

Thorns, a Novel Natural Plants for Adsorption of Lead (II) Ions from Wastewater Equilibrium, Isotherm, Kinetics and Thermodynamics

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Abstract: Thorns, a novel plant material, were found to exhibit excellent adsorption capacity over a wide range of Pb(II) concentration. It was characterized by Fourier transform infrared spectroscopy and Scanning Electron Microscopy to support the adsorption of Pb(II) ions. Effect of different parameters likes pH, contact time, initial concentration and different electrolytes was investigated using batch process to optimize conditions for maximum adsorption. The adsorbent data were analyzed using Langmuir, Freundlich, isotherm equations at 30°, 40° and 50 °C. Thermodynamic parameters such as standard enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) were also evaluated and the results indicated that adsorption of Pb(II) is spontaneous and endothermic. Various kinetics models including the Pseudo-first-order kinetics, Pseudo-second-order kinetics and Intraparticle diffusion models have been applied to the experimental data to predict the adsorption kinetics. Kinetic study was carried out by varying initial concentration of Pb(II) at constant temperature and it was found that pseudo-second-order rate equation was better obeyed than pseudo-first-order equation supporting that chemisorptions process was involved.

Keyword: Adsorption, Thorns, Lead, Equilibrium, Isotherms, Kinetics, Thermodynamic.

INTRODUCTION

The continuously excess of pollution, it's occur by fast excess of developing in the industrial production technology, that leads to find the best methods to reduce this great amount of many types of pollutants that released to environment, subsequently safe the humans, animals and plants from that risky effect. Heavy metals pose a great risk to humans and the environment, when it's accumulate in tissues of humans, plant and animals, because it contains high toxicity, perseverance and un-degradable elements also if it's in small concentration. Chromium, Lead, Mercury, Copper, Zinc and Cadmium are frequently sense in wastewaters of industrial activities, which are originate as of pesticides, mining tricks, industry of battery, smelting, refinery of uranium, metal plating, and so forth.

Over the years some techniques applied to get rid of the ions of heavy metal ions from soils and manufacturing plants waste solution. Many traditional techniques utilized to recovery ions of metal from wastewater take in: ion-exchange, electro dialysis, solvent extraction, phyto-extraction, reverse osmosis, chemical precipitation, adsorption and ultra-filtration [1].

Agriculture activities uses huge quantity from raw materials that used to product it, that produce the wastes from solid materials and liquid solution. Utilizing Fertilizers, pesticides and dyes product occur vast amounts of hazardous chemicals wastes whilst rice husk, coffee husk, biogases, peanut shell and sawdust regarded as from the solid wastes[2]. In the last time, the researchers trend to used the solid wastes result from agricultural activities as a media to adsorbed the hazardous chemical wastes, that achieve this words "waste to treat waste". Depending on this theory, treatment of industrial wastewater become easy by low cost materials to adsorption the heavy metals, that was a big problem in management of wastewater. Because of concerns of environmental plus the interesting to get pure water, putted more guidelines and regulating the limitation to control on the effluent of hazardous and toxic

materials to the rivers, lakes and the surface water. That means brought about creating hazardous waste reuse strategies to reduce it for a less amounts rid it in surface water. The following treatment of wastewater must have advanced techniques to removing hazardous compounds[3]. Auxiliary strategies are utilized related to cutting edge techniques to separate the refractory natural mixes and inorganic compounds (non-biodegradable) [4]. For removing the hazardous elements and the heavy metals use the advanced technique such as; membrane separation [5], ion exchange [6], lime precipitation, neutralization, metal hydroxide precipitation [7], electrolytic methods [8] and adsorption[9]. However, these processes are costly, Utilizing resins of ion- exchange and activated carbon are very costly in preparation and operation in many countries of third world particularly[10]. There are a large quite applications for adsorption technique because, there are found many adsorbents kind utilized to remove the metals such as; Silica gel, zeolite, activated carbon, Clay and adsorbents from agricultural waste like; husk of coffee [10], shells of peanut [11], bagasse [12], rice husk [13] and sawdust [14]. Therefore, utilizing natural, low cost waste from agricultural activities, plentiful, pollutants adsorption from wastewater be able to greatly cheap by observe to processes physicochemical similarly[15]. Agriculture waste utilizing to remove the metals didn't research by details, according to my knowing, there is no paper published utilized Thorns for Lead(II) ions removal from wastewater.

Adsorption with agriculture adsorbents low cost has been efficiently practical to eliminate toxic compounds from contamination water. Lead is a main worry due to its normal use in industrial world with its nature like; toxic, non-degradable.

The Lead persistent toxicity to the environment and humans is also familiar and high Lead concentrations cause gastrointestinal annoyance, cancers of bone and lung[16]. Latest years, used diverse adsorbents to elimination Lead(II) ions from contaminated solutions. On the other hand, novel adsorbents by local availability, great adsorption capability and economical composed materials are still desirable. Characteristic materials have phenomenal possibility Concerning illustration modest adsorbents. Different adsorbents have been utilized within secret word quite some time for lead particle removal, however, those investigation Furthermore improvement for new adsorbents may be constant. Biomaterials for example, cashew nut shells[17], low cost Fly Ash[18], ground nut shell[18], zeolite [19], Activated Carbon Derived from Waste Biomass [20], Modified and Non modified Carbon Nano-tubes[21], Cane Papyrus[22], Multi-Walled Carbon Nano-tubes as a super sorbent [23], a modified lignin hydrogel [24], Gamma Irradiated Minerals [25], Synthetic Polymers[26], modified walnut shells[27], natural clays[28] etc. have lately been utilize the Pb(II) elimination from waste water. Thorns flora are medium size plants or plant with flowers to look like a Thorns since of the cylindrical stalk.

This worth of effort need been embraced should investigate the adsorption behavior Of this guaranteeing novel material stick thorns towards Pb(II) ions. Those impact about parameters for example, introductory result pH, substantial metal concentration, and contact run through might have been analyzed.

A few characterization strategies (FTIR, SEM) were likewise utilized to recognize those progressions On stick Thorns should determine its materialness in the adsorptive evacuation for Pb(II). This substance up till now need to be tried in favor of the adsorption about overwhelming metals from watery result Also In this way it's phenomenal adsorption capacity, simplicity about availability, non-toxic nature, inexpensiveness and so forth. Provide for those principle advancement of the display investigation.

MATERIALS AND PROCEDURE

The Preparation of Adsorbent

The Adsorbent Preparation (Thorns) was collected from farmlands in the Al- Mustansiriyah University / Baghdad – Iraq.

The grass were cautiously separate from the plant stalk and wash carefully by valve hose to get rid themed, and remains soil particles after that dried by sun for 10 days. The dehydrated biomass was ground to fine particles by a hammer mill also weigh. Powder resultant was classified by systematic sieves. The Particles in 100-300 μm were used for simulated wastewater samples. The adsorbent showed a fluffy and highly porous and rough microstructure containing some voids and cracks which is suitable for the adsorption of Pb(II) ions. The Pb(II) ions concentration in aqueous solution was analyzed using Atomic Absorption Spectrometer (AAS). Mechanical shaker with regulating velocity, time was used for agitation and pH meter was used for all pH measurements. The chemical composition of the adsorbent was analyzed using X-ray Fluorescence spectrometer. The chemical composition of the adsorbent is presented in (Table I).

Table 1: Chemical Composition of Thorns

Compound	
Moisture (%)	69.1
Ash (%)	23.3
Protein (% dry weight)	21.0
Fat (%)	< 1.0
Ca (% dry weight)	26.7
P (mg/g dry weight)	1.4
Astaxanthin (mg/kg dry weight)	65.4

Surface area of the adsorbent was $30.3\mu\text{m}^2$ (Table 2). The Thorns normal diameter was in range $10 < D < 20\mu\text{m}$ and the adsorbent was classified as a mesoporous material. Similarly, reported BET surface areas of $2\mu\text{m}^2$ and $2.52\mu\text{m}^2$ for activated carbon from macadamia nuts used for phenol removal and maize tassels for heavy metal removal from polluted waters, respectively although adsorbents with higher surface areas have been widely reported in literature.

Table 2: Grain Statistics

Data channel: Topography forward
Number of grains: 121
Total projected area (abs. $30.3\mu\text{m}^2$)
Total projected area (rel.): 1.66 %
Mean grain area: 251×10^{-15} m^2
Mean grain size: $0.41\mu\text{m}$
Total grain volume (zero): $39\mu\text{m}^3$
Total grain volume (minimum): $1.27\mu\text{m}^3$
Total grain volume (laplacian): $1.50\mu\text{m}^3$
Total projected boundary length: $191\mu\text{m}$

Used 1g of milled Thorns to adsorption Pb(II) ions onto the surface of Thorns using mechanical shaker at 25°C and speed at 200 rpm. The adsorbent dosage effect was investigated by changeable the adsorbent initial mass between (5–100) g. The most favorable dosage obtained was used for consequent process. Likewise, the pH effects, Pb(II) initial concentration removal was initiated by contacting (0.0 to 5.0) g of the adsorbent with a 100 mL Pb(II) solution in a closed cylindrical plastic vessel of 250 mL volume. and (5–120) min, respectively. The percentage removal of Pb(II) ions from aqueous solution was estimated by using Equation (1):

$$\text{Adsorption}(\%) = \frac{[C_i - C_f]}{C_i} \times 100 \quad (1)$$

where, C_i and C_f are the final and initial metal ions concentrations, respectively.

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

where, q_e is the amount of metal adsorbed in mg/g, C_i and C_e represent initial and equilibrium concentrations of metal ions in aqueous phase. V is the volume of the solution in liters (L) and w is the weight of the adsorbent used in grams.

Adsorbate solution

Lead solution was prepared by using the Lead sulfate ($\text{PbSO}_4 \cdot 6\text{H}_2\text{O}$) in an analytical mark (Molar mass of $\text{PbSO}_4 \cdot 6\text{H}_2\text{O}$ is 411.3543 g/mol)(Table 3). The solution of Pb^{+2} ions was prepared to containing 1000 mg/L of Pb^{+2} ions. In the study all solutions prepared by double distilled water. Sulfuric acid and sodium hydroxide solutions with 1M concentration were used to adjust the pH value.

Temperature Studies

The temperature effect on the Pb(II) adsorption was studied through changeable the doses of adsorbent starting 0.1 to 1.0 gm on initial concentration of Pb(II) 50 mg /L, with constant volume (50 ml) of the solution. These beakers were reserved into water bath shaker at diverse temperatures (30, 40 and 50°C) used for 5hr and after that filtered.

Table 3: Elemental composition of PbSO₄.6H₂O

Symbol	Element	Atomic weight	Atoms	Mass percent
Pb	Lead	207.2	1	50.3702 %
S	Sulfur	32.065	1	7.7950 %
O	Oxygen	15.9994	10	38.8945 %
H	Hydrogen	1.00794	12	2.9404 %

pH Studies

Pb(II) solution in 50 ml volume, containing 50 mg /LPb(II) was in use in a glass as well as adjusted the solution through adding 0.1 M H₂SO₄ or 0.1 M NaOH with pH meter, after that The solution treat with the adsorbent in 0.5g after the equilibrium achievement and final Pb(II)concentration determined. The % adsorption calculated from Eq.(1) by subtract initial concentration from final concentration. The equilibrium or final also record. To study electrolyte effect, similar method repeat with(50 mg/L)solution ofPb(II)setwithinKNO₃(0.5M).

Study the Capacity of Breakthrough

The study used glass column was taken 1gm adsorbent. Pb(II) ions solution in 50 mg/l concentration and 1000ml, the flow rate in the column was 10mL/min initial concentration (C₀) was passed through . In 500 mL fractions the effluent was collected and to the (AAS). By plotting volume versus C/C₀ of the effluent was obtained the capacity curve of breakthrough.

Electrolytes Studies

The different electrolytes effect likes Na₂SO₄,CaSO₄, NaHCO₃, NaCl , MgSO₄and H₂SO₄on the adsorption of Pb(II) was investigated. Solution in 50 ml volume and (50 mg/L)Pb(II) concentration was ready on top of electrolytes treat through 0.5 g of adsorbent. The Pb(II)quantity adsorbed in these electrolytes attendance were after that determined because its describe before.

Adsorption Study

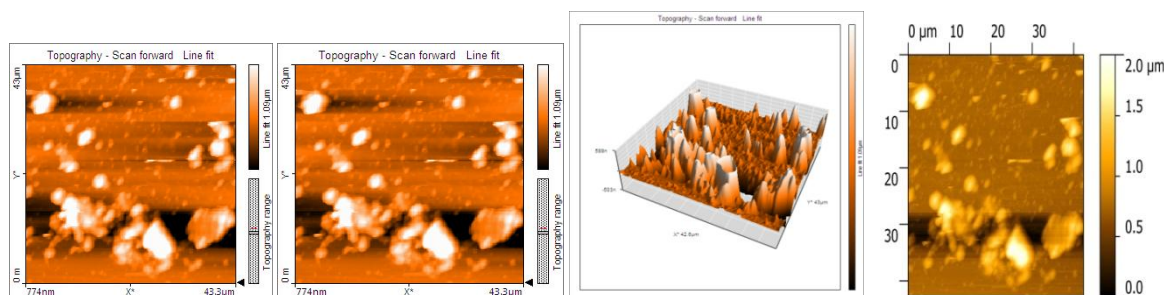
Adsorption investigations were conveyed out by clump procedure. The measure about 0.5g adsorbent might have been set for a tapered flask to which 50 mlPb(II) result for fancied focus might have been included to a 250mL tapered the mixture and flask might have been shaken over temperature-controlled shaker hatchery to 24hr. For filtration paper used filter paper (No.50) kind (Whatman). The final solution of metal ions in the filtrate analyzed by atomic Absorption spectrophotometer (AAS). Total Pb(II)ions adsorbed was intended with subtract last concentration from first concentration.

RESULTS AND DISCUSSION

Infra-red Spectroscopy: The results from the Fourier transform infra-red showed a broad peak at 4000 cm⁻¹ with a high transmittance frequency, which can be attributed to either -OH or -NH groups. As shown in Fig. 1, the band observed at 3000 cm⁻¹ is possibly due to C-H stretching vibrations of saturated aliphatic compounds , while the band at 2865 cm⁻¹ can be attributed to -NH bending vibration of primary amines .

A small peak was observed at 1725 cm⁻¹ and corresponds to the (C-C) stretching vibrations of aromatic rings . The peaks observed at 1373 cm⁻¹,1319 cm⁻¹ and 1242 cm⁻¹ corresponds to the C-O stretch of alcohols, carboxylic acids, esters or ethers. The absorption band at 831 cm⁻¹ can be due to the presence of an alkyl halide.

Also confirmed that mucilage extracted from Diceriocaryum species contains carboxyl functional group. The presence of acidic functional groups is responsible for its adsorptive property. The stated clearly from their studies of natural plant materials that the biochemical characteristics of acidic functional groups are responsible for their metal ion uptake[29].



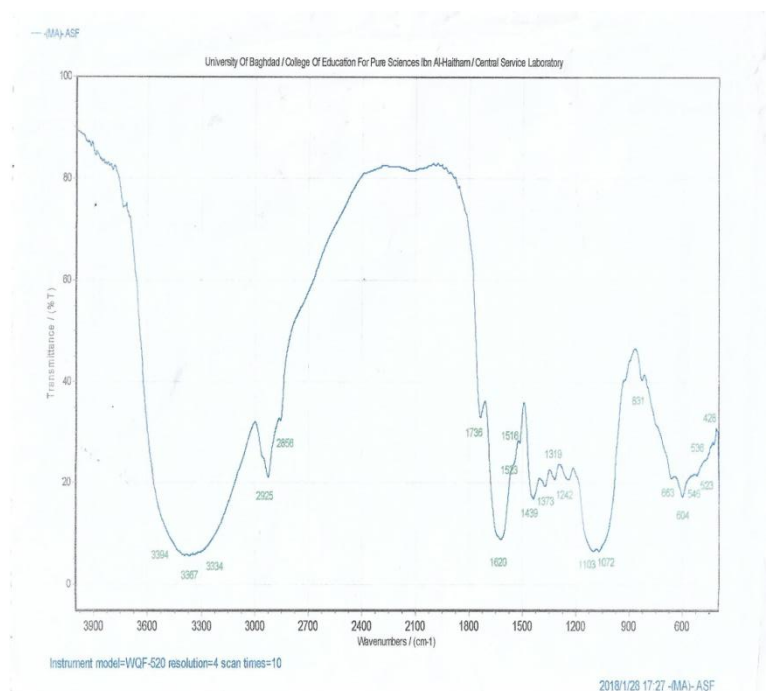


Fig.1: Results from the Fourier transform infra-red

Zero Charge Point

The zero charge point of the adsorbent was determined by addition of solid method . 50 mL DDW transfer to a sequence of beakers and these solutions has initial pH adjusted roughly among 1 to 10 with each 0.1 M NaOH or 0.1 M H₂SO₄ solution. The solutions in these initial pH was correctly record, after that add 0.5 g adsorbent to every beaker and allowable the mixture 24 h to equilibrate, with irregular manual trembling. The supernatant solution final pH was then noted [29].

Effect of pH

The %Pb(II) adsorption increased by raise the initial pH and reach to greatest pH at 6. Adsorption also affected with final pH or the equilibrium solution pH. The adsorption mechanism can be explain on the initial pH basis, equilibrium pH, the adsorbent surface charge and the metal speciation. The effect of pH on Pb(II) ions adsorption onto Thorns is shown in **Fig.2**. Lead(II) ion elimination was fast affected by change in the equilibrium solution pH. Adsorption of Pb(II) was 40 % at pH 1, 65% at pH 4, 90% at pH 5 and 98.5% at pH 6. The removal efficiency was decrease in experiential at pH value of after 7 (90%) and 75% at pH 8. This may be because at and after pH 7 [Pb(II) exist as Pb⁺² ions (in great amount) with the formation of Pb(OH)₂ (tiny amount)]. The maximum adsorption of Pb⁺² ions occur at pH=6. Higher values of pH (pH>7), Pb⁺² ions started precipitation [30].

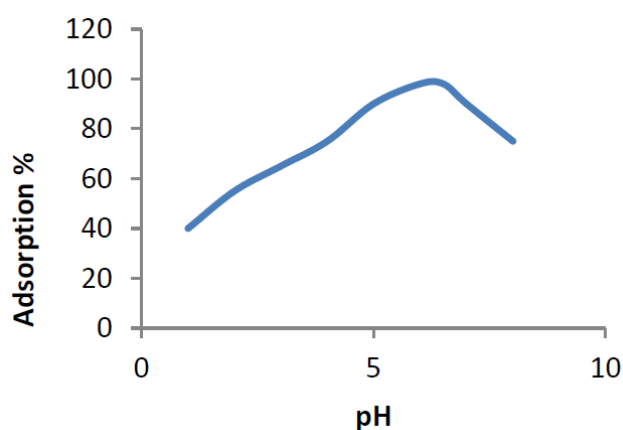


Fig. 2: Effect of pH on the adsorption efficiency of Pb(II) ions onto Thorns

Breakthrough Capacity

The most efficient column method creating the best use of the concentration gradient between the residual in the solution and that solute adsorbed by the adsorbent is breakthrough curve. The column is operational until the metal ions in the effluent start appearing and for practical purposes the working life of the column is over called breakthrough point. That is essential in the method design since it straight affect the possibility and process economics Fig.3 show to Pb(II) solution in 220 mL could be passed through column with none detect Pb(II) in the waste matter. The capacity of breakthrough be establish to be 45 mg/g.

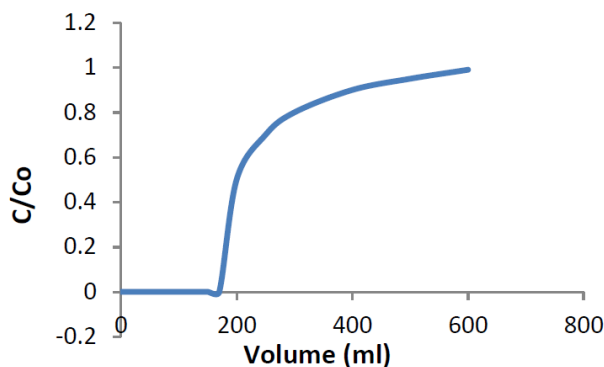


Fig. 3: Breakthrough curve of Pb(II)

Contact time and Pb(II) Initial Concentration Effect

The contact time Effect on the adsorption of Pb(II) ions was determined through analyze the remaining Pb(II) into solution after contact time starting (5 to 300) min. Batch process Experiments were perform using at room temperature. 1gm add of adsorbent to 100ml solution in diverse Pb(II) initial concentrations (10–50 mg/L). The Samples were withdrawn from beakers after specific time period and analyze for remaining metal content. The metal mechanism uptake normally depends on the adsorbent mass that contact with the heavy metals initial concentration. Small concentrations the specific site is dependable for adsorption, whilst in case of increase concentrations of metal the specific site is saturated with adsorption sites are packed. The Pb(II) initial concentration effect on the amount of adsorption that is shown in Fig.4. Increasing adsorption with time and achieve maximum for all the concentrations. Capacities of the adsorption 10, 30 and 50 mg/l, initial Pb (II) concentrations were establish to be 2.4, 2.7 and 3 mg/g, respectively. Increasing driving force by means of increasing Pb(II) ions concentration might be causes this result. The metal ions uptake at any particular concentration increased with contact time. Fig.4 show that the rate is rapid then it slow down awaiting it reach stability. This is due to the fact that a great amount of residual vacant plane site is obtainable for adsorption through first step by the time raise, the residual vacant plane site is not easy to be in use because of disgusting forces between the bulk phases and solute molecules on the solid. On the other hand, by increasing Pb(II) ions initial concentration also increasing the contact time and need to achieve equilibrium. From experimental the equilibrium is attain at (50, 15 and 5) min for (50, 30 and 10) mg/L of Pb(II) concentrations, respectively.

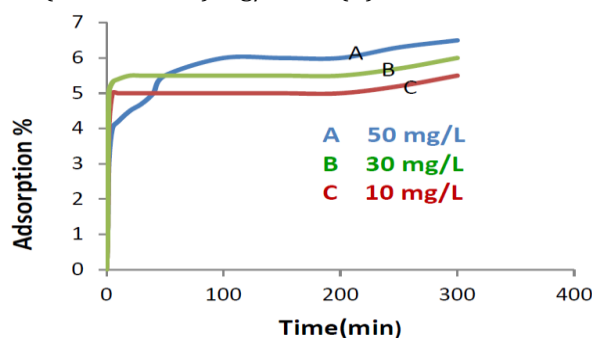


Fig.4: Efficiency adsorption of Pb+2 ions with contact time onto Thorns

Adsorption Isotherms

To optimize the adsorption design system for the Pb(II) ions removal from wastewater, it is significant to give details about association among equilibrium concentration of residual metal ion in solution (C_e) and adsorbed Pb(II) ions per unit mass of adsorbent (q_e). The adsorption isotherm figures study by

correct them to diverse isotherm models of adsorption is significant step to get the appropriate isotherm model of adsorption to use for design purpose. investigational data were fitted within the , Freundlich, Langmuir models at different temperatures. To calculate the data suitability, determination coefficient (R^2) that evaluate between calculated data and experimental data for both model. Consistent with model of Langmuir[31] adsorption occurs on a homogenous surface form adsorbate monolayer with steady adsorption temperature for all sites with no interface among adsorbed molecules . The Langmuir model may be known as linear form :

$$\frac{l}{q_e} = \frac{l}{q_{\max}} + \left\{ \frac{l}{b q_{\max}} \right\} \frac{l}{C_e} \quad (4)$$

where, C_e is the equilibrium concentration ions of Pb(II) in the solution (mg/L), q_e is the Pb(II) adsorbed quantity per adsorbent unit weight (mg /g), q_{\max} is the Pb(II) required amount to form monolayer (mg/g) and b is a constant related to adsorption energy(L/mg) that represent enthalpy of adsorption that differ with temperature. The q_{\max} and b values were calculated at diverse temperatures from the intercept and slope of the linear plots of $1/q_e$ versus $1/C_e$. From this model, the data obtain indicate that is applicability at diverse temperature(30,40 and 50) °C , however data were fixed greatest by high temperatures(40 and 50)°C like indicate through high determination coefficient (R^2). The value of q_{\max} and b increase by rising temperature representing adsorption higher heat by rising temperature and confirm the adsorption endothermic nature. **Fig.5** representing that the adsorption conform to Langmuir model indifferent temperature . The adsorption capacity and the greatest Cr^{+3} ions concentration adsorbed was calculate from the intercept and slope of the scheme. The adsorption process agreement to Langmuir model was determined using Equation (5):

$$R_l = \frac{l}{(1+bC_0)} \quad (5)$$

where, (R_l) separation factor, (C_0) initial concentration of metal (mg/L) and (b) langmuir coefficient (l/mg). $R_l > 1$ indicate an unfavorable adsorption monolayer process, $R_l = 1$ linear, $0 < R_l < 1$ favorable and $R_l = 0$ irreversible. From this study the result obtain is R_l values between (zero to one), representing a favorable adsorption process. This implies that chemisorptions process duly explains the Cr^{+3} ions adsorption onto Thorns.

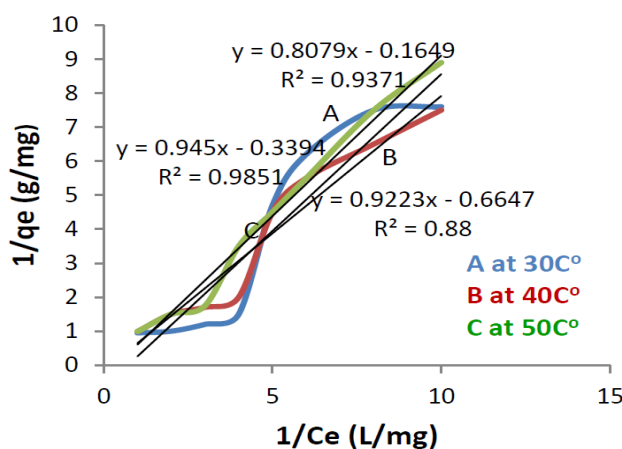


Fig. 5: Langmuir Isotherm adsorption plot for Pb+2 ions onto Thorns in different temperature.

The Freundlich model[32] is an empirical equation based on the adsorption of adsorbate onto heterogeneous surface. The linear form of Freundlich model can be represented as.

$$q_e = K_f C_e^{1/n} \quad (6)$$

where C_e is the equilibrium concentration in mg/L, K_f is the Freundlich constant which indicate the adsorbent qualified adsorption ability correlated to bonding energy and n is the heterogeneity factor representing the difference from linearity of adsorption and is also recognized as Freundlich coefficient. Equation (7) was obtained by taking the logarithm of Equation (6):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

A plot of $\log q_e$ versus $\log C_e$ in different temperature should produced directly line and values of $1/n$ and K_f can be calculated from the slope and intercept. The data obtain from this model indicate that the values of K_f and n increased with the increase in temperature from 30 to 50 °C as shown in Fig.6.

Freundlich model was best obeyed at 50 °C because of high R². The n values between 0.0 and 1.0 indicated favorable adsorption.

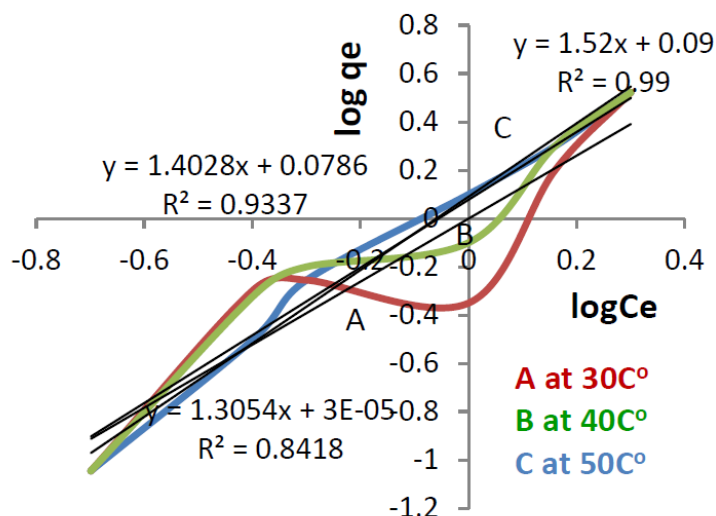


Fig.6: Freundlich Isotherm adsorption plot for Pb+2ions onto Thorns in different temperature.

Adsorption Kinetics

The rate constants were calculated using pseudo-first-order [33] and pseudo-second-order kinetics models. The first-order rate expression is given below

$$\log(q_e - q_t) = \log q_e - \left\{ \frac{K_1 t}{2.303} \right\} \quad (8)$$

where q_e is the amount of Pb(II) adsorbed per unit weight of adsorbent at equilibrium or adsorption capacity (mg/g), q_t is the amount of Pb(II) adsorbed per unit weight of adsorbent at any given time t, K₁ is the rate constant for pseudo-first-order model. The values of K₁ and q_e were calculated from slope and intercept of the linear plot of ln (q_e - q_t) versus t at various concentrations. A plot of log (q_e - q_t) versus t gave straight lines confirming the applicability of the pseudo-first-order rate equation Fig.7.

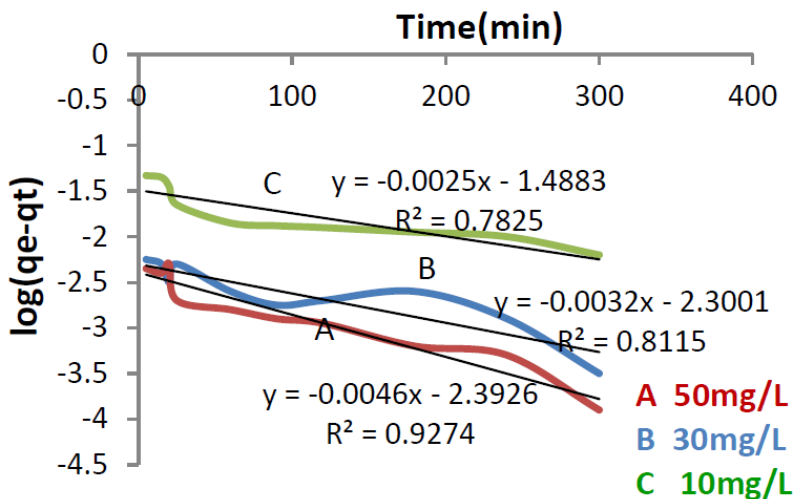


Fig.7: Pseudo first order kinetics for Pb+2ions adsorption onto Thorns.

The pseudo-second-order rate expression is used to describe chemisorptions involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange [34]. The pseudo-second-order kinetic rate equation is given as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left\{ \frac{1}{q_e} \right\} t \quad (9)$$

where K₂ is the pseudo-second-order adsorption rate constant in (g/ mg.min). The K₂ and q_e values were calculated from the intercept and slope of the linear plots of t/q_t versus t at various Pb(II)

concentrations. directly line plots of t/q_t versus t indicate the pseudo-second-order model applicability (Fig.8).

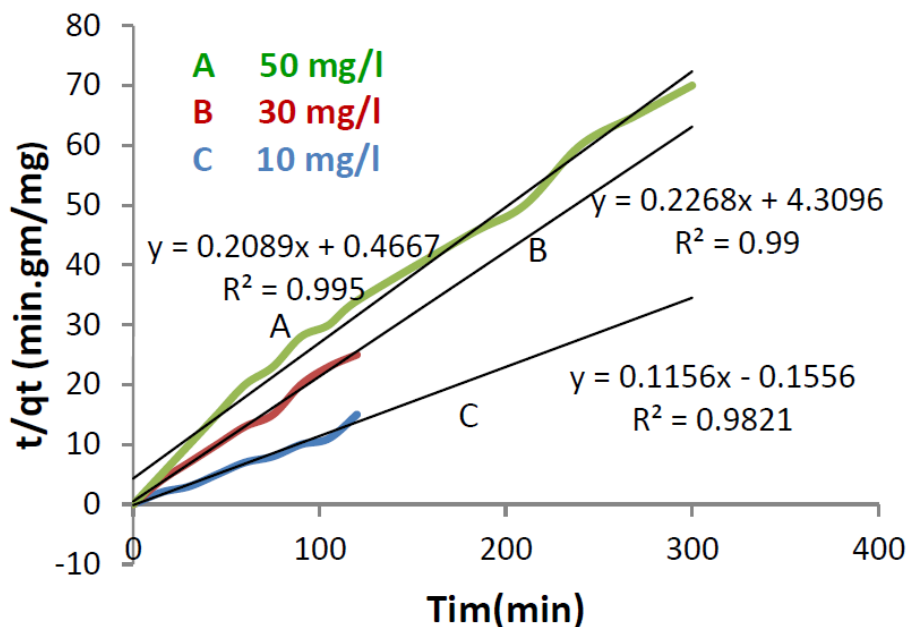


Fig. 8: Pb+2 ions Adsorption onto Thornsby Ho's Pseudo-Second-order model.

Table 3: Pb²⁺ ions Adsorption onto Thornsby Lagergren rate equation constants and Pseudo-second-order rate equation constant.

Concentration	Lagergren rate Equation		Pseudo-second-order rate equation	
	K ₁	R ²	K ₂ g/mg.min	R ²
10 mg/l	0.0025	0.7825	0.1156	0.9821
30 mg/l	0.0032	0.8115	0.2268	0.9900
50 mg/l	0.0046	0.9274	0.2089	0.9950

Table 3 provides data of pseudo-first-order rate constants K₁, pseudo-second-order rate constants K₂, R₂, calculated equilibrium adsorption capability q_e and investigational equilibrium adsorption capability at diverse initial Pb(II) concentrations. It establishes that q_e values from pseudo-first-order model differ significantly from the experimental values showing that the system did not follow pseudo-first-order model. The values of q_e were very close to q_e values in pseudo-second-order kinetic model at different initial Pb(II) concentrations as compared to pseudo-first-order model representing that pseudo-second model was superiorly obeyed. The data also shows that the values of determination coefficient (R²) for pseudo-first-order model (Table 3) are lesser as compared to pseudo-second-order kinetic model at diverse initial concentration values [35].

Thermodynamic Study

The effect of Pb(II) ions adsorption on the temperature was calculated on a temperature range starting 30, 40 and 50 °C. The Gibbs energy change (ΔG°) indicates the degree of spontaneity of an adsorption process, and a higher negative value reflects a more energetically favorable adsorption. Thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using the following relations [34]:

$$\Delta G^\circ = -RT \ln K_c \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

where R is the universal gas constant (8.314 J/mol.K), T is the temperature (K) and K_c is the thermodynamic equilibrium constant without units. The enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption are obtained from the following equation

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

According to Equation (9), (ΔH°) and (ΔS°) parameters can be calculated from the slope and intercept of a plot of $\ln K_c$ versus $1/T$, respectively **Fig.9**.

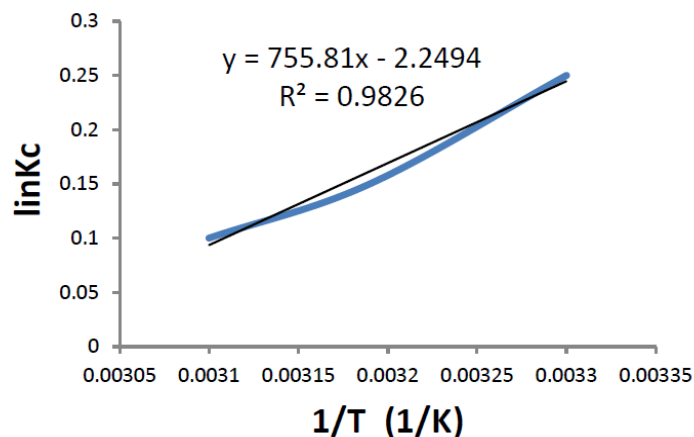


Fig. 9: Thermodynamic Parameters for Pb^{+2} ions Adsorption onto Thorns

These parameters of thermodynamic can present imminent into the kind and method of an adsorption procedure. Free energy ΔG° values change are depressing confirm that adsorption of $Pb(II)$ ions is thermodynamically and natural approving while ΔG° became further negative by raise into temperature (-0.27,-0.39 and -0.63)KJ/mol. at (30,40 and 50) $^\circ C$ respectively, representing high dynamic power and therefore resultant in upper capacity of adsorption by upper temperature. The ΔH° value in positive that indicate the process of adsorption is endothermic (0.756 KJ/mol.). A little but positive value of ΔS° (0.0225 KJ/mol.K) at the range of temperature from 30–50 $^\circ C$ recommended enlarged chance in the interface of solid-solution for the reason that a little molecules of water are dislodge through $Pb(II)$ ions adsorption[35].

Effect of Electrolytes

The contaminated water with $Pb(II)$ also contains a new ions number that may possibly power the adsorption procedure. In this work evaluate the $Pb(II)$ ions adsorption activities within the attendance salted solution in 0.05–0.1 M of different electrolytes like to sulphate, carbonate and chloride separately at the first concentration of $Pb(II)$ ions 50 mg/L. Different electrolytes effect on the $Pb(II)$ ions adsorptions listed in Table 6. $Pb(II)$ ions adsorption is decrease by raise the electrolytes concentration like to Na_2SO_4 , $CaSO_4$, $NaCl$, $NaHCO_3$, $MgSO_4$, H_2SO_4 . That can be qualified to greater than before opposition for adsorption sites between $Pb(II)$ ions and electrolyte ions as well as decrease the $Pb(II)$ ions activity[36]. The electrolytes influence and their result in poisonous pollutants removal using natural materials has been observed in recent past [37,38]. Many studies showed that reduce the metal ions adsorption into the electrolytes ions attendance. However, $Pb(II)$ ions adsorption enlarged by rising Na_2SO_4 concentrations which may be due to raise in final pH of the Na_2SO_4 solution with increased concentration (pH 7–8.5) as report in (Table 4).

Table 4: The % adsorption onto electrolytes Influence of Pb^{+2} ions at 50 mg/L.

Electrolytes	% Adsorption	
	0.05M	0.1M
$MgSO_4$	82	54
Na_2SO_4	95	62
$NaCl$		
$CaSO_4$		
$NaHCO_3$		
H_2SO_4		

CONCLUSION

The adsorption ability of powdered Thorns has been investigated and found effective for the removal of $Pb(II)$ ions from wastewater. The removal concentration was dependent on the time of equilibrium. The experimental results showed that the adsorbent always had a higher capability to adsorb $Pb(II)$ ions and the maximum adsorption could be possible from the aqueous solution at pH 6. At higher temperatures the isotherm of Freundlich, Langmuir were greatest obeyed. The $Pb(II)$ ions adsorption was affected with rising the different electrolytes concentration. Kinetic data show the pseudo-second-order model confirm improved applicability that the $Pb(II)$ ions adsorption was nature chemical sorption. Thermodynamic

data indicate the Pb(II) ions adsorption was endothermic and natural. Column experiments showed that the breakthrough began at 220 mL .

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REFERENCES

- [1] An, H. K., Park, B. Y. and Kim, D. S. (2001). Crab shell for the removal of heavy metals from aqueous solution. *Water Res.*,35, 3551-3556.
- [2] Mohammed Jaafar Ali Alatabe, Ahmed Alaa,(2017). Isotherm and Kinetics studies, Adsorption of Chromium(III)Ions from Wastewater Using Cane Papyrus. *Themed Section: Engineering andTechnology*, 3,2394-4099.
- [3] V.Mavrov ,S.Stamenov, E.Todorova, H.Chmiel and T.Erwe(2006).New hybrid electrocoagulation membrane process for removing selenium from industrial wastewater.201(1-3),290-296.
- [4] Mlayah, S. Jellali, (2015). Study of continuous lead removal from aqueous solutions by marble wastes: efficiencies and mechanisms. *Int. J. Environ. Sci. Technol.* (2015)12:2965–2978.
- [5] Myzairah H., Zaini U., Mohamed N., Tony H., Gustaf O., Hashim H. and Nurfarhain . R.,(2013).Optimization of Parameters Affecting Adsorption of Nickel (II), Zinc (II) and Lead (II) on Dowex 50 W Resin Using a Response Surface Methodology Approach. 6 (3): 106-118.
- [6] E. Kurt, O. Gecici, M. Serteser, Ö. Güler, (2007). The effects of electroconvulsive therapy on ghrelin, leptin and cholesterol levels in patients with mood disorders. *Neuroscience Letters* Nov. 2007 426(1):49-53. DOI: 10.1016/j.neulet.2007.08.018.
- [7] Alatabe, M. J. (2012). Removal of Lead Ions from Industrial waste Water. *Journal of Environmental Studies*, 9:1-7.
- [8] Mohammed Jaafer Ali Alatabe, Crystallization in Phase Change Materials. *IJSRSET* 2018,4(1), 93-98.
- [9] A. Dubey • S. Shiwani,(2012). Adsorption of lead using a new green material obtained from Portulaca plant . *Int. J. Environ. Sci. Technol.* (2012) 9:15–20 DOI 10.1007/s13762-011-0012-8.
- [10] Berhe S., Ayele D., Tadesse A., Mulu A.,(2015). Adsorption Efficiency of Coffee Husk for Removal of Lead (II) from Industrial Effluents: Equilibrium and Kinetic Study. *International Journal of Scientific and Research Publications*,2015, 5(9).
- [11] OuYang, X.-K., Yang, L.-P., and Wen, Z.-S. (2014). "Adsorption of Pb(II) from solution using peanut shell as biosorbent in the presence of amino acid and sodium chloride," *BioRes.* 9(2), 2446-2458.
- [12] R. Shiralipour,T. Hamoule and K. Manochehripour, (2018) . Research Article Removal of Pb (II) From Contaminated Water by Bagasse Adsorbent Modified with Dithizone. *Jundishapur J Health Sci*July; 10(3):e62360. Published online 2018 June 27. doi: 10.5812/jjhs.62360..
- [13] T. Naiya,A. Bhattacharya,S. Mandal,S. KumarDas, (2009). The sorption of lead(II) ions on rice husk ash. *Journal of Hazardous Materials*,2009, 163,(2-3), 1254-1264
- [14] S. Yadla1, V.Sridevi and ,C.Lakshmi,(2012). Adsorption Performance Of Fly Ash For The Removal Of Lead. *International Journal of Engineering Research & Technology.* 2012,1(7).
- [15] Alatabe, M. J., Adsorption of Copper (II) Ions from Aqueous Solution onto Activated Carbon Prepared from Cane Papyrus. *Pollution*, 2018,4(4): 649-662.
- [16] Senthil Kumar Ponnusamy, (2015).Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: Optimization by response surface methodology. *Water Resources and Industry*, (2015), 11(C):64-70. DOI: 10.1016/j.wri.2015.07.002
- [17] C. Siripatana, A. Khuenpetch, R. Phromrak, W. Saengngoen and K. Nuithitikul,(2017). Kinetic Study of Adsorption of Lead (II) Ions onto Cashew Nut Shells. *Journal of Engineering and Applied Sciences.* 2017,12(7);1819-1824. DOI: 10.3923/jeasci.2017.1819.1824.
- [18] X.Yang,L.Yang,Z. Wen(2014).Adsorption of Pb(II) from Solution using Peanut Shell as Biosorbent in the Presence of Amino Acid and Sodium Chloride.*Bioresources*,9(2),Mar. 2014.
- [19] Kelly B., Payne, and Tarek M. Abdel-Fattah(2004). Adsorption of Divalent Lead Ions by Zeolites and Activated Carbon: Effects of pH, Temperature, and Ionic Strength. *JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH Part A—Toxic/Hazardous Substances &*

- Environmental Engineering Vol. A39, No. 9, pp. 2275–2291, 2004.DOI: 10.1081/LESA-200026265.
- [20] M. Erdem, S.Ucar, S. Karagöz, and T. Tay,(2013). Removal of Lead (II) Ions from Aqueous Solutions onto Activated Carbon Derived from Waste Biomass. *The Scientific World Journal*, 2013, Article ID 146092, 7 pages. <http://dx.doi.org/10.1155/2013/146092>
- [21] N. QUYEN, T. TUYEN, D. KHIEU, H. HAI, D. TIN, P. LAN and I. KIYOSHI(2018). Lead ions removal from aqueous solution using modified carbon nano-tubes .*Bull. Mater. Sci.* (2018) 41(6). <https://doi.org/10.1007/s12034-017-1541-7>.
- [22] Mohammed Jaafar Ali Alatabe, A Novel Approach for Adsorption of Lead(II) Ions from Wastewater Using Cane Papyrus.*Journal of petroleum research & studies* No.18, Jan. 2018, pp.29-42.
- [23] M. Tehrani, P. Azar , P. namin, S. Dehaghi,(2014). Removal of Lead Ions from Aqueous Solution Using Multi-Walled Carbon Nanotubes: The Effect of Functionalization. *J. Appl. Environ. Biol. Sci.*, 2014, 4(2)316-326.
- [24] Q.Yao,J. Xie, J. Liu, Y. Liu,(2014). Adsorption of lead ions using a modified lignin hydrogel. *Journal of Polymer Research*.Jun. 2014, 21(6). DOI: 10.1007/s10965-014-0465-9
- [25] J. Olivares, G.Barrera, C. Alonso, C. Díaz, M. Mercado, and F. Núñez,(2016). Adsorption of Lead Ions from Aqueous Solutions Using Gamma Irradiated Minerals. *Journal of Chemistry*, Vol. 2016, Article ID 8782469, 7 pages. <http://dx.doi.org/10.1155/2016/8782469>.
- [26] F. D. Alsewailam, S. A. Al-Dzhilil,(2016). Synthetic polymers and their blends for removing lead from aqueous solutions.*Journal of Water Chemistry and Technology*. Mar. 2016,38 (2),89–95.
- [27] R. Wolfová , E. Pertile and P. Fečko,(2013).Removal of lead from aqueous solution by walnut shell.*Journal of Environmental Chemistry and Ecotoxicology*, Jun.2013,5(6),159-167,
- [28] Mohammed Jaafar Ali Alatabe, Ahmed Alaa Hussein. Adsorption of Nickel Ions From Aqueous Solution Using Natural Clay. *Al-Nahrain Journal for Engineering Sciences*.2018,21(2), 223-229.
- [29] B.M. Babic, S.K. Milonjic , M.J. Polovina, B.V. Kaludierovic(1999). Point of zero charge and intrinsic equilibrium constants of activated carbon cloth. *Carbon*. 1999, 37, 477–481.
- [30] Mohammed Jaafar Ali Alatabe, Phase Change Materials for Thermal Energy Storage. *Journal of Petroleum Research & Studies*, 2012, NO.5 , E-69-E-93.
- [31] Langmuir I (1916) The constitution and fundamental properties of solids and liquids. *J Am ChemSoc* 38:2221–2295, (76 pages)
- [32] Freundlich HMF (1906) Over the adsorption in solution. *J Phys Chem*57:385–471,(87 pages).
- [33] Lagergren S (1898) About the theory of so called adsorption of soluble substances. *Kun Sven VetenskapademHandl*. 24:1–39,(40 pages).
- [34] Mohammed Jaafar Ali Alatabe, A Novel Approach for Adsorption of Copper(II) Ions from Wastewater Using Cane Papyrus. *International Journal of Integrated Engineering*, 2018,10 (1), 96-102.
- [35] Ho YS, McKay G (1998) A comparison of chemisorptions kinetic models applied to pollutant removal on various sorbents. *ProcSaf Environ Prot* 6:332–340, (9 pages).
- [36] A.Rouff, R.Reeder,N.Fisher,(2005). Electrolyte and pH effects on Pb(II)–calcite sorption processes: the role of the PbCO₃(aq) complex. *Journal of Colloid and Interface Science* (2005) 286(1):61-67.
- [37] F. Ghamouss ,D. Lemordant and L.Monconduit,(2015) Efect of Adsorption or Electro-Adsorption of Electrolyte Components at Interfaces on the Electrochemical Performances of Li-Ion Batteries. *ECS Trans.* 2015, 64(24), 1-9. doi: 10.1149/06424.0001ecst
- [38] A.Selatnia, A. Boukazoula, N. Kechid, M.Z. Bakhti, A. Chergui, Y. Kerchich(2004). 135 Biosorption of lead (II) from aqueous solution by a bacterial dead *Streptomyces rimosus* biomass. *Biochemical Engineering Journal* 19 (2004) 127– 135. doi:10.1016/j.bej.2003.12.007.