EUROPEAN JOURNAL OF BIOMEDICAL AND PHARMACEUTICAL SCIENCES
http://www.ejbps.com

ISSN 2349-8870
Volume: 5
Issue: 02
659-670
Year: 2018

ISOTHERMAL KINETICS AND THERMODYNAMIC STUDIES ON ADSORPTION OF Pb(II) IONS USING ACTIVATED CARBON

T. Chandrasekaran[1], A. Arun Kumar[2] and K. Riaz Ahamed*

[1]Assistant Professor, Dhanalakshmi Srinivasan Institute of Research and Technology, Siruvachur. Perambalur, Tamilnadu, India.
[2]Assistant Professor, Dhanalakshmi Srinivasan Engineering College, Perambalur. Tamilnadu, India.
*Assistant Professor, PG and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli-620020, Tamilnadu, India.

***Corresponding Author: Dr. K. Riaz Ahamed**
Assistant Professor, PG and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli-620020, Tamilnadu, India.

Article Received on 05/12/2017 **Article Revised on 25/12/2017** **Article Accepted on 14/01/2018**

ABSTRACT
The possibility of using *Glycosmis mauritiana* carbon for removal of lead (II) ions from aqueous solution as a low cost adsorbent was explored. Distribution of lead (II) ions between the solid and liquid phases in batch studies was described by isotherms like Langmuir adsorption and Freundlich models. The adsorption process shows better represented by the Langmuir isotherm model. The maximum adsorption capacity of lead (II) ions was measured through the Langmuir model. The data of Pseudo-second order rate equation was better suited for the adsorption process. A dynamic mode study also conducted to analyze the ability of *Glycosmis mauritiana* to remove lead (II) ions from aqueous solution. Present study revealed that carbon prepared from *Glycosmis mauritiana* can be used for the removal of lead (II) ions from the aqueous solution and low cost water treatment techniques can be developed using this adsorbent.

KEYWORDS: adsorption; *Glycosmis mauritiana*; Freundlich isotherm; Langmuir; pseudo-second order.

1. INTRODUCTION
Worldwide 780 million people still lack access to improve drinking water sources. It is urgent to implement basic water treatment in the affected areas (mainly in developing countries) where water and wastewater infrastructure are often non-existent. Due to the climatic change, water has a challenge in both quality and quantity. Heavy metals from wastewater of many industries, such as batteries, tanneries, electrical, electroplating, fertilizers, pesticides, mining, refining ores, etc are some of the industrial sources releases heavy metals to our environment.[1,2] The water bodies get polluted in large scale by human activities like industrial discharge, agricultural wastes, urbanization, domestics waste, mining etc. and disturbing the normal use of water for irrigation, agriculture, public supply and aquatic life because its normal function and properties are affected by the pollution. The changes in colour, odour and taste are undesirable in water shows the presence of the impurities like dissolved minerals, gasses and organic constituents. These wastes are invariably discharging directly and cause pollution to the environment. Even at low concentration, heavy metals show the toxic effect to aquatic animals, flora and human beings, even at relatively low concentrations. The water pollution may constitute organic and inorganic pollutants that include oxygen-demanding wastes, disease–causing agents, plant nutrients, sewage, synthetic organic components and oil.

Heavy metal toxicity may result in damaged or reduced mental and central nervous function, lower energy levels, damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's ailment, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals (or their compounds) may cause cancer. The accumulation of lead, nickel, copper and zinc in the liver tissue of sheep grazed on sewage sludge-treated pastures. Lead concentrations in the liver of lambs were higher than copper and zinc. They determined that the mean concentrations of cadmium, nickel and lead were two to four-folds higher in liver of ewe than lamb, at the same time copper concentrations were five-fold lower. Therefore, this is our accountability to preserve our environment neat and clean by means of utilizing different preventive measures.[3]

Various methods are suggested for such a reduction. These methods includes chemical and electrochemical oxidation[4,5], microbiology treatment[6,7], ion-exchange and membrane separation[8], coagulation[9], foam separation[10] and various adsorption techniques.[11-13] The adsorptive methods appear to provide the required efficiency for water purification and have advantages when it comes to practical implementation due to for example a comparably low cost. Activated carbons have a large capacity to adsorb surfactants because of their large specific surface areas and hydrophobic nature. Hence, there is a growing demand to find low-cost and efficient, locally available adsorbents for the sorption of copper such as the sugar beet pulp[14], peanut hull[15], Cinnamomum camphora leaves powder[16], Litter of poplar forests[17], Lentil shell, Wheat shell, Rice shell[18], Herbaceous peat[19], T. grandis L.f. leaves powder[20], Base treated rubber leaves[21], Pine cone powder[22], Spent grain[23], Tree fern[24], Groundnut shells[25], Pretreated Aspergillus niger[26], Cedar sawdust, crushed brick[27], saw dust[28], etc.

In present work, carbon prepared from stem of the plant *Glycosmis mauritiana* using sulphuric acid as a activating agent. Hence, aim of the present study is to utilize *Glycosmis mauritiana* as a cheap renewable material for preparation of activated carbon by chemical treatment with sulphuric acid, followed by carbonization. The adsorption experiments in batch mode were performed to evaluate the potentiality of the prepared activated carbon for the adsorption of Pb(II) ions from aqueous solution. The effects of initial concentration was investigated. The study also includes modeling of adsorption data as well as the equilibrium experimental data were assessed using isotherm and kinetic sorption models to elucidate adsorption mechanism.

2. MATERIALS AND METHODS

2.1. Adsorbent

The raw *Glycosmis mauritiana* was collected and treated with sulphuric acid. The treated *Glycosmis mauritiana* was used as an adsorbent. This natural waste was thoroughly rinsed with water to remove dust and soluble material and was allowed to dry at room temperature. The above dried natural waste was ground to a fine powder. The resulting material was sieved in the size range of 0-53µ mesh particle size, named as GMC-2.

2.2. Adsorbate

All the chemicals used were of analytical reagent (AR) grade. Stock solution of 100 mg/L of lead (II) ion was prepared from $Pb(NO_3)_2$ in double distilled water. Desired test solutions lead (II) ions were prepared using appropriate subsequent dilutions of stock solution. The range in concentrations of lead (II) ions prepared from standard solution varied between 100 to 500 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

2.3. Adsorption experiments

Batch adsorption experiments were carried out by shaking the flasks at fixed period of time using a rotary shaker. Following a systematic process, the removal of lead (II) ions from aqueous solutions by the use of GMC-2 in a batch system was studied in the present research work. The data obtained in batch studies were used to calculate the equilibrium metal adsorptive quantity by using the following mass balance relationship.

% Adsorption = $(C_0 * C_e) / C_0 \times 100$……..(1)

Where, C_0 is the initial concentration of adsorbate (mg/L), C_e is adsorbate concentration (mg/L).

2.4. Isothermal studies

Equilibrium adsorption isotherms (capacity studies) are of fundamental importance in the design of adsorption systems since they indicate how metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of metal concentration. When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the surface of the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a clearly defined distribution of metal ions between the solid and liquid phases. Heavy metal ion concentrations ranged from 100 to 500 mg L^{-1} with a different adsorbent mass (100 – 500 mg) and keeping all other conditions constant. The obtained experimental data were fitted with the Freundlich and Langmuir models in order to calculate the adsorption capacity of the selected adsorbents.

2.4.1. Langmuir isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir adsorption model assumes that uptake of adsorbate occurs on a homogeneous surface by monolayer adsorption without any interaction between the adsorbed ion. It also considers that there is no transmigration of the adsorbate in the plane of the surface of the adsorbent. The Langmuir adsorption isotherm has been successfully rapplied to many real sorption processes.[6]

The Langmuir equation is given by equation $q_e = \frac{bq_m C_e}{1+q_m C_e}$ ……...(2)

The linear form of Langmuir isotherm: $C_e/q_e = 1/q_m b + C_e/q_m$…(3)

Where, qe is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of metal ions in solution (mg/L), q_m (mg/g) represents the maximal adsorption capacity under the experimental conditions and b is a constant related to the energy of adsorption. The essential characteristics of the Langmuir isotherm can be described by a separation factor[8] R_L which is defined as.

$R_L = 1/(1+bC_0)$……..(4)

Where, b is the Langmuir constant and C_0 is the initial concentration of the metal ion. The values of R_L indicate the shape of the isotherm as follows.[9]

R_L value Types of isotherm
R_L>1 Unfavorable
R_L = 1 Linear
0 < R_L < 1 Favorable
R_L= 0 Irreversible

2.4.2. Freundlich isotherm

The Freundlich isotherm is an empirical model that considers adsorption energies on the uneven adsorbing surface and is applicable to the adsorption of single solute within a fixed range of concentration. The linear form of Freundlich adsorption model is given by following equation.[10] The value of n is not only a measure of the deviation from linearity but informs about the heterogeneity degree of the adsorption sites. The values of n>1 for the adsorption of Pb (II) ions on GMC-2 shows favorable adsorption.

Freundlich isotherm: $\ln q_e = \ln K + (1/n) \ln C_e$ …….(5)

Where, q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of metal ions in solution (mg/L), q_m (mg/g) represents the maximal adsorption capacity under the experimental conditions and "b" is a constant related to the energy of adsorption. The linear plots of $\ln C_e$ versus $\ln q_e$ clearly reveal that adsorption of metal ion on GMC-2 adsorbent follow the Freundlich model. The values of K_F and n are derived from the intercepts and slope respectively are shown.

The R^2 values for metal ion adsorption on adsorbent are close to unity for both adsorption models. It indicates that the adsorption of metal ion follows the Langmuir and Freundlich adsorption isotherms. The value of n greater than unity for metal ion corresponds to multilayer adsorption of metal ion onto the adsorbent.

2.5. Kinetic Study

Kinetics of adsorption is a characteristic responsible for the efficiency of adsorption. Although a range of models is available to study the kinetics of adsorption, First order, Pseudo-second order, and Intra-particle diffusion models were used to study the kinetics of metal adsorption onto GMC-2. Adsorption kinetics experiments were carried out by varying the initial concentration of metal ion (100 - 500 mg/L) with the optimum adsorbent dose 0.2 g. The samples were shaken and then withdrawn at different time intervals, filtered and analyzed.

2.5.1. Pseudo-first-order kinetics

The adsorption kinetics may be described by Pseudo-first order equation. The pseudo-first order equation of Lagergen,

$dq/dt = k_1(q_e - q_t)$……..(6)

By integration of above equation in the conditions (t = 0, q_t = 0 and t = t, q = q_t) gives;

$\log(q_e - q_t) = \log q_e - k_1 t / 2.303$……(7)

Where, q_e and q_t are the amounts of metal ion adsorbed per unit mass of adsorbent at equilibrium and at time t (min), and k_1 (min^{-1}) is the first order rate constant. Values of k_1 can be obtained from linear plots of log (q_e - q_t) versus t and are given for metal adsorption on GMC-2.

2.5.2. Pseudo-second order kinetics

The adsorption kinetics may be described by pseudo-second-order kinetics model.[11]

$dq/dt = k_2(q_e - q)$ …….(8)

By integrating the above equation into the boundary conditions (t=0, q=0) and (t = t, q = q_t), we obtain.

$t/q_t = 1 / (k_2 q_{e2}) + t/q_e$……(9)

where, k_2 (g/mg/min) is the second order rate constant, q_t (mg/g) is the amount adsorbed at time t (min) and q_e is the amount of adsorbed at equilibrium (mg/g). This model is more likely to predict the kinetics of adsorption with chemical adsorption being the rate-controlling step. The values of rate constants (k_2), calculated from the linear plots of t/q_t versus t, along with q_e values.

2.5.3. Weber and Morris model

Weber and Morris proposed intra-particle diffusion model, which can be written as,

$q_t = k_{id} t^{1/2} + C$…….(10)

where, q_t (mg/L) is the amount adsorbed at time t (min), k_{id} ($mg/g/min^2$) is the rate constant of intra-particle diffusion and 'C' is a constant which gives an idea about the boundary layer thickness. The larger the intercept, the greater is the boundary layer effect. The plots of q_t versus $t^{1/2}$ obtained for the adsorption metal ion (100 mg/L) onto GMC-2 carbon at a different dose (100 - 500 mg). The intraparticle rate constant k_{id} and intercept C (mg/g). The linear plots of q_t versus $t^{1/2}$ with zero intercept indicate that intra-particle diffusion alone determines the overall rate of adsorption.

2.6. Thermodynamic studies

In adsorption, thermodynamic parameter plays an important role to determine whether the adsorption process occurs randomness, spontaneity to know the nature of the process (exothermic or endothermic). The thermodynamic parameters include a change in enthalpy (ΔH), change in entropy (ΔS), and change in Gibbs free energy (ΔG).

Thermodynamic parameters are considered to determine the process due to the transfer of unit mole of solute from solution onto the solid-liquid interface. The concept of thermodynamic assumes that in an isolated system where the energy cannot be lost or gained, the entropy change is the driving force. Enthalpy change (ΔH) is considered to

be important thermodynamic function and useful to determine the adsorption nature. The positive (ΔH) value indicates that the process is endothermic. The negative (ΔH) indicates the process is exothermic. The important parameter is entropy change (ΔS) whereas it explains about the spontaneity occurs in the adsorption process. The following equations were used to calculate the thermodynamic parameters (ΔG, ΔH, ΔS) [5,6]. The Gibb's free energy change of the adsorption process is related to the equilibrium constant by the classic Van't Hoff equation. The equation is,

$\Delta G = - RT \ln K_0$

Where, ΔG - is free energy of activation (KJ/mo1), R - is the universal gas constant (8.314 J/K/mo1), T - is temperature (K), K_0 - is equilibrium constant of adsorption, The equilibrium constant (K_0) calculated from the following equation,

$K_0 = C_{Ae}/C_e$

Where, C_{Ae} - is the adsorbed metal ion concentration at equilibrium (mg/L), C_e - is the equilibrium concentration of metal ion in solution (mg/L). By substituting all values in Gibb's free energy equation, ΔG can be calculated. Standard enthalpy change (ΔH) and standard entropy change (ΔS) of adsorption are calculated by using Van't Hoff relationship. According to thermodynamics, Gibb's free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation,

$\Delta G = \Delta H – T\Delta S$

Combining the above equations, we get,

$\ln K_0 = \Delta S/R - \Delta H/RT$

The enthalpy and entropy can be calculated from Van't Hoff plot of ln K_0 Vs 1/T.

3. RESULTS AND DISCUSSION

3.1. Isothermal studies

3.1.1. Langmuir isotherm

The Langmuir adsorption isotherm has been successfully applied to many adsorption processes and has been the most widely used. The Langmuir adsorption isotherm study has been done by varying the initial concentration of metal ion from 100 to 500 mg/L, with different mass of the adsorbent (100 to 500 mg) keeping all other conditions constant. A plot of C_e/q_e versus C_e indicates a straight line of slope $1/q_m$ and an intercept of $1/q_mb$ were shown in Table-1.

Where, C_e is the equilibrium concentration (mg/L), qe is the amount of metal ion adsorbed (mg/g), q_m is q_e for a complete monolayer (mg/g); b is adsorption equilibrium constant. The essential characteristic of a Langmuir isotherm, related to the isotherm shape, can be expressed in terms of a dimensionless constant separation factor, also called the equilibrium parameter R_L. The Langmuir plots of Pb(II) ions are shown in Figure -1. The adsorption of Pb(II) ions onto GMC-2 carbon follows the Langmuir isotherm model for metal adsorption. The value of q_m and b were evaluated and given in Table-2. In the present study, the computed values of R_L are found to be a fraction as in the range of 0 to 1, indicating that the adsorption process is favourable for the removal of M^{2+} ions by using GMC-2 carbon as an adsorbent. The R_L value decreases with increase in dose of the adsorbent as shown in Table-3. The high value of correlation coefficient R^2 indicates a good agreement between the parameters and confirms the monolayer adsorption of metal ion on the adsorbent surface.

3.1.2. Freundlich isotherm

The Freundlich isotherm assumes that the adsorption occurs on the heterogeneous surface at sites with different energy of adsorption and with non-identical adsorption sites that are not always available. The plots of Freundlich adsorption isotherm plots of metal (Pb, Cd and Cu) ions were shown in Figure-2. The K_F value is related to the adsorption capacity; while the 1/n value is related to the adsorption intensity. A plot of log C_e versus log q_e from the values in Table-4 gives a straight line. K_F and 1/n were determined from the intercept and the slope, respectively and the results are given in Table-5. The value of the correlation coefficient (R^2) obtained in this case indicates that the Langmuir isotherm model fits better than the Freundlich isotherm model.

3.2. Adsorption kinetics

The adsorption kinetics of lead (II) ions onto GMC-2 carbon, was investigated with the aid of three kinetic models, namely pseudo-first order model, pseudo-second-order model and Weber and Morris's intraparticle diffusion model to analyze the experimental data.

3.2.1. Pseudo-first order kinetic model

The pseudo-first-order rate model of Lagergren is based on solid adsorbent capacity and generally expressed as follows

$\log_{10} (q_e - q_t) = \log q_e – k_1t / 2.303$…….(11)

Where, q_e is the amount of solute adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_t is the amount of solute adsorbed at any time (mg/g) and k_1 (min^{-1}) is the adsorption rate constant. Values of k_1 calculated from the plots of log ($q_e – q_t$) vs t at different initial concentrations are summarized in Table-6 and plot shown in figure-3.

The values of rate constants obtained in linear plot of log ($q_e – q_t$) versus t for studied metal ions on GMC-2 applicability of Lagergren equation of 100 to 500 mg/L of metal ions were 0.015 - 0.0148 x 10^{-2} s^{-1} for Pb (II) ions. The correlation coefficient values low with the experimental values. These results suggest that the pseudo first-order model does not show good agreement with this kinetic model. The K_1 values of the metal ion as shown in Table-7.

3.2.2. Pseudo-second order kinetic model

The pseudo-second order model can be expressed as

$t/q_t = 1/(k_2 q_{e2}) + t/q_e$

where, k_2 (g/mg/min) is the rate constant of the pseudo-second-order equation, q_e (mg/g) is the maximum adsorption capacity, and q_t (mg/g) is the amount of adsorption at time t (min). The plot of t/q_t vs t shows a linear relationship shown in figure-4. The value of q_e (mg/g) and k_2 (g/mg/min) are determined from the slope and intercept of the plot. From Table-8, it can be seen that the calculated coefficient of determination (R^2) was very close to unity with the experimental values. These results suggest that the pseudo-second-order model shows good agreement with the experimental one describes the adsorption kinetics of the present system. This decrease in k_2 values at higher concentrations seems due to the repulsion between the adsorbed and the non-adsorbed Pb^{2+} ions shown in Table-9.

3.2.3. Intraparticle diffusion

To gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the intra-particle diffusion plays an important role in the extent of adsorption and can be expressed as,

$q_t = k_{id}\, t^{1/2} + C$

Where, the k_{id} is the intraparticle diffusion constant (mg/g min) and the intercept (C) reflects the boundary layer effect. The value of q_t were linearity correlated with the values of $t^{1/2}$ and the rate constants K_{id} was directly evaluated from the slope of the regression line indicating that two or more steps take place. In first stage, the sharper portion represents the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intra-particle diffusion is rate controlling. The third portion is the final equilibrium stage where intra particle diffusion starts to slow down due to extremely low solute concentrations in the solution. The larger the intercept, the greater is the boundary layer effect. The values of k_{id} were calculated from slopes of the plots of q_t vs $t^{1/2}$ and are presented in Table-10.

k_{id} values decrease with increase in the dose of the adsorbent, which reveals that the rate of adsorption is governed by the diffusion of adsorbed Pb(II) ions within the pores of the adsorbent as shown in Table-11. The R^2 values are close to unity indicating the applicability of this model. This may confirm that the intra-particle diffusion is the rate-limiting step.

From the above consideration, the pseudo-second-order kinetic model provided the best correlation for all the adsorption process, whereas the intra-particle diffusion model fit well for an initial period of adsorption process shown in figure-5. Hence, it was concluded that the pseudo second- order kinetic model represented the rate limiting step in adsorption, followed by the intra-particle diffusion model.

3.3 Thermodynamic studies

Temperature is found to be an important parameter for the adsorption of metal ions dealing with the thermodynamics of the adsorption process. An increase or decrease in temperature should cause a change for metal removed or adsorbed by the GMC-2. The change in temperature causes a change in thermodynamic parameters like ΔG, ΔH and ΔS. These parameters help to understand the adsorption mechanism. Parameters like ΔG, ΔH and ΔS provide valuable information about the adsorption process was shown in Table – 12.

The studies performed using GMC-2 has not accounted for the values of thermodynamic parameters, yet they describe the role of temperature as causing a decrease in the metal adsorption shown in figure - 6. The ΔG addresses the possibility and feasibility of a certain reaction. The positive value of ΔG shows the process non-spontaneous of the process. The increase in ΔG value, with temperature shows the increased probability of the adsorption process energy of adsorption found below 20 KJ/mol, which follows physisorption.[29] The respective value of the change in free energy increased from 8.7998 - 10.6245 K/mol for lead ions as listed in Table - 13.

Positive values of ΔS showed a good affinity of metal ion towards the GMC-2 carbon and increased randomness at the solid solution interface during the adsorption process. Positive values of ΔS showed an increase in entropy, stability of the adsorption and irreversible nature of the adsorption process. The corresponding values of change in entropy (ΔS) was 0.2071 KJ/mol/K for Pb^{2+} ion respectively.

On one hand, ΔH shows the route of energy in the system. A positive value shows an endothermic process and a negative value indicates an exothermic process. This also contributes to decide whether a certain adsorbent can be used for the removal of metal ions at elevated temperature or not. ΔH indicated the process was exothermic and an increase in temperature caused a decrease in the adsorption capacity. The value of ΔH was calculated from ln K_0 versus 1/T plot and was found to be - 43.5789 KJ/mol for Pb^{2+} ions. This confirmed that metal ion adsorption by GMC-2, under studied conditions, was exothermic.

3.4 Scanning Electron Microscope (SEM) and X- ray Diffraction Studies (XRD)

Scanning Electron Microscope techniques have been used to characterize the pore structures of the activated carbons. The recent developments in images analysis techniques can provide more in depth analysis and interpretation of the microscopic images of the carbon surfaces in the adsorption process. SEM micrograph of GMC carbon shows rough areas and pores on the surfaces. The presence of more porosity can hold more solute from solution during adsorption[30] observed

similar observation for *Glycosmis mauritiana* stem activated carbon as shown in Figure – 4.8. After adsorption of metal ions the carbon have been filled by adsorbate as shown in Figure – 7.

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of the materials. If the material under investigation is crystalline, well-defined peaks will be observed while non-crystalline or amorphous systems show a hollow instead of well-defined peak.[31] Adsorption reaction may lead to a change in the molecular and crystalline structure of the adsorbent and hence an understanding of the molecular crystallinity of the adsorbent and the resulting changes thereof would provide valuable information regarding adsorption reaction. Examination of the X-ray diffraction patterns of the GMC-2 carbon was shown in Figure – 8. The diffractogram does not exhibit a horizontal basic line. This shows that the major part of the matter of the GMC-2 carbon was amorphous. However, two diffraction peaks (2θ = 25°, 29°) emerged from the basic line indicated the presence of a low degree of crystalline nature.[32] After adsorption of the metal ions the peaks are disappeared and it confirms the adsorption of metal ions.

Table-1: Data for Langmuir isotherm on adsorption of Pb(II) ions.

Conc. of Pb(II) ions(mg/L)	Time = 210 min, pH = 6.0, Conc. of Pb(II) ion = 100 - 500 mg/L.									
	$1/C_{eq}$, mg/L					$1/q_e$, mg/g				
	Weight of the adsorbent (mg)					Weight of the adsorbent (mg)				
100	**100**	**200**	**300**	**400**	**500**	**100**	**200**	**300**	**400**	**500**
200	17.55	19.31	19.3	22.71	29.7	2.14	4.06	5.79	7.02	7.15
300	8.58	8.98	9.42	9.9	12.45	1.17	2.21	3.22	3.96	4.11
400	5.44	5.76	6.03	6.23	6.89	0.86	1.54	2.23	2.86	3.16
500	3.86	4.02	4.2	4.44	4.71	0.7	1.29	1.81	2.27	2.38

Table-2: Constants for Langmuir isotherm on adsorption of Pb(II) ions.

Weight of the adsorbent (mg)	100	200	300	400	500
b, (mg/L)	3.4843	1.7513	1.3387	0.8110	0.6031
q_m, (mg/g)	2.7333	3.1722	2.8731	4.7977	8.9139

Table-3: Data for separation factor (R_L) on adsorption of metal ions.

[Pb(II)]ini., C_0, mg/L	R_L					Correlation coefficient (R^2 value)				
	Dose of the adsorbent (mg)									
100	**100**	**200**	**300**	**400**	**500**	**100**	**200**	**300**	**400**	**500**
200	0.0032	0.0030	0.0029	0.0021	0.00106	0.999	0.998	0.998	0.997	0.993
300	0.0017	0.0015	0.0015	0.00103	0.00054					
400	0.0011	0.0010	0.00102	0.00069	0.00036					
500	0.0008	0.00076	0.00076	0.00052	0.00027					

Table-4: Data for Freundlich isotherm an adsorption of Pb(II) ions.

Time = 210 min, pH = 6.0, Conc. of Pb (II) ion = 100-500 mg/L.									
log C_e, mg/L					log q_e, mg/g				
Weight of the adsorbent (mg)					Weight of the adsorbent (mg)				
100	**200**	**300**	**400**	**500**	**100**	**200**	**300**	**400**	**500**
4.043	3.947	3.947	3.785	3.516	3.842	3.203	2.849	2.656	2.638
4.758	4.913	4.535	4.615	4.386	4.248	3.814	3.333	3.029	3.192
5.214	5.156	4.903	5.079	4.977	4.758	4.170	3.604	3.554	3.453
5.557	5.516	5.110	5.417	5.358	4.959	4.353	4.012	3.785	3.546
5.834	5.804	5.200	5.731	5.688	5.110	4.448	4.101	3.896	3.737

Table-5: Freundlich isotherm constants on adsorption of Pb(II) ions.

Weight of the adsorbent (mg)	100	200	300	400	500
K_f	5.4954	2.7606	2.6765	1.0592	9.2045
1/n	0.7400	0.7010	0.9880	0.6820	0.4900
R^2	0.984	0.976	0.969	0.970	0.981

Table-6: Data for Pesudo-first order reaction.

Time (min)	Time = 210 min, pH = 6.0, Conc. of Pb (II) ions = 100 mg/L				
	log (q_e - q_t)				
	100 mg/L	200 mg/L	300 mg/L	400 mg/L	500 mg/L
30	1.191437	1.413283	1.49246	1.527224	1.753771
60	1.112253	1.367524	1.413283	1.45467	1.643724
90	0.890393	1.258374	1.316369	1.316369	1.49246
120	0.714288	1.191437	1.112253	1.112253	1.191423
150	0.4133	0.890421	0.71433	0.890393	1.015339

Table-7: Constants value of Pseudo- first order reaction.

Weight of the adsorbent (mg)	100	200	300	400	500
K_1 x 10^{-2}, s^{-1}	0.015	0.0094	0.0143	0.0124	0.0148
R^2	0.966	0.951	0.982	0.805	0.828

Table-8: Data for Pseudo- second reaction.

Time (min)	Time = 210 min, pH = 6.0, Conc. of Pb (II) ion = 100 mg/L.				
	(t/q_t)				
	100 mg/L	200 mg/L	300 mg/L	400 mg/L	500 mg/L
30	0.8274	0.5516	0.5265	0.4455	0.7222
60	1.5444	1.0530	0.9652	0.8273	1.1062
90	2.0441	1.4479	1.3365	1.1209	1.3396
120	2.5741	1.8533	1.5977	1.3627	1.4506
150	3.0483	2.0685	1.8099	1.6088	1.7064
180	3.4750	2.2419	2.0441	1.7820	1.8318
210	4.0540	2.6156	2.3848	2.0791	2.1371

Table-9: Constants of Pseudo-second order reaction.

Weight of the adsorbent (mg)	100	200	300	400	500
K_2 x10^{-2}, s^{-1}	0.0670	0.0265	0.0214	0.0178	0.0081
q_e	58.82	100.00	111.11	125.00	142.85
R^2	0.995	0.975	0.985	0.989	0.979

Table-10: Data for Intra-particle diffusion model on adsorption of metal ions.

$t^{1/2}$	Time = 210 min, pH = 6.0, Conc. of Pb(II) ion = 100 mg/L				
	Q_t				
	100 mg	200 mg	300 mg	400 mg	500 mg
5.4772	29.007	16.057	11.395	9.323	8.495
7.7459	33.05	18.647	13.122	10.619	9.945
9.4868	37.294	21.755	15.194	12.69	11.81
10.9545	41.438	25.755	17.611	14.762	12.639
12.2475	47.654	27.452	19.683	16.057	13.675
13.4164	50.762	28.488	21.41	17.093	14.503

Table-11: Values of K_{id} on adsorption of metal ions.

Weight of the adsorbent (mg)	100	200	300	400	500
K_{id}	2.815	1.689	1.298	1.037	0.770

Table – 12: Thermodynamic studies of the metal ions.

Thermodynamic studies on M^{2+} ions			
T	1/T	K_0	ln K_0
		Pb^{2+}	Pb^{2+}
308	0.003247	31.078	3.4365
313	0.003195	33.668	3.5165
318	0.003145	41.438	3.7242
323	0.003096	41.438	3.7242
328	0.003049	49.208	3.8960

Table – 13: Thermodynamic constants of the metal ions.

Metal ion	Conc. of Metal solution (mg/L)	T (K)	ΔG (KJ / mol)	ΔS (KJ / mol / K)	ΔH (KJ/mol)
Pb^{2+}	100	308	8.7998	0.2071	-43.5789
		313	9.1510		
		318	9.8462		
		323	10.3173		
		328	10.6245		

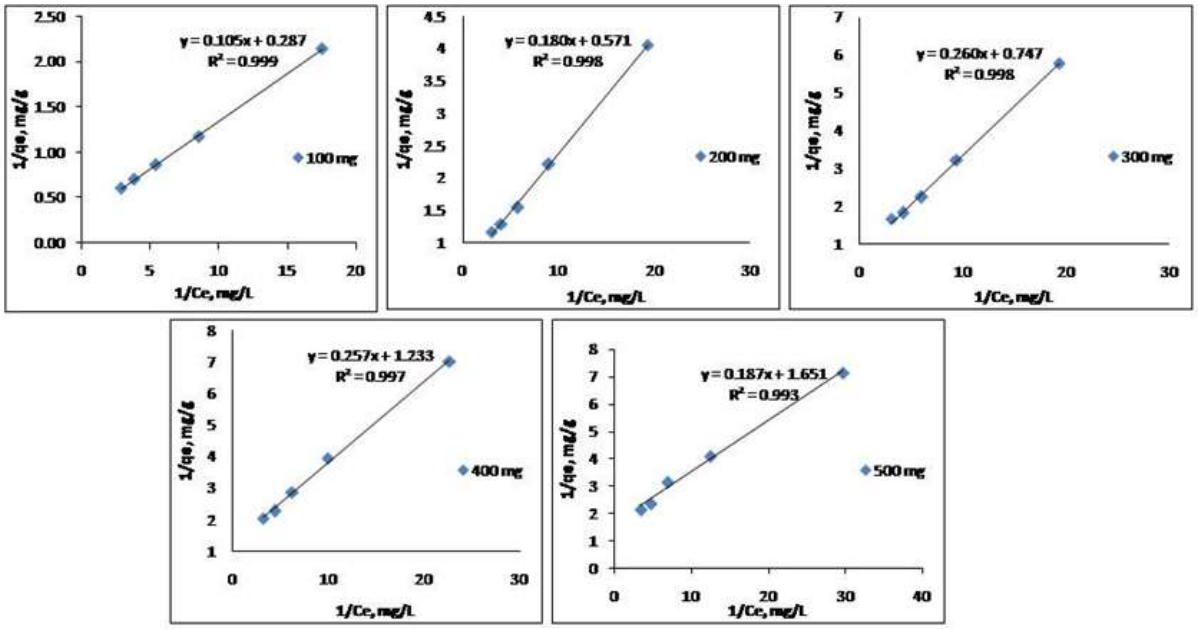

Figure 1: Plots of Langmuir isotherm.

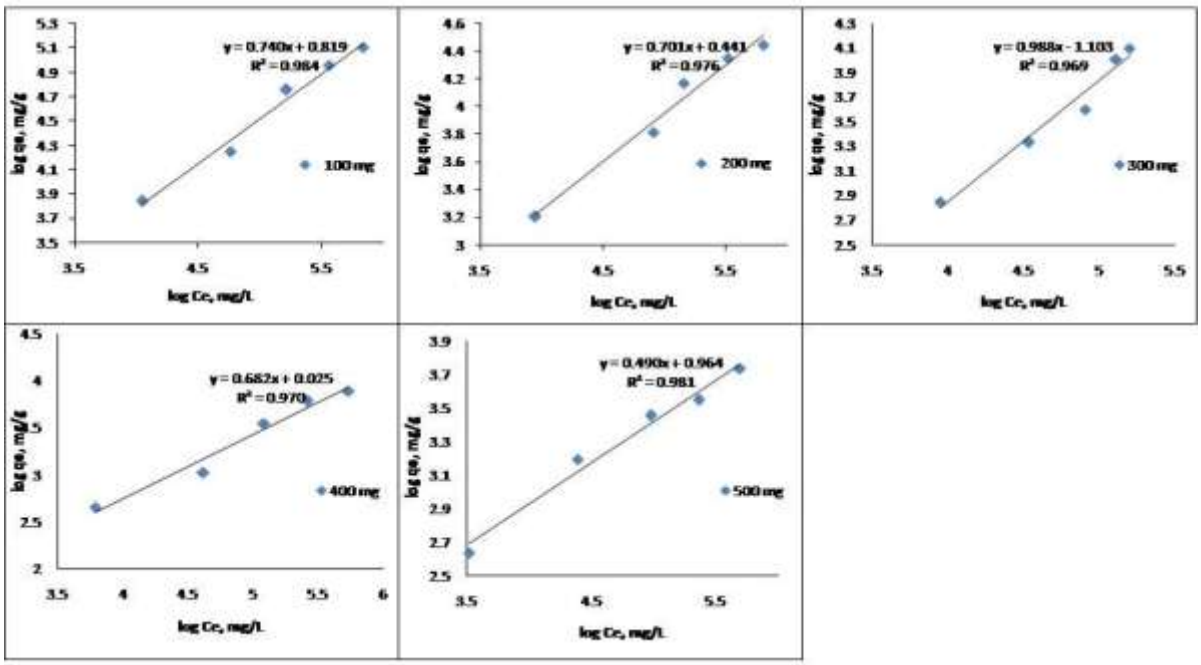

Figure 2: Plots of Freundlich isotherm.

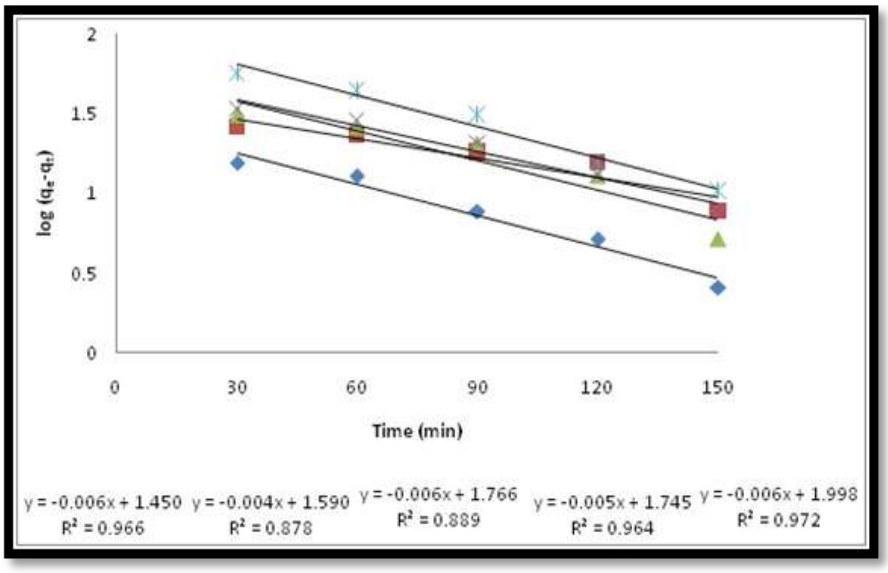

Figure-3: Plots of Pseudo- first order reaction.

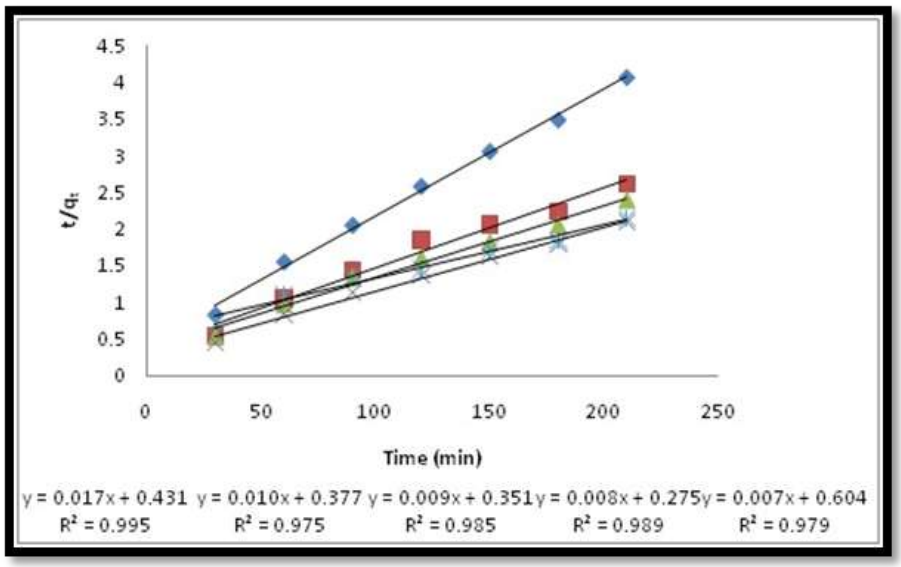

Figure-4: Plots of Pseudo-second order reaction.

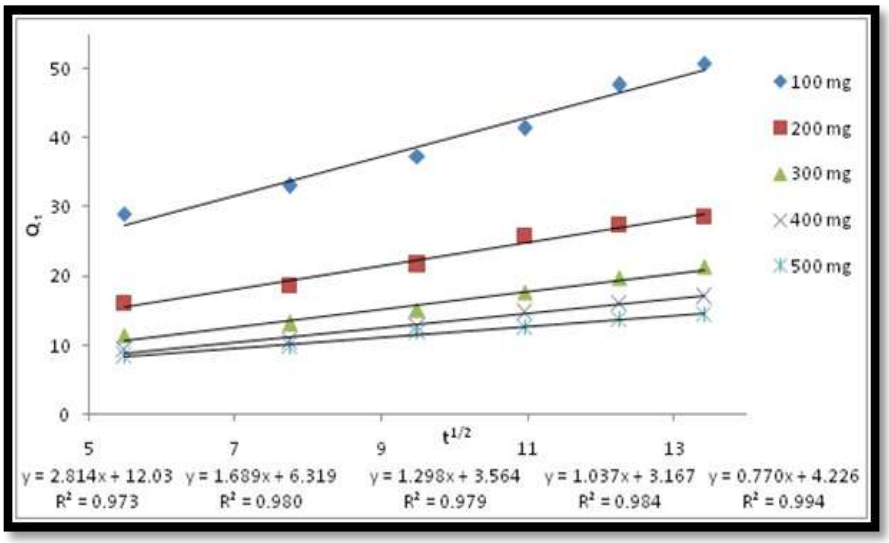

Figure-5: Plots of Intra-particle diffusion.

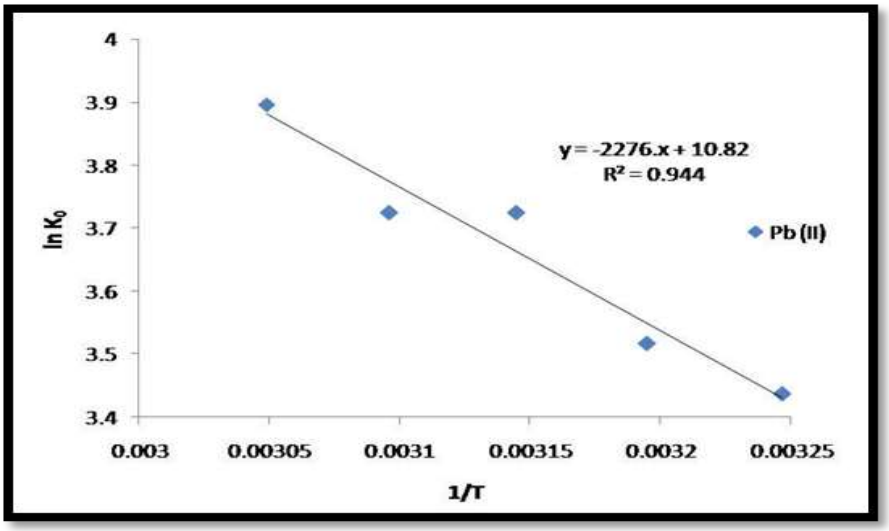

Figure-6. Thermodynamic plot of metal ions (Pb^{2+}) on GMC–2 carbon.

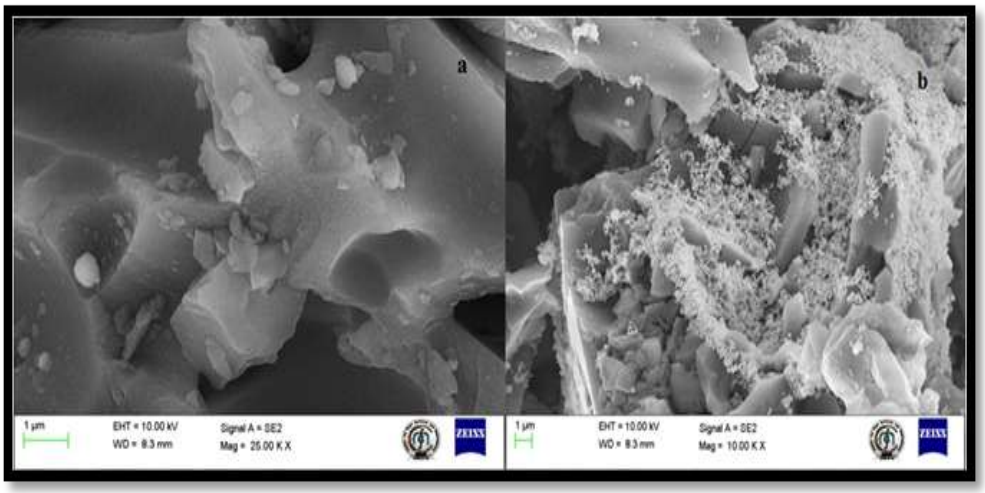

Figure-7. SEM image of a) GMC-2, b) Pb adsorbed GMC-2 carbon.

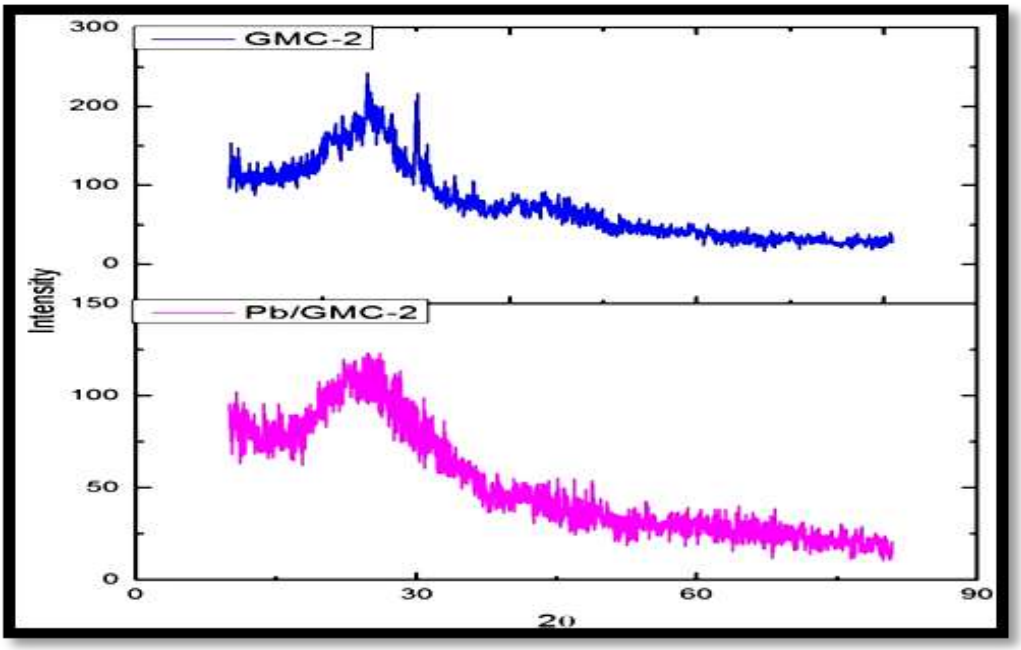

Figure-8. XRD peaks of GMC-2, Pb adsorbed GMC-2 carbon.

4. CONCLUSION

The present work is to utilize the stem part of the plant *Glycosmis Mauritiana* for the preparation of activated carbon. The properties of adsorption on the removal of metal ion from aqueous solution using adsorbent prepared from *Glycosmis Mauritiana* contains only limited studies have so far been conducted by batch study method. Therefore, studies were carried out on the removal of Pb(II ions from aqueous solutions, using carbon derived from stem of this plant. From the equilibrium adsorption capacity, the isotherm studies related to applicability of monolayer or heterogeneous layer adsorption. The characteristic parameters for both isotherms and their related R^2 values have been determined. The result concludes that the adsorption of studied metal ion undergoes Langmuir adsorption isotherm to fit the experimental data better than the other isotherms tested although the generalized isotherm also represented the data reasonably well. Kinetics studies were used to study of rate constants involved in adsorbent and adsorbate species. Pseudo-second-order kinetics was found to be more suitable as compared to the pseudo first-order due to the inclusion of both adsorbent and adsorbate species in adsorption of Pb^{2+} ions onto GMC-2. The thermodynamic study shows the adsorption of lead ion onto GMC-2 carbon was found to be an exothermic and physisorption in nature.

ACKNOWLEDGEMENT

The authors would like to thank the Head of the Department of Chemistry, Jamal Mohamed College for performing the research work in the laboratory.

REFERENCES

1. K. Banerjee, S. T. Ramesh, P.V. Nidheesh, K.S. Bharathi, A Novel Agricultural Waste Adsorbent, Watermelon Shell for the Removal of Copper from Aqueous Solutions, Iranica J. Energy Environ, 2012; 3: 143–156.
2. Q. Manzoor, R. Nadeem, M. Iqbal, R. Saeed, T.M. Ansari, Organic acids pretreatment effect on Rosa bourbonia phyto-biomass for removal of Pb(II) and Cu(II) from aqueous media, Bioresour. Technol, 2013; 132: 446–452.
3. J.S. Merrie, N. Saswathi, S.V. Ramakrishna, R. Sheela, Biosorption of chromium VI by free and immobilized Rhizopus arrhizus. Environmental Pollution, 1999; 104: 421-442.
4. K. Ikehata, M.G. El-Din, Degradation of recalcitrant surfactants in wastewater by ozonation and advanced oxidation processes: a review, Ozone Sci. Eng, 2004; 26: 327–343.
5. M. Panizza, M. Delucchi, G. Cerisola, Electrochemical degradation of anionic surfactants, J. Appl. Electrochem, 2005; 35: 357–361.
6. E. Pérez-Carrera, V.M. León, P.A. Laramartín, E. González-Mazo, Influence of the hydrophilic moiety of anionic and nonionic surfactants on their aerobic biodegradation in seawater, Sci. Total Environ, 2010; 408: 922–930.
7. U. Tezel, M. Tandukar, R.J. Martinez, P.A. Sobecky, S.G. Pavlostathis, Aerobic biotransformation of n-tetra decyl benzyl dimethyl ammonium chloride by An enriched pseudomonas spp. community, Environ. Sci. Technol, 2012; 46: 8714–8722.
8. I. Kowalska, Ion-exchange–ultrafiltration system for surfactants removal from water solutions, Desalin. Water Treat, 2011; 25: 47–53.
9. Aboulhassan, S. Souabi, A. Yaacoubi, M. Baudu, Removal of surfactant from industrial wastewaters by coagulation flocculation process, Int. J. Environ. Sci. Technol, 2006; 3: 327–333.
10. S. Boonyasuwat, S. Chavadej, P. Malakul, J.F. Scamehorn, Anionic and cationic surfactant recovery from water using a multistage foam fractionator, Chem. Eng. J, 2003; 93: 241–252.
11. M.C. Gonzalez-Garcia, L.M. Gonzalezmartin, M.A. Gallardo-Moreno, A.V. Gomez Serrano, L. Labajosbroncano, F.M. Bruque, Removal of an ionic surfactant from wastewater by carbon blacks adsorption, Sep. Sci. Technol, 2002; 37: 2823–2837.
12. N. Schouten, L.G.J. Van Der Ham, G-J.W. Euverink, A.B. De Haan, Selection and evaluation of adsorbents for the removal of anionic surfactants from laundry rinsing water, Water Res, 2007; 41: 4233–4241.
13. A.V. Sineva, A.M. Parfenova, A.A. Fedorova, Adsorption of micelle forming and non-micelle forming surfactants on the adsorbents of different nature, Colloids Surf. A, 2007; 306: 68–74.
14. Z. Aksu, I.A. Isoglu, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, Process Biochem, 2005; 40: 3031–3044.
15. C.S. Zhu, L.P. Wang, W.B. Chen, Removal of Cu(II) from aqueous solution by agricultural by-product: Peanut hull, J. Hazard. Mater, 2009; 168: 739–746.
16. H. Chen, G. Dai, J. Zhao, A. Zhong, J. Wu, H. Yan, Removal of copper(II) ions by a biosorbent-Cinnamomum camphora leaves powder, J. Hazard. Mater, 2010; 177: 228–236.
17. M. Dundar, C. Nuhoglu, Y. Nuhoglu, Biosorption of Cu(II) ions onto the litter of natural trembling poplar forest, J. Hazard. Mater, 2008; 151: 86–95.
18. H. Aydin, Y. Bulut, C. Yerlikaya, Removal of copper(II) from aqueous solution by adsorption onto low-cost adsorbents, J. Environ. Manage, 2008; 87: 37–45.
19. R. Gundogan, B. Acemioglu, M.H. Amla, Copper(II) adsorption from aqueous solution by herbaceous peat, J. Colloid Interface Sci, 2004; 269: 303–309.
20. Y.P. Kumar, P. King, V.S.R.K. Prasad, Equilibrium and kinetic studies for the biosorption system of copper(II) ion from aqueous solution using Tectona grandis L.f. leaves powder, J. Hazard. Mater, 2006; 137: 1211–1217.

21. W.S.W. Ngah, M.A.K.M. Hanafiah, Biosorption of copper ions from dilute aqueous solutions on base treated rubber (Hevea brasiliensis) leaves powder: kinetics, isotherm, and biosorption mechanisms, J. Environ. Sci, 2008; 20: 1168–1176.
22. A.E. Ofomaja, E.B. Naidoo, S.J. Modise, Removal of copper(II) from aqueous solution by pine and base modified pine cone powder as biosorbent, J. Hazard. Mater, 2009; 168: 909–917.
23. S. Lu, S.W. Gibb, Copper removal from wastewater using spent-grain as biosorbent, Bioresour. Technol, 2008; 99: 1509–1517.
24. Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, Process Biochem, 2002; 37: 1421–1430.
25. S.R. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust, Sep. Purif. Technol, 2005; 43: 1–8.
26. M. Mukhopadhyay, S.B. Noronha, G.K. Suraiskhumar, Kinetic modelling for the biosorption of copper by pretreated Aspergillus niger biomass, Bioresour. Technol, 2007; 98: 1787-1787.
27. R. Djeribi, O. Hamdaoui, Sorption of copper(II) from aqueous solutions by cedar sawdust and crushed brick, Desalination, 2008; 225: 95–112.
28. S. Larous, A.H. Meniai, M.B. Lehocine, Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust, Desalination, 2005; 185: 483–490.
29. Sengil, I. A., M.Özacar, M. Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes. J. Hazard. Mater, 2008; 157(2–3): 277–285.
30. Raffiea Baseri, J., Palanisamy, P. N. and Sivakumar, P. Preparation and characterization of activated carbon from *Thevetia peruviana* for the removal of dyes from textile waste water Adv. Appl. Sci. Res, 2012; 3(1): 377–383.
31. Namasivayam, C., Kavitha, D. IR, XRD and SEM studies on the mechanism of adsorption of dyes and phenols by coir pith carbon from aqueous phase. Microchemical. J, 2006; 82(1): 43–48.
32. Lua, A. C., Yang, T. Effect of activation temperature on the textural and chemical properties of potassium hydroxide activated carbon prepared from pistachio nut shell. J. Colloid Interface Sci, 2004; 274: 594–601.