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Effective removal of Lead (II) from aqueous solutions using Sugarcane bagasse (*Saccharum officinarum L.*)

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Abstract

In the present study sugarcane bagasse (*Saccharum officinarum L.*) was studied as a cost effective biosorbent for Pb(II) ions was investigated using batch technique. FTIR analysis of the biosorbent revealed that hydroxyl, carbonyl and carboxyl groups which are involved in the uptake of lead (II) ions. SEM represents porous structure with large surface area. The effects of operational factors including solution pH, biosorbent dose, initial lead (II) ions concentration, contact time and temperature on the biosorption efficiency were studied. The experimental equilibrium biosorption data were fitted by four widely used two-parameters Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin isotherm equations. Simple kinetic models such as pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intraparticle diffusion rate mixing equation were employed to determine the adsorption mechanism. Thermodynamic studies were also carried out. The results showed that sugarcane bagasse (*Saccharum officinarum L.*) was a low-cost capable sorbent to seize Lead(II) from wastewater

Keywords: Adsorption kinetics, biosorption, Lead (II) ions, Thermodynamic study. Biosorption, lead (II), sugarcane bagasse (*Saccharum officinarum L.*), adsorption isotherm

Introduction

The release of heavy metals into aquatic systems has become a matter of concern over the last few decades. The pollutants of severe apprehension include lead, zinc, cadmium, chromium, mercury, uranium, selenium, arsenic etc. due to pollutants' carcinogenic and mutagenic nature. These poisonous materials may be resulting from mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the production of electrical equipment, paints, alloys, batteries, pesticides or preservatives. Lead is a toxic heavy metal of significant environmental and occupational concern. Lead is one of the heavy metal, considered as toxic pollutants which find its way to the water bodies through industries like metal production, phosphate fertilizers, electrical wiring, manufacture of batteries, pigments, electroplating, air conditioning tubing and plumbing. Severe lead poisoning can cause encephalopathy, with permanent damage, while moderate lead poisoning result in neurobehavioral and intelligent deficit (Chen et al., 2007). The presence of lead in drinking water, even in low concentrations may cause anaemia, hepatitis and nephritic syndrome (Zulkali et al.) The procedures used in general for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Juang and Shiau, 2000). These techniques apart from being economically expensive have disadvantages like incomplete metal removal and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content. In this situation, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous effluents (Volesky and Holan, 1995). The process of heavy metal removal by biological materials is known as biosorption. The focus of this work is to study the possible use of sugarcane bagasse (*Saccharum officinarum L.*) as an efficient biosorbent for removal of lead (II) ions from aqueous solutions by conducting batch experiments.

Materials and Methods

Chemical and reagent: All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of metal solutions. The desired pH of the metal ion solution was adjusted with the help of dilute hydrochloric acid and sodium hydroxide.

Preparation of lead (II) solution

Preparation of lead (II) ions solution The stock solution of 1000 ppm of lead (II) ions was prepared by dissolving 0.1 g of lead metal (AR grade) in 100 ml of double distilled water and further desired test solutions of lead (II) ions were prepared using appropriate subsequent dilutions of the stock solution

Preparation of biosorbent

The Sugarcane bagasse (*Saccharum officinarum* L.) was collected locally and washed with several times with distilled water to remove the surface adhered particles, dirt, other unwanted material and water soluble impurities and water was squeezed out. The washed biosorbent was then dried at 50°C overnight and grounded in a mechanical grinder to form a powder. The powder was sieved and a size fraction in the range of 100-200 µm will be used in all the experiments. This powder was soaked (20 g/l) in 0.1 M nitric acid for 1 hour. The mixture was filtered and the powder residue was washed with distilled water, several times to remove any acid contents. This filtered biomass was first dried at room temperature and then dried in an oven at 105°C for 1-2 hrs. For further use, the dried biomass was stored in air tight plastic bottle to protect it from moisture.

Instrumentation

The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model no. Eq-610) using a combined glass electrode. The concentration of Lead(II) in the solutions before and after equilibrium was determined by using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) technique. Biosorbent was characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM) and X-ray diffraction (XRD).

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis

The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biosorbent. The biomass samples were examined using FTIR spectrometer (model: FT/IR-4100typeA) within range of 400-4000 cm⁻¹. All analysis was performed using KBr as back ground material. In order to form pellets, 0.02 g of biomass was mixed with 0.3 g KBr and pressed by applying pressure.

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis

The Scanning Electron Microscope (SEM) was used to see the porosity of the biosorbent. The samples were covered with a thin layer of gold and an electron acceleration voltage of 10 KV was applied and then Scanning Electron Micrograph was recorded.

Experimental procedure

The static (batch) method was employed at temperature (300C) to examine the biosorption of Lead (II) by biosorbent. The method was used to determine the adsorption capacity, stability of biosorbent and optimum biosorption conditions. The parameters were studied by combining biosorbent with Lead(II) solution in 250 ml separate reagent bottles. The reagent bottles were placed on a shaker with a constant speed and left to equilibrate. The samples were collected at predefined time intervals, centrifuged, the content was separated from the adsorbent by filtration, using Whatmann filter paper and amount of Lead (II) in the supernatant/filtrate solutions was determined by ICPAES. The following equation was used to compute the percent removal (% Adsorption) of Lead(II) by the adsorbent,

$$\% \text{ Ad} = \frac{(C_i - C_e)}{C_i} \times 100$$

where C_i and C_e are the initial concentrations and equilibrium concentrations of the Lead(II) in mg/L. The equilibrium adsorptive quantity (q_e) was determined by the following equation,

$$q_e = \frac{(C_i - C_e)}{w} \times V$$

where q_e (mg metal per g dry biosorbent) is the amount of Lead(II) biosorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used. Desorption Study: To evaluate desorption efficiency, Lead(II) loaded biosorbent was dried after equilibrium sorption experiments. The dried biosorbent was contacted with 0.1 M nitric acid (HNO₃), 0.1 M hydrochloric acid (HCl) and 0.1M sulphuric acid (H₂SO₄) separately for 3 hours to allow Lead(II) to be release from biosorbent. The samples were separated from the biosorbents by filtration, using Whitman filter paper and amount of Lead(II) in the supernatant/filtrate solutions was determined by ICPAES to find out desorption efficiency. Desorption efficiency was calculated from the amount of metal adsorbed on the biosorbent and the final metal concentration in the biosorption medium.

Desorption

$$\text{efficiency}(\%) = \frac{\text{released metal ions in mg/L}}{\text{initially adsorbed metal ions in mg/L}} \times 100$$

Results and discussion

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis

The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biosorbent. The biosorbent samples were examined using FTIR spectrometer (Model: FT/IR4100typeA) within range of 400-4000 cm⁻¹. All analysis was performed using KBr as back ground material. a FTIR analysis was carried out and the spectra are shown in Fig.1. (a and b). As seen in the figure unloaded biosorbent displays a number of absorption peaks, reflecting the complex nature of biosorbent. The broad peak at 3401 cm⁻¹ is the indicator of -OH and -NH groups. The peaks located at 1752 cm⁻¹ are characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biosorbent. The peaks observed at 1120 cm⁻¹ are due to C-H and C-O bonds. The -OH, NH, carbonyl and carboxyl groups are important sorption sites. As compared to simple biosorbent, biosorbent loaded with

Lead(II) the broadening of -OH peak at 3401 cm^{-1} and carbonyl group peak at 1752 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of Lead(II).

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis

The surface morphology of Sugarcane bagasse (*Saccharum officinarum* L.) was examined using Scanning Electron Microscopy (SEM), before and after biosorption and the corresponding SEM micrographs were obtained at an accelerating voltage at 10 kv at 10000 x magnification and are presented in Figure (a and b). At such magnification, the Sugarcane bagasse (*Saccharum officinarum* L.) particles showed rough areas of surface within which micropores were clearly identified.

Effect of pH

For Lead(II) stability pH is one of the most important parameter which controls the surface properties of biosorbents, functional groups and ionic state of metal's species. The optimization of pH was done by varying the pH in the range of 1-8 for biosorption of Lead(II) and pH trend observed in this case is shown in Figure 4. It was found that at pH 5 the biosorption process was maximum with 94.87% and after increasing pH, biosorption was decreases. As the pH of the solution increases, charges on the surface of biosorbent becomes negative, this leads to generation of repulsive forces between Lead(II) & biosorbent and inhibits adsorption and resultantly percent Lead(II) uptake may slightly decrease.

Effect of biosorbent dose concentration

Biosorbent dosage is an important parameter studied while conducting batch mode studies. The sorption capacity of Sugarcane bagasse (*Saccharum officinarum* L.) onto Lead(II) by varying its dosage from 1 g/L to 15 g/L is shown in Figure 5. From the results it was found that biosorption of Lead(II) increases with increase in biosorbent dosage and is highly dependent on biosorbent concentration. Increase in biosorption by increase in biosorbent dose is because of increase of ion exchange site ability, surface areas and the number of available biosorption sites (Naiya et al., 2009). The point of saturation for Sugarcane bagasse (*Saccharum officinarum* L.) was found at 5 g/L of biosorbent dose with 94.87% of removal efficiency. The decrease in efficiency at higher biosorbent concentration could be explained as a consequence of partial aggregation of adsorbent which results in a decrease in effective surface area for metal uptake (Karthikeyan et. al. 2007). Hence, biosorbent dose 5 g/L was chosen for all further studies.

Effect of initial Lead (II) concentration

The effect of initial Lead (II) concentration from 5 mg/L-250 mg/L on the removal of Lead(II) from aqueous solutions at biosorbent dose concentration 5 g/L and at optimum pH 5 at 30°C was studied. On increasing the initial Lead(II) concentration, the total Lead(II) ions uptake decreased slightly when Lead(II) concentration increases from 5 mg/L - 250 mg/L.

Effect of contact time

In order to optimize the contact time for the maximum

uptake of Lead(II) onto biosorbent, contact time was varied between 10 minutes-240 minutes on the removal of Lead(II) from aqueous solutions in the concentration of Lead(II) 10 mg/L and biosorbent dose 5 g/L at optimum pH 5.0 at 30°C. The results obtained from the biosorption capacity of Lead(II) onto Sugarcane bagasse (*Saccharum officinarum* L.) showed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for biosorption of Lead(II) ions onto Sugarcane bagasse (*Saccharum officinarum* L.) was 180 minutes with 78.47 % removal. The rapid uptake of Lead(II) is due to the availability of ample active sites for sorption. A further increase in the contact time has a negligible effect on the biosorption capacity of Lead(II) biosorption. So a contact time of 180 minute was fixed for further experiments.

Effect of temperature

The effect of temperature on removal of Lead(II) from aqueous solutions using Sugarcane bagasse (*Saccharum officinarum* L.) was studied at different temperatures from 20°C-40°C. The influence of temperature is depicted in Figure 8. The percentage removal of Lead(II) increased from 69.17% to 77.50% in the range of temperature 20°C-40°C respectively. It can be clearly seen from the figure that, increase in temperature the percentage removal increased slowly. The increase in biosorption capacity with the increase in temperature indicates that the biosorption process is endothermic in nature.

Effect of agitation rate

The effect of agitation rate on removal of Lead(II) from aqueous solutions at biosorbent dose 10 mg/ml and at optimum pH 5 at 30°C was studied at different agitation rate such as 40 rpm, 80 rpm, 120 rpm, 160 rpm and 200rpm. The efficiency was highest at 120rpm with percentage removal 78.47 %. So, 120 rpm was chosen for all further biosorption studies.

Desorption study

In application of real wastewater, desorption of heavy metal ions in the biosorbent is important process. Sugarcane bagasse (*Saccharum officinarum* L.) was the most effective waste biosorbent with desorption efficiency 41.82% (0.1 M hydrochloric acid), 44.24% (0.1 M nitric acid) and 46.70% (0.1 M sulphuric acid). Sulphuric acid has shown highest desorbed capacity of Lead(II) followed by hydrochloric acid and nitric acid from Sugarcane bagasse (*Saccharum officinarum* L.)

Adsorption isotherm models

The analysis of the adsorption isotherms data by fitting them into different adsorption isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter adsorption isotherm models: Langmuir, Freundlich, DubininKaganer-Redushkevich (DKR) and Temkin. Adsorption isotherms results for biosorption of Lead(II) by Sugarcane bagasse (*Saccharum officinarum* L.) is shown below;

Langmuir adsorption isotherm (Langmuir, 1918)

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by;

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

where q_m is the maximum biosorption capacity of adsorbent (mg g⁻¹). b is the Langmuir biosorption constant (L mg⁻¹) related to the affinity between the biosorbent and biosorbate. Linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants and is represented as:

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m}$$

The linear plots of $1/q$ vs $1/c_e$ is shown in Figure 10 (a). The two constants b and q_m are calculated from the slope ($1/q_m \cdot b$) and intercept ($1/q_m$) of the line. The values of q_m , b and regression coefficient (R^2) are listed in Table 1.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the biosorbate and biosorbent which is calculated using following equation;

$$R_L = \frac{1}{1 + b C_i} \quad (4.1)$$

where b is the Langmuir constant and C_i is the maximum initial concentration of Lead(II). The value of separation parameters R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation: to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to 0.0714-0.7938 for concentration of 5 mg/L250 mg/L of Lead(II). They are in the range of 0-1 which indicates favorable biosorption (Malkoc and Nuhoglu 2005).

Frenudlich adsorption isotherm (Frenudlich, 1939)

Freundlich equation is represented by;

$$q = K C_e^{1/n}$$

where K and n are empirical constants incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively. Linearized Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

Equilibrium data for the adsorption is plotted as $\log q$ vs $\log C_e$, as shown in Figure 10 (b). The two constants n and K are calculated from the slope ($1/n$) and intercept ($\log K$) of the line, respectively. The values of K , $1/n$ and regression coefficient (R^2) are listed in Table 1.

The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is chemical process; if $n > 1$, then adsorption is a physical process. A relatively slight slope and a small value of $1/n$ indicate that, the biosorption is good over entire range of concentration. The n value in Freundlich equation was found to be 1.1870. Since $n > 1$, this indicates that biosorption is a physical process biosorption of Lead(II)

ions onto Sugarcane bagasse (*Saccharum officinarum L.*). The higher value of K (7.4404) indicates the higher adsorption capacity for the Polyvinyl alcohol- alginate- Glutaraldehyde immobilized Sugarcane bagasse (*Saccharum officinarum L.*)

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm (Dubinin and Radushkevich, 1947): Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as;

$$\ln q_e = \ln q_m - \beta \epsilon^2$$

where q_m is the maximum biosorption capacity, β is the activity coefficient related to mean biosorption energy and ϵ is the polanyi potential, which is calculated from the following relation;

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (10)$$

Equilibrium data for the adsorption is plotted as $\ln q_e$ vs ϵ^2 , as shown in Figure 10 (c). The two constants β and q_m are calculated from the slope (β) and intercept ($\ln q_m$) of the line, respectively. The values of adsorption energy E was obtained by the following relationship,

$$E = \frac{1}{\sqrt{-2\beta}} \quad (11)$$

The E value was found to be 0.5773 KJ mol⁻¹. The mean free energy gives information about biosorption mechanism whether it is physical or chemical biosorption. If E value lies between 8 KJ mol⁻¹ and 16KJ mol⁻¹, the biosorption process take place chemically and $E > 8$ KJ mol⁻¹, the biosorption process of the physical in nature (Olivieri and Brittenham, 1997). In the present work, E value (1.5812 KJ mol⁻¹) which is less than 8 KJ mol⁻¹, the biosorption of Lead(II) ions onto Sugarcane bagasse (*Saccharum officinarum L.*) is of physical in nature (Sawalha et al., 2006).

Temkin adsorption isotherm (Temkin and Pyzhev, 1940): Linearized Temkin adsorption isotherm is given by the equation;

$$q_e = \frac{RT}{bT} \ln(A_T C_e) \quad (12)$$

where bT is the Temkin constant related to heat of biosorption (J/mol) and A_T is the Temkin isotherm constant (L/g). Equilibrium data for the adsorption is plotted as q_e vs $\ln C_e$, as shown in Figure 10(d). The two constants bT and A_T are calculated from the slope (RT/bT) and intercept ($RT/bT \cdot \ln A_T$) of the line. The values of A_T, bT and regression coefficient (R^2). The various constants and regression coefficient R^2 obtained from adsorption isotherms (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) are summarized in Table 1.

Adsorption kinetics: As aforementioned, a lumped analysis of adsorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a)

the pseudo-first-order equation (Lagergren 1898) (b) the pseudo-second-order equation (McKay et al., 1999) (c) Elovich equation (Chien and Clayton 1980) (d) Weber & Morris intra-particle diffusion equation (Weber and Morris, 1963) are presented below;

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$

$$q_t = k_i t^{0.5} + c$$

where q_e (mg g⁻¹) is the solid phase concentration at equilibrium, q_t (mg g⁻¹) is the average solid phase concentration at time t (min), k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of α (mg g⁻¹ min⁻¹) and β (g mg⁻¹) are Elovich coefficients representing initial biosorption rate and desorption constants, respectively. k_i (mg g⁻¹ min^{-1/2}) is the intraparticle diffusion rate constant, c is intercept.

If the adsorption follows the pseudo-first-order model, a plot of $\ln(q_e - q_t)$ against time t should be a straight line. Similarly, t/q_t should change linearly with time t if the adsorption process obeys the pseudo-second order model. If the adsorption process obeys Elovich model, a plot of q_t against $\ln t$ should be a straight line. Also a plot of q_t against $t^{0.5}$ changes linearly the adsorption process obeys the Weber and Morris intraparticle diffusion model. Kinetic plots depicted in Figure 8 (a) (b) (c) and (d) (Septum et al., 2007).

Biosorption of Lead (II) onto biosorbent was monitored at different specific time interval. The Lead (II) uptake was calculated from the data obtained. From the Lead(II) uptake was plotted against time to determine a suitable kinetic model, the adsorption data was fitted into pseudo-first-order model, pseudo-second-order model, Elovich models and the Weber & Morris intra-particle diffusion model. The pseudo-first-order model was plotted for $\ln(q_e - q_t)$ against t (Figure 11 (a)). The values of k_1 and q_e values were calculated from the slope (k_1) and intercept ($\ln q_e$) of the plot and shown in Table 2. Pseudo-first-order model showed the correlation value ($R^2 = 0.1870$) being lower than the correlation coefficient for the pseudo-second-order model. Kinetic biosorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the ions adsorbed onto it (Septum et al., 2007).

The pseudo-second-order model was plotted for t/q_t against t (Figure 11 (b)). The values of q_e and k_2 are calculated from the slope ($1/q_e$) and intercept ($1/k_2 q_e^2$) of the plot and values are shown in Table 2. Pseudo-second-order kinetic model showed the strongest correlation ($R^2 = 0.995$). This suggests that Lead (II) biosorption occurs in a monolayer fashion and which relies on the assumption that chemisorption or chemical adsorption is the rate-limiting step. Lead (II) reacts chemically with the specific binding sites on the surface of biosorbent.

The Elovich model was plotted for q_t against $\ln t$ (Figure 11 (c)). The values of β and α are calculated from the slope ($1/\beta$) and the intercept ($\ln(\alpha\beta)/\beta$) of the plot and values are shown in Table 2. The Elovich model has been used with the assumption that the actual adsorption surface is energetically heterogeneous (Thomas and Thomas, 1997).

The Weber & Morris intra-particle diffusion model was plotted for q_t against $t^{0.5}$ (Figure 11 (d)). The value of k_i and c are calculated from the slope (k_i) and intercept (c) of the plot and values are shown in Table 2. The Weber and Morris intra-particle diffusion model showed a ($R^2 = 0.9395$) being lower than the correlation coefficient for the pseudo-second-order model. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intra-particle pore diffusion is not only rate-limiting step (Weber and Morris, 1963).

The plot of intra-particle diffusion model showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of biosorbent or the boundary layer diffusion of solute molecules. The second portion describes ion stage, where intra-particle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of biosorption (Panday et al., 1986).

Determination of thermodynamic

The effect of temperature on removal of Lead(II) from aqueous solutions in the concentration of Lead(II) 10 mg/L and biosorbent dose concentration 5 mg/ml with optimum pH 5.0 was studied. Experiments were carried out at different temperatures from 20°C-40°C. The samples were allowed to attain equilibrium. Sorption slightly increases from. The equilibrium constant (Catena and Bright, 1989) at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations;

$$K_c = \frac{C_{Ae}}{C_e}$$

$$\Delta G^0 = -RT \ln K_c$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the amount of Lead(II) biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). ΔG^0 , ΔH^0 and ΔS^0 are changes in standard Gibbs free energy (kJ/mol), standard enthalpy (kJ/mol) and standard entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K).

The values of ΔH^0 and ΔS^0 were determined from the slope and the intercept from the plot of $\ln K_c$ versus $1/T$ (Figure 12). The values of equilibrium constant (K_c), standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) calculated in this work were presented in Table 3. The equilibrium constant (K_c) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intra-particle diffusion. The value of standard Gibbs free energy change (ΔG^0) is small and negative and indicates the spontaneous nature of the biosorption. The values of ΔG^0 were found to decrease as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The value of ΔH^0 was positive, indicating the endothermic

nature of the biosorption of Lead(II) Sugarcane bagasse (*Saccharum officinarum* L.). The positive values of ΔS^0 shows an affinity of biosorbent and the increasing

randomness at the solid solution interface during the biosorption process.

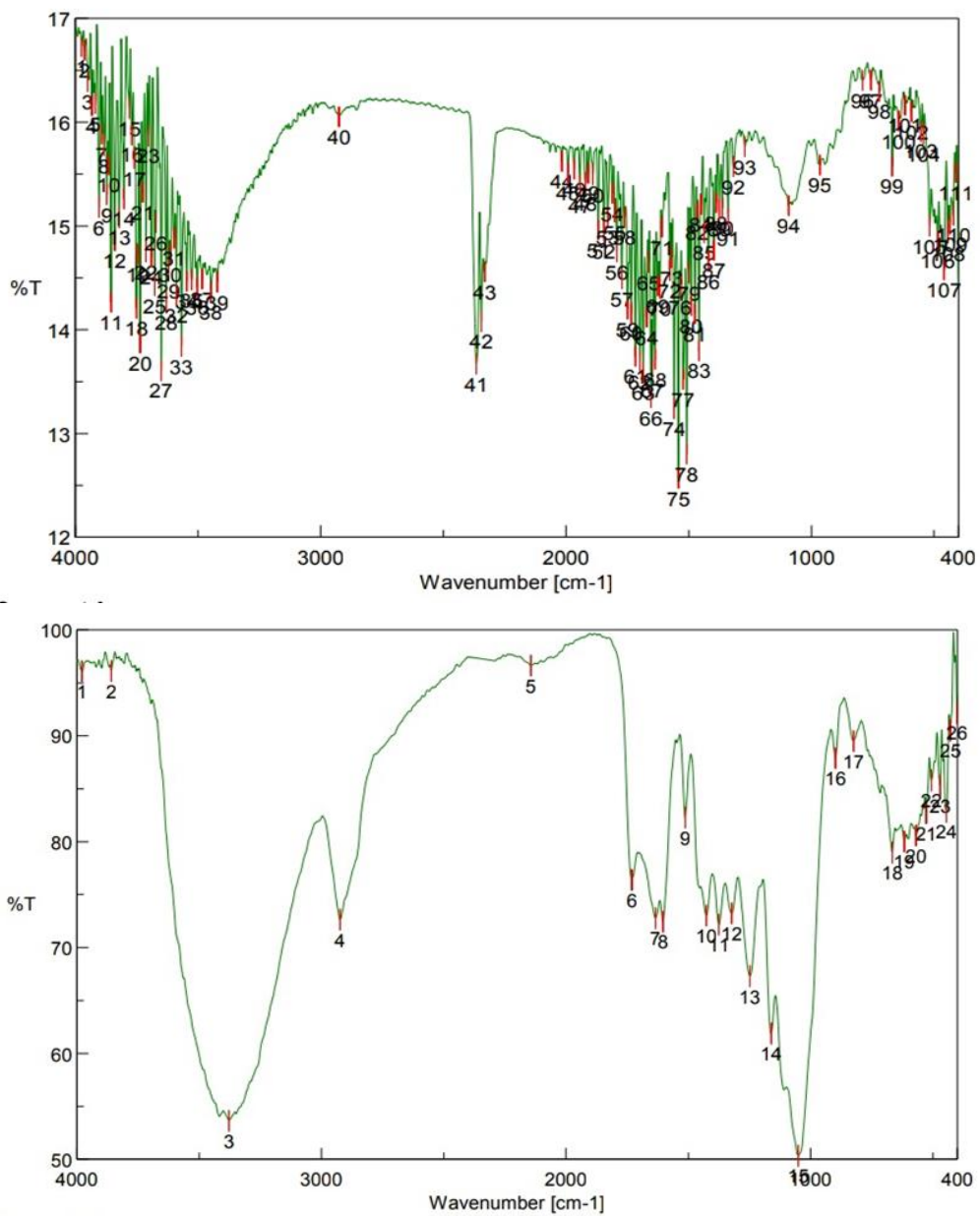


Fig.1: FTIR spectra of Sugarcane bagasse (*Saccharum officinarum* L.) (a) Unloaded with Lead (II) (b) Loaded with Lead (II)

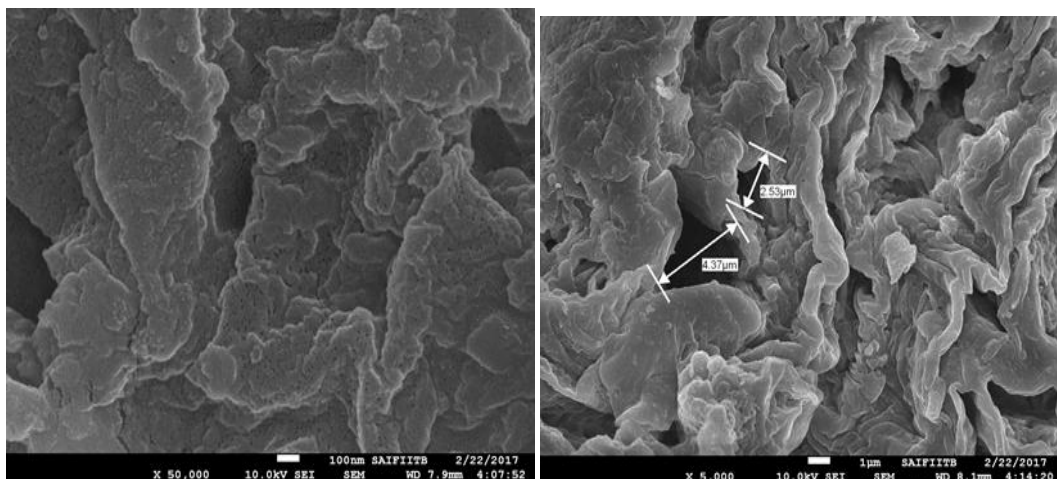


Fig.2: Scanning Electron Microscope (SEM) analysis of Sugarcane bagasse (*Saccharum officinarum* L.) (a) Unloaded with Lead (II) (b) Loaded with Lead (II)

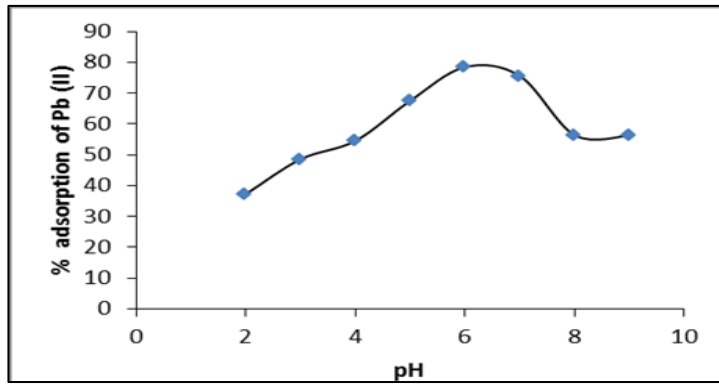


Fig.4: Effect of pH on Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30⁰C)

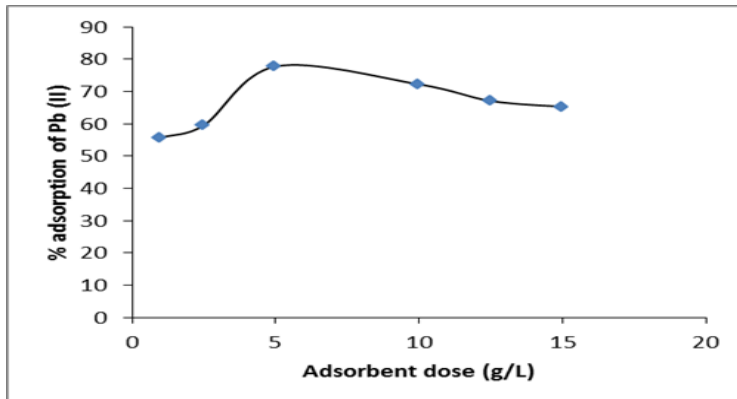


Fig.5: Effect of biosorbent dose concentration on Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30⁰C)

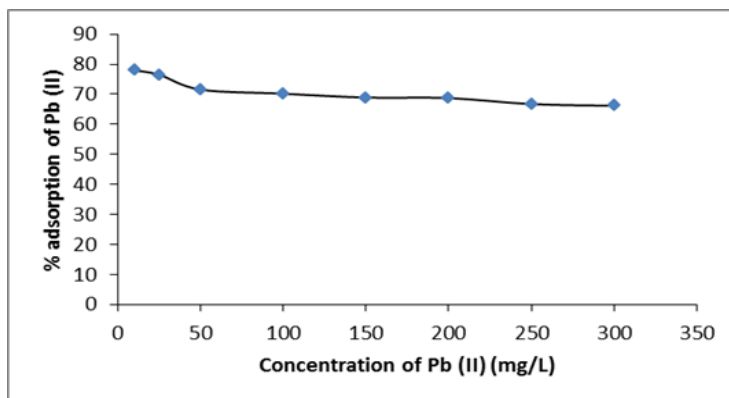


Fig.6: Effect of lead (II) concentration on Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30⁰C)

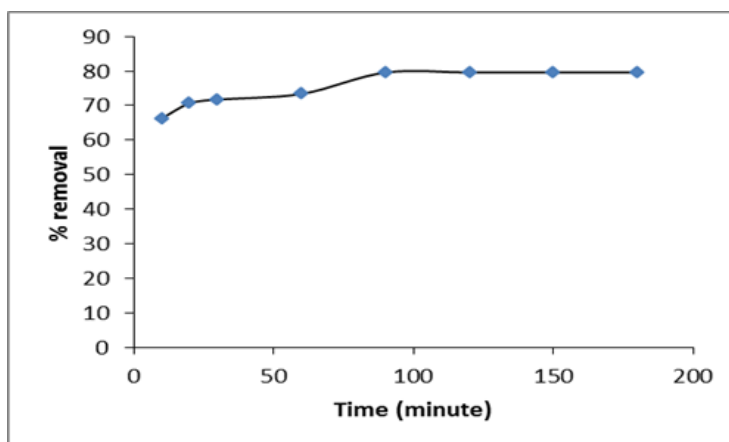


Fig.7: Effect of contact time on Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30⁰C)

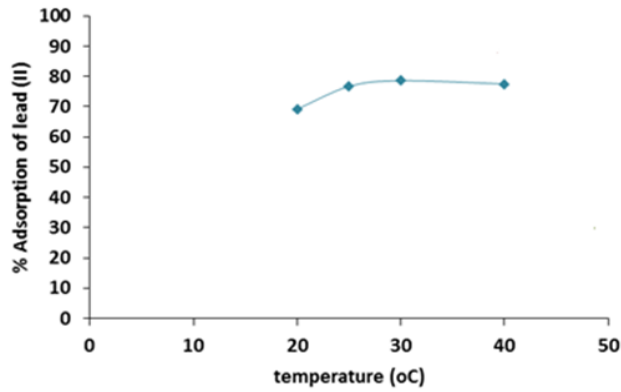


Fig.8: Effect of temperature on Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30⁰C)

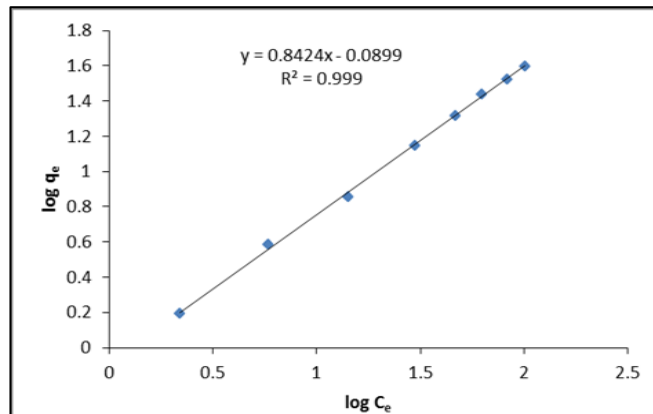


Fig.9: Effect of agitation rate on on Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30⁰C)

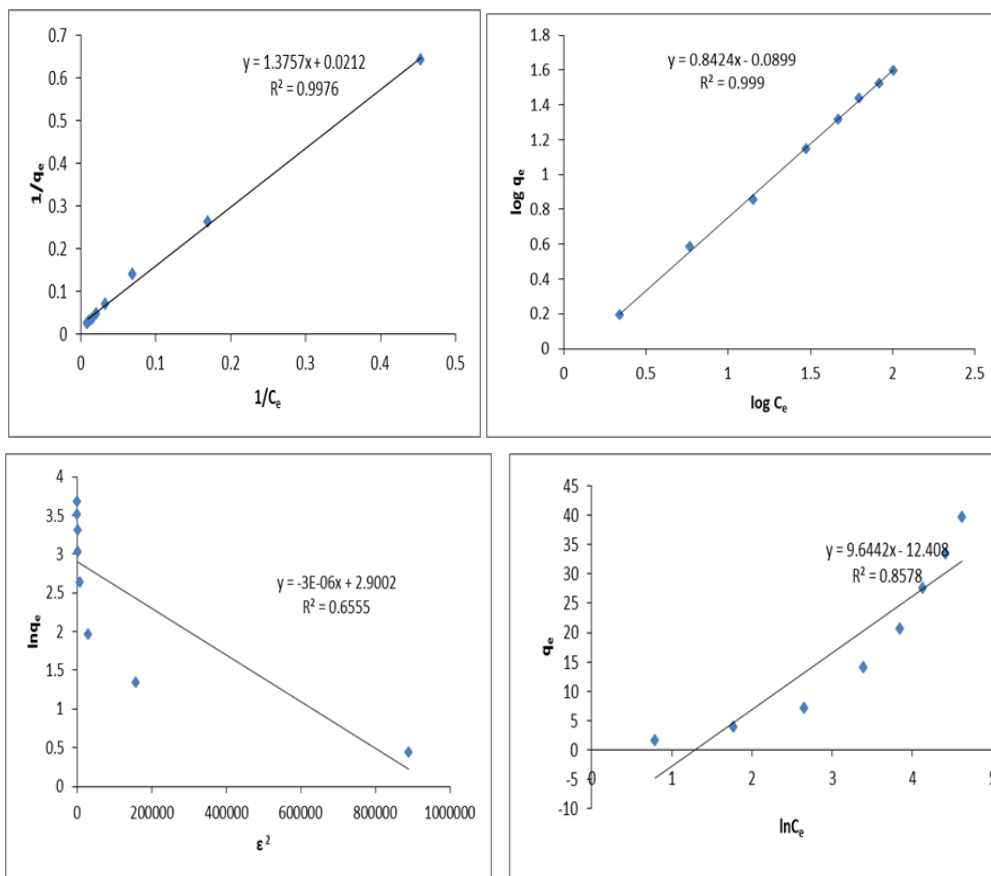


Fig.10: Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30⁰C)

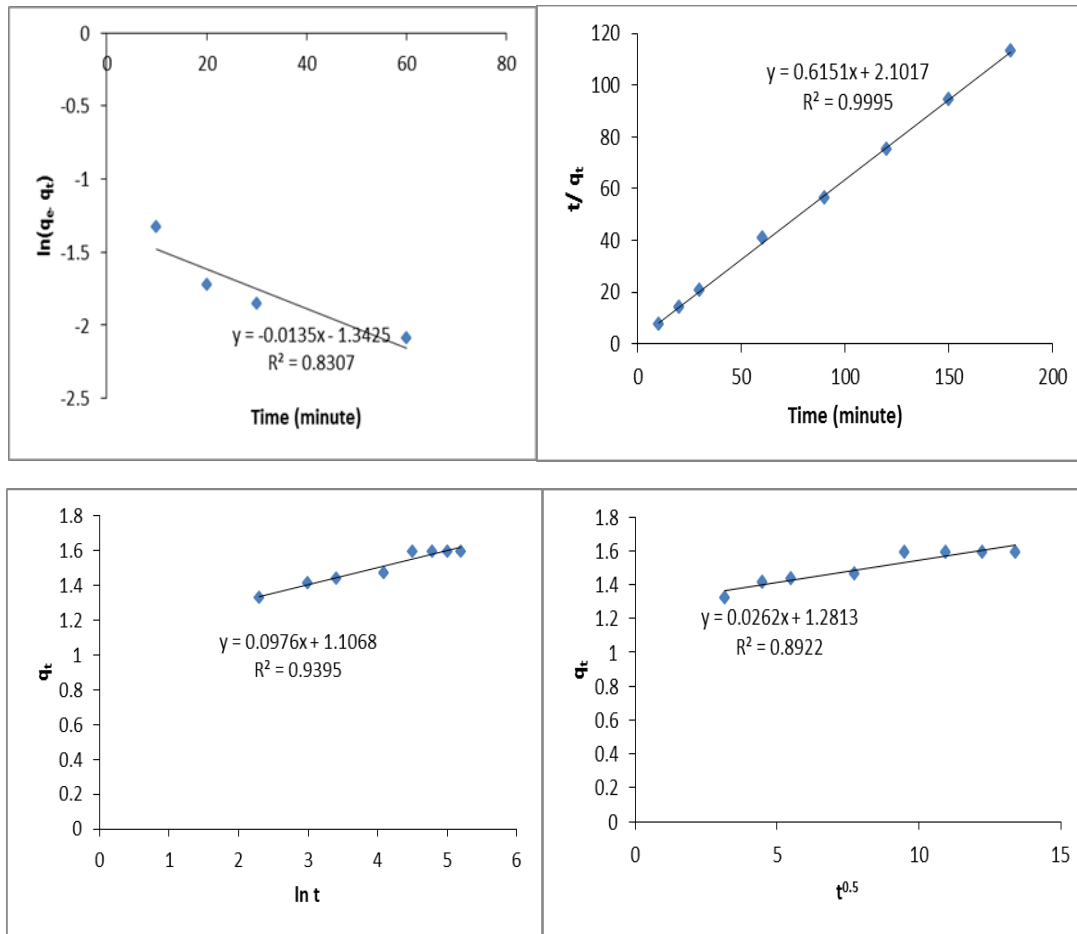


Fig.11: Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffusion equation, for biosorption of Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30°C)

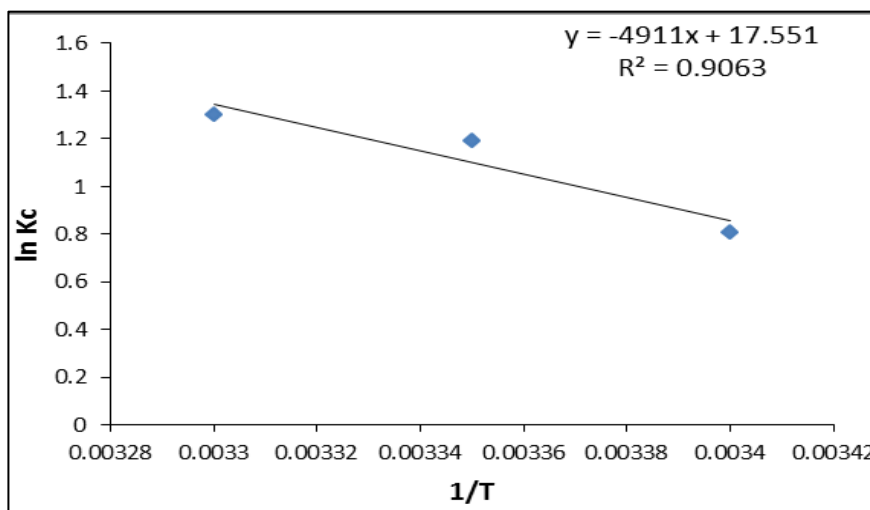


Fig.12: Plot of $\ln Kc$ against $1/T$ for determination of thermodynamic parameters for Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30°C)

Table 1: Adsorption isotherm constants for Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.)

Langmuir parameters			Freundlich parameters			DKR parameters				Temkin parameters		
q_m	B	R^2	K	$1/n$	R^2	B	q_m	E	R^2	A_T	b_T	R^2
47.1698	0.0154	0.9976	0.8130	0.8424	0.9990	-3×10^{-6}	18.1777	0.5773	0.6555	0.2762	261.2079	0.8578

Table 2: Adsorption kinetic data for for Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.)

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intraparticle diffusion model		
q_e	k_1	R^2	q_e	k_2	R^2	a	β	R^2	Ki	C	R^2
0.2611	0.0135	0.8307	1.6257	0.1800	1.9995	8.211×10^3	10.2459	0.9395	0.0262	1.2813	0.8922

Table 3: Thermodynamic parameters of Lead (II) biosorption by Sugarcane bagasse (*Saccharum officinarum* L.)

Sr. No.	Time (min)	K	Kc	$-\Delta G^0$	ΔH^0	ΔS^0
1	20 ⁰ C	293	2.2435	1.968	34.910	145.919
2	25 ⁰ C	298	3.2881	2.949		
3	30 ⁰ C	303	3.6663	3.272		
4	40 ⁰ C	313	3.4444	3.218		

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