Studies on Removal of Arsenic from an Aqueous Solutions onto *Peltophorum Pterocarpum Leaves* Powder: Equilibrium and Kinetic Studies

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ABSTRACT:

In present study, the biomass is derived from the leaves of peltophorum pterocarpum and it has been investigated to remove the arsenic ions from waste water. The effects of various parameters viz. pH, contact time, biosorbent dosage, biosorbent size and temperature on the biosorption processes were systematically studied. Experimental data was modeled by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms. It was observed that arsenic biosorption best fitted to the Langmuir isotherm. The mean sorption energy (E) calculated from D–R model, indicated physical adsorption. The study of the thermodynamic parameters revealed the exothermic, spontaneous and feasible nature of biosorption process. The pseudo-second-order rate equation described the kinetics of arsenic biosorption with good correlation coefficients than pseudo-first-order equation. The biomass of peltophorum pterocarpum leaves was found to be effective for the removal of arsenic with 88.3% sorption efficiency at a concentration of 20mg/L of arsenic solution, and thus uptake capacity is 25.64 mg As/g of biomass. The peltophorum pterocarpum leaves powder biomass could be used as a low-cost biosorbent for arsenic removal.

Keywords: Arsenic, peltophorum pterocarpum leaves powder, Biosorption, Isotherm models, Kinetic models, Thermodynamics.

Introduction:

Arsenic is a metalloid, having properties of both metals and nonmetals. The anthropogenic sources are responsible for the presence of Arsenic in the environment[1]. 10 mg/L was established as the guideline value for arsenic in drinking water by the World Health Organization (WHO) in 1993[2]. Arsenic contamination in drinking ground water caused by industrial effluents and some agricultural activities is a world-wide problem. Arsenic is responsible for potentially toxicity in humans such as as chronic effects for many intakes of food and drinking water with arsenic contamination. The chronic effects include skin diseases, cancer, neurological, etc.[3-6]. Arsenic intake results as a slow poison that effects the human health and existence[5]. Arsenic occurrence in the environment was due to human activities such as mining, pesticides use, smelting of non-ferrous metals, burning of fossil fuels and timber treatment[2]. In the industrial sector, arsenic is mainly used as a wood preservative and hence, it can also be used in industries of dyes, pigments and paints. It is also used in glass preparation and mentors manufacturing[7]. Arsenic concentration in the rural areas averaged between 0.6 and 0.9 mg/L, and between 3.2 and 5.6 mg/L for rivers influenced by industrial discharges. A very small quantity of arsenic is used in human and

animal medical treatments as well as care products, and it is added in many food supplement products also. New and very old technologies used for removing arsenic from contaminated water have been developed, including oxidation, precipitation, coagulation and filtration, adsorption, ion exchange and membrane filtration like reverse osmosis and nanotechnology[3]. Each of the new and old technology processes has their advantages and disadvantages point of view which make the choice or select a suitable processing[8]. Comparing between all the advantages and disadvantages of above mentioned processes, the adsorption technique is one of the most popular methods for arsenic removal from aqueous solutions, and wastewater, and is now considered as highly efficient and low cost method for waste water treatment. During the last decades, the use of biosorbents has become interesting due to high adsorption capacities, low costs and regenerability of the sorbent. In the present work conversion of agricultural waste material like Peltophorum pterocarpum leaves powder into biosorbent. The objective of this work is to test the sorption capacities and kinetic and thermodynamic studies of arsenic onto Peltophorum pterocarpum leaves powder. Finally, it will be evaluated by the Freundlich, Langmuir, D-R isotherms can describe the arsenic biosorption capacity of Peltophorum pterocarpum leaves powder.

Experimental procedure

Preparation of biomass

peltophorum pterocarpum leaves were collected from nearby area and washed with water to remove dust particles. The washed biosorbent were then totally dried in sunlight for 10 days. The dried leaves were then cut into small pieces and powdered using domestic mixer. In the present study the powdered materials in the range of 75-212 μm average particle size were then immediately used as biosorbent without any pre-treatment.

Preparation of stock solution

Arsenate solution was prepared by dissolving solid Na_2HAsO_47H2O in distilled water. Ionic strength of solutions was adjusted by adding (0.1N) HNO_3 and(0.1N) NaOH were used for pH adjustment. All chemicals used in this work were of analytical grade.

Biosorption Experiments:

Arsenic removal capacity of peltophorum pterocarpum leaves powder was investigated by varying pH, initial arsenic ions concentration, biomass dosage and, temperature, while keeping the volume of reaction mixture as 30ml. Mixing was carried out in orbital shaker at 180 rpm. Samples were collected and filtered using What man filter paper. Residual arsenic in solution was measured using Atomic Absorption Spectroscopy. Triplicate experiments were conducted and the mean values have been recorded. Blank experiments were also run to ensure biosorption.

Biosorption capacity:

In order to estimate the uptake of the arsenic ions, a whole arrangement experiments were performed at different process variables for the Peltophorum pterocarpum leaves powder biosorbent. The metal uptake of arsenic onto Peltophorum pterocarpum leaves powder

utilizing the accompanying mathematical expression[15]:

$$q = \frac{V(C_i - C_f)}{1000w} \qquad (1)$$

Where q is the amount of metal biosorbed by Peltophorum pterocarpum leaves powder biosorbent (mg/g), C_i is the initial concentration of solute in the solution before biosorption (mg/l),C_f is the final concentration of solute in the solution after adsorption (mg/l), V is the volume of the metal solution and w is the mass of the Peltophorum pterocarpum leaves powder biosorbent.

RESULTS AND DISCUSSION
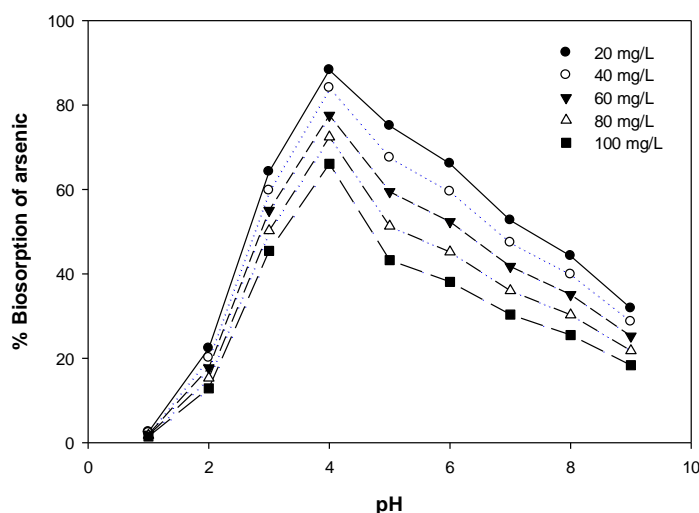
Effect of pH:

**Fig.1: Effect of pH on arsenic removal by Peltophorum pterocarpum
leaves powder for 0.1g/30ml of biosorbent concentration.**

The variation of pH of metal solution is highly effected on the biosorption process for the removal of metal ions from aqueous solutions using Peltophorum pterocarpum leaves powder as a biosorbent. This parameter is directly effects the surface charges of the biosorbent as well as the degree of ionization of different metal ions in the aqueous solution. The effect of pH on biosorption of arsenic at constant temperature (303 K) and time of agitation 60 min is shown in Fig. 1. The maximum removal of efficiency 88.31% is obtained at pH 4.0. It was observed that biosorption capacity is very low at strong acidic medium (pH = 1–3). After pH 3, biosorption efficiency, increase sharply up to pH 4 because more metal binding sites could be exposed and carried negative charges, with subsequent attraction of the positively charged metal ions with the biosorbent surface.
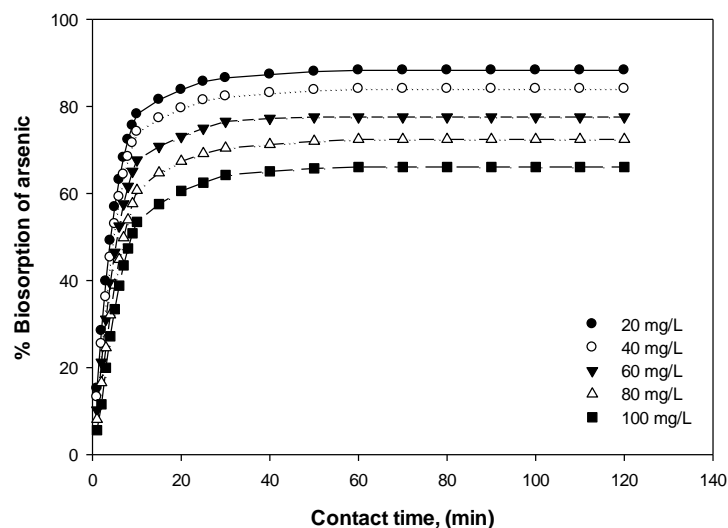
Effect of contact time:

**Fig.2: Effect of contact time on arsenic removal by peltophorum
pterocarpum leaves powder for 0.1g/30ml of biosorbent concentration.**

The biosorption experiments were conducted for different arsenic concentrations from 20 mg/l- 100 mg/l with the function of agitation time and biosorption capacity of Peltophorum pterocarpum leaves powder are demonstrated in Fig.2. The biosorption effectiveness of arsenic ions increases gradually with increasing contact times and reaches equilibrium at around 60 min, at which point the maximum amount of arsenic is removed from the solution.
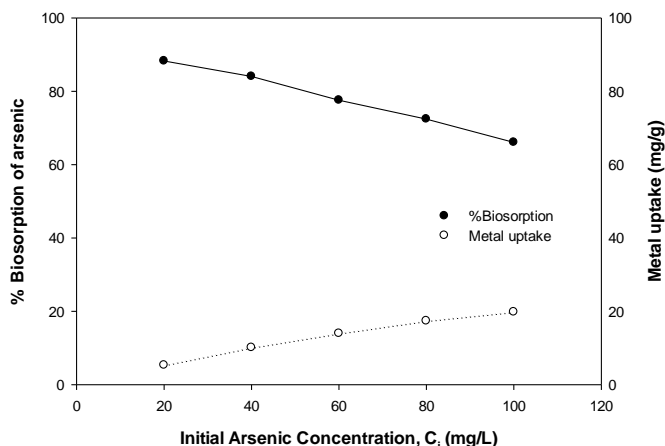
Effect of initial metal ion concentration:

Fig.3: Effect of metal ion concentration on biosorption capacity of arsenic by Peltophorum pterocarpum leaves powder of 0.1g/ 30ml of biosorbent concentration.

The Fig.3. Demonstrates the biosorption behavior by using Peltophorum pterocarpum leaves powder biosorbent at the different solute concentration in stock solution from 20 mg/l - 100mg/l, optimum pH 4.0, agitation time 60 min, the weight of Peltophorum pterocarpum leaves powder biosorbent is 0.1 grams and the temperature is 303K. The outcomes got from the data, investigated that the biosorption efficiency has declined from 88.31 % - 66.08% and the amount of arsenic deposited on the surface of the Peltophorum pterocarpum leaves powder biosorbent is increased from 5.29 mg/g-19.82 mg/g with increases solute concentration. At lower concentrations, all arsenic ions present in solution could interact with the binding sites and accordingly the rate biosorption was higher than those at higher initial arsenic ion concentrations. At higher concentrations, the lower biosorption yield is due to the saturation of biosorption sites.
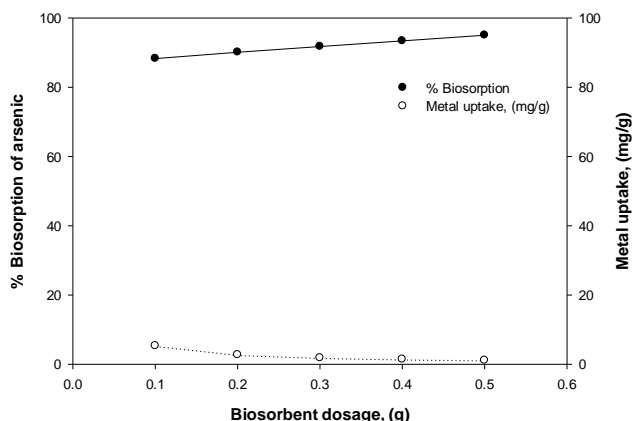
Effect of biosorbent dosage:

Fig.4: Effect of biosorbent dosage on removal and arsenic uptake by peltophorum pterocarpum leaves powder for 20mg/l metal solution concentration.

Fig.4 depicts the effect of biomass dosage on removal of arsenic from the solution containing 20 mg/l arsenic with different amounts of biomass at equilibrium. Biosorption capacity of the Peltophorum pterocarpum leaves powder was increased from 88.31% to 95.03% with an increase of Peltophorum pterocarpum leaves powder dosage from 0.1 g to 0.5 g. and metal uptake decreased from 5.2 to 1.1mg/g. This increase is obviously due to the availability of more binding sites on surface area.
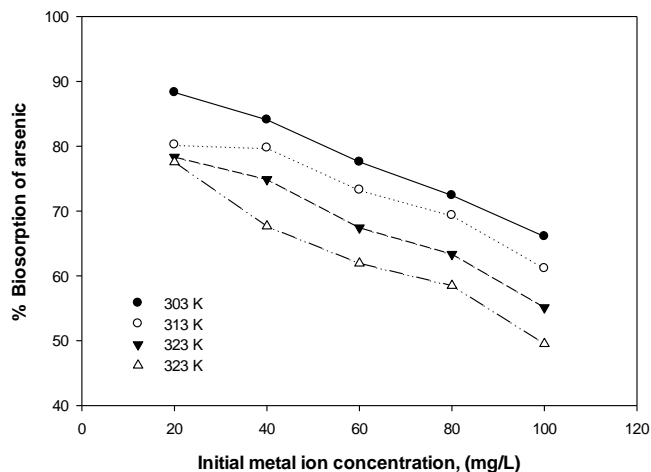
Effect of Temperature:

Fig.5: Effect of temperature on arsenic removal by *Peltophorum pterocarpum leaves powder* for 20 mg/l metal and 0.1g/30ml of biosorbent concentration.

The rate of adsorption is a function of initial metal ion concentration as well as its temperature. The percent biosorption of arsenic onto the Peltophorum pterocarpum leaves powder was shown in Fig.6 as a function of the initial metal ion concentration at 303, 313, 323 and 333 K. The percentage biosorption of arsenic on the peltophorum pterocarpum leaves powder was decreased from 88.32 to 66.08% as the temperature increased from 303 to 333 K at 20 mg/l. The percentage biosorption at higher temperature levels shows a decreasing trend because at lower temperatures, all arsenic ions present in solution could interact with the binding sites and thus the percentage biosorption was higher than those at higher temperatures.
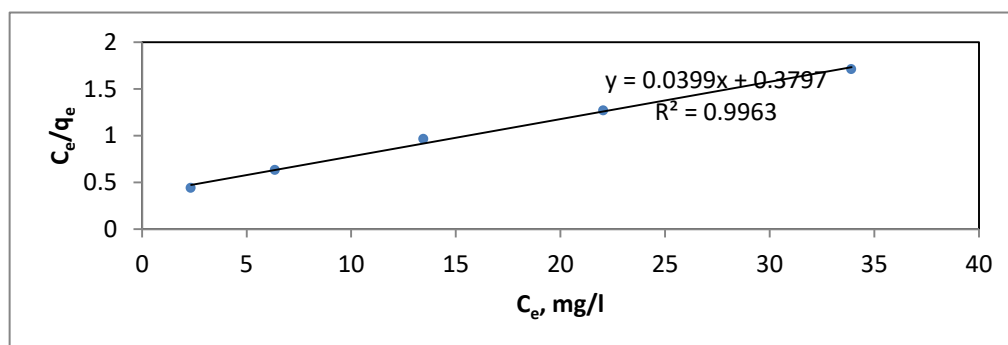
Equilibrium modeling:

Langmuir Isotherm

Fig. 6: Langmuir biosorption isotherm at 0.1g/30ml of biosorbent concentration.

Equilibrium studies are carried out to predict maximum arsenic removal by Peltophorum pterocarpum leaves powder. Experiments were conducted at 20mg/l by fixing other parameters as constant. Langmuir and Freundlich models were used in establishing equilibrium relation between arsenic ions biosorbed onto the Peltophorum pterocarpum leaves powder(q_e) and residual arsenic ions in solution (c_e). Langmuir isotherm has been extensively used for dilute solutions in following linear form [9]

$$\frac{C_e}{q_e} = (\frac{C_e}{a}) + \frac{1}{ab} \qquad (2)$$

where, 'a' is maximum metal uptake per unit mass of adsorbent to form complete monolayer and 'b' represents the affinity of binding sites. The plot of (c_e/q_e) against (c_e) indicates the applicability of this model. From the graph equilibrium data were well fitted by Langmuir model.
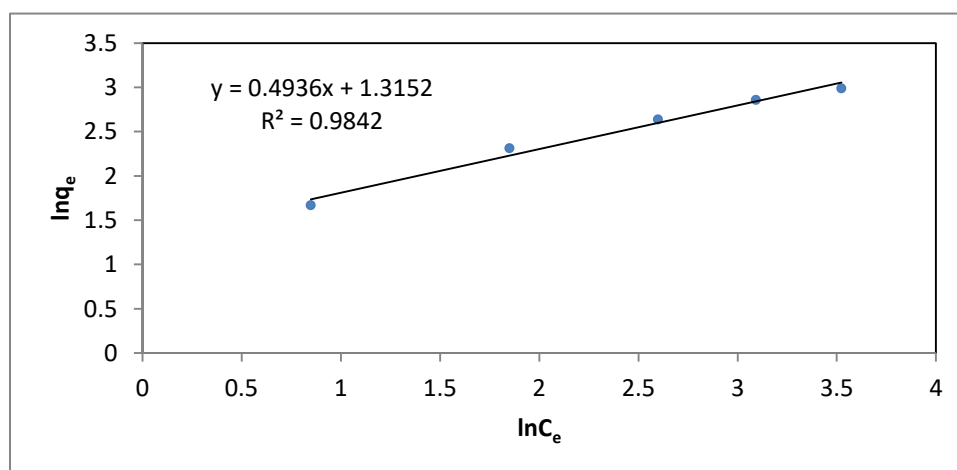
Freundlich Isotherm:

Fig7: Freundlich biosorption isotherm at 0.1g/30ml of biosorbent concentration

Freundlich model can be described by the equation given below[9]

$$q_e = K_f C_e^{1/n} \qquad (3)$$

where, the value of k_f and n are indicators of biosorption capacity and intensity. The linear plot of log (q_e) against log (c_e) describes the fitness of the this model.

Dubinin–Radushkevich isotherm:

D–R isotherm model is used to determine the nature of biosorption process as physical or chemical. The linear form of this model is expressed as [10]

$$\ln q_e = \ln q_m - \beta\, \varepsilon^2 \qquad (4)$$

Where q_e and q_m are equilibrium and maximum metal uptake (mol/g) respectively, β is activity coefficient represents mean biosorption energy (mol^2/J^2) and ε is the Polanyi potential which is calculated from the following equation[11]

$$\varepsilon = RT\, \ln(1 + \frac{1}{c_e}) \qquad (5)$$

The mean biosorption energy (E, kJ/mol) is calculated from

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (6)$$

If E value is between 8 and 16 kJ/mol, the biosorption process follows chemically and if E < 8 kJ/mol, the biosorption process is of a physically[16-17]. The mean biosorption energy was calculated as 5.79 kJ/mol for the biosorption of arsenic ions.
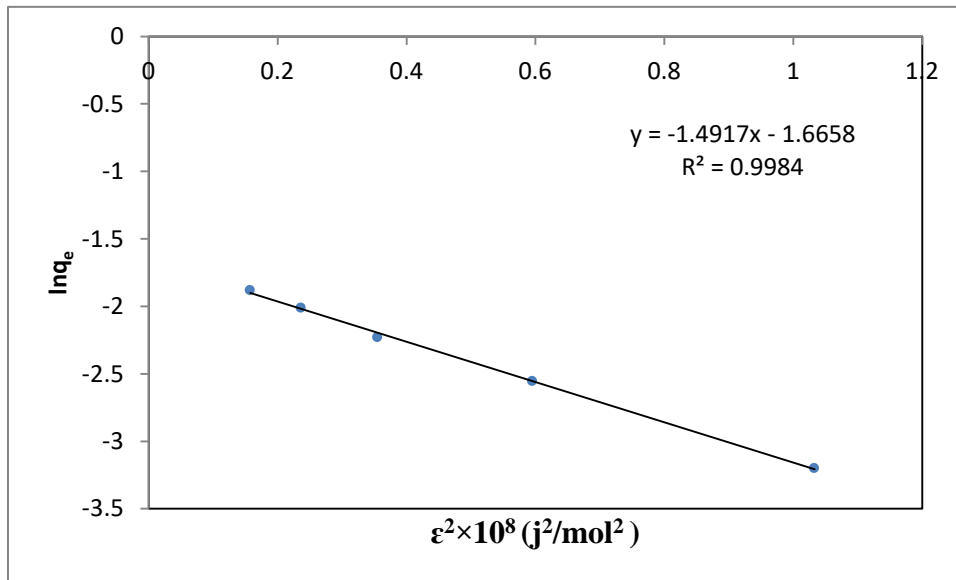

Fig8: D-R biosorption isotherm at 0.1g/30ml of biosorbent concentration

Table1: Constant values of Langmuir, Freundlich, D-R constants

Isotherm	Isotherm constants and coefficients	
Langmuir	$q_{max}(mg/g)$	25.64
	$k_l(l/mg)$	0.102
	R^2	0.996
Freundlich	$K_f(mg/g)$	3.724
	1/n(g/l)	0.493
	R^2	0.984
Dubinin – Radushkevich	β	1.491×10^{-8}
	E(KJ/mol)	5.79
	$q_{max}(mg/g)$	18.9×10^{-2}
	R^2	0.998

5. Kinetic studies

5.1 The Pseudo First-Order Equation

The kinetics equation proposed by Lagergren has been used to describe the biosorption of biosorbate from an aqueous solution. The pseudo first-order model is described by the following

Equation[12]

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad (11)$$

where q_e is the amount of metal ion adsorbed on biosorbent at equilibrium (mg/g), q_t is the amount of metal ion adsorbed on biosorbent at time 't' (mg/g) and k_1 is Lagergren constant

(min^{-1}). Integrating the above equation and transforming to log scale

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (12)$$

Linear plot of $\ln(q_e - q_t)$ against time indicates whether this kinetic model is applicable or not for biosorption process. The results of kinetic parameters are shown in table2.
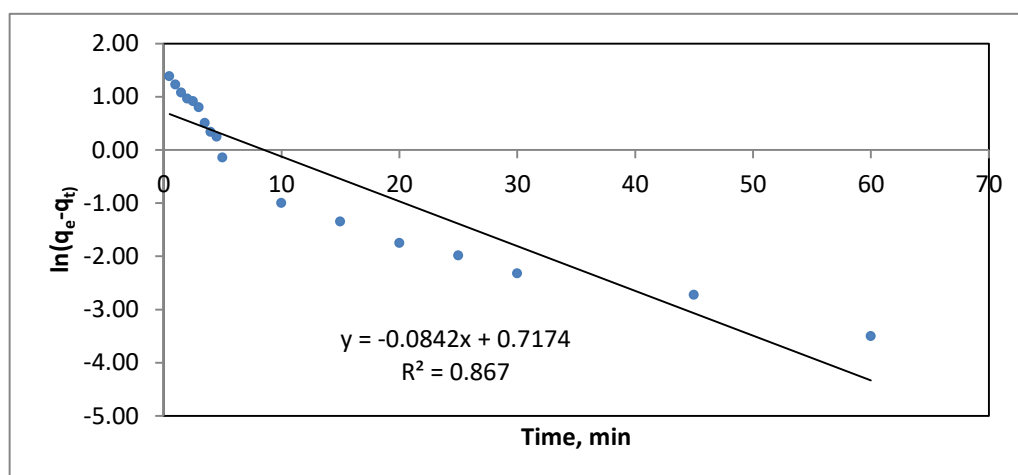

Fig9: pseudo first order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

5.2 The Pseudo Second-Order Equation

The pseudo second-order kinetic model is given as [13]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (13)$$

Where q_e = amount of adsorbed metal ion on biosorbent at equilibrium (mg/g), q_t = amount of adsorbed metal ion (mg/g) on biosorbent at time't', k_2 = second order rate constant (g/mg min). A linear plot of t/q vs t indicates whether this model of biosorption is applicable for this case or not.

The values of constants of kinetic models obtained from the plots for biosorption of arsenic onto peltophorum pterocarpum at 303^0K are shown in Table 2.The data showed good agreement with the pseudo second-order kinetic model ($R^2 = 0.999$). However, the value of the determination coefficient (R^2) indicates the applicability of the pseudo second-order model for describing the experimental results to a higher degree of accuracy. In addition, Fig.12 and Table 2, show that the q values (q_e,cal) determined from the pseudo second-order model were closer to the experimental q values (q_e, exp) than those determined from the pseudo first-order model.
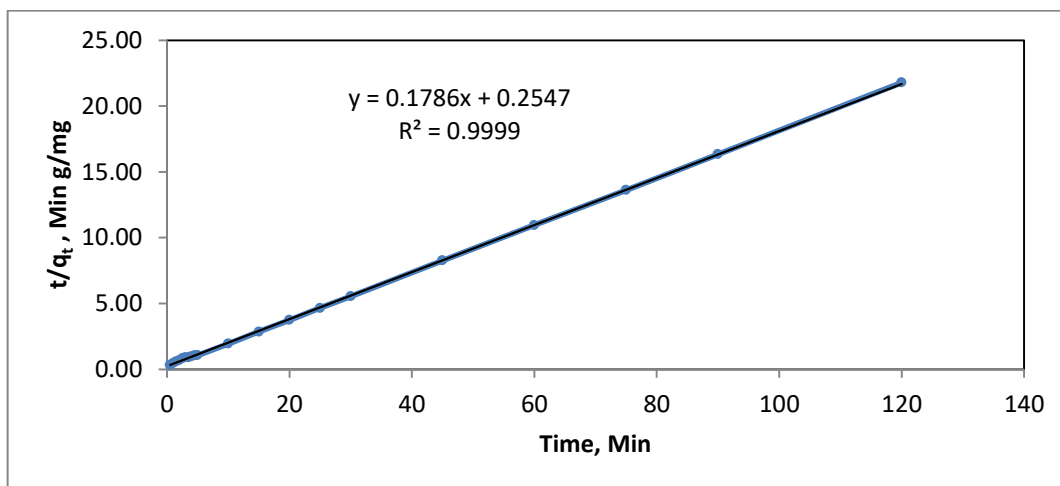
Fig10: pseudo second order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

Table.2: Biosorption rate constants, q_e estimated and coefficient of correlation associated to the pseudo-first and second-order biosorption for the Peltophorum pterocarpum leaves powder biomass

Metal	$q_{e\ Exp}$ (mg/g)	Pseudo first order			Pseudo second order		
		$K_1(min^{-1})$	q_e cal(mg/g)	R^2	K_2	q_e cal(mg/g)	R^2
Arsenic	5.2	0.084	2.048	0.867	0.124	5.617	0.999

Thermodynamic Studies:
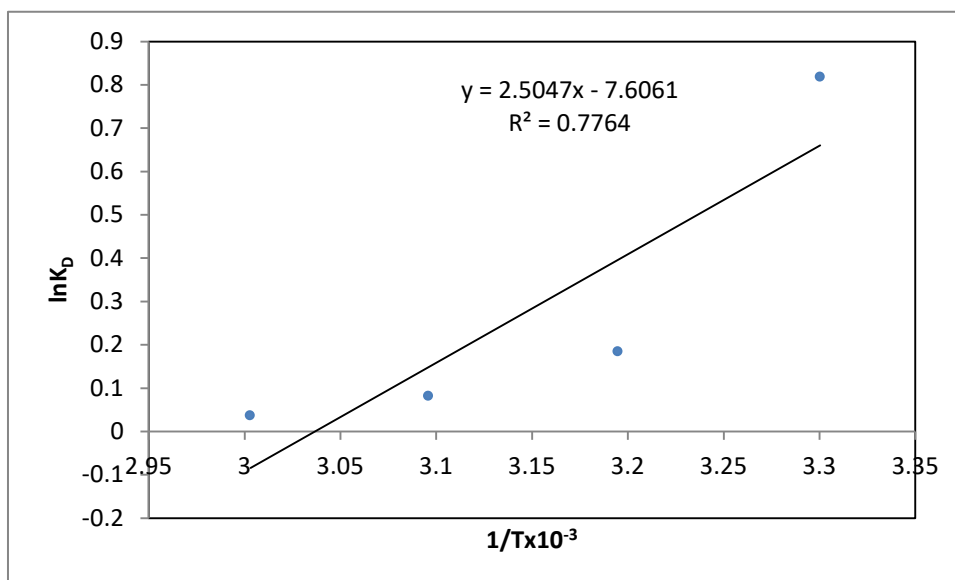

Fig.11 : Plot of ln(K_D) vs. 1/T for the estimation of thermodynamic parameters for biosorption of arsenic onto Peltophorum pterocarpum leaves powder biomass.

The thermodynamic energy functions ΔS^0 and ΔH^0 were calculated from the linear plot of log K_D versus 1/T shown in Fig.11 and ΔG^o was calculated from equilibrium constants (K_D). In this study, the negative values of ΔG^o confirm the natural possibility of process with high preference of arsenic at low temperatures. The value of ΔH^o for biosorption of arsenic onto peltophorum pterocarpum leaves powder was obtained as −20.81 kJ/mol. The negative value of ΔH^o reflects that the sorption process is exothermic and spontaneous[14].

CONCLUSION:

The biosorption potential prepared from the biomass of Peltophorum pterocarpum for the removal of arsenic from aqueous metal solutions was investigated. The batch mode experiments were conducted by varying one parameter at a time to find out effect of individual process parameters. It was found that the process is strongly affected by following independent factors i.e., initial metal ion concentration, biomass dosage and the pH of the solution. Peltophorum pterocarpum was found to be very competent and effective in removing arsenic ions (88.31%) and also the maximum removal rate was achieved within 60 min of contact time at optimum pH of 4. The equilibrium data was well described by Langmuir model. Thermodynamic parameters (ΔH^0, ΔS^0 and ΔG^0) of the arsenic ions indicate that the process is exothermic and proceeds spontaneously for the Peltophorum pterocarpum.

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