Study the adsorption of lignin on surface of poly vinyl chloride

Zainab Naeif Majeed
Polymer Research Unit , College of Science
Al-Mustansiriya University

Abstract

In this work, polyvinyl chloride(PVC) was utilized as a strong adsorbent for the expulsion of lignin from fluid arrangement utilizing a shower techniques. The got an outcome infer that the lignin adsorbs onto PVC are driven by entropy impact, exothermic and nonspontaneous forms, additionally, the outcomes have as demonstrated that Freundlich isotherm fitted a harmony information well. as per Dubinin – Radushkevich isotherms the adsorption limit of PVC (qmax) is ٢,٨٣٠٣ mg/g, the mean free vitality (EDR) esteem an ascertained by examinations of a balance information with Dubinin – Radushkevicha condition show that the adsorption components are hydrogen holding .the lignin was expelled by (٣٩,٢٪) at PH measure up to ٢ and at ٣٠ C^o .

Key word: lignin, poly vinyl chloride, adsorption

Introduction

Lignin as a standout amongst the most bounteous natural polymers on the earth is the by – result of paper and rising cellulose ethanol enterprises .it is a nebulous (i.e. it has no long-run request of molecules), profoundly cross – connected and a sweet-smelling polymer of phenyl propane joins together ,with a complex basic heterogeneity that makes up its specific protection from microbial debasement .besides it might contain hydroxyl, ether and carbonyl gatherings. Many investigations have demonstrated that lignin can possibly act like an adsorption material because of its high adsorption limit[١,٢] . Also, lignin adsorption limit can be improved by concoction techniques, for example, the expansion of practical gatherings or cross-linking[٣].

In this way the surface lignin has attracted expanding consideration late years. Surface lignin focus has been accounted for to be three to five time higher than the comparing mass lignin fixation for both Kraft softwood and Kraft hardwood pulp[٤,٥]. These high surface lignin fixations have incited various discourse and theory about the impact if surface lignin on ensuing procedures, for example, fading and between fiber holding. Lain and Stenius[٦] found that surface lignin strongly affected fading stages. The

adsorption of material, for example, Xylan and lignin on mash filaments amid pulping has been accounted for in a few studies[٧].however, the instrument of this procedure isn't yet evident. it has been named as re-testimony retake, sorption, and precipitation, which demonstrates some shows some irregularity in understanding the essentials included. The goal of this examination to acquire a comprehension of the balance and thermodynamic adsorption of lignin on PVC. The Freundlich, Dubnin – Radishkeich and summed up isotherm conditions were utilized to analyze the harmony information. The impacts of time, temperature, fixation and PH of the arrangement are examined. The point of this work to think about the capacity of PVC as a surface to expel the lignin as mechanical waste from the contamination water.

Experimental materials and methods

The lignin utilized was (B.D.H Co.),as abundant of dirty was without facilitate purging .the adsorption isotherm share been dictated by permitting contamination arrangement of know starting focus to be blended with precisely weighted measure of PVC in a firmly shut cup at a specific temperature and PH. The measure of PVC in the slurry has been (٠,٧) gm/١٠ ml arrangement. A consistent blending at a steady temperature and PH was accomplished utilizing a shaker water shower. The pre-arrangement have been balance for one ٦٠ minutes. Polymer subjected to examination utilizing ultra violet-noticeable system (UV-VISBLE) at (٢١٨) nm, the same exploratory was accounted for at various starting focus , temperatures and PH.

The measure of lignin adsorbed in mg/g was computed utilizing the accompanying condition ٢:

$Qe = V(Co-Ce) / ms$…….(١)

Where Qe is the amount of adsorbed Cr(VI) on lignin mg/g. $C_{\cdot}$ and C_e are the initial and equilibrium concentration in solution mg/L respectively, and m_s is the mass of PVC.

Equilibrium isotherms

The equilibrium data of lignin adsorption were correlated with the models of Freundlich, Dubinin - Radushkevich and Generalized isotherem equations. The linearized Freundlich equation is shown below:

$\text{Log } q_e = \log K_f + ١/n \log C_e$……..(٢)

Where qe is the measure of lignin adsorbed per unit mass of adsorbent(mg/g), Ce is the balance grouping of lignin is the arrangement (mg/L). The Freundlich recipe in an experiential condition and in like manner, the model accept that the measure of adsorbate on the adsorbent

surface increments by expanding the adsorbate fixation. The most extreme adsorption limit with regards to the Freundlich condition can be controlled by utilizing the articulation given by:

$$\boldsymbol{kf = \frac{qm}{Ce^{1/n}}} \qquad \text{……(٣)}$$

Where log q_m = logq_e when $C_e = C_o$.

Dubinin-Radushkevich isotherem

The linearized Dubinin-Radushkevichequation is shown below:

$$Lnq_e = lnq_m - k\varepsilon^{٢} \qquad \text{……(٤)}$$

The parameter Ɛ can be found from the equation :

$$\varepsilon = RT\, ln[١ + ١/C_e] \qquad \text{……(٥)}$$

Where qe is the measure of lignin adsorbed per unit mass of adsorbent(mg/g),qm is the most extreme adsorption capacity(mg/g).

R is the gas consistent (٨،٣١٤ J.mol-١.K-١) and T is the total temperature .in this way, the Dubinin – Radushkevich isotherm can be utilized anticipate balance adsorption information at deferent temperatures. the model depicts the adsorption of subcritical vapors onto miniaturized scale pore solids following a pore filling system. The mean free vitality adsorption (E) is the free vitality of progress when one mole of particle moved from vastness in the answer for the surface of the sorbent [٨].

E is computed from the estimation of K utilizing the condition :$\boldsymbol{E = \frac{1}{\sqrt{(2K)}}}$

……..(٦)

Generalized isotherm equation:

The linearizedGeneralized isotherm[٩] equation is shown below.

$$\boldsymbol{log\left[\frac{qm}{qe} - 1\right] = logk_G - N_b logC_e} \qquad \text{……..(٧)}$$

Where qe is the measure of lignin adsorbed per unit mass of adsorbent(mg/g),Ce is the balance convergence of lignin in arrangement (mg/L),qmis the greatest adsorption capacity(mg/g). KG is the immersion steady (mg/L), Nb the helpful restricting consistent, the plotted log[(qm/qe) - ١] of versus log Ce was utilized to decide the estimations of KG and Nb from the slant and the block separately.

Result and discussion:

Adsorption study:

The result concerning lignin adsorption by PVC are presented in figure (١) at (٣٠٣) k and PHs (٤،٧and ٩).

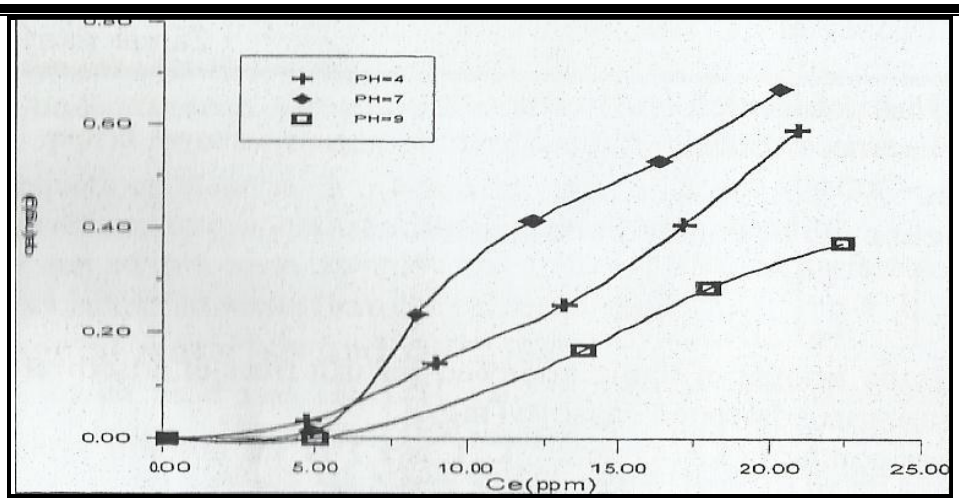

Figure (١): adsorption isother of lignin on PVC at different PHs and at ٣٠٣ k

This figure demonstrates that the solid power of connection amongst lignin and PVC at PH=٧. The outcomes got demonstrated that the adsorption limit (qe)of the two colors diminished with expanding PH and indicated comparable adsorption design.

The outcomes demonstrated that ,the greatest expulsion of lignin with PVC was seen at the lower PH esteems where the holding between lignin with PVC expanded while this holding diminished at higher PH .the measure of lignin adsorbed at harmony is expanded from ١٠,٣٨٪ to ١٦,٥٪ with diminishing the PH from ٩ to ٤, while the present evacuation of lignin in common PH was ١٨,٧٢٤٪.

Adsorption isotherms:

The examination of harmony information is critical to outline and enhance a working system ,and furthermore with a specific end goal to build up a condition that can be utilized to looked at changed adsorption materials under various operational conditions. in the present study,various two parameters adsorption isotherms models; Freundlish and Dubinin-Radushkevich (D-R), conditions ٢ and ٤ were utilized to think about the connection between that harmony focus Ce (ppm) and the sorption balance qe(mg/g), (figure ٢ and ٣). table(١) portrays the isotherm constants and relationship coefficients ($R^{٢}$) of these isotherms for the adsorption of lignin on PVC.

Table (١): Isotherm constants for the adsorption of lignin on PVC

Freundlich isotherm constants			
Kf(mg/g)	١/n	Q_e(mg/g)	$R^{٢}$
٩,٤٦٤٥x١٠$^{-٣}$	١,٤٩٤	١,٩٤٧٩	٠,٩٦٤٢
Dubinin-Radushkevich isotherm constants			
K(mol^{٢}KJ^{٢})	E(KJ/mol)	Q_m(mg/g)	$R^{٢}$

٠,٩٦٣١	٢,٨٣٠٣	٠,٠١٢٦٤٩	٨x١٠-٥

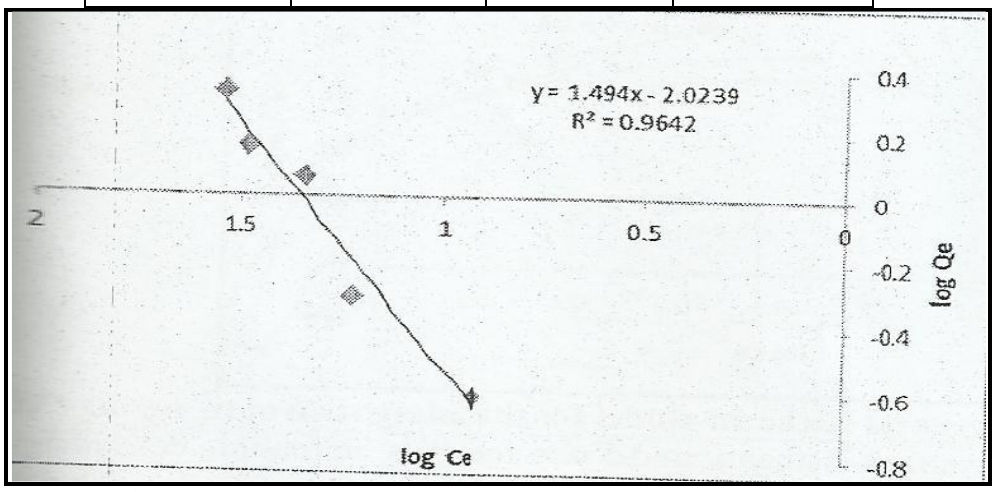

Figure (٢): Freundlich isotherm model for adsorption of lignin on PVC

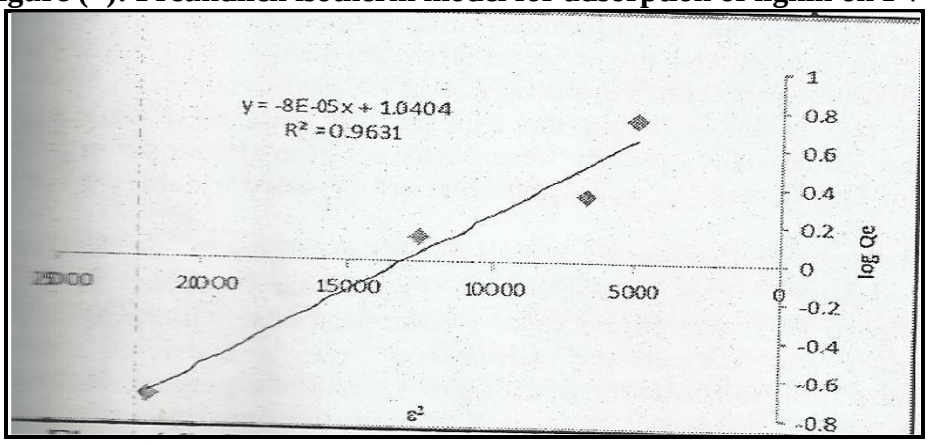

Figure (٣): D-R isotherm model for adsorption of lignin on PVC

The experimental data were further analyzed using the generalized isotherm , figure (٤) shows the plot of {log (q_m / q_e)-١} versus log C_e; the intercept gave log K_G and the slope gave N_b constants.

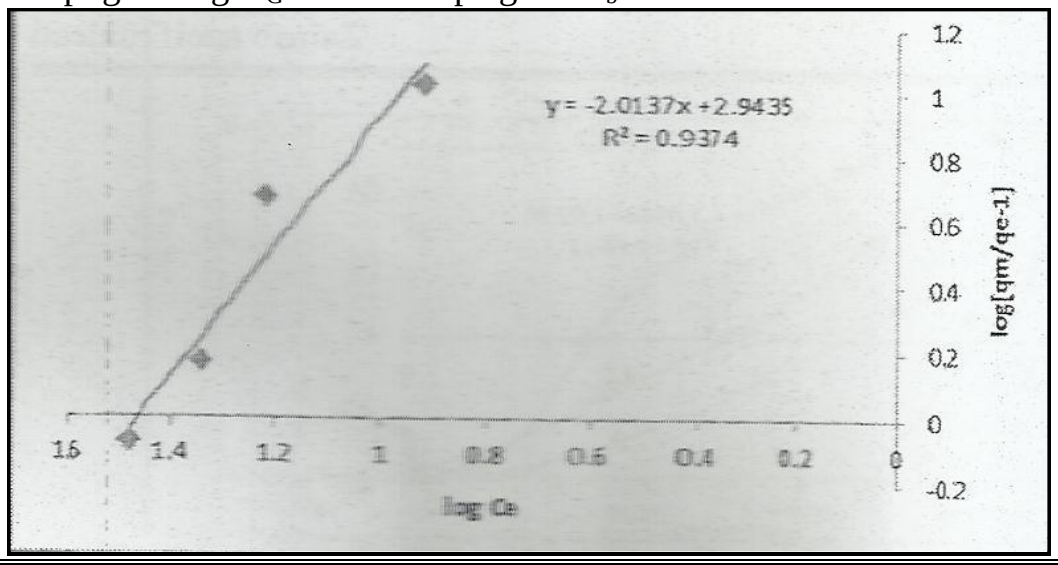

Figure (٤): General isotherm model for the adsorption of lignin on PVC

The summed up isotherm display was observed to be plausible depicting the harmony information with a high connection coefficient (R^2=٠,٩٣٧٤), the estimations of kf and Nb were (٨٧٨,٠١١) and (٢,٠١٣٧) individually. The Freundlich isotherm condition presumes that the adsorbent surface is comprise of restricting site with various restricting vitality and the more grounded site gets involved first and that the coupling quality declines inside wrinkling level of locales occupation [١٠].

Results demonstrate that the model is fitting the exploratory – information well with high connection R^2,the estimations of Kf and ١/n were acquired from the incline and the capture of the plot Log Ce and log qe separately and revealed in table (١) and figure(٢).

The incline ١/n means that the surface heterogeneity or surface intensity[١١],the estimation of ١/n got from Freundlich isotherm for the adsorption of lignin on PVC was observed to be more prominent than one ,which demonstrates that the adsorption was agreeable adsorption ,which includes solid associations between the atoms of adsorbate[١٢] and the percent evacuation (R%) of lignin by PVC was likewise assessed at beginning focus ٥٠ ppm which equivalent to ٣٩,٢٪.

Effect of temperature

The underlying rate of adsorption is diminished by an expansion in temperature, the adsorption limit is diminished with increments of temperature the getting away inclination of particles from the interface , and in this way lessens the degree of adsorption, a decline in the rate of lignin adsorption from decreases the time required to achieve equilibrium[١٣] as observed in figure(٥).

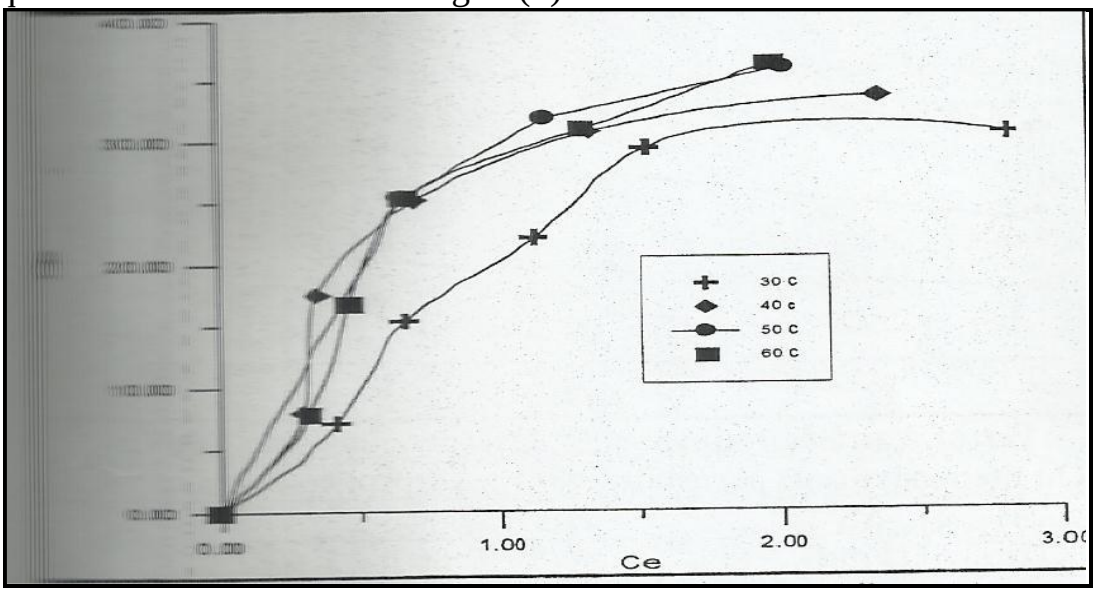

Figure (٥): Adsorption of lignin on PVC at different temperature

In order to evaluate the efficiency of the removal process of lignin by pvc ,thermodynamic parameters including ΔG^o (KJ.mol^{-1}),ΔH^o (KJ.mol^{-1}) and ΔS^o (J.mol^{-1}.K^{-1})were calculated by applying the following of equation(١٤):

$$lnK_d = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{.....(٨)}$$

$$K_d = q_e/C_e \quad \text{.....(٩)}$$

$$\Delta G = -RTlnK_d \quad \text{.....(١٠)}$$

Where kd is the adsorption conveyance coefficient, Ce is the focus (mg/L) of remained lignin in the arrangement at balance, R is the widespread gas steady (٨,٣١٤J.mol-١. K-١) and T is the total temperature which lies in the range (٣٠٣-٣٣٣)k in this examination. The ΔGo esteem shows the level of the immediacy of adsorption process and the little positive esteem reflects less vigorously ideal adsorption. The ΔHo and ΔSo esteems are gotten from the slant and block of the plot of ln Ko versus ١/T as appeared in figure (٦). The estimations of relationship coefficients (R٢) at acidic PH and the thermodynamic parameters are given in table(٣).

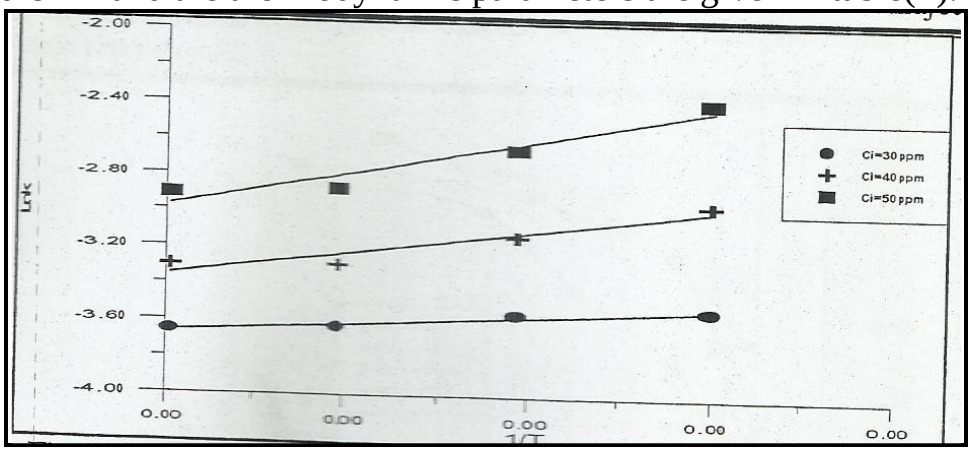

Figure (٦): Plot of Vant Hoff equation for adsorption of lignin on PVC

Table (٣): The thermodynamics parameters for the adsorption lignin on pvc

C_o(ppm)	ΔH^o (KJ.mol^{-1})	ΔS^o (J.mol^{-1})	ΔG^o(KJ.mol^{-1})				R^2
			٣٠C^o	٤٠C^o	٥٠C^o	٦٠C^o	
٣٠	-٣,٨٣٤	٤١,٩٣١	٧,٤٦٧	٩,٢٥٢	٩,٧٤٥	١٠,١١٨	٠,٩٥٧٩
٤٠	-١٠,٢٤٧	٥٨,٦١٠	٧,٤٣٦	٨,١٤٦	٨,٨٤٣	٩,١٣٩	٠,٩١٥١
٥٠	-١٥,٣٠٩	٧٠,٦٨١	٥,٩٩٩	٦,٨٩٦	٧,٧٢٣	٨,٠٥٥	٠,٩٣٦٩

As indicated by the outcomes recorded in the table (٣), the estimation of ΔGo demonstrates that the adsorption procedure of lignin happened non immediately. The negative estimations of ΔHo affirm the exothermic idea of adsorption(١٥).

The negative estimation of ΔSo of lignin recommends positive adsorption[١٦]. The positive estimations of entropy describe the expanded issue of the framework, because of loss of the water which encompasses the lignin particles at the sorption of PVC. This could propose that the main impetus of the adsorption procedure is by entropy impact. This perception was shown by another trial result[١٧].

Conclusions:

This expulsion of lignin from their fluid arrangements by adsorption on PVC is led. The impact of contact time at various PH arrangement is resolved .the outcomes demonstrated a sharp increment in the take-up level in the initial ٥ minutes. The rate of adsorption is then achieved balance inside a hour for lignin.

The direct connection coefficients of Freundlich and Dubinin-Radushevich were gotten and comes about have demonstrated that Freundlich isotherm fitted the balance information well.

Examination of adsorption limits is completed at various PHs.it was discovered that the expulsion limit of the lignin is higher in the acidic medium.

The thermodynamic parameters of the adsorption framework are assessed in the scope of ٣٠٣-٣٣٣K and at various pHs. The acquired outcomes demonstrated that the adsorption could happen non precipitously and is exothermic in nature. The estimations of ΔSo gave a sign of the expansion in the confusion of the considered framework and proposed that, the adsorption procedure could be driven by entropy change.

References

١. Xueyan Guo, Shuzhen Zharg and Xiao-quanShan,"Adsorption of metal ions on lignin", Journal of Hazardous Materials,١٥١,١٣٤,(٢٠٠٨).
٢. Hengky Harmita, Karthikeyan K.G.,and Xuejun Pan ,"Copper and cadmium sorption onto kiaft and organosolv lignins ", Bioresource Technology,١٠٠,٦١٨٣,(٢٠٠٩).
٣. Durga P, KatsutoshiI., Keisuke O., Tatsuya O., Atsushi M., Masamitsu F., and Kenjiro M., "Adsorption of heavy metals on crosslinked lignocatechol : a modified lignin gel Reactive and Functional Polymers", ٦٢,١٢٩, (٢٠٠٥).
٤. Laine ,J. and Stenius, P., "Surface Characterization of Unbleached Kraft Pulps by Means of ESCA", Cellulose , ١,١٤٥,(١٩٩٤).
٥. Heijnession , A., Simonson, R. and Westermark, U., "Removal of Lignin-rich Surface Material from Unbleached Kraft Fibres", Holzforscchung, ٤٩(٤),٣١٣,(١٩٩٥).

٦. Laine,J.and Stenius ,P.,"The Effect of ECF and TCF Bleaching on the Surface Chemical Composition of Kraft Pulp as Determined by ESCA", Nordic Pulp Paper Res.J.,٣,٢٠١,(١٩٩٦).
٧. Alexander M., "The Retake of Xylan during Alkaline Pulping:A Critical Appraisal of the Literature", Holzforschung , ١٩, ١١٨, (١٩٦٥).
٨. Ahmed El Nemr , Azza K., Ola A and Amany El –Sikaily. "Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed", Journal of Hazardous Materials,١٥٢,٢٦٣,(٢٠٠٨).
٩. Fikret K .,and Serpil O., "Biosorption performance of powdered activated sludge for removal of different dyestuffs Enzyme and Microbial Technology",٣٥,٢٦٧-٢٧١,(٢٠٠٤).
١٠. Khambhaty Y., Mody K., Basha S., and Jha B.,"Kinetics , equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine Aspergillus niger",Chemical Engineering Journal, ١٤٥, ٤٨٩, (٢٠٠٩).
١١. Khezami L., and Capart R., "Removal of chromium (VI)from aqueous solution by activated carbons : kinetic and equilibrium studies ,Journal Hazard Mater,.B١٢٣,٢٢٣,(٢٠٠٥).
١٢. Foo and K.Y., and Hameed B. H.,"Insight into the modeling of adsorption isotherm system ",Chemical Engineering Journal,١٥٦,٢,(٢٠١٠).
١٣. Mc kay G.,"The removal of color from effluent using various adsorbents-III silica : pate processes", Water reseach,١٤,١٥, (١٩٨٠).
١٤. Emad A.S. Al-Hyali, Faiz M.Al-Abady, and Ihmood K.H.J, "Thermodynamic and Kinetic Study Of Benzothiozoles Derived dyes Adsorption by Activated Carbon",National Journal of Chemistry,٤٠,٦٨٠-٦٩١,(٢٠١٠).
١٥. Zainab N.M.,SalahA.A,andRashaA.D.,"Study the adsorption of eosin Y dye on Iraqi clay",Journal of Karblaa University ,٢٠١٢,(under press).
١٦. Smith, J. M. ,and Van Ness, H.C.," Introduction to chemical engineering thermodynamics"٤thed.,Mc-Graw Hill, Singapore, (١٩٨٨).
١٧. Suten, D., and Bilba, D.,"Equilibrium and kinetic study of reactive dye Brilliant Red HE-٣B Adsorption by activated charcoal", Acta Chim.Solv.,٥٢,٧٣,(٢٠٠٥).

دراسة امتزاز اللجنين على سطح البولي فاينيل كلورايد

زينب نايف مجيد

وحدة ابحاث البوليمر، كليةالعلوم، الجامعة المستنصرية

الخلاصة

تضمن هذه البحث استخدام فاينيل كلورايد كمادة مازة صلبة لازالة اللجنين من محاليه المائية بطريقة الوجبة الواحد. اشارت النتائج التي تم الحصول عليها ان امتزاز هذه الملوث على (pvc) يسير بتاثيرالانتروبي وان عملية الامتزاز هي عملية الامتزاز هي عملية لا تلقائية وباعثة للحرارة .من خلال ايزوثيرم Dubinin–Radushkevich وجد ان سعة امتزاز ال PVC (qmax) تساوي ٢,٨٣٠٣ والطاقة الحرة المحسوبة من معادلة Dubinin–Radushkevich تشير ان ميكانيكية الامتزاز هي تاصرهيدروجيني. ان النسبة المئوية للجنين المزال كانت ٣٩,٢% عند دالة حامضية (PH) مساوي الى ٢ و بدرجة حرارة ٣٠ درجة مئوية.