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RESEARCH ARTICLE

USABILITY STUDY OF SPENT BLACK TEA LEAVES AND POMEGRANATE PEEL IN ADSORPTION OF TETRACYCLINE HYDROCHLORIDE ANTIBIOTIC

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ABSTRACT

Adsorption of tetracycline hydrochloride (TCH) from aqueous solutions by using spent black tea leaves (SBTL) and pomegranate peel (PP) wastes as low cost and available adsorbents are studied in this paper. Batch adsorption experiments were Investigated to study the sorption behaviour of (SBTL) and (PP) towards TCH as a function of initial concentration, reaction time, dosage of (SBTL) and (PP) wastes, pH and temperature. Time dependent experiments showed that adsorption reached equilibrium at 180 and 30 min for both (SBTL) and (PP) respectively. The adsorption of TCH is found to be better in acidic pH for both wastes. Equilibrium isotherms were tested by applying Freundlich, Langmuir, Tempkin and Dubinin–Radushekevich (D-R) models and it was found that the equilibrium data could be well described by Tempkin for the adsorption process on (SBTL) wastes and by (D-R) for the adsorption on (PP) wastes. Four kinetics models including simple - first - order pseudo – first – order, second – order, pseudo – second – order models were employed and the experimental results were found to be follow Pseudo - second-order equation for both wastes with a good correlation coefficients ($R^2 >$ 0.99). Thermodynamic parameters such as ΔH°, ΔS° and ΔG° have been determined and the findings data suggested that the physisorption is predominant. The positive values of ΔH° and ΔS° confirm that the adsorption process is endothermic and increased the randomness of the system interface. The negative value of ΔG° indicates the adsorption process is spontaneous and favourable. In order to support that Physisorption is the predominant the values of activation energy E_a and sticking probability S were calculated, the values of S and Ea indicates the applicability of (SBTL) and (PP) to be used as an effective pharmaceutical adsorbents of TCH from aqueous solutions and of TCH overdose.

INTRODUCTION

Tetracycline hydrochloride (TCH) is a broad-spectrum polyketide antibiotic produced by the streptomyces genus of actinobacteria, indicated for use against many bacterial infections and exert their antimicrobial effect by inhibition of protein synthesis. Tetracycline is also used as a biomarker in wild life to detect consumption of medicine or vaccine - containing baits(1) and in genetic engineering tetracycline used in transcriptional activation. In cancer research(2) tetracycline has been used to switch off leukemia and to do so reliably, when added to their drinking water. Drug overdoses can involve people of any age, it is most common problem in very young children, happens when too much of a drug or poison is taken, more than the medically recommended dose, leading to a toxic effect on the body. The major principles applied in the emergency treatment of accidental poisoning by drug are dilution, emesis and adsorption. in cases where no specific antidotes exist, preventation of further absorption of a drug from the oral route is by use of oral adsorbents(3). Many types of adsorbents such as activated carbon (4-10), clays(11-15), polymers(16-17), synthetic carbon and resin(18-19), carbon nanotubes (20-22), and etc. have been used either for adsorption of chemical compounds and drugs or to prevent further absorption of drug overdose. As a result of the modern science trends to use cheep, safe and wide spread availability agricultural wastes adsorbents, therefore, the production of a low-cost has become a focus to researchers. The objective of the present paper have been to employ two agricultural wastes, spent black tea leaves (SBTL) and pomegranate peel (PP) as an adsorbents and complementary to works of many researchers(23-31) and to study the feasibility of these wastes in the removal of TCH overdose to our knowledge have no adsorption studies of TCH on these wastes are reported in the literature.

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MATERIALS AND METHODS

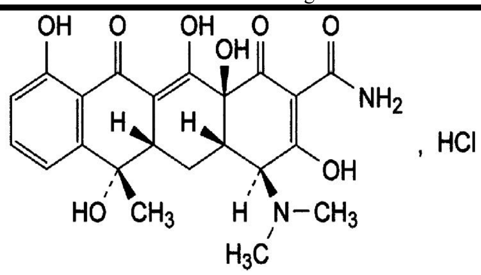
Preparation of Black Tea Leaves and Pomegranate Peels Wastes

Spent black tea leaves were collected from Coeffe shops and Cafteria in Al-najaf-al-ashraf governarate, Iraq. Samples of tea leaves were steep under stirring with bioling water (100°C) overnight to extract coloured of compounds from the leaves, after that samples were filtered and washed with distilled water until the filterate was colourless, then the leaves were oven dried at 100°C for 5 h., finally the dried leaves were ground and stored in blastic bags at room temperature. The pomegranate peels were collected from the beverage shopes, were air dried in the sun, grainding and powdered into samller grain by using mortar and pestle, the resulting powder was then subjected to the same treatment gives above of the black tea leaves.

Preparation of synthetic (TCH) solution

Tetracycline hydrochloride 250 mg (TCH) used as adsorbate, obtained from Samaraa drugs industry company, Iraq (S.D. I). Table (1) showed some physical and chemical properties of (TCH) (32). A stock solution of 200 mgL^{-1} was prepared by diluting appropriate amount of (TCH) with 500 ml distilled water in volumetric flask, different concentrations were prepared by dilution of the stock solution to the initial concentrations ranging from 10 - 100 mgL^{-1}. All

Table (1). Properties of tetracycline hydrochloride

Specification sheet		Structure of drug
Emprical formula	$C_{22}H_{24}N_2O_8$,HCl	
Molar mass	288.78	
Melting point	480.9 °C	
Solubility	Water	
Appearance	Yellow, crystalline powder.	
		(4*S*,4a*S*,5a*S*,6*S*,12a*S*)-4-(Dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide hydrochloride.

reagents used were of analytical grade and were supplied from B. D. H. England.

Effect of contact time

To estimate the time to reach equilibrium, 15 ml of standard solution of TCH at pH 6 was added in to 50ml volumetric flasks to 0.1 g of both SBTL and PP. The mixtures were put in the shaker water bath GCA. Percision scientific chicago, U.S.A set at 28 ° C and the time period was varied from 15 min. to 210 min. After each 15 min. the flask was removed from the shaking water bath, then the solution was filtered, centrifuged at 3000 rpm for 15 min. Centrifuge, Magafuge1.0, Herouse sepatech and analyzed using a spectrophotometer Biochrom Ltd, combridge CBu of J, England at the λ_{max} = 358 nm, from the results, the time to attain equilibrium was found 180, 30 min. for SBTL and PP respectively.

Optimization of adsorbent dosage

To determine the optimium adsorbent dosage, experiments were carried out by adding different weights of the SBTL or PP ranging from 0.05 to 0.4 g to 15 ml of desired concentration of TCH in 50 ml conical flask at pH 6, temperature 28° C and agitated for 180 min. of SBTL and 30 min. of PP. Aliquots concentration was analyzed to determine the extent of adsorption of TCH at equilibrium. The results showed that the best weights one 0.2g for SBTL and 0.3g for PP.

Batch adsorption studies

Batch adsorption experiments were carried out by adding 0.2 g when we used SBTL and 0.3 g when used PP as adsorbents in to 100 ml conical flask filled with 50 ml of TCH solution of known initial concentration ranging from 10 to 100 mgL^{-1}. The conical flasks were sealed and placed inside the shaker water bath at 28°C and shaking speed 150 rpm for 180 min. In case of using SBTL and 30 min., when using PP adsorbents, the samples were then withdrawn, filtered and centrifuged at appropriate time interval.The residual TCH concentration at equilibrium was estimated spectrophotometrically at λ_{max} = 358 nm. The amount of TCH adsorbed on to SBTL and PP, Q_e (mgg^{-1}) was calculated using the following equation[33]:

$$Qe = \frac{V_{sol}(C_o - C_e)}{M}$$

Where C_o, C_e are the initial and equilibrium TCH concentrations (mgL^{-1}), V_{sol}. is the volume of the solution (L) and M is the weight of the dry adsorbent used (g). The removal efficiency was calculated from the following equation:

$$\%Removal = \left(\frac{C_\circ - C_e}{C_\circ}\right) \times 100$$

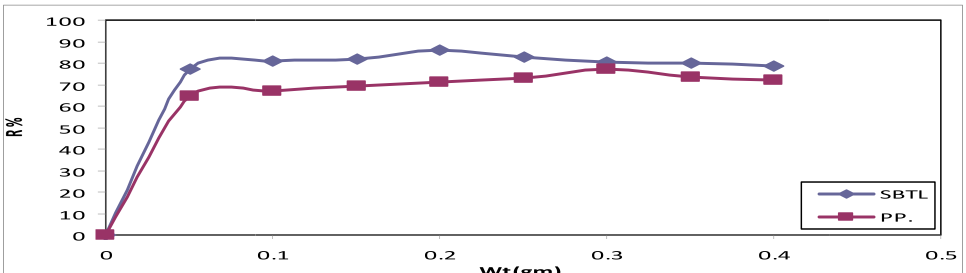


Fig.(1):Effect of whieght on the percent removal of TCH on SBTL and PP. wastes at pH=6, temperature 28 °C and initial conc. 100 mgL^{-1}

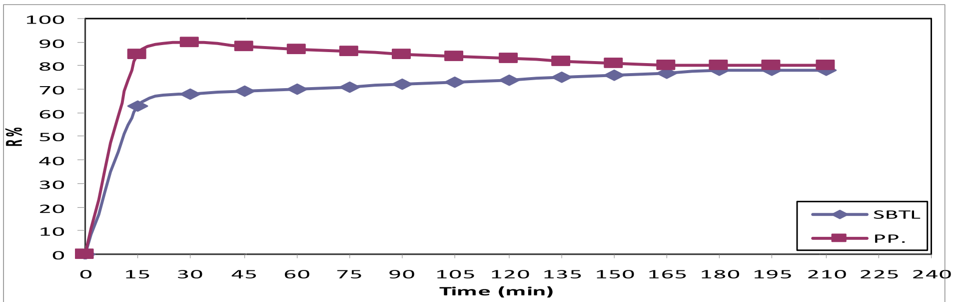


Fig.(2):Effect of contact time on the percent removal of TCH on SBTL and PP. wastes at pH=6, temperature 28 °C and initial conc. 100 mgL^{-1}

The effect of the pH on TCH adsorption was studied in the range of 2 - 10 by adding dilute CH_3COOH or NH_3. To evaluate the kinetics studies of TCH adsorption on both surfaces, simple - first -order, pseudo - first - order, second - order and pseudo-second-order models were used. The adsorption isotherms were also determined using a set of models such as, Freundlich, Langmuir, Tempkin and D-R isotherms at pH 6 and initial concentration in the range of 10 to 100 mgL^{-1}. The adsorption studies were also carried out at various temperatures in the range of 28 to 58 °C, to evaluate the thermodynamic parameters.

RESULTS AND DISCUSSION

Effect of Adsorbent Dosage

A number of experiments were achieved with different dosage of both adsorbents at initial TCH concentration of $100mgL^{-1}$. Results shown in Fig.1. from the figure, The extent of adsorption of TCH increased with increasing adsorbents dosage up to a point, after that the increasing of adsorbents dosage did not increase the TCH uptake. The saturation occurred at 0.2gm and 0.3gm for SBTL and PP respectinely.

Effect of the Contact Time

In order to study the effect of contact time on the percent removal of TCH from aqueous solution, experiments were carried out at initial concentration of 100 mgL^{-1}, different contact times ranging from 15 to 210 min., dose of SBTL was 0.2gm and of PP was 0.3gm, pH=6 and temperature 28°C. The percentage removal of the TCH solution by the adsorption on SBTL and PP is shown in Fig. 2. For SBTL the equilibrium was attained with in 180 min. and the percent removal was 78% of TCH solution, whereas the time required for the adsorption on PP to a achieve equilibrium was 30 min. and the percent removal was 90% of the TCH solution.

Adsorption Equilibrium

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm, and it is important from both a theoretical and a practical point of view [34]. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes, the applicability of the isotherm models to the adsorption study done was compared by the correlation coefficients, R^2 values[35]. A set of isotherm models have been tested; Freundlich, langmuir, Tempkin and Dubinin-Radushkevich (D-R).

Freundlich Isotherm Model

Freundlich isotherm is derived to a model of the multilayer adsorption and for the adsorption on heterogeneous surfaces, the linearized form of Freundlich equation is given by[36] :

$$\text{Log } q_e = \log k_f + 1/n \log C_e$$

where k_f and n are Freundlich constants , q_e is the extent of TCH adsorbed per unit mass of adsorbent (mgg^{-1}) and C_e is the equilibrium concentration of TCH (mgL^{-1}). Aplot of log q_e against log C_e would give the values of n and k_f from the slope and intercept respectively. The slope[35] of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero, while k_f represents the quantity of adsorbate on to the adsorbent. The values of Freundlich constants with the correlation coefficients are shown in Table 2 and Fig. 3. The results shows a poor of fitting with experimental data of TCH adsorption on to both SBTL and PP wastes.

Langmuir Isotherm Model

To understand the adsorption isotherm, the Langmuir equation is perhaps the most widely used model due to its simplicity and strong theoretical reasoning behind [37]. This model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. In addition the model assumes uniform energies of sorption on to the surface and no transmigration of the sorbate. The linearzed form of the langmuir isotherm equation is represented as [36]:

$$C_e/q_e = 1/k_L q_m + C_e/q_m$$

Where q_e (mgg^{-1}) is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of sites, C_e (mgL^{-1}) is the equilibrium concentration of TCH in solution, q_m(mgg^{-1}) is the monolayer adsorption capacity of the adsorbent and K_L(Lmg^{-1}) is the adsorption energy. The related parameters are summarized in Table 2, and the linearized Langmuir equation is shown in Fig.4. The results reveal the Langmuir model is not able to describe the experimental data properly, poorless of fitting on both wastes.

Tempkin Isotherm Model

Tempkin isotherm assumes that heat of adsorption decreases linearly with the adsorption on to the surface at a particular temperature, and the adsorption is characterized by uniform distribution of binding energies[38-39]. The Tempkin has generally been applied in the following linear form:

$$Qe = B \ln A + B \ln Ce$$

Where B = RT/b

A plot of qe versus ln Ce enables one to determine the constants A and B, Table. 2 are listed the Tempkin constants and the correlation coefficients, Fig. 5, is shown the plot of this isotherm. The Tempkin equation represents a better fit of experimental data of TCH uptake by SBTL waste, less agreement with D-R equation, poorless of fitting of Freundlich and Langmuir equations.

Dubinin - Radushkevich (D-R) model:

This isotherm model was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. In general (D-R) isotherm model is subjected to experimental data to determine the nature of adsorption ⁄ biosorption processes either physical or chemical process, and this model is applicable at low concentration and can be used to describe sorption on both homogeneous and heterogeneous surfaces[40-41]. The linear form of (D-R) isotherm equation is[36] :

$$\ln qe = \ln qm - KD\, R\, \varepsilon^2$$
$$\varepsilon = RT \ln[1 + (1/Ce)]$$

Table (2). Isotherms parameters of TCH sorption on to SBTL and PP at 28 °C and pH=6

Freundlich				Langmuir			Tempkin			D-R		
Surface	$K_f\, g^{-1}(1-n)g^{-1}\, L^{1/n}$	n	R^2	K_L Lmg-1	q_m mgm^{-1}	R^2	B $Jmol^{-1}$	A Lmg^{-1}	R^2	B $mol^2\, J^{-2}$	q_m mgg^{-1}	R^2
SBTL	9×10^{-5}	0.24	0.851	-0.044	-2.16	0.836	7.86	0.12	0.982	-3.03	18.69	0.95
PP.	1×10^{-5}	0.22	0.908	-0.043	-1.19	0.525	5.15	0.11	0.907	-3.63	11.48	0.93

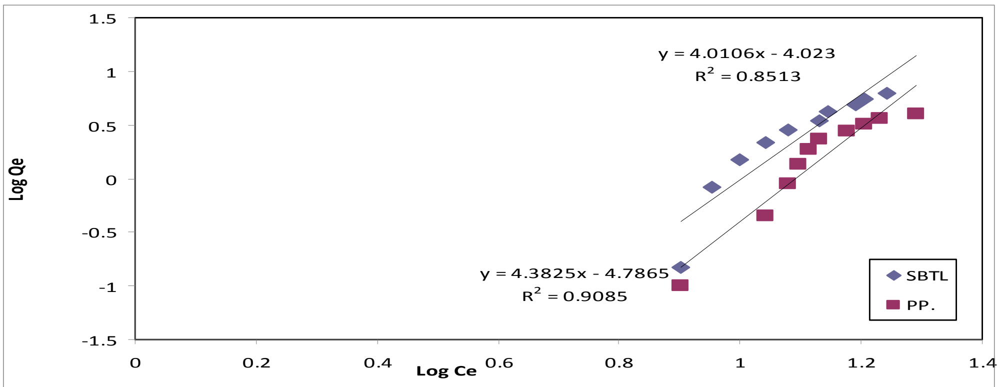


Fig.(3) : Freundlich equation for the sorption of tetracycline hydrochlorid on SBTL and PP at 28 °C and pH=6

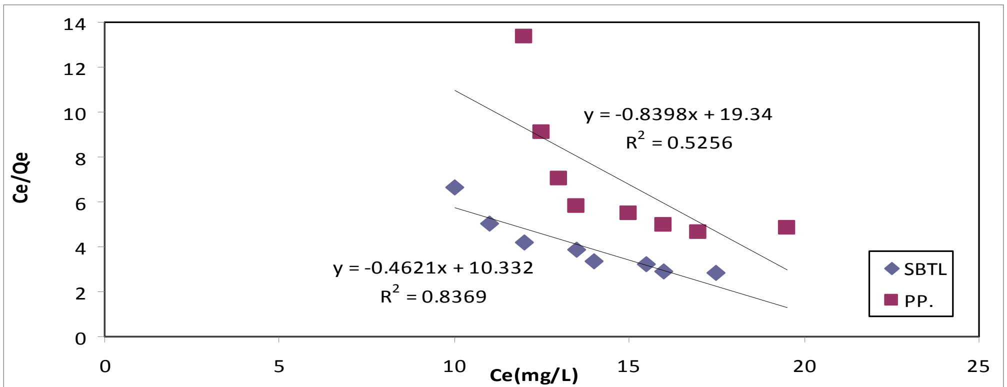


Fig.(4) : Langmuir equation for the sorption of tetracycline hydrochlorid on SBTL and PP at 28 °C and pH=6

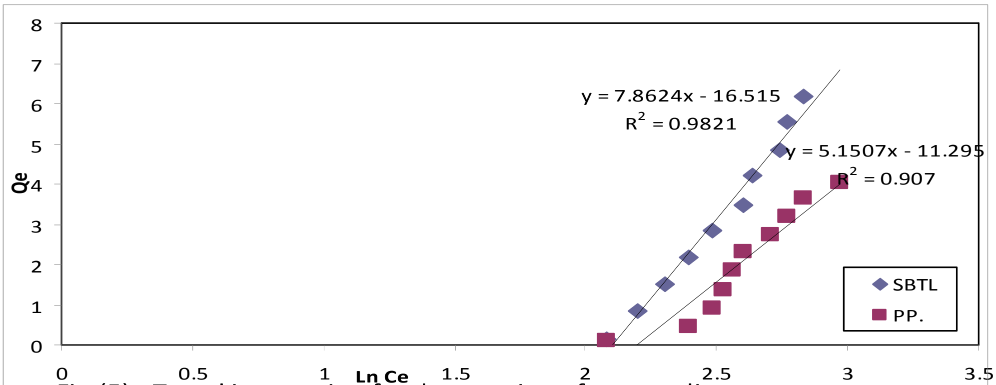


Fig.(5) : Tempkin equation for the sorption of tetracycline hydrochlorid on SBTL and PP at 28 °C and pH=6

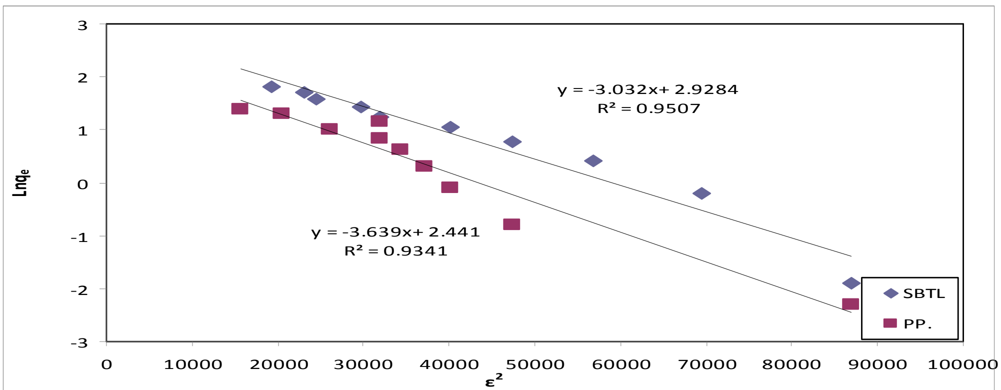


Fig.(6) : Dubinin-Radushkevich (D-R) equation for the sorption of tetracycline hydrochlorid on SBTL and PP at 28 °C and pH=6

q_m is the (D-R) monolayer capacity (mgg^{-1}) , K is a constant related to adsorption energy, ε is the polany adsorption potential, R is a gas constant, T is the absolute temperature, C_e is the equilibrium concentration. A plot of in q_e versus ε^2 is shown in Fig. 6. The values of (D-R) constants and correlation coefficients are listed in Table 2. The data points of this model seem to be a goodness of fitting with experimental data of TCH uptake by pomegranate peel waste, and seem to be less agreement with the Tempkin, Freundlich equation and poorless of fitting with Langmuir equation.

Adsorption Kinetics

In order to evaluate the adsorption kinetics of TCH on to SBTL and PP wastes, different kinetic models are used to fit the experimental data which were analyzed using simple - first - order, pseudo-first - order , second - order and pseudo - second - order equations as shown (27-28 ,36 , 38 , 42)

ln Ct = k1 t + ln C_oSimple-first- order
ln (qe-qt) = ln qe – k′1t Pseudo-first-order
1/Ct = k2t + 1/C_oSecond- order
t/qt = 1/k′2qe + 1/qetPseudo-second-order

Where q_e and q_t are the amount of TCH sorbed (mgg^{-1}) at equilibrium and at any time respective ; k_1, k'_1 (min^{-1}) and k_2, k'_2 (g mg^{-1} min^{-1}) are the simple - first -order, pseudo – first – order , second – order and pseudo – second – order rate constants of adsorption respectively ; C_o and C_t are the initial and at any time TCH concentrations (mgL^{-1}). The values of rate constants with the correlation coefficients for these models are shown in Table 3, and the models plots are shown in Figs. 7-10. The correlation coefficients for the pseudo - second - order kinetic model has a high value greater than 0.99 indicating that the pseudo - second - order adsorption mechanism of the TCH on to both wastes (SBTL and PP) is predominant. Similar finding have already been reported in the literature [12 ,35 ,43- 45].

pH Dependence

The infleunce of pH on the adsorption of TCH antibiotic to SBTL and PP was investigated at various pH values in the range of 2 – 10 and 28°C. Fig.11 shows the percent removal of TCH with respect to pH change. As shown in Fig.11 it can be observed that he extent of adsorption increased with increasing in pH of TCH solution til pH 6 then decreased with increasing in pH value. This observation attributed to the tetracycline antibiotics group, which are amphoteric

Table (3). Kinetic parameters for TCH sorption on to SBTL and PP at 28 °C and pH=6

	Simple 1st order			Pseudo 1nd order			2nd order			Pseudo 2nd order		
Surface	**qe** mg/g	K min-1	R^2	qe mg/g	K_1 min-1	R^2	qe mg/g	K_2 mgg-1 min-1	R^2	qe mg/g	K_2 mgg-1 min-1	R^2
SBTL	30.38	-0.094	0.981	2.251	-1.083	0.891	31.446	0.003	0.97	11.918	0.848	0.999
PP.	39.884	0.093	0.902	0.897	0.324	0.971	40.983	-0.002	0.892	6.849	-0.78	0.998

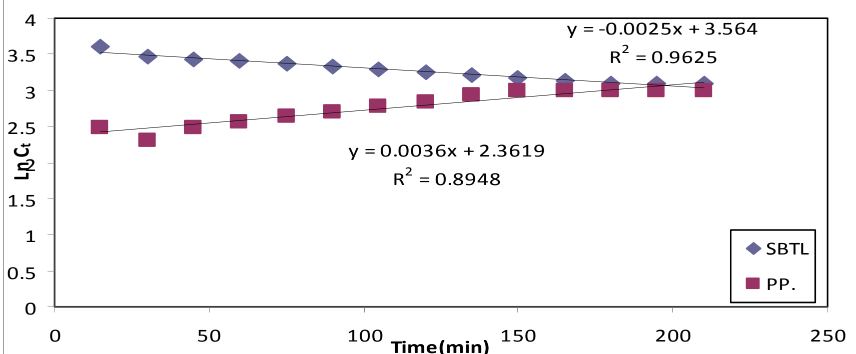


Fig.(7): Simple first order adsorption of tetracycline hydrochlorid on SBTL and PP at 28 °C , pH=6 and intial TCH conc. 100mgL^{-1}

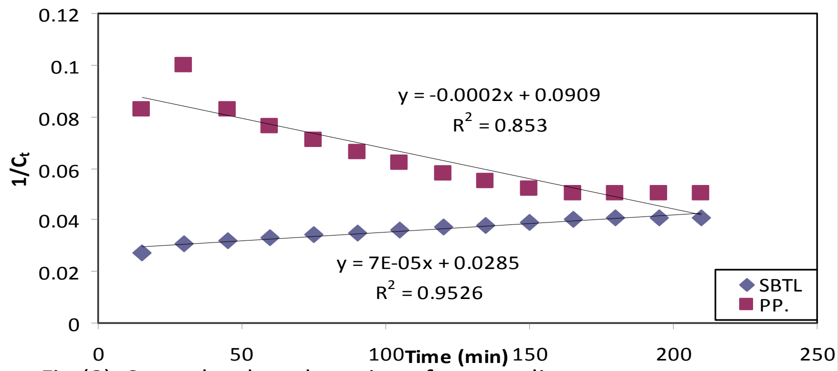


Fig.(8): Second-order adsorption of tetracycline hydrochlorid on SBTL and pp at 28 °C ,pH=6 and initial TCH conc. 100mgL^{-1}

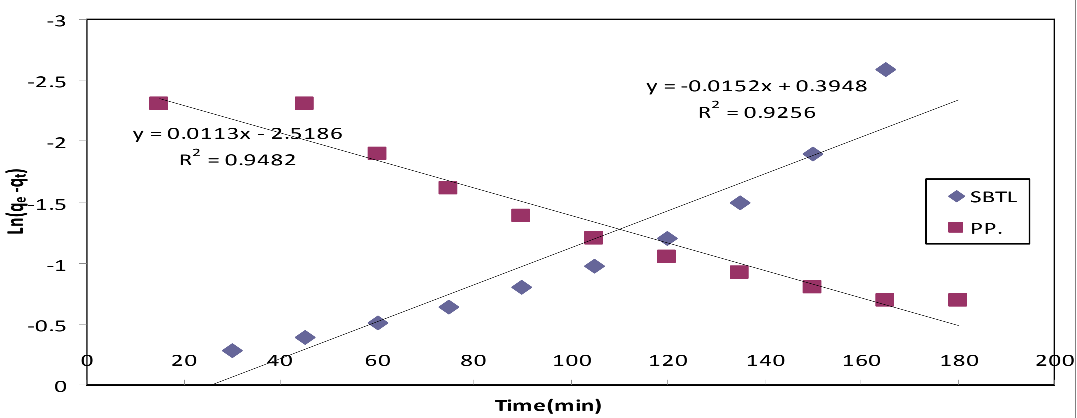


Fig.(9): Pseudo -first order adsorption kinetic data of tetracycline hydrochlorid on SBTL and PP at 28 °C and pH=6 and initial conc. 100mgL^{-1}

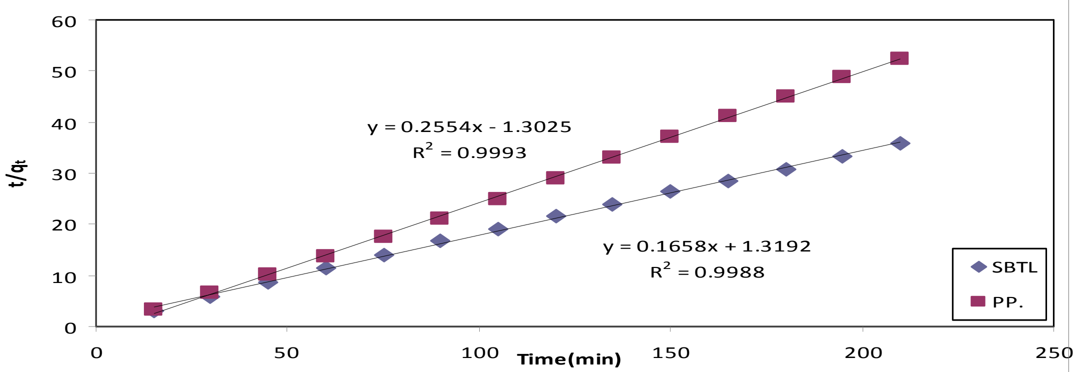


Fig.(10): Pseudo-second order adsorption kinetic data of tetracycline hydrochlorid on SBTL and PP at 28 °Cand pH=6 and initial conc. 100mgL^{-1}

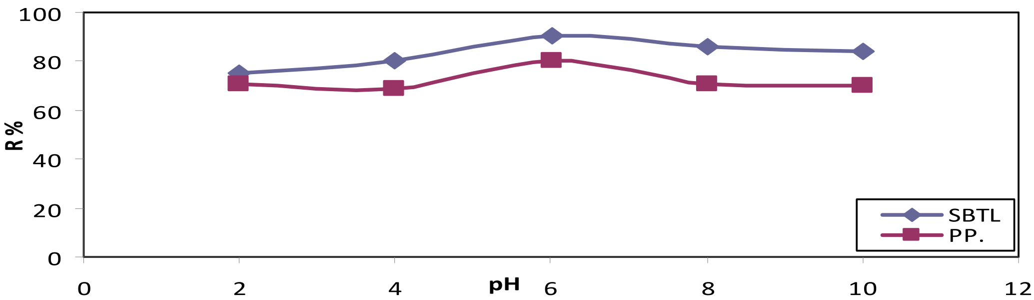


Fig. (11) : Effect of pH on percentage removal of tetracyclin hydrocloride on to SBTL and PP at 28 °C and TCH conc. 100mgL^{-1}

molecules having multiple ionizable functional groups, acquire tricarbonyl amide, phenolic diketon and dimethyl amine moieties, in addition, tetracycline is characterized by three dissociation constants and exists as cationic, Zwitterionic and ionic species under acidic, neutral and alkaline conditions[46-47]. At low pH value the presence of H^+ ions which competing with cations group of the TCH. At pH 6. The concentration of the H^+ is lowered and the adsorption of TCH increases. At pH > 7, the OH^- ion concentration is increased and adsorbed on the SBTL and PP, this may result a repulsion forces between the negatively charge of TCH and the surface of both wastes and so the adsorption of TCH will be reduced. Similar finding were reported in the literature[48-50].

Temperature dependence

The data of TCH adsorption on to SBTL and PP at different temperatures ranging from 28°C to 58°C have been studied. It is clear from Fig.12 that the removal percent of TCH on to both wastes was increased by increasing the temperature from 28°C to 58°C, indicating that the adsorption process is an endothermic and favourable at high temperature, some researchers have been reported this findings[51]. Furthermore to know the type of adsorption mechanism predominant, the value of activation energy E_a and sticking probability S were calculated from the experimental data by using the following equations [36]:

$$S = (1 - \theta) \exp(-Ea / RT)$$
$$\theta = 1 - C_e / C_o$$

Where θ is the surface coverage, C_o and C_e are the initial and equilibrium TCH concentrations mgL^{-1} respectively. Fig.13. Shows the linear plot of log 1 – θ against (1 / T) with the slope (E_a / 2.303R) and intercept log S. The positive value of activation energy Ea indicates that the adsorption mechanism is a diffusion controlled - process such result have been reported[52]. The value of sticking probability is S<<1 which indicate that the adsorption process is physisorption. Thermodynamic parameters were calculated to evaluate the thermodynamic feasibility of the TCH adsorption. Which necessary to conclude wether the process is spontaneous or not, the Gibb's free energy change, ΔG°, is an important criterion for spontaneity[37]. Both enthalpy ΔH° and entropy ΔS° parameters must be considered in order to determine the Gibb's free energy of the process, the following equation had been used to calculate these parameters:

$$\ln k_c = -\Delta H^o/RT + \Delta S^o/R$$
$$\Delta G^o = \Delta H^\circ - T \Delta S^\circ$$

Where K_c is linear sorption distribution coefficient, R is the ideal gas constant (8.314 J mol^{-1}) and T is the temperature (K). Fig.14 shows the relationship between Ln K_c and temperature, the negative values of ΔG° indicate the adsorption process is spontaneous in nature, furthermore, the positive value of ΔS° suggests the increased randomness at the solid solution interface during the adsorption of TCH , the same findings have been reported in literature[53]. Table 4,5 shows the thermodynamic parameters, activation energy and surface coverage of TCH adsorption on to SBTL and PP at the temperature range (28 - 58° C) and pH = 6.

Table (4). Thermodynamic parameters, activation energy and sticking probability for TCH sorption on to SBTL

T(K)	1000/T (K^{-1})	S^*	Θ	- Log (1-Θ)	- Ln K	- ΔG $kJmol^{-1}$	+ ΔH $kJmol^{-1}$	+ ΔS $Jmol^{-1} k^{-1}$	$+E_a$ kJmol-1
301	3.322		0.82	0.756	1.039	9.319			
311	3.215		0.85	0.823	0.855	9.629			
321	3.115	0.0028	0.86	0.869	0.732	9.939	0.012	31.37	0.01
331	3.021		0.88	0.92	0.597	10.249			

Table (5). Thermodynamic parameters, activation energy and sticking probability for TCH sorption on to PP

T(K)	1000/T (K^{-1})	S^*	Θ	- Log (1-Θ)	- Ln Kc	- ΔG $kJmol^{-1}$	+ ΔH $kJmol^{-1}$	+ ΔS $Jmo1^{-1} k^{-1}$	$+E_a$ kJmol-1
301	3.322		0.82	0.805	1.577	0.598			
311	3.215		0.85	0.815	1.512	0.618			
321	3.115	0.0409	0.86	0.825	1.445	0.638	0.004	2.599	0.003
331	3.021		0.88	0.83	1.41	0.658			

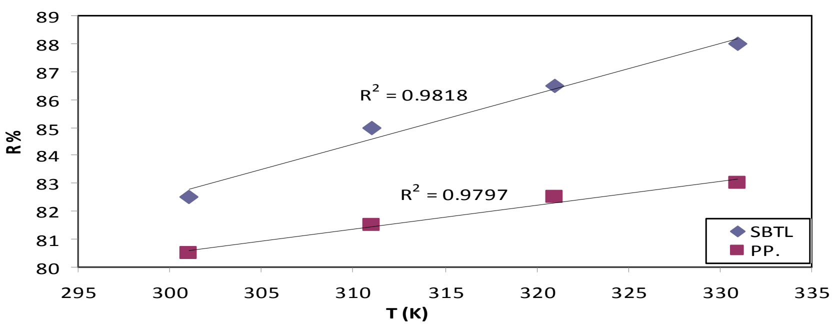


Fig.(12): Effect of temperature on the adsorption of tetracycline hydrochlorid solution on SBTL and PP at 28 °C,pH=6 and TCH conc. 100mgL-1,

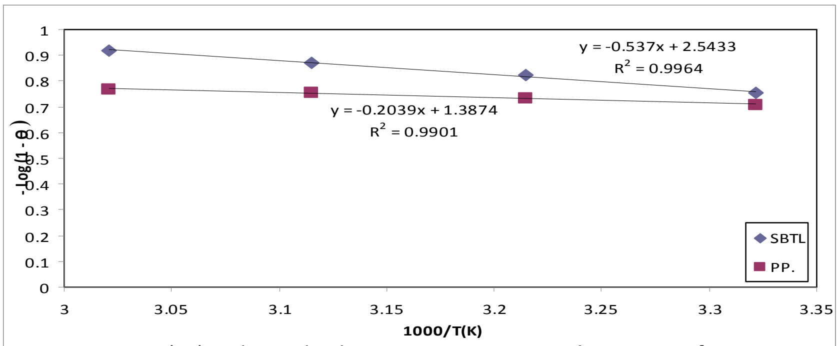


Fig.(13): Relationship between temperature and Log 1- Θ of tetracycline hydrochlorid adsorption on to SBTL and at 28 °C,pH=6 and TCH conc. 100mgL-1,

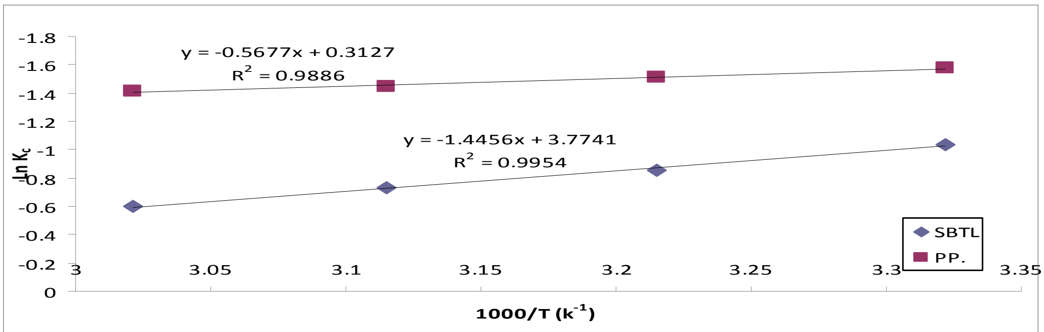


Fig.(14): Relation between temperature and Ln Kc for tetracycline hydrochlorid on SBTL and PP at pH=6, and initial conc. 100mgL^{-1}

Conclusion

The results of this study shows that SBTL and PP has a suitable adsorption capacity for the removal of TCH from aqueous solution. The effect of various parameters such as sorbent dosage, contact time, pH, TCH concentration and temperature was studied. The equilibrium data were analyzed by using Freundlich, Langmuir, Tempkin and D-R isotherm models and the results are well fitted to Tempkin and D-R equations. It was found that the equilibrium was reached within 180 and 30 min. For SBTL and PP wastes respectively , also it was found that the optimum pH value of the TCH adsorption was 6 .The kinetic studies follow the pseudo-second-order model . Effect of temperature on adsorption process shows that adsorption is an endothermic, spontaneous and the mechanism is physisorption because of low activation energy. The present work demonstrates that (SBTL) and (PP) agricultural wastes to be used as effective pharmaceutical adsorbents of TCH adsorption from aqueous solution.

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