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Mechanism of Lead (II) Biosorption By*delonixregia*leaves and Bark: Combined Sorbent Effect

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ABSTRACT: The toxicity of Pb(II) on living mechanisms has led to severe ecological and health issues. In this paper, Delonixregialeaves (DRL), Delonixregia tree bark (DRB) have been used as biosorbents for the removal of Lead (II) from aqueous solutions. The biosorption studies were carried out using each biosorbent singly and the combination of the two in equimolar proportions respectively. The concentrations of the metal ions adsorbed were determined by atomic absorption spectroscopic (AAS) method. Biosorption experiments were performed as a function of pH, contact time, particle size, biosorbent dosage, temperature, initial concentration of the biosorbates. The maximum removal of Lead (II) was obtained at pH 5 after two hours.Biosorption Kinetics data obtained in this study fitted satisfactorily to the pseudo-first-order rate equation for all the biosorbents. The experimental equilibrium biosorption data were tested for Langmuir and Freundlich models, and the Freundlich model fitted better for all the biosorbents with correlation coefficient (R^2) ranges 0.997 - 0.999. Thermodynamic parameters such as Gibbs free energy, enthalpy and entropy evaluated from experimental data predict the nature of the biosorption, revealed thatbiosorption of Lead (II) was exothermic. The optimum uptake of Lead (II) was achieved at 25 °C. The results show that a large proportion of Lead (II)wereadsorbed at higher percentage when the combined form of the biosorbents was used as compared to when the biosorbents were used singly.

Key Words: Mechanism, Biosorption, Lead(II), Sorbent, *Delonixregia*

INTRODUCTION

The major problem faced today world wide is contamination of the environment especially water by toxic heavy metals. Heavy metal solutions are widely used in industrial activities such as metal finishing, electroplating, painting, dyeing, photography, surface treatment and printed circuit board manufacture (Sohail *et al*). Lead is non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain, and can be readily absorbed into the human body (Wong *et al.*, 2003). It is released into the environment in a number of ways: by process engaged in lead acid batteries, pulp and paper, petrochemicals, refineries, printing, pigments, photographic materials and explosive manufacturing, ceramics, glass, paint, oil, metal, phosphate fertilizer, electronics, wood production and also combustion of fossil fuel, forest fires, mining activity, automobile emissions, sewage wastewater, and sea spray, to mention just a few examples (Jalali *et al.*, 2002; Conrad *et al.*, 2007).

There are several methods of effluent treatment. They involves sedimentation, equalization, neutralization, aerated lagoons, trickling filters, activated sludge process, oxidation ditch, oxidation pond, anaerobic digestion, Ion Exchange , Electrodialysis , Evaporation , Chemical Precipitation, Reverse Osmosis , Electro deposition, Chemical Reduction, Adsorption etc.However, these methods have serious limitations in addition to high cost and biosorption with its distinct advantages has emerged as an alternative technology.

Plant materials are easily available and relatively inexpensive and have therefore been widely utilized as adsorbents, by different researchers in the investigations of biosroption processes (Qaiser, *et al.*, 2009 and references there in). *Delonixregia*is a species of flowering plant noted for its flamboyant display of flowers, in many tropical parts of countries around the world it is

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grown as an ornamental tree and has low nutritional requirements.

In this study, the mechanism of biosorption of Pb (II) by *Delonixregia* Leaves and Bark : combined sorbent effects has been rarely reported and this provides a premise of its use for this research in the removal of these toxic and valuable heavy metals Pb (II)from sewage and industrial effluents.

MATERIALS AND METHODS

Preparation of Biosorbents

*Delonixregia*tree leaves (DRL) and barks (DRB) were collected from the Parks and Gardens in Wuse, Abuja. The leaves and barks were washed with tap water to remove sandy particles and rinsed with distilled water. They were then cut into small segments and air-dried until almost all the moisture evaporated, groundwith electric grounder and sieved into different particle sizes of0.061mm, 0.235mm, 0.330mm, 0.391mm, 0.533 and 1.330mm. Each part was soaked in 0.1M NaOH solution for two hours to remove the lignin content. Excess alkalinity was removed by neutralizing with 0.1 M HCl and then washed severally with distilled water till the washings were free from colour and turbidity. The washed biosorbents were oven dried at 50 °C for 24 hours and stored in the desiccator for the study.

Batch Biosorption Studies

The stock solution of Lead (II) was prepared by dissolving 1.63g of $Pb(NO_3)_2$ in 100cm^3 of distilled water. The pH of the solution was adjusted using 0.1M HCl and/or 0.1 NaOH. A concentration range of 100mg/l-600mg/l were subsequently obtained from the stock solution by dilution. The influence of pH, initial concentration,contact time, adsorbentdose, particle size and temperature were investigated at 25 °C, and except in the investigation of a specific factor where a range of values were used, studies were carried out at optimum values of these factors.

Batch biosorption studies were carried out in 250 ml flasks with 100ml of the working biosorbate solution of different concentrations and 2g of biosorbent was then introduced into each flask.The flasks were agitated for 120 minutes on a mechanical shaker. The mixture in the respective flask was filtered after the agitation using Whatman filterpaper and the lead concentration in the filtrate was determined by flame atomic absorption spectrophotometry (model AA-6200) at 283.30nm. All studies were confirmed from three independent replicates and the mean value was determined for each set of experiment. The percentage of Pb (II) removal from solution was calculated using the following equation:

Percentage removal = $100(C_i - C_f) / C_i$

Where C_i and C_f are the initial and final concentration of the metal in solution, respectively.

RESULTS AND DISUSSION.

Results

Effects of initial concentration on Biosorbents

The experiments revealed that percentage removal of Pb (II) by biosorbents decreased with increasing Pb (II) concentration at pH 5, 25^{o}C after 2 hours as shown in figure 1.

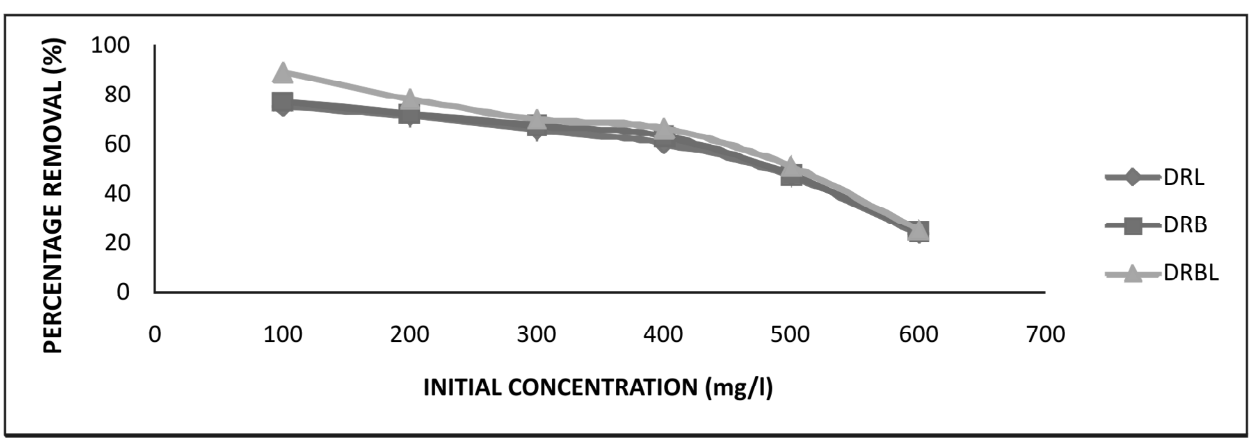

Figure 1: Biosorption of Pb (II) with variations in initial concentration by the biosorbents

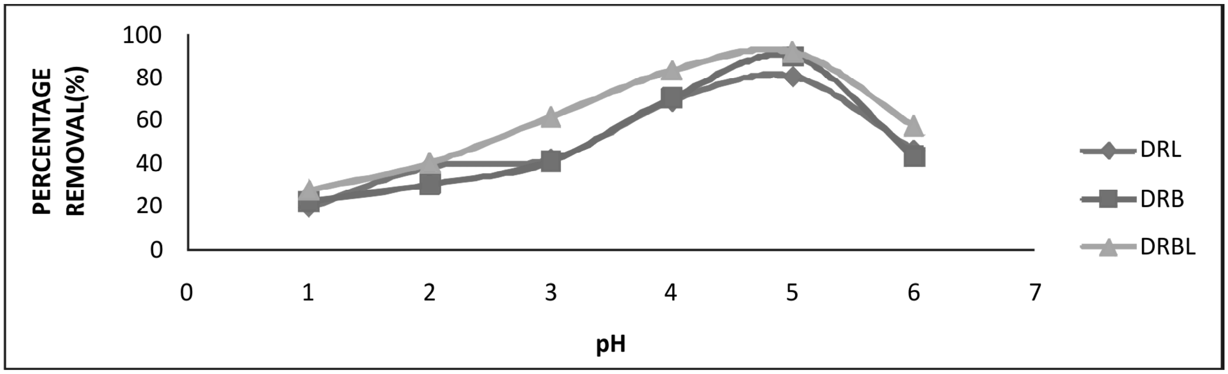

Figure 2: Biosorption of Pb (II) with contact time by biosorbents

Effects of pH

The experiments carried out at 600mg/l, 25 °C in 2 hours and it was observed that there was pH increase between pH 1 and 5 where the maximum biosorption was attained. Below pH 5 there was sharp decrease in percentage removal to pH 8 when biosorbents were used.

EFFECTS OF CONTACT TIME

Biosorbents system with Pb (II)

The climax of percentage removal of Pb (II) was reached after one hour and maintained the equilibrium. It occurred with 600mg/L, 25 °C and pH 5 as revealed in figure 3.

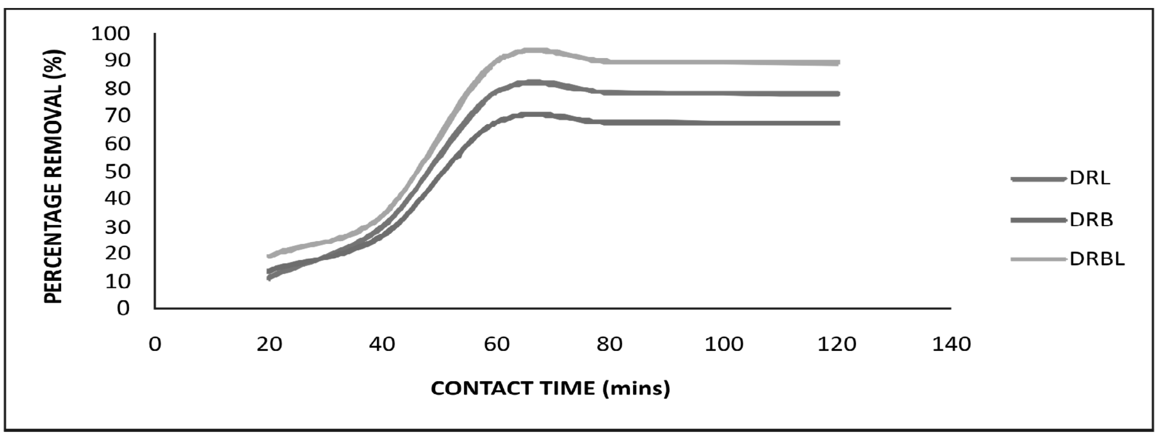

Figure 3: Biosorption of Pb (II) with contact time by biosorbents.

Effects of biosorbent sizes

The reduction in percentage removal of Pb (II) was observed as the particle sizes increases. It occurred with 600mg/L, 25^{0}C and pH 5 as revealed in figure 4.

Effects of biosrbent dosage

There was increase in percentage removal of Pb (II) as the dosage increases at 25^{0}C and pH 2 after two hours as revealed in figure 5.

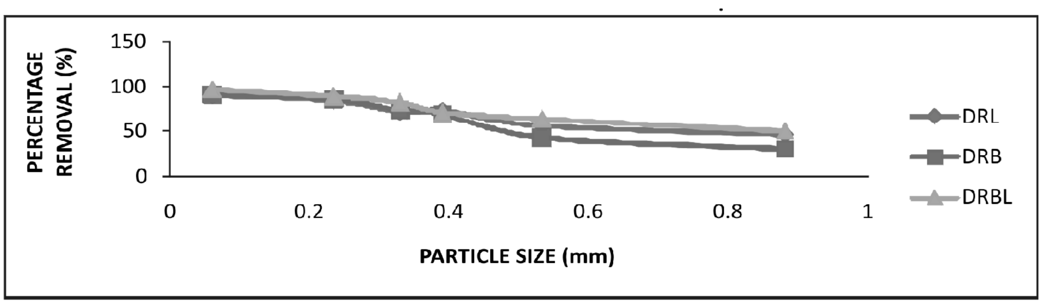

Figure 4: Biosorption of Pb (II) with Particle Sizes by biosorbents

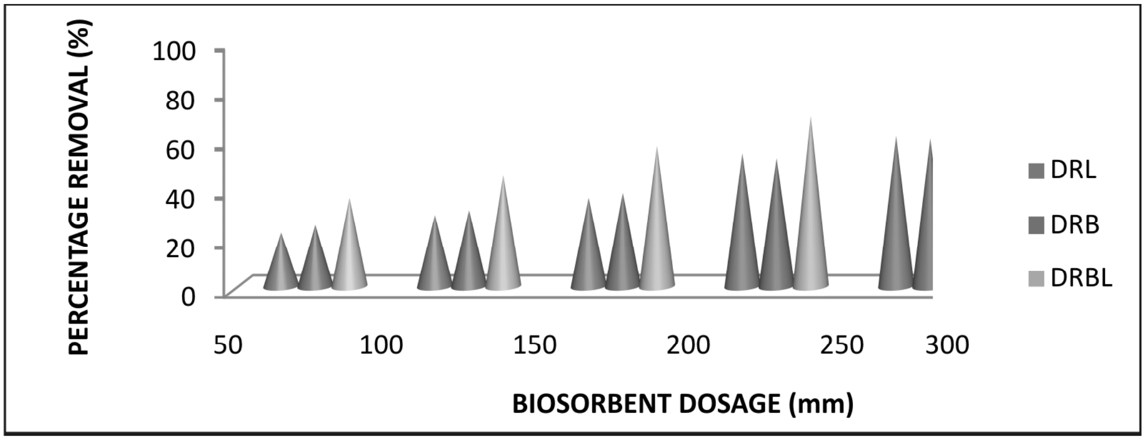

Figure 5: Biosorption of Pb (II) with Biosorbent Dosage of biosorbents

Effects of temperature

The decrease in percentage removal of Pb (II) was observed as the temperature increased at 100mg/ L and pH 5 in 2 hours as revealed in figure 6.

KINETICS STUDIES

The study of biosorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of biosorbate uptake at the solid– solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process. The results obtained from the experiments were used to study the kinetics of metal ion biosorption.

The rate kinetics of metal ionadsorption onbiosorptionswasanalyzed using pseudo-first order and pseudo-second order .The conformity betweenexperimental data and the model predictedvalues was expressed by correlationcoefficients (r^2).

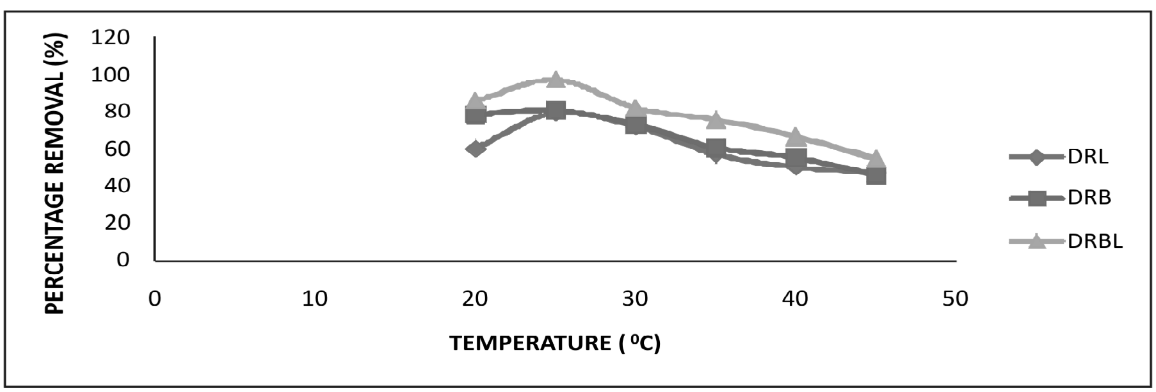

Figure 6: Biosorption of Pb (II) with Temperature by biosorbents

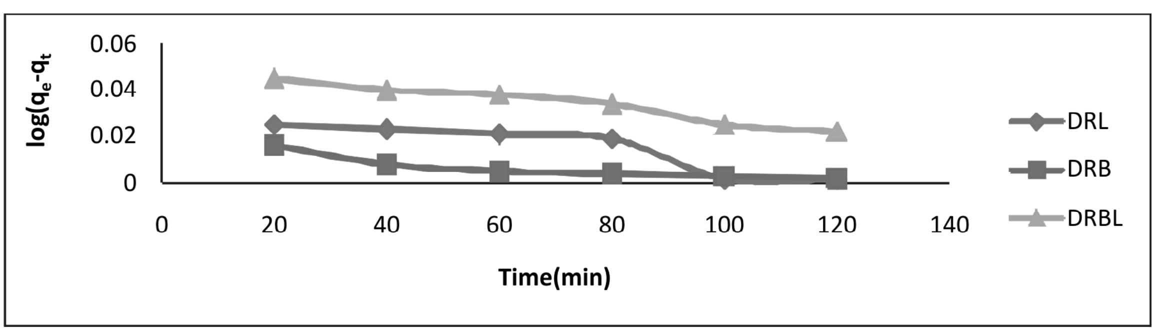

Figure 7: Pseudo-first order for the biosorption of Pb (II) by biosorbents

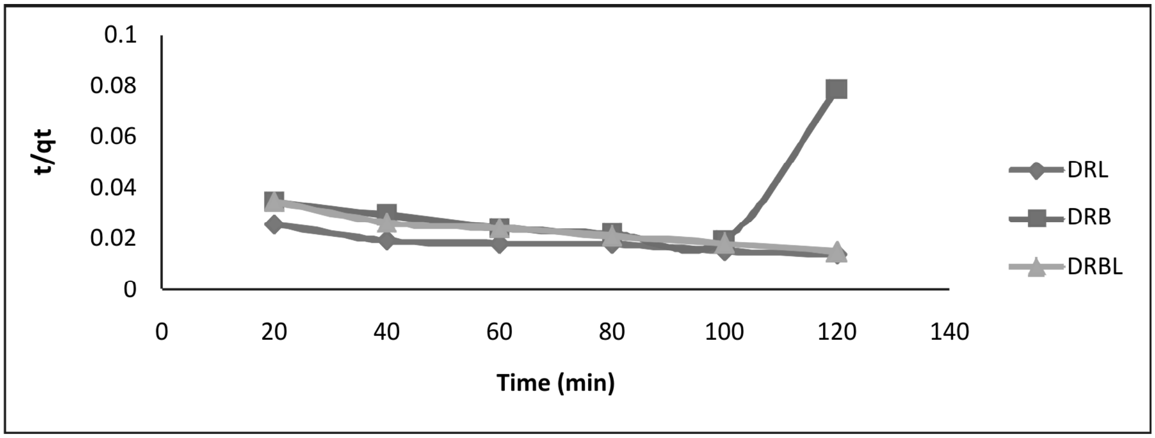

Figure 8: Pseudo-second order for the biosorption of Pb (II) by biosorbents

Biosorption Isotherm

To find out the mechanisticparameters associated with Pb (II) biosorption, the results obtained bythe biosorption experiments were analyzed byLangmuir and Freundlich models.

The theoretical Langmuirisotherm models is best known to all theisotherm models, and describes thebiosorption of a solute from a liquid solution.

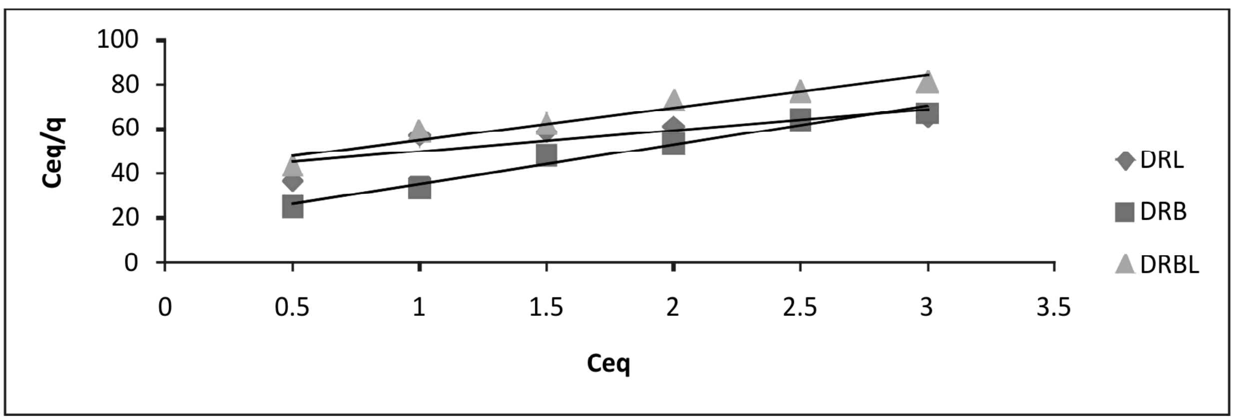

Figure 9: Langmuir isotherms of Pb (II) by biosorbents

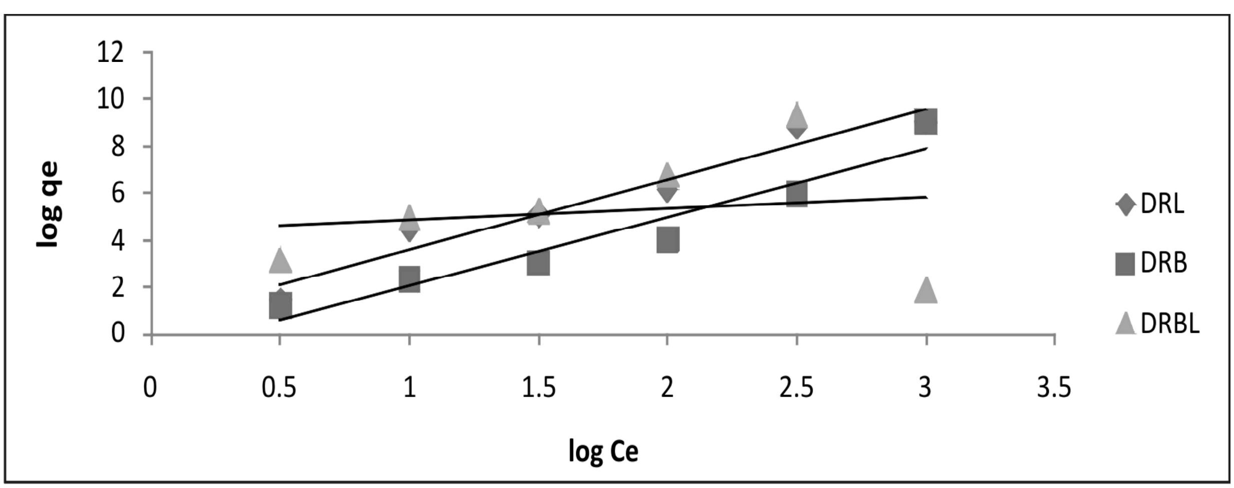

Figure 10: Freundlich isotherms of Pb (II) by biosorbents

Thermodynamic Studies

Thermodynamic parameters such as Gibbs free energy change ΔG , standard enthalpy change ΔH and standard entropy change ΔS were also found out to give more information about the nature of sorption process as shown in figure 11a, 11b and 11c respectively.

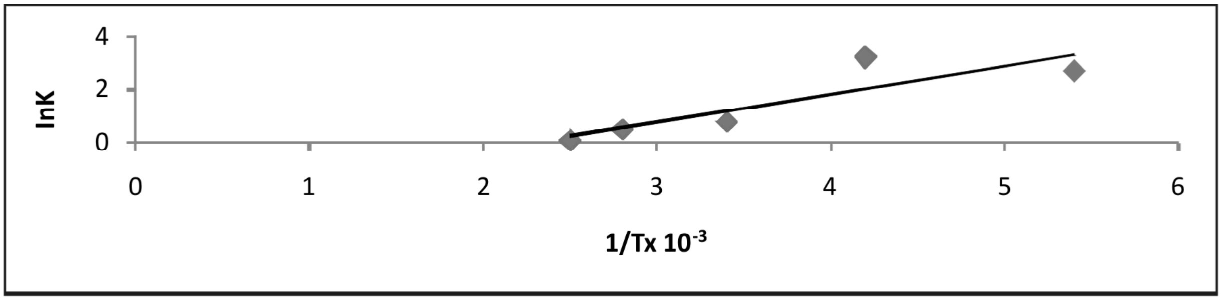

Figure 11a: Biosorption Thermodynamics of Pb (II) with DRB

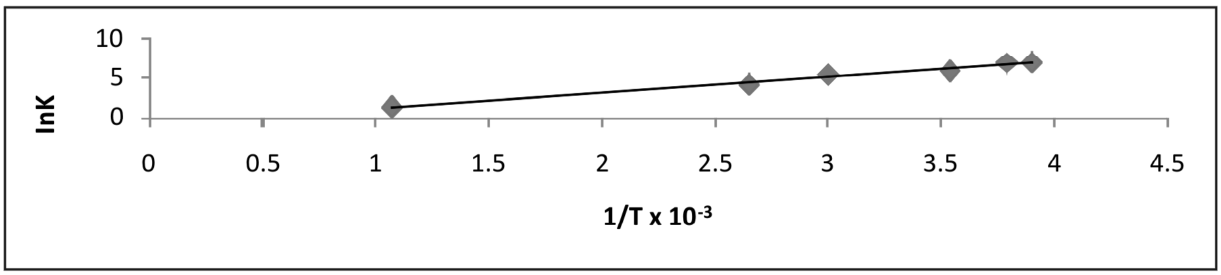

Figure 11 b: Biosorption Thermodynamics of Pb (II) by DRL

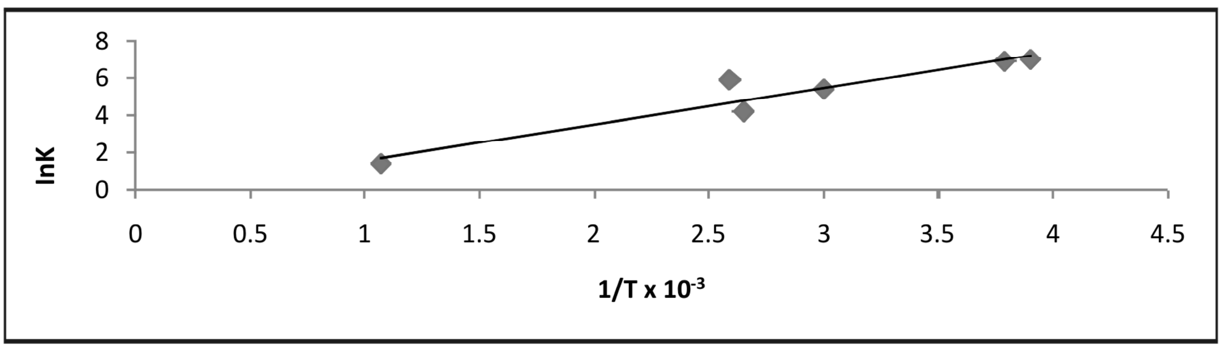

Figure 11 c: Biosorption Thermodynamics of Pb (II) by DRBL

DISUSSIONS

Effects of Initial Concentration of Pb (II) by Biosorbents

The effect of initial concentration of Pb (II) in the aqueous solution on the percentage removal of Pb (II) at equilibrium is shown in Fig1. At an optimum agitation time of 120 mins for DRB, DRL, and DRBL, the percentage removal of Pb (II) from the aqueous solution was decreased. It was observed that lesser percentage of Pb (II) is removed at higher concentration in the aqueous solution. Such behavior can be attributed to the increase in the amount of biosorbate to the unchanging number of available active sites on the biosorbent (since the amount of biosorbent is kept constant).

Effect of biosorbent size on percentage removal of Pb (II) by biosorbents

The results for biosorptive removal of Pb (II) with respect tobiosorbent sizes are shown in Fig.3. The percentage removal ofPb (II) is increased with decreasing size of the biosorbent. Fora biosorbent dosage of 1.5g, 100mg/L of Pb (II) concentrationand 50mL of aqueous solution, the metal % removal decreasesfrom 91.01% to 30.00% as the size increases from 0.061mm to1.330mm. This phenomenon isexpected since as the size of the biosorbent decreases, surfacearea of the particle increases, thereby the number of activesites on the biosorbent is better exposed to the biosorbate.Hence, the metal uptake would be increased.

Effect of biosorbent dosage on the biosorption of Pb (II)

Fig. 4 represents the variation in the percentage removal of Pb (II) with biosorbent dosage at optimum agitation time for different biosorbent sizes 0.061mm, 0.235mm, 0.330mm, 0.391mm, 0.533mm and 1.330mm. It is evident from the results that the fraction of the metal removed from the aqueous phase increases with an increase in the biosorbent amount. Such behaviour is obvious since the metal uptake capacity of the biosorbent increases as its dosage is increased. This is so because the number of active sites available for metal uptake would be more as the amount of the biosorbent increases.

Effects of pH on Pb (II) removal from aqueous solution on biosorbents

The pH of the solution has a significant impact on the removal of heavy metals, since it determines the surface charge of the biosorbent, the degree of ionization and speciation of the biosorbate. Fig.2 is a plot drawn between % removal of lead and pH of the aqueous solution. The percentage removal of lead is maximum at pH value 5 . Downward trend of the % biosorption is noted with an increase in pH above 5. Low pH depresses biosorption of lead, which is due to competition of lead with H+ ions for appropriate sites on the biosorbent surfaces. However, with increasing pH, this competition weakens and lead ions replace H+ bound to the biosorbent for forming part of the surface functional groups such as – OH, - COOH etc.

Effects of Temperature *on Pb (II) removal from aqueous solution on biosorbents*

Temperature plays a major role in the biosorption of heavy metals on activated carbon, regardless of the fact that the magnitude of the heat effect for the biosorption process is one of the most important criteria for the efficient removal of heavy metals from the wastewater. Temperature changes will affect a number of factors in heavy metal ion biosorption. These factors include: (i)) the stability of the metal ion species initially placed in solution; (ii) the stability of biosorbents-metal complex depending on the biosorption sites; (iii) the effect of temperature on the biosorbents configuration; (iv) the ionization of chemical moieties on the biosorbents.

The effect of temperature on biosorption of Pb (II) was studied by varying the temperature in the range 20-45ºC. As depicted by Figure 6, the change in temperature affected the biosorption of Pb (II). The temperature higher than 40°C caused a change, in the texture of the biomass and thus reduced its biosorption capacity. The biosorbents contained more than one type of sites for metal binding. The effect of temperature on each site is different and contributes to overall metal uptake.

Effects of Contact time on Pb (II) removal from aqueous solution by biosorbents

The optimum agitation time is determined by agitating 50ml of aqueous solution containing 100mg/L of Pb (II) with varying biosorbent dosages ranging from 50mg to 300mg and with different biosorbent sizes in 2 hr. The removal of Pb (II) increases with time and attains saturation in about 120 mins for the biosorbents. In figure 11, the rate of percent metal removal is higher in the beginning due to a larger surface area of the biosorbent being available for the biosorption of the metals. As time increases, more amount of Pb (II) gets adsorbed onto the surface of the biosorbent and surface area available decreases. Normally, the biosorbate forms a thin layer over the surface, which is only one molecule thick. When this monomolecular layer covers the surface, the capacity of the biosorbent is exhausted.

Kinetic Studies on the Biosorption of Pb (II) by biosorbents

In the kinetic study of the biosorption process, data from the kinetic studies were fitted into the pseudo-first-order and pseudo-second-order models. Kinetic biosorption of pollutants in wastewaters has been studied using predominantly pseudo-first-order (Langergren, 1898) and pseudo-second-order models (Ho and McKay, 2000). The linearized forms of pseudo-first-order and pseudo-second order models are given by equations 1 and 2.

$$\ln (qe\text{-}qt) = \ln qe - K_1 t \qquad 1$$

$$(t / qt) = 1 / (k_2\, qe_2) + (t / qe) \qquad 2$$

A plot of ln (qe-qt) against t was made and values of k_1 and qe were obtained from the slope and intercept, respectively. K_2 is the rate constant of pseudo-second order biosorption. A plot of (t/qt) against t gives (1/qe) as slope and (1/ k_2 qe_2) as intercept from which k_2 can be obtained. Both models are tested for suitability using their correlation coefficient, R^2 (Ho and McKay, 2000).

As can be seen from figure 9, the calculated *q*e determined from the plot of the pseudo-second-order model for Pb (II) at various concentrations differs from the experimental *q*e.

This implies that the model is not very good in explaining the kinetics of the biosorption of the metals. On the other hand, the pseudo-first-order model as shown in figure 9 fits the kinetics better, as their correlation coefficient is close to 1 (i.e., 0.99)for Pb (II) solutions at various concentrations. The calculated qe are very close to the experimental qe. All these imply that pseudo first order kinetics best explain the observed rate, suggesting that biosorption is the rate-limiting step; and that biosorption of the Pb (II) solutions involves one species, in this case, the biosorbent particles.

Biosorption isotherm of Pb (II) removal by biosorbents

Equilibrium batch biosorption experiments resulted in points of the biosorption isotherm, which was approximated by the *Langmuir* model.

The Langmuir isotherm is represented in the linear form as:

$$Ce / qe = 1 / b\, Q0 + Ce / Q0 \qquad 3$$

Q0 and *b is* Langmuir constants related to the capacity and energy of sorption respectively. The values of *Qo*and b and correlation coefficient obtained from the Langmuir model are shown in figure 9.

The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exist a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site behaving according to the Langmuir isotherm.

The sorption data of Pb (II) sorption onto the biosorbents was also fitted to Freundlich isotherm, in the following linear form:

$$\log qe = \log K_f + 1/n \log Ce \qquad 4$$

Where, *qe* is the amount of metal ion adsorbed per gram of adsorbent (mg/g). Ce is the equilibrium concentration of metal ion in solution (mg/L). K_f and *1/n* are Freundlich constants, indicating the biosorption capacity and biosorption intensity, respectively. The K_f and *1/n* values were calculated from intercept and slope of the plot respectively. Where n > 1 indicates the affinities decrease with increasing biosorption density. Evaluation of the coefficient of K and n can be accomplished using the linearized form of equation.

Biosorption Thermodynamics of Pb (II) by biosorbents

The thermodynamic parameters, namely the values of enthalpy (ΔH^o), entropy (ΔS^o) and Gibbs free energy (ΔG^o) of the sorption are useful in defining whether the sorption reaction is either endothermic or exothermic, alongside the spontaneity of the biosorption process.

Figure 11 a-c is the illustration of the graph of ln ko against 1/T. It was observed that the adsorption of Pb (II) rose with increasing values of temperature. Also, the value of ΔH^o was found to be positive.

The positive ΔH^o value confirmed that the biosorption process is endothermic for Pb (II), which is an indication of the existence of a strong interaction between biosorbents and Pb (II).

Besides, the Gibbs free energy change (ΔG^o) was negative at different temperatures indicating the feasibility and spontaneity of the biosorption reaction. The decrease in ΔG^o with the increase of temperature indicated that efficient biosorption was higher at higher temperature. At higher temperature, ions are readily dehydrated, and therefore their biosorptions become more favourable.

The positive values of entropy change, ΔS^o, reflected the affinity of the biosorbents towards Pb (II) ions in aqueous solutions and may suggest some structure changes in biosorbents. The results indicated the higher randomness tendency at the biosorbents and biosorbates interface during the Pb (II) biosorption onto the biosorbents. It was noticed that the equilibrium uptake of lead ions was affected by temperature and it increased with the increasing temperature up to 45°C.

CONCLUSIONS

In this study, batch biosorptionexperiments for the removal ofPb(II) from aqueous solutions have beencarried out using Delonixregia Leaves (DRL), Barks (DRB) and combined effect (DRBL).The biosorption characteristics have beenexamined at different Initial concentration, pH values, contacttime, biosorbent dosages, particle sizes and temperature.

The Langmuir biosorption isotherm modelswere better fitted to represent theexperimental data. Experimental data obtained from ratekinetics were better described by pseudo- firstorder model than pseudo-second ordermodel as evident from correlation coefficientvalues (r^2). The calculated thermodynamic parameters (ΔG, ΔH and ΔS 0) showedthat the biosorption of Pb (II) onto *the biosorbents* was feasible,spontaneous and exothermic under examinedconditions. This work illustrated analternative solution for the management ofthe unwanted biological materials where *Delonixregia*, one of the fast-growing plant, could be utilized as abiosorbent for the removal of heavy metalsfrom the low strength wastewater.

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