Results and Discussion: Characterization of Bio-sorbent:

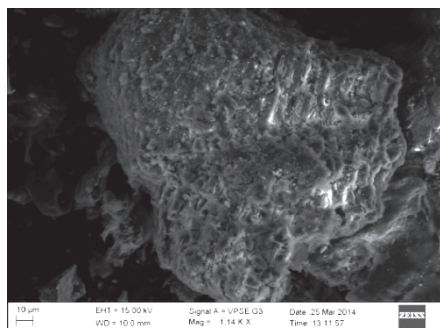


Fig 1(A) SEM image of raw *P. spicigera*

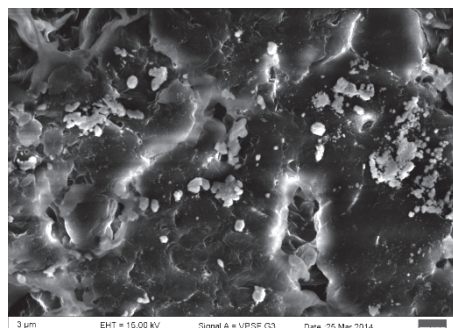


Fig 1(B) SEM image of Mercury loaded *P. spicigera*

Fig 1, SEM image shows the surface morphology of *P. spicigera* of unloaded (A) and loaded (B) Hg (II) ions were analyzed with different magnifications of 1.14X and 4.00 X with the biosorbent size 100 μm . Fig 1 (A) shows rough surface and large surface area before the biosorption and Fig 1 (B) shows that the Hg (II) metal has been accumulated as thick crystals on the surface of the biosorbent.

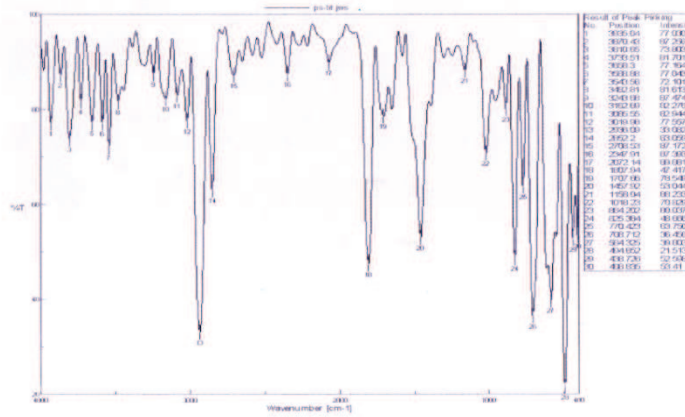


Fig. 2 (A) FTIR spectra of unloaded *P. spicigera*

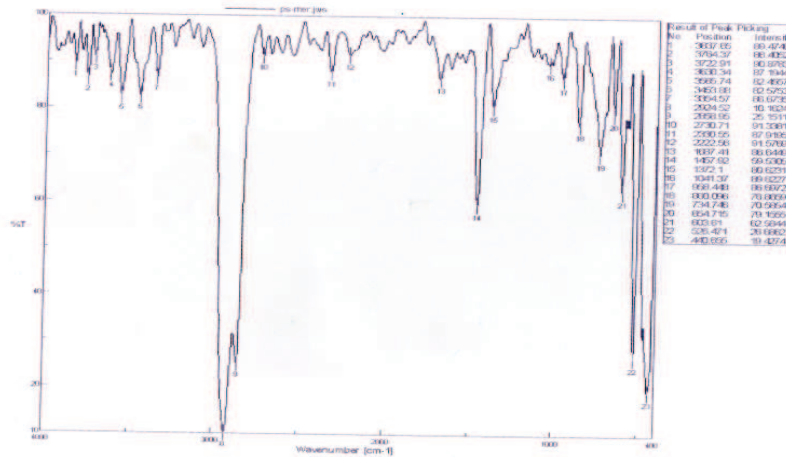


Fig. 2 (B) FTIR spectra of loaded *P. spicigera*

Fig 2 (A) and Fig 2 (B) are the FTIR characterization of raw biosorbent and metal loaded biosorbent, respectively. The range of FTIR spectra was from 400-4000 cm^{-1} , reveals the presence of functional groups which is

responsible for the biosorption process. The peak ranging from 3000-3800 cm^{-1} indicates the presence of stretching N-H bonded hydroxyl (Park *et al.*, 2005) and O-H (free) groups. The peak at 2924 and 2730 cm^{-1} shows the presence of carbonyl group stretching from aldehydes and ketones. The biosorption peak ranging from 2100-2400 cm^{-1} are due to C-H stretching, while a peak at 1687 cm^{-1} attributed to C=O stretching. The biosorption peak at 1457 and 1372 cm^{-1} characterise the presence of Nitroso N=O stretching and S=O sulfonyl groups which is associated with stretching aromatic rings. The spectral data confirms the presence of O-H, N-H, carbonyl and carboxylic groups in the biomass.

The results of the various parameters studied during the biosorption experiments could be summarized as follows:

Effect of pH: The ability to bind metals in solution has been shown to be a function of pH (Denizli *et al.*, 2004). At lower pH, H^+ ions compete with metal cations for the exchange sites in the system. The heavy metal cations are completely released under circumstances of extreme acidic conditions (Forstner and Wittmann, 1981). The batch biosorption study done at pH ranges of 2.0-7.0 and the results obtained are shown in Fig (3). Maximum uptake of Hg (II) was recorded at pH 6 with the percent removal of 94.09, while at higher pH (>7), hydroxo species of the metals are formed and do not bind to the adsorption sites on the surface of the biosorbent (Kacar *et al.*, 2000) causing a reduction in percent adsorption. Similar findings of Hg (II) removal were observed by using nonviable *Bacillus sp.* from a tropical estuary (Carlos Green-Ruiz, 2006).

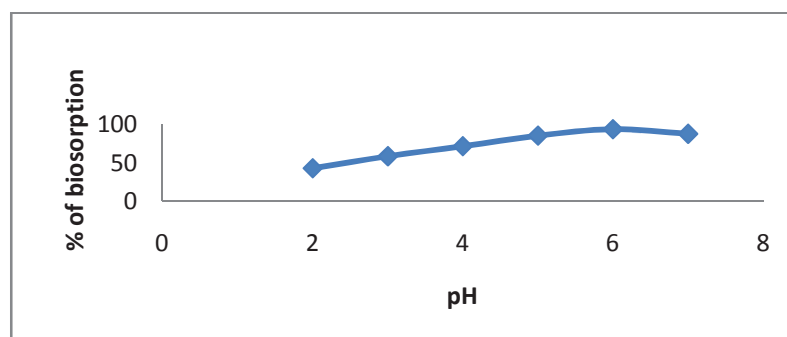


Fig. 3 Effect of pH on biosorption of Hg (II) by *P. spicigera*

Effect of biosorbent dosage: The effect of biosorbent dosages on Hg (II) biosorption by pods powder of *P. spicigera* was studied with biosorbent dosage range from 0.5- 4.0 g/L taking initial Hg (II) concentration of 200 mg/L at optimum pH of 6.0. Fig 4 shows the increase in the percent removal of Hg (II) from 51.0 to 94.09 with increase in the biosorbent dose from 0.5 to 4.0 g/L. Increase in the adsorption with increasing dose of adsorbent is due to the increase in surface area and more adsorption sites available and hence increasing the removal efficiency (Mall *et al.*, 2006; Ola Abdel Wahab, 2007).

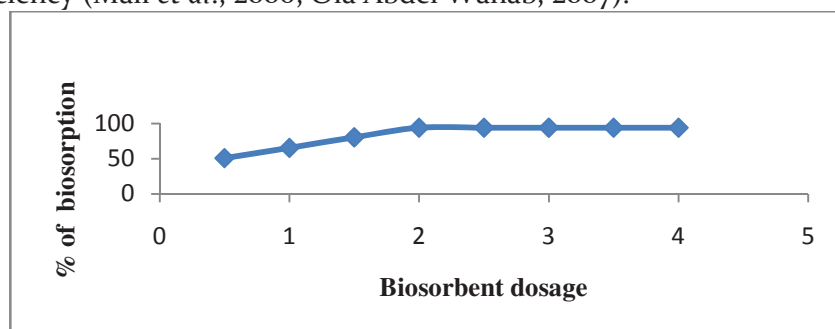


Fig. 4 Effect of biosorbent dosage on biosorption of Hg (II) by *P. spicigera*

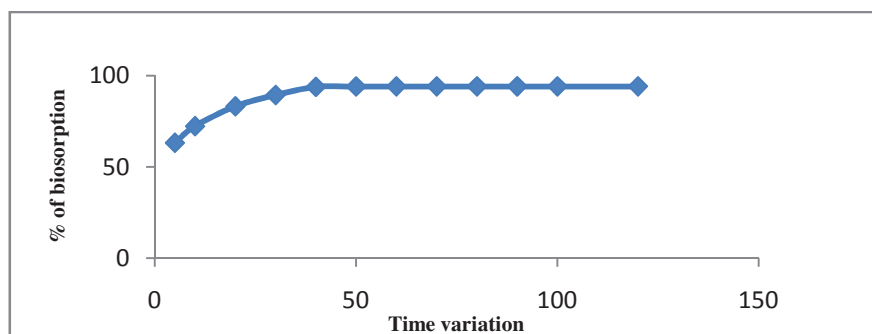


Fig. 5 Effect of contact time on biosorption of Hg (II) by *P. spicigera*

Effect of contact time: Fig 5 depicts the effect of contact time on Hg (II) biosorption by pods of *P. spicigera*. The result shows that biosorption capacity of Hg (II) increased as the contact time increased from 5-120 min with the percent removal increasing from 63.25 to 94.09. The optimum contact time for maximum biosorption reached was 60 min because of the

availability of maximum adsorption sites. The biosorption percent becomes constant due to decrease in the number of available sites which in turn remains constant (Deepa *et al* 2014). Similar findings were reported by using Jute Nanofibre for removal of Hg (II) (Vijay Baheti *et al.*, 2013).

Effect of metal ion concentration: The effect of metal ion concentration on biosorption of Hg (II) is depicted in Fig 6. The other parameters such as pH, contact time and adsorbent dose were kept constant but the concentration was varied from 25-300 mg/L. The result showed that the percent removal of Hg (II) was higher at lower concentration and decreased with increase in concentration from 98.3 to 62.73. This may be due to the fact that at lower concentration the ratio of the initial Hg (II) surface area available was low and subsequently fractional sorption became independent of the initial concentration (Salem *et al.*, 2011).

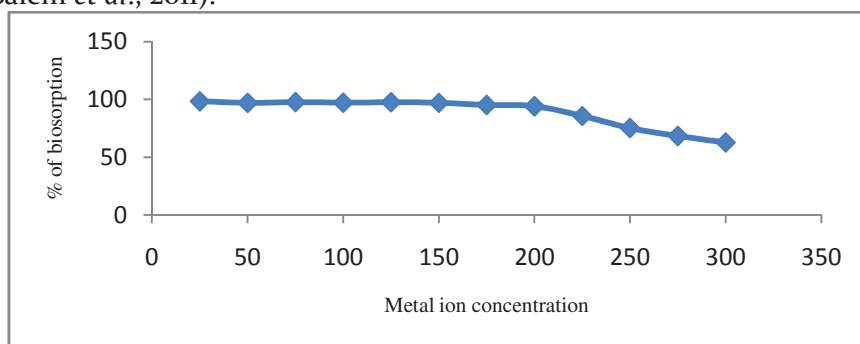


Fig. 6 Effect of metal ion concentration on biosorption of Hg (II) by *P. spicigera*

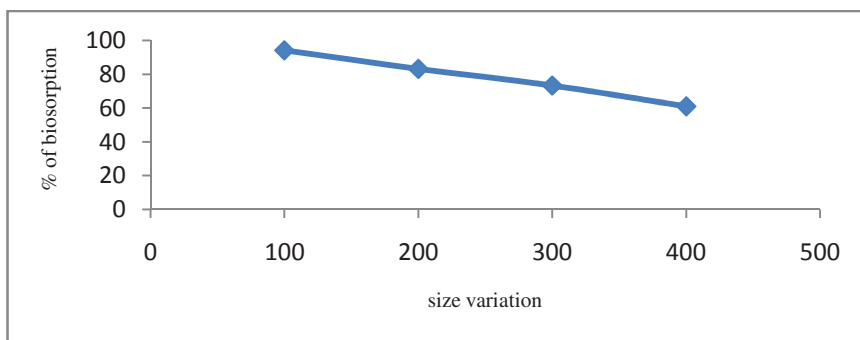


Fig. 7 Effect of particle size on biosorption of Hg (II) by *P. spicigera*

Effect of particle size: A series of experiment was conducted to understand the biosorption capacity with respect to different particle sizes from an aqueous solution using *P. spicigera*. The particle sizes were varied from 100 to 400 μm . Fig. 7 depicts that as the particle size increases, the percent biosorption capacity decreases from 94.09 to 60.9. This shows that, as the particle size increases the saturation capacity of metal ion adsorption gets decreased. This may be due to smaller particles have large surface area and thus the percentage biosorption is more.

Biosorption Kinetics: In order to understand the potential rate controlling steps involved in the biosorption process of Hg (II) onto pods of *P. spicigera*, pseudo first order and pseudo second order kinetics were applied by fitting experimental data at variable time and their respective correlation coefficients (R^2) data.

Pseudo first order kinetics was first described by Lagergren (1898) in order to describe adsorption based on solid capacity and is generally expressed in linear form as $\log (q_e - q_t) = \log q_e - k_1 / 2.303 t$ (3)

Where q_e is the amount of metal adsorbed (mg g^{-1}), q_t is the amount of metal adsorbed at time t (mg g^{-1}), K_1 is the rate constant of pseudo first order adsorption ($1/\text{min}$).

Fig. 8 shows the straight line of $\log (q_e - q_t)$ versus time, the intercept and slope of the plot can be determined by q_e and K_1 values, respectively. The calculated R^2 value shows that it is not good agreement with the pseudo first order as shown in Table 1 and shows that they were concentration dependent.

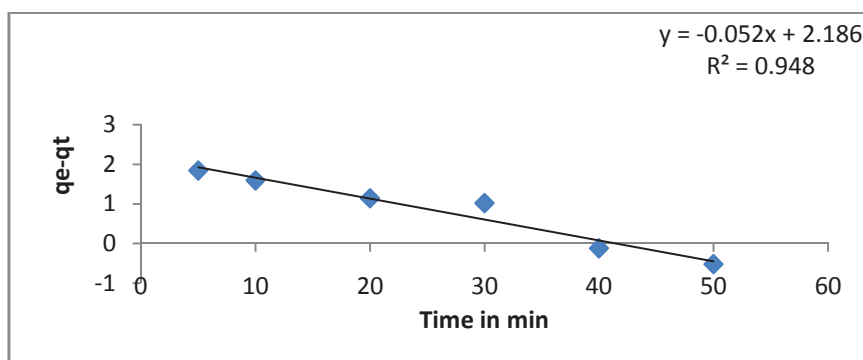


Fig. 8 Pseudo first – order sorption Kinetics for Hg (II) by *P. spicigera*
In pseudo second order (Fig 9) the amount of metal greatly influences the adsorbent surface and the metal adsorbed at equilibrium can be given in

terms of amount adsorbed in linear form as

$$dq/dt = K_2 (q_e - qt)^2 \quad (4)$$

Where qt and q_e are the amounts of metal adsorbed at time t and at equilibrium (mg g^{-1}) and K_2 ($\text{g.mg}^{-1} \text{min}^{-1}$) is the pseudo second order adsorption rate constant.

The initial adsorption rate (h) is defined as the product of $K_2 q_e^2$ and expressed as $\text{Rate } (h) = K_2 q_e^2 \quad (5)$

Where K_2 and h values are determined from the slope and intercept of the plots t/q against t

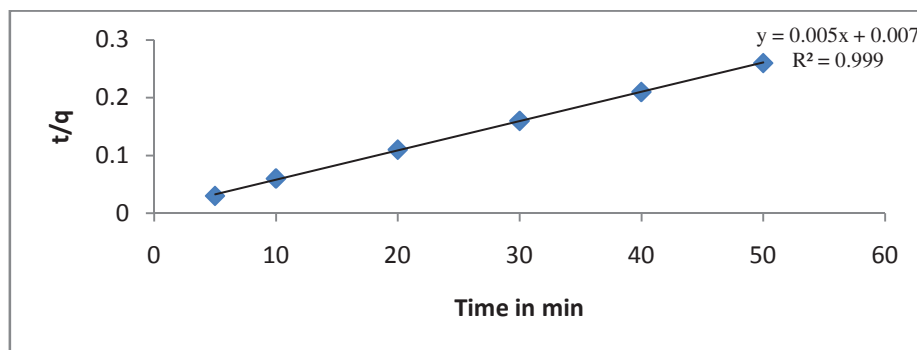


Fig. 9 Pseudo second – order sorption Kinetics for Hg (II) by *P. spicigera*

Metal	Pseudo first order			Pseudo second order			
	q_e (mg/g^{-1})	K_1 (min^{-1})	R^2	q_e (mg/g^{-1})	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2	h
Hg (II)	0.317	0.034	0.948	3.981	0.0005	0.999	1.507

Biosorption Isotherms: Biosorption of metal ions can be classified into two types: the Langmuir Model (Langmuir, 1918) in which the amount of metal uptake by the biomass reaches equilibrium and the Freundlich Model (Freundlich, 1939) in which the amount of metal uptake by the biomass increases with time (Chang and Hong, 1994).

The application of Langmuir adsorption isotherm studies which is a monolayer biosorption, were carried out with fixed initial biosorbent dose and varied metal ion concentration and it is represented in the linear

form which determines the slope and intercept as follows:

$$C_e / q_e = 1/ b q_{max} + C_e/ q_{max} \quad (6)$$

Where, b and q_{max} are Langmuir constants expressing the equilibrium constant of adsorbent and adsorbate, respectively. Fig 10 shows the plot between C_e/ q_e and values of q_{max} and b are 17.85 and 0.055, respectively as shown in Table 2. Langmuir model does not fit easily with Mercury ion biosorption on *P. spicigera* with correlation coefficient of 0.887.

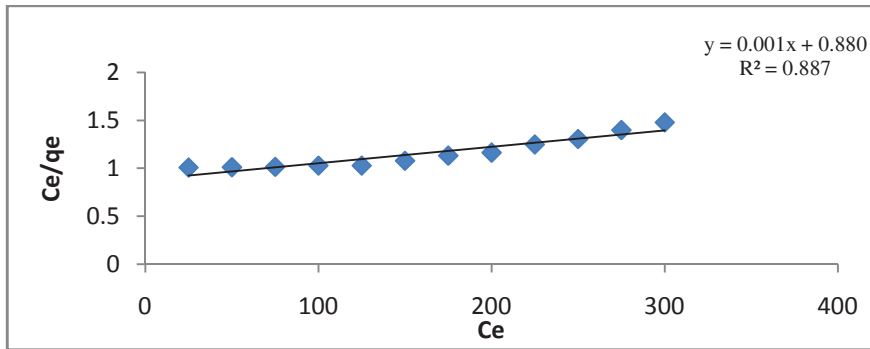


Fig. 10 The linearized Langmuir adsorption isotherms of Hg (II) by *P. spicigera*

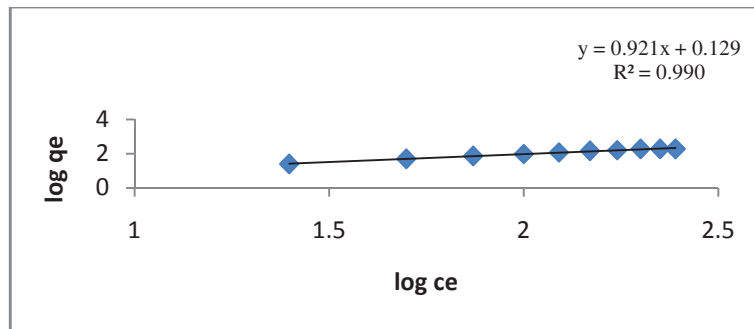


Fig. 11 The linearized Freundlich adsorption isotherms of Hg (II) by *P. spicigera*

Table 2 Langmuir and Freundlich constants for Hg (II) biosorption by <i>P. spicigera</i>						
Metal	Langmuir			Freundlich		
	q_{max}	b	R^2	K_f	$1/n$	R^2
Hg (II)	17.85	0.055	0.887	16.60	0.95	0.990

The heterogeneous surface energies by multilayer biosorption was described by Freundlich isotherm and expressed in linear form as (Netzer and Wilkinson, 1974) $\log (q)=\log \left(K_f\right)+1 / n \log \left(C_e\right)$ (7)

Where, q is the amount of metal adsorbed per unit weight of the adsorbent at equilibrium (mg q^{-1}), C_e is the equilibrium of metal concentration (mg L^{-1}), K_f is the measurement of adsorption capacity (mg/g) based on Freundlich isotherm, n is the adsorption equilibrium constant.

Fig. 11 shows the plot between $\log C_e/q_e$ and $\log C_e$ which better fit in this model compared to Langmuir, shows higher correlation coefficient (R^2 0.990) calculated from slope and intercept. Table.2 shows the values of K_f and n as 16.60 and 0.95 respectively which correspond to favorable biosorption.

Biosorbent	q_{\max}	Reference
<i>Spirogyra hyalina</i>	18.18	Cini Oommen (2012)
Treated sawdust (<i>Acacia arabica</i>)	20.6	Meena <i>et al.</i> , (2008)
Wheat bran	70	Farajzadeh, Monji, 2004
Dates nut carbon	1.16	Rao <i>et al.</i> , (2009)
<i>Eucalyptus camaldulensis</i> bark	33.1	Ismaiel <i>et al.</i> , (2013)
Activated carbon prepared from sugarcane bagasse	35.71	Asasian <i>et al.</i> , (2012)
<i>P. spicigera</i>	17.85	Present study

* q_{\max} is equilibrium and maximum adsorption capacity (mg/g)

Conclusion: Present investigation shows the pods powder of *P. spicigera* is an effective and inexpensive biosorbent which is used for the removal of Hg (II) in the aqueous solution. The biosorbent is mainly dependent on factors like pH, contact time, biosorbent dose, metal ion concentration and particle size. The result revealed that the percent removal of Hg (II) in aqueous solution under optimized conditions was 94.09% with pH 6.0, contact time 60 min, biosorbent dose 2 g/L, metal ion concentration 200

mg/L and particle size of 100 μm . Kinetics was best suited with Pseudo second order equation and Isotherms fit good with Freundlich model with correlation coefficient of (R^2) 0.990.

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