Biosorption Studies of Cyanide Ion from Wastes by Spent Black Tea Leaves

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الخلاصة

ان الدراسة الحالية مهتمة لامتزاز ايون السيانيد من المحاليل المائية باستعمال نفايات اوراق الشاي السوداء (SBTL) كسطح ماز للامتزاز عند الاتزان لتراكيز ايون السيانيد بين ٥٠ -٣٠٠ملغم/لتر .تم دراسة تأثير الدوال التالية منها زمن الاتزان ، محلول الدالة الحامضية ،درجة الحرارة و كمية المادة الممتزة .وبينت النتائج ان كمية الازالة حوالى ٩٠% لتركيز ٥٠ ملغم/لتر لايون السيانيد عند درجة ٣٧ درجة مئوية وبدالة حامضية PH=8 . حللت النتائج باستعمال ايزوثيرمات فرندلش ولانكماير لامتزاز باستعمال معادلة الخط المستقيم عند درجات حرارة مختلفة .وجد ان مستقيمات فرندلش للامتزاز هي الافضل لامتزاز ايون السيانيد على سطح SBTL .تم حساب الدوال الثرموديناميكية عند ثلاث درجات حرارية مختلفة واستخلص من نتائج امتزاز ايون السيانيد انه تلقائي وماص للحرارة .كما تم دراسة حركية الامتزاز باستعمال معادلة المرتبة الاولى الكاذبة والمرتبة الثانية الكاذبة . بينت النتائج ان المرتبة الثانية الكاذبة الأفضل من المرتبة الأولى .

Abstract

The present study is concerned with the adsorption of cyanide ion (CN^-) from aqueous solutions using the wastes of spent black tea leaves (SBTL) as an adsorbent Batch adsorption experiments were carried out at equilibrium conditions for concentrations of cyanide ion between 50 and 300mgL^{-1} .The parameters examined in this study were the effect of contact time ,solution pH , temperature and amount of adsorbent .The results showed that significant amounts about 90% of 50 mgL^{-1} cyanide ion was removed at 37°C and solution pH= 8.The equilibrium adsorption isotherms have been analyzed by the Freundlich and Langmuir equations using Linearized correlation coefficient at different temperatures. The Freundlich is found the best represent the equilibrium data for cyanide-SBTL system. Thermodynamic parameters were calculated at three different temperatures and the obtained values support the conclusion that the cyanide ion adsorbs by spontaneous and endothermic process. To examine the kinetic of the adsorption process, models of pseudo-first-order and pseudo-second-order were applied. The data showed that the pseudo –second-order model was best-fit model.

Key Words: *cyanide ion , Adsorption ,isotherm, spent black tea leaves*

Introduction

Cyanide ion and its compounds from electroplating and mining industries are responsible for the contamination of lakes , crecks and rivers. From the environmental and economic point of view, the management of such a contaminating but valuable resource is very important. Cyanide is a highly toxic species .Short-term exposure can cause rapid breathing , tremors and other neurological effects. Long –term exposure can cause weight loss , thyroid deficiency and nerve damage .The mean lethal dose for the human adult is 50-200 mg L^{-1} ,but for freshwater invertebrates it is only 0.028-2.295 mgL^{-1} .Thus, cyanide –contaminated effluents should not be discharged into the environment without detoxification to meet cyanide satutory limits [1]. Adsorption is the one of the most important physiochemical processes that occur types of the solid-liquid and soild-gas interfaces [2]. Many types of the biomaterials are low-cost agricultural waste and available in a large amount have been used as an adsobent for removal of environmental pollutants from wastewaters, such as ,modified rice hulls [3], rice husk[4,5], coconut husk [6], natural cellulose [7], saw dust [8], banana pith [9], etc. In the present work a wastes of spent black tea leaves were used as an adsorbent and complementary to the works of many researchers to study the feasibility of this waste in the removal of environmental pollutants such as, metal ions [10-12], dye [13-14] and some organic compounds [15]. The aim of this work was to investigate the adsorption behaviour of (SBTL) on CN^- adsorption .However there are no available data on CN^- adsorption by spent black tea leaves from aqueous solution .

Materials and Methods

Chemicals

Sodium cyanide with a purity > 95% was obtained from Fluka ,silver nitrate was purchased from Fluka and with a purity> 96%,Analar reagent grade concentrated hydrochloric acid, sodium hydroxide (B.D.H) were used to adjust pH values of solutions. Distilled water was used in all experiments.

Spent Black Tea Leaves preparation

Samples of black tea leaves wastes were obtained from commercially available black tea leaves ,about 5g of dried leaf was weighted and placed in the conical flask containing 250ml of boiling distilled water for 5min ,and allowed to cool to room temperature ,then the solution was discarded .After that spent black tea leaves were recovered again with 250ml distilled water discarded also ,then the wastes were washed with distilled water five times in order to remove coloured and some soluble compounds, after that the wastes of spent black tea leaves were dried at 80°C ,then soild was grounded a fine powder in a grinding mill and sieved to get size fraction < 200µm .

Equilibrium Studies

The adsorption experiments were conducted by batch method where samples of 0.1g of (SBTL) were placed in a 50ml conical flask and equilibrated with 20 ml of NaCN solution of known concentration which ranging from 50 to 300mgL^{-1} and at pH 7.0.The mixture was agitated at a constant temperature (room temperature)on a thermostatic water bath shaker (shaking Inducator . GCA./Percision Scientific Chicago, U.S.A) of know time (15min) and in a constant speed (200rpm).After reach equilibrium the solution was filtered .The solutions pH was in the range of 2-12 adjusted by diluted HCl or NaOH .Standard silver nitrate solution was used to standardization the amount of cyanide at equilibrium (Volumetric method) and using the following equation:

$$qe = \frac{(Co - Ce)V}{w}$$

Where qe is the metal uptake capacity (mg/g),C_o is the initial dye concentration (mgL^{-1}) , C_e the equilibrium dye concentration (mgL^{-1}), V the volume of the solution (L) and m the weight of the dry adsorbent used (g).

The percentage removal of cyanide was calculated by the following equation :

$$\%CN\ removal = \frac{C0-Ce}{Co} x100$$

Where C_o,C_e (mgL^{-1}) are initial and equilibrium cyanide concentration respectively, V(ml) is the volume of the solution and W(g) is the mass of the adsorbent .

Kinetics studies

A 0.1 g of (SBTL) was added to 20 ml of sodium cyanide solution with initial concentration of 250mgL^{-1} .This mixture was agitated on shaker water bath at a constant speed in a temperature controlled and at pH=7 .Samples were filtered and the filtrate was titrated with standard silver nitrate solution at different time ranging from 10 to 120 min.

Results and Discussion

Effect of pH on Cyanide ion adsorption

The effect of initial pH on adsorption of cyanide ion was studied from pH 2 to 12 at 37°C at initial cyanide concentrations 50,150 and 250mgL^{-1} , adsorbent weight of 0.1 g and contact time of 15min .The extent of cyanide ion adsorption depends on solution pH and on the properties of (SBTL) .Fig.1 shows the change of the percent removal with the change of pH value, about 90% of CN^- removal was observed at pH 7-8 at 50mgL^{-1} CN^- concentration. Previously ,other researchers also showed that the cyanide wastewater remediation by adsorption method was very efficient at dilute cyanide ion concentrations(16-17).At low pH values ,the surface of the (SBTL) would acquires hydrogen ions which enhance the cyanide ion interaction with adsorbent sites. As the pH increased the surface charge on the adsorbent become negative ,and a small decrease in cyanide adsorption was observed which due to the electrostatic repulsion .

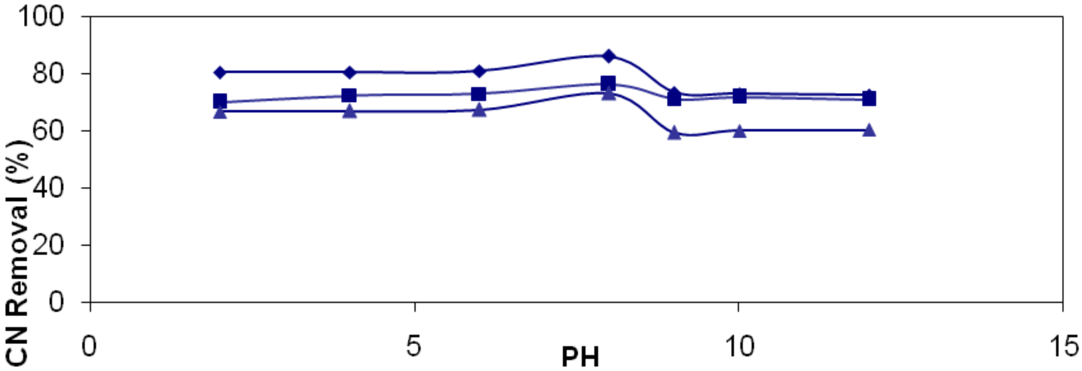

Fig. 1: Effect of pH on Adsorption Of CN (50,150 250$mg.L^{-1}$) Onto 0.1g SBTL at Temperature 37°C

Effect of (SBTL) dose on Cyanide ion adsorption

The effect of (SBTL) dose for removal of cyanide ion was carried at four different mass ranging from 0.01 , 0.1 , 0.25 , 0.5g for initial cyanide ion concentration of 250 mgL^{-1} .Fig.2 shows that the percent removal of cyanide ion was increased from 80 % to 95% when the (SBTL) dosage was increased from 0.01 to 0.5g .

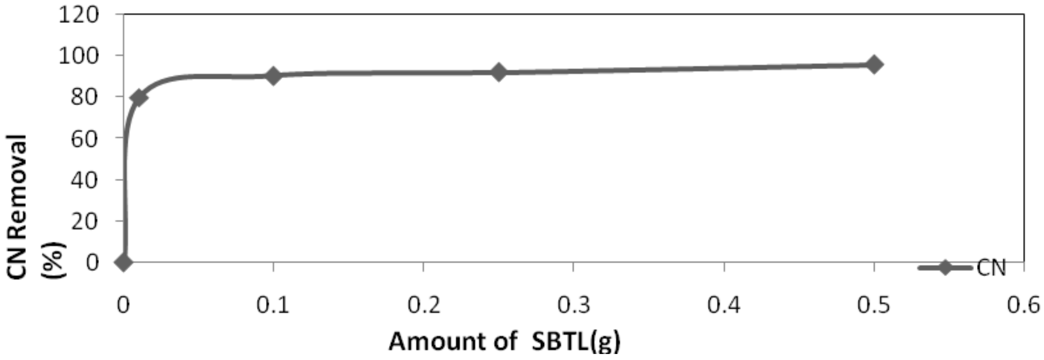

Fig.2: Effect of SBTL Dosage CN^- Removal ,Co=250$mg.L^{-1}$ at pH=7 Agitation Speed 200 rpm and Temperature 37°C

Effect of contact time on Cyanide ion adsorption

The time need to reach equilibrium for the removal of the CN^- at two concentration of 100 and 250 mgL^{-1} by (SBTL)from aqueous solution was estimated as shown in Fig.3,it was observed the percent removal of CN^- increases with increase in contact time to some percent and remain constant when reach contact time above 15min .That indicated that (SBTL) taken 15min, to remove 80-95% of 100 and 250 mgL^{-1} of CN^- concentration respectively.

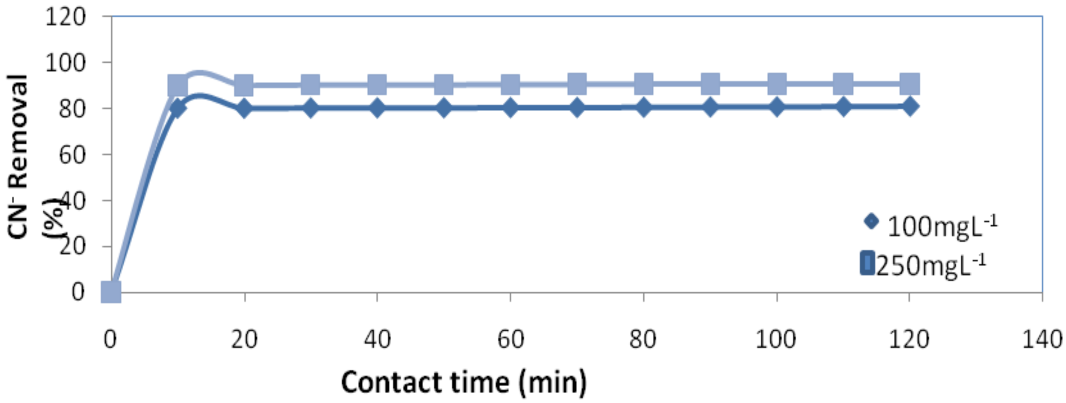

Fig. 3: Effect of Contact Time on The Removal of CN^- With Initial Concentrations 100,250$mg.L^{-1}$ at 37°C and pH=7

Effect of temperature on Cyanide ion adsorption

Adsorption experiments were performed at different temperatures 37,39 and 41°C for the initial CN^- concentration 250mgL^{-1}, equilibrium time 15 min and pH=8 . Fig.4 shows the influence of temperature on the adsorption of CN^- onto (SBTL) .The equilibrium adsorption capacity decreased from 87.4 to 70.3 mgg^{-1} when the temperature increased from 37 to 41°C,As it was indicated the endothermic nature of adsorption .

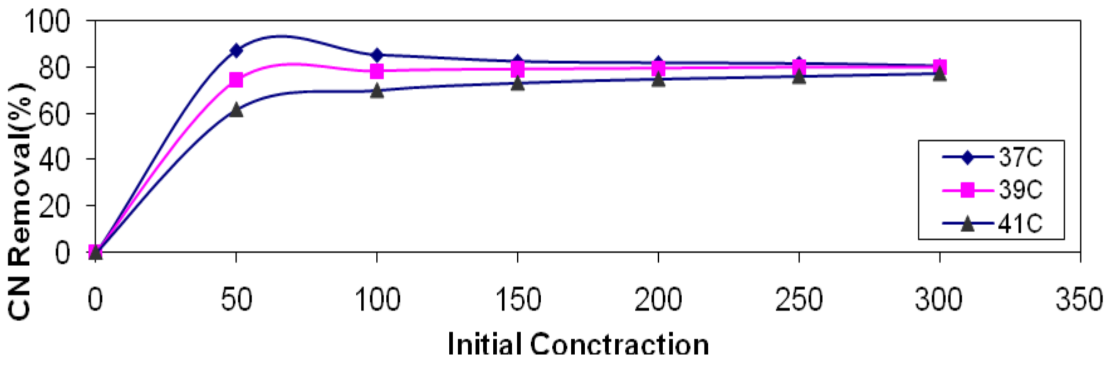

Fig. 4: Effect of Temperature on CN Adsorption Uptake, at pH=7, Adsorption Dose 0. 1g

Adsorption isotherms

Isotherms are the equilibrium relation between the concentration of the adsorbate on the solid phase and in the liquid phase [18] .An adsorption isotherm is characterized by certain constant values which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants [19].The experimental equilibrium adsorption data were analyzed using two models Freundlich and Langmuir by using the following equations [20]:

$$\text{Log } Qe = \log K_f + \frac{1}{n}\log Ce \qquad \text{Freundlich equation}$$

$$\frac{Ce}{Qe} = \frac{1}{K} + \frac{a}{K}\, Ce \qquad \text{Langmuir equation}$$

Where K_f is relative to the adsorption capacity and n is related to adsorption intensity. The Langmuir constant ,K is related to energy of adsorption and a is corresponding to complete monolayer. **Figures 5** and **6** illustrate the Freundlich and Langmuir models. The constants of CN^- adsorption onto (SBTL) were calculated from intercepts and slopes of these plots ,are presented in **Table 1**. The values of correlation coefficient (R^2) of Langmuir equation was slightly lower than of Freundlich equation at all temperature,which indicating that the Freundlich equation show the best fitting from Langmuir equation. The values of n and k changed with the rise of temperature which showed that CN^- is favourably adsorbed by (SBTL) and confirming that the process is endothermic.

Table 1: Isotherms constants for CN adsorption onto SBTL at 25°C and PH=7

Isotherm model	parameters	Temperature		
		37°C	39°C	41°C
Freundlich	$K_f(Lmg^{-1})$	2.700	4.412	1.005
	n	0.567	0.546	0.877
	R^2	0.921	0.892	0.768
Langmuir	$K_L(Lmg^{-1})$	16.39	35.71	71.43
	a	21.51	35.99	56.85
	R^2	0.292	0.805	0.692

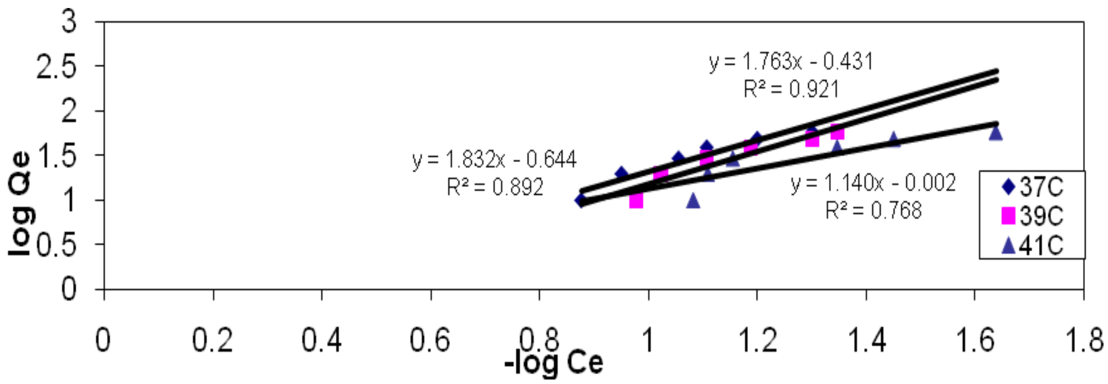

Fig.5: Freundlich Isotherm at Different Temperature

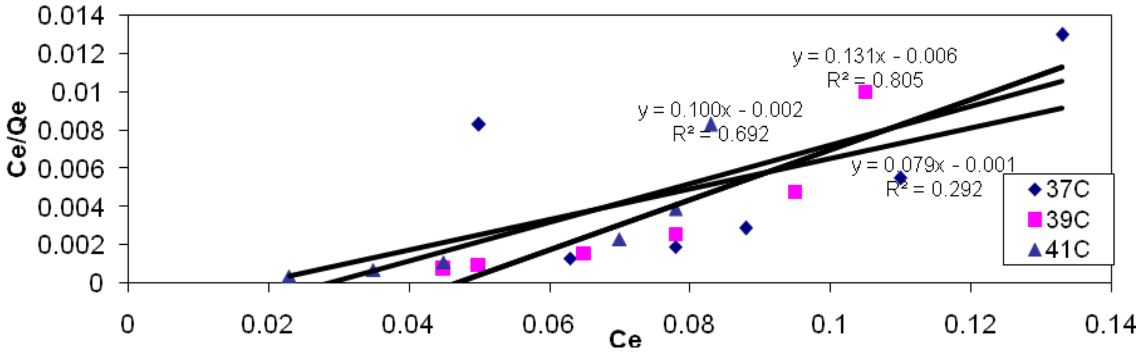

Fig. 6: Langmuir Isotherm at Different Temperature

Adsorption Kinetics

In order to calculate the rate constants of the adsorption process of CN^- on the (SBTL) , pseudo-first -order and pseudo- second -order kinetics models were studied .

The pseudo –first –order (Lagergren models) ,is expressed by equation [21]:

$$\log(qe - qt) = \log qe - \frac{K1}{2.303}t$$

Where qe,qt(mgg^{-1}) are the amount of cyanide ion at equilibrium and adsorbed at time t and $K_1(min^{-1})$ is the rate constant , the plot of log(qe-qt) versus t Fig.7 should give a straight line with correlation coefficient (R^2 = 0.975),which suggests the applicability of this kinetic model only over the initial stage of the adsorption process .

The pseudo- second- order kinetic model is given as follows[21]:

$$\frac{t}{qt} = \frac{1}{K2q2} + \frac{1}{qe}t$$

Where qt,qe (mgg^{-1}) are the amount of CN^- adsorbed at any time t and at equilibrium respectively, K_2($gmg^{-1}min^{-1}$) is the rate constant .The plot of $\frac{t}{qt}$ versus t should give a linear relationship Figure 8 with correlation coefficient (R^2=0.998).

The validity of each kinetic models was tested by the values of correlation coefficients R^2. **Table 3** illustrates the kinetic parameters of cyanide ion adsorption on (SBTL) .It is important to note that for pseudo- first -order and the value of correlation coefficients (R^2) were slightly lower than those of a pseudo -second- order model indicating that pseudo -second -order model is better obeyed than other models.

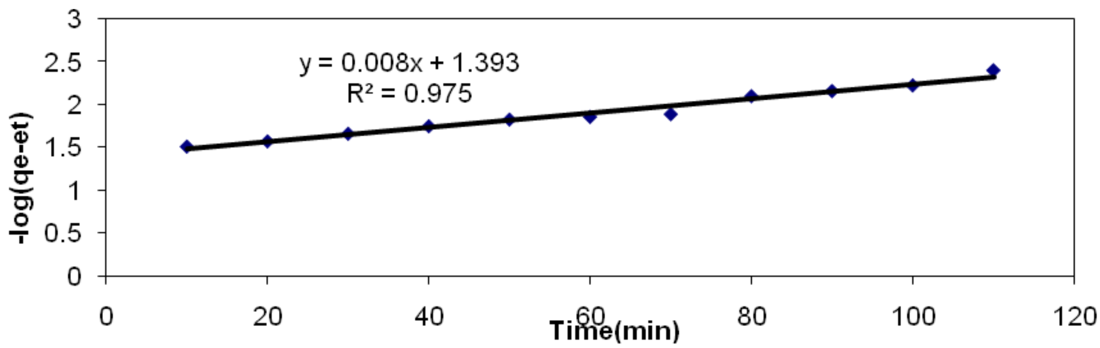

Fig . 7: Pseudo First Order Kinetic Model

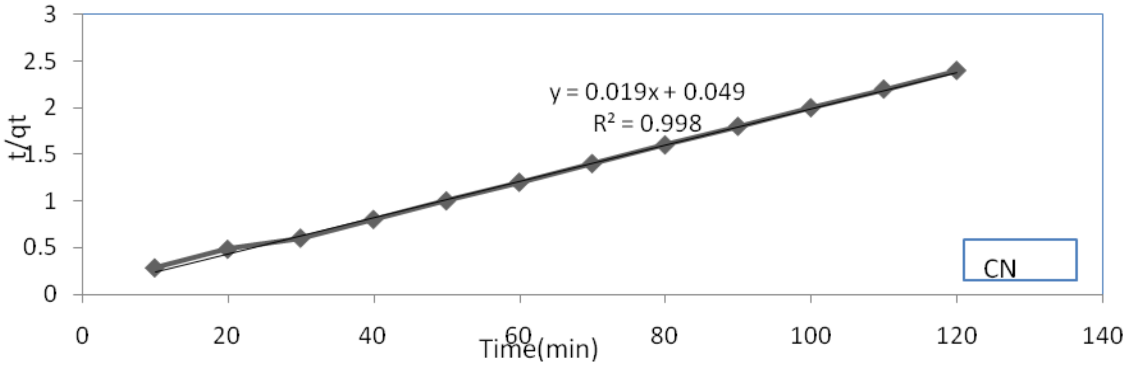

Fig. 8: Pseudo Second Order Kinetic Model

Thermodynamic Study

Thermodynamic parameters were calculated to elucidate CN^- adsorption mechanism on (SBTL) and to evaluate the thermodynamic feasibility of the adsorption process .The standard thermodynamic functions were calculated by the equation:

$$\ln Kc = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Where R is the ideal gas constant (8.314 J $mol^{-1}k^{-1}$) ,T the temperature (K) and Kc is the apparent equilibrium constant which calculated from the equation:

$$Kc = \frac{Cad}{Ceq}$$

Where Cad and Ceq are the concentrations of cyanide ion on the (SBTL) and at equilibrium respectively .

The plot of ln Kc verses 1/T Fig.9 given a straight line from which ΔH°, ΔS° can be calculated from the slope and intercept .

In order to further support the assertion that physical adsorption is the predominant mechanism ,the values of activation energy (Ea) and sticking probability (S*) were estimated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows [22] :

$$S^* = (1-\theta)\, e^{-Ea/RT}$$

$$\theta = \left[1 - \frac{Ce}{Co}\right]$$

The value of sticking probability (S*) lies in the range $0 < S^* < 1$ and its temperature dependent ,the plot of Log (1-θ) verses 1/T Fig.10 gives a straight line with intercept of logS and slope Ea/2.303R .**Table 2** shows the values of ΔG°,ΔH° ΔS°, Ea ,S* and θ of adsorption of cyanide ion onto (SBTL) at the experimental temperature and pH=7. The negative values of ΔG° indicate the spontaneous nature of the adsorption process at a given temperature ,the positive values of ΔH° suggest the endothermic process, while the negative values of entropy characterize the decreased randomness of the system due to higher uptake of the cyanide ion by the (SBTL).

Table 2: Thermodynamic Parameter of Adsorption of Cyanide Ion onto SBTL at Experimental Temperature and pH=7

Temperature(°C)	Kc	-ΔG KJ mol^{-1}	ΔH KJ mol^{-1}	ΔS KJ mol^{-1}	Ea KJ mol^{-1}	S*	θ
37	1199.5	18.276					0.9997
39	1702.2	18.697	32.26	71.78	177.17	4.077	0.9998
41	2606.2	20.539					0.9999

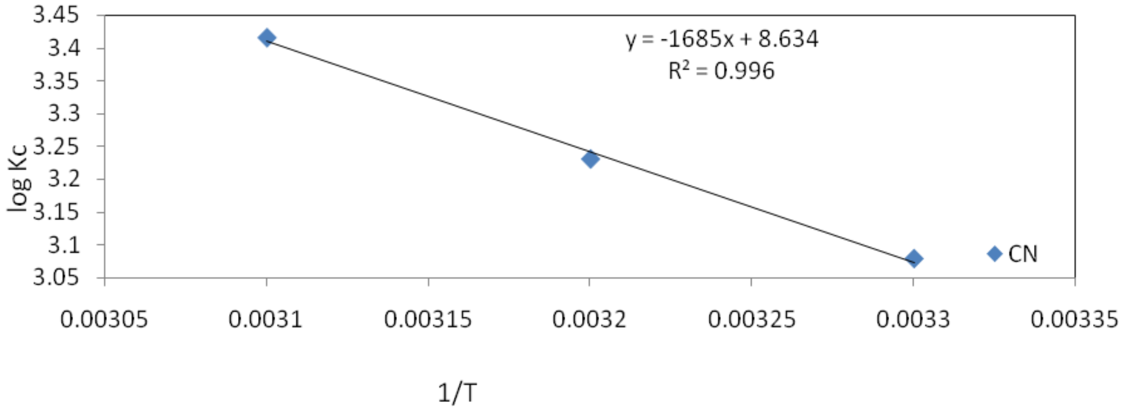

Fig. 9: Plot of Ln Kc Versus 1/T for The Adsorption of CN^- (250mg.L^{-1}) onto SBTL at pH=7 and 37°C

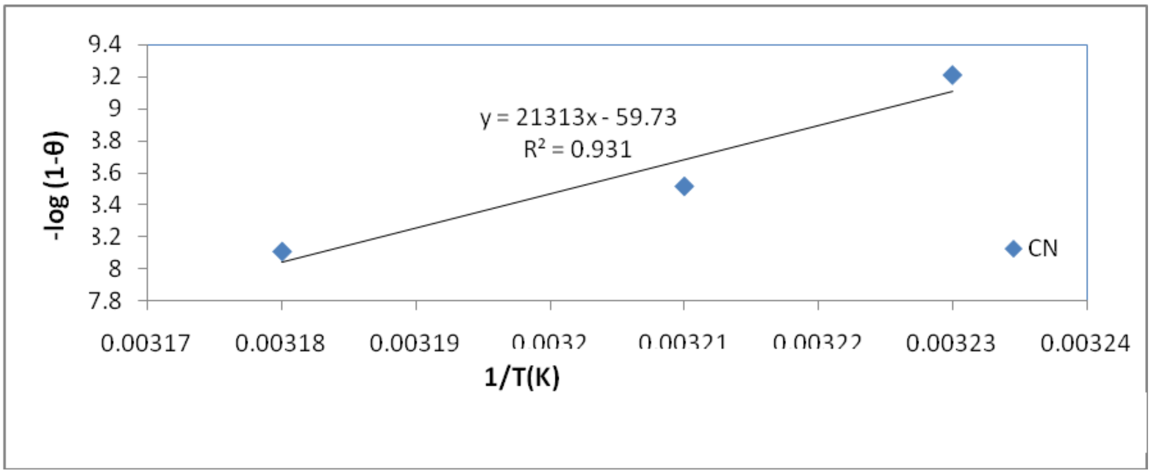

Fig. 10: Plot of Log(1-θ)versus 1/T for The Adsorption of CN 250mgL-1 onto (SBTL) at pH=7 and 37°C

Conclusion

- The present study showed that the batch adsorption process for removal of CN^- from aqueous solution onto (SBTL) is dependent on initial concentration ,solution pH, adsorbent dose ,contact time and temperature .The equilibrium is reached with about 15min.The highest percent removal is at pH 7 and 37°C.
- The equilibrium data follows Freundlich and Langmiur isotherm equations, the Freundlich isotherm equation was found to be the best correlation coefficient(R^2) than Langmuir isotherm equation at the studied concentration and temperature .
- The kinetic study was also discussed based on pseudo- first- order and pseudo- second-order .The results indicated that the pseudo –second- order kinetic model provided the best correlation coefficient(R^2).
- The thermodynamic parameters (ΔG°, ΔH°, ΔS°, Ea , S*,θ) indicates endothermic and spontaneous nature of the physisorption process.
- It may be concluded that the (SBTL) could be used as low-cost plant source waste adsorbent for the removal of CN^- from aqueous solutions.

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