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EQUILIBRIUM, THERMODYNAMICS AND KINETICS STUDY OF DOXYCYCLINE ADSORPTION FROM AQUEOUS SOLUTION USING SPENT BLACK TEA LEAVES AND POMEGRANATE PEEL WASTES

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ABSTRACT

Pharmaceutical antibiotics also known anti-bacteria, which inhibit the growth of bacteria and various infections. Doxycycline (DOC) is a member of the tetracycline antibiotics which is frequently used to treat many different bacterial infection such as Chronic Prostitutes, Pelvic inflammatory disease and etc. Also Doxycycline has been demonstrated to reduce the invitro. growth of human breast and Prostate cancer cell, but at the sometime they have a negative effect on the environment when its presence in the industrial waste water . Adsorption of Doxycycline from aqueous solutions by Spent Black Tea Leaves (SBTL) and Pomegranate Peel (PP) wastes asl low- cost and available adsorbents has been studied in this work. Batch adsorption experiment were investigated to study the sorption behaviour of (SBTL) and (PP) towards DOC as a function of initial concentration, reaction time, adsorbent dosage, pH and temperature. Time dependent showed that the adsorption process reached equilibrium at 150 and 90 min. for both (SBTL) and (PP) respectively. Four adsorption isotherms equations were employed including Freundlich, Langmuir, Tempkin and Dubinin–Radushekevich (D-R) equations. The equilibrium data could be well described by D-R equation for the adsorption process on (SBTL) waste and by freundlich for the adsorption on (PP) waste . Also four kinetics equations. including simple - first - order pseudo – first – order, second – order, pseudo – second –order were applied and the resulting data were found to be follow pseudo – second –order equation for both wastes. Findings therrmodynamics data suggested that the physical adsorption is predominant, and the negative value of ΔH° and ΔS° confirm that the adsorption process is exothermic and decreased the randomness of the system interface. The positive values of ΔG° indicates the adsorption process is non-spontaneous. Furthermore the value of activation energy (Ea) and sticking probability (S) were calculated to assess the applicability of (SBTL) and (PP) as an effective adsorbents of DOC from aqueous solutions.

INTRODUCTION

Doxycycline (DOC) is a member, of the tetracycline antibiotics , it fights bacteria in the body and is frequently used to treat many different bacteria infections such as Chronic Prostitutes, Sinusitir, Pelvic inflammatory disease (Sweet *et al*., 1988; Gjonnaess and Holten, 1978), Nickettsial infections (Walker *et al*., 2008) and is also effective the treatment of Lyme disease (Nadelman *et al*., 1992; Nadelman *et al*., 2001; Karlsson *et al*., 1994) and Chrlichiosis (Weinstein, 1996; Karlsson *et al*., 2001). Doxycycline has been demonstrated to reduce the invitro growth of human breast and prostate cancer cells (Duiverivoorden *et al*., 1997; Fife *et al*., 1995). The removal of such compounds at such low concentration consist a difficult problem, so many advanced methods one used for the treatment of waste water, these processes have been found to be limited, because they often involve high capital and operational costes and also, these methods become in efficient when pollutants one present in trace concantrations (Gharbani *et al*., 2012). Among the treatment options, adsorption had been found to be superior to other techniques for water treatment in term of initial cost, simplicity of design, ease of operation and insensitivity of toxic substsnces, subsequently the adsorbent can be regenerated (Behi and Mayank, 2011). The safety of Activated Charcoal (AC) is remarkable, since AC is a non-reactive substance and is not absorbed systematically; oral

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administration results only in occasional constipation and combined administration of charcoal with sufficient dose of cathartic (Afonne *et al*., 2002). Recent studies has been focused on the use of residues coming from both industrial and agricultural sources as safe and wide spread availability adsorbents. Batch adsorption experiments were investigated to study the sorption behaviour of (SBTL) and (PP) towards DOC. The purpose of this work is to assessment the adsorption of Doxycycline solutions onto two types of biomass residues, Spent Black Tea Leaves (SBTL) and Pomegranate Peel (PP) as a result of the modern science trends to use cheep, safe, low cost and wide spread availability agricultural wastes (Hassan and Ali, 2013; Hussein and Alam, 2012; Hassan *et al*., 2012; Khadeem, 2013), and to complementary the works of many researchers (Meilan *et al*., 2012; Shukla and Quraishi, 2010).

Experimental

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, The pomegranate peels were collected from the beverage shopes, preparation of these wastes have been described elsewhene (Hassan and Ali, 2013).

Preparation of Doxycycline (DOC) Solution

Doxycycline (DOC) used as adsorbate, obtained from Samaraa drugs industry company, Iraq (S. D. I). Table 1 showed some physical and chemical properties of (DOC) (BPI, 2007). A stock solution of 200 mgl^{-1} was prepared by adding appropriate amount of DOC with 500ml 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 reagents used were of analytical grade and were supplied from B. D. H, England.

Effect of Contact Time

Batch adsorption method was carried out at 28^{o}C, 50 ml of (DOC) solutions of known concentration (100 mg/l) at pH = 6 were shaken in the shaker water bath (GCA. Percision scientific chicago, U. S. A) at the certain speed (150 rpm) with a required dose of both adsorbents (0.1 gm). To estimate the time to reach equilibrium, the time period was varied from 15 min. to 210 min., after each 15 min. the solution was filtered, centrifuged at 3000 rpm for 10 min using (Centrifuge, Magafuge 1.0, Herouse sepatech) then the solution was filtered and analyzed using a spectrophotometer (Biochrom Ltd, combridge CBu of J, England) at the λ_{max} = 275 nm, from the results, the time to attain equilibrium was found 150, 90 min., for (SBTL) and (PP) respectively.

Effect 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 DOC in 50 ml conical flask at pH 6, temperature 28° C and agitated for 150 min of (SBTL) and 90 min. of (PP). Aliquots concentration was analyzed to determine the extent of adsorption of DOC at equilibrium. The results showed that the best weights are 0.05g for (SBTL) and 0.15g for (PP).

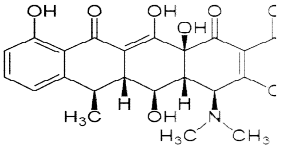
Equilibrium Studies

Batch adsorption experiments were studied by adding 0.05 g of SBTL and 0.15 g of PP in to 100 ml conical flask filled with 50 ml of DOC solution of known initial concentration ranging from 10 to 100 mgl^{-1} at pH=6. The conical flasks were sealed and placed inside the shaker water bath at 28°C and shaking speed 150 rpm for 150 min. in case of using SBTL and 90 min. when using PP adsorbents, the samples were then withdrawn, filtered and centrifuged at appropriate time interval. The residual DOC concentration at equilibrium was estimated spectrophotometrically and the amount of DOC adsorbed, Q_e (mgg^{-1}) was calculated using the following equation (Hassan *et al*., 2012):

Where C_o, C_e are the initial and equilibrium DOC 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 (Hassan and Ali, 2013):

The effect of the pH on DOC adsorption was studied in the range of 2 - 10 by adding dilute CH_3COOH or NH_3.

Table 1. Properties of Doxycycline (DOC)

Doxycycline		
Specification sheet		Structure
Emprical formula	$C_{22}H_{24}N_2O_8$	
Molar mass	444.34 g/mol	
Melting point	201 ^{o}C	
Source	Iraq (S . D . I)	
Solubility	Very soluble in water	
Appearance	Yellow crystalline	(4S,4aR,5S,5aR,6R,12aS)-4-(dimethylamino)- 3,5,10,12,12a-pentahydroxy- 6-methyl- 1,11-dioxo- 1,4,4a,5,5a,6,11,12a-octahydrotetracene- 2-carboxamide

Batch Kinetic Studies

Batch adsorption experiments were carried out at at 28°C on both wastes, 50 ml 0f DOC solution of known initial concentration (100 mg/l) was shaken at the agitation speed 150 rpm with a required dose of adsorbents for the specific period of equilibrium time and at pH=6, samples were withdrawn at different time intervals.

RESULTS AND DISCUSSION

Effect of Adsorbent Dosage

A number of experiments were achieved with different dosage of both adsorbents at initial DOC concentration of 100 mgL^{-1}.

Results shown in Fig. 1. from that figure, The extent of adsorption of DOC increased with increasing adsorbents dosage up to a point, after that the increasing of adsorbents dosage did not increase the DOC uptake. The saturation occurred at 0.05gm and 0.15gm for SBTL and PP respectively.

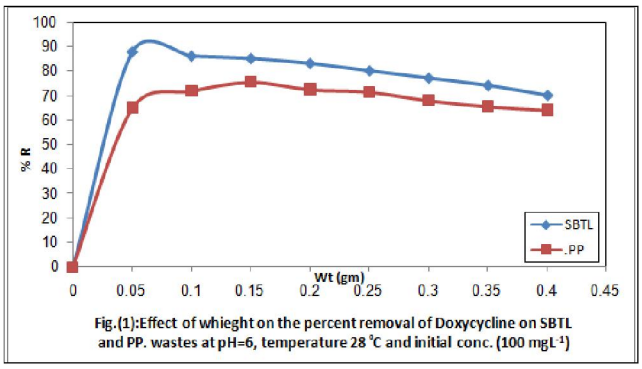


Fig.(1):Effect of whieght on the percent removal of Doxycycline on SBTL and PP. wastes at pH=6, temperature 28 °C and initial conc. (100 mgL⁻¹)

Effect of the Contact Time

In order to study the effect of contact time on the percent removal of DOC from aqueous solution, experiments were carried out at initial concentration of 100 mgL^{-1}, different contact times from 15 to 210 minutes, dose of (SBTL) 0.05gm and (PP) 0.15gm, pH=6 and temperature 28°C. The percentage removal of the DOC solution by the adsorption on (SBTL) and (PP) is shown in Fig. 2. For (SBTL) the equilibrium was attained with in 150 min. and the percent removal is (89%) of DOC solution, whereas the time required for the adsorption on (PP) to a achieve equilibrium was 90 min. and the percent removal is (83%) of the DOC solution.

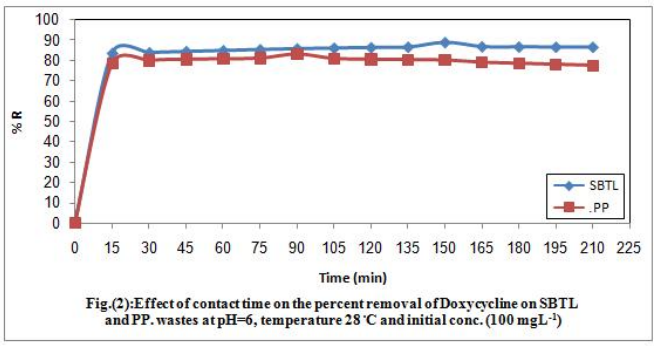


Fig.(2):Effect of contact time on the percent removal of Doxycycline on SBTL and PP. wastes at pH=6, temperature 28 °C and initial conc. (100 mgL⁻¹)

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. 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 values. 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 (Liangliang *et al*., 2010):

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

where k_f and n are Freundlich constants, q_e is the extent of DOC adsorbed per unit mass of adsorbent (mgg^{-1}) and C_e is the equilibrium concentration of DOC (mgL^{-1}). Aplot of log q_e against log C_e would give the values of n and k_f from the slope and itercept respectively. The slope (Haris and Sathasivam, 2009) 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 show a better fit of experimental data of DOC uptake by (pp) waste, less agreement with (D-R), poorless of fitting with Langmuir and Tempkin

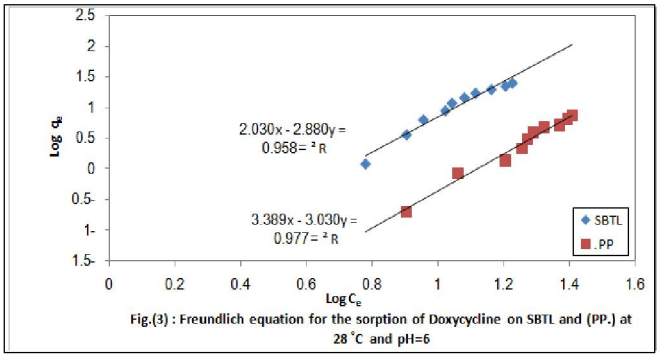


Fig.(3) : Freundlich equation for the sorption of Doxycycline on SBTL and (PP.) at 28 °C and pH=6

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 (Sohn and Kim, 2005). 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 (Liangliang *et al*., 2010):

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

Where q_e (mgg^{-1}) is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of sites, Ce (mgl^{-1}) is the equilibrium concentration of DOC 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

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

	Freundlich			Langmuir			Tempkin			D-R		
Surface	K_f mg^{-1} $(1\text{-}n)g^{-1}$ $L^{1/n}$	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}	2
SBTL	0.009	0.347	0.958	-0.06	-3.365	0.603	24.411	0.152	0.950	-2.05	36.812	0.982
PP.	0.0004	0.329	0.977	-0.034	-1.336	0.857	6.089	0.102	0.804	-3.639	11.455	0.934

Langmuir model is not able to describe the experimental data properly, poorless of fitting on both wastes.

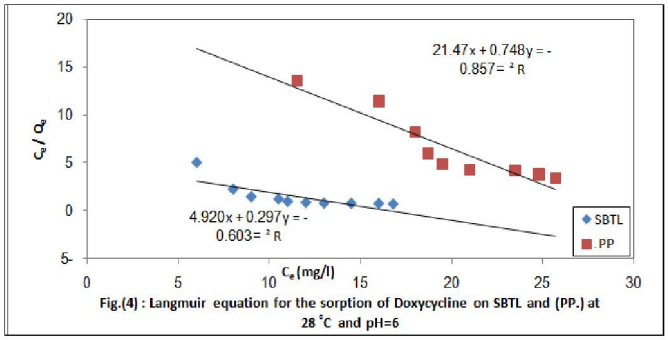


Fig.(4) : Langmuir equation for the sorption of Doxycycline on SBTL and (PP.) at 28 °C and pH=6

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 (Mohammad *et al*., 2013; Hameed *et al*., 2008). The tempkin has generally been applied in the following linear form:

$Q_e = B \ln A + B \ln C_e$

Where, $B = RT/b$

A plot of q_e versus $\ln C_e$ 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 can be used to describe the sorption of DOC onto (SBTL) waste, but less of fitting onto (PP) waste.

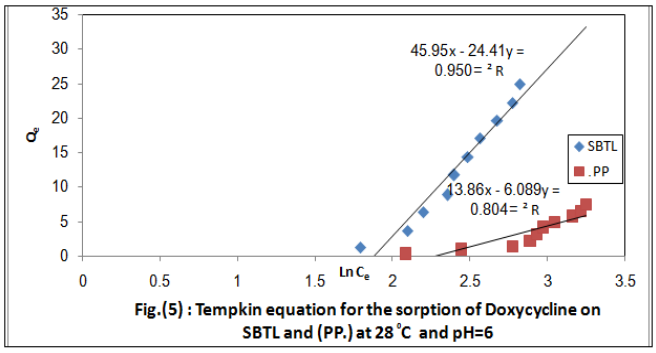


Fig.(5) : Tempkin equation for the sorption of Doxycycline on SBTL and (PP.) at 28 °C and pH=6

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 (Itodo *et al*., 2010; Qok, 2013). The linear form of (D-R) isotherm equation is (Liangliang *et al*., 2010):

$\ln q_e = \ln q_m - K_D R \varepsilon^2$

$\varepsilon = RT \ln[1 + (1/Ce)]$

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 DOC uptake by spent black tea leaves waste (SBTL), and seem to be less agreement with the Freundlich andTempkin equations but poorless of fitting with Langmuir equation.

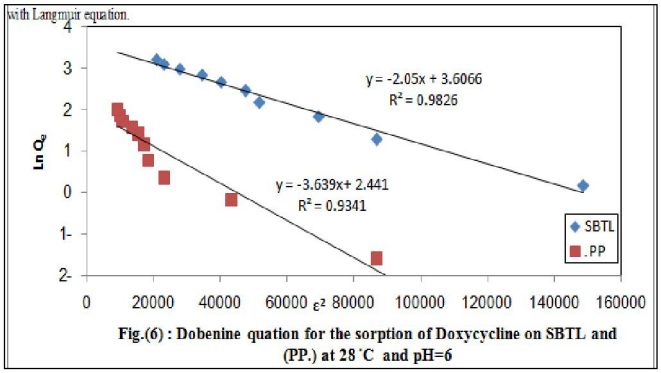


Fig.(6) : Dobenine quation for the sorption of Doxycycline on SBTL and (PP.) at 28 °C and pH=6

Adsorption Kinetics

In order to evaluate the adsorption kinetics of DOC on to (SBTL) and (PP) wastes, different kinetic models are used to fit the experimental data which were analyzed by using simple - first - order, pseudo-first - order, second - order and pseudo - second - order equations as shown (Liangliang *et al*., 2010; Mohammad *et al*., 2013; Juanjuan and Li, 2011)

$\ln q_t = k_1 t + \ln q_o$	Simple-first- order
$\ln (q_e - q_t) = \ln q_e - k'_1 t$	Pseudo-first-order
$1/q_t = k_2 t + 1/q_o$	Second- order
$t/q_t = 1/k'_2 q_e + 1/q_e t$	Pseudo-second-order

Where q_e and q_t are the amount of DOC sorbed (mgg^{-1}) at equilibrium and at any time respectively; 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, pseudo – second – order rate constants of adsorption respectively; q_o are the initial amount of DOC sorbed (mgg^{-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 results reveal that the pseudo - second - order adsorption mechanism of the DOC on to both wastes (SBTL) and (PP) is predominant.

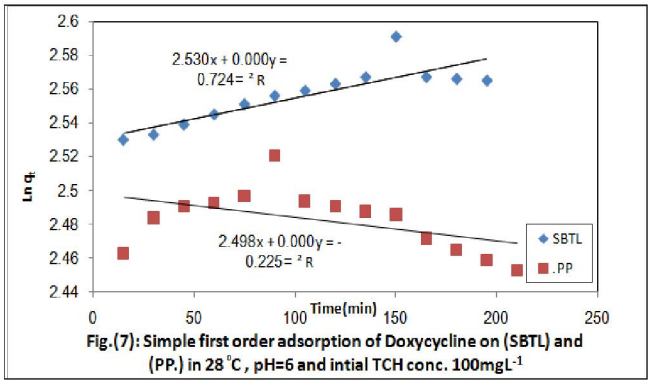


Fig.(7): Simple first order adsorption of Doxycycline on (SBTL) and (PP.) in 28 °C , pH=6 and intial TCH conc. 100mgL-1

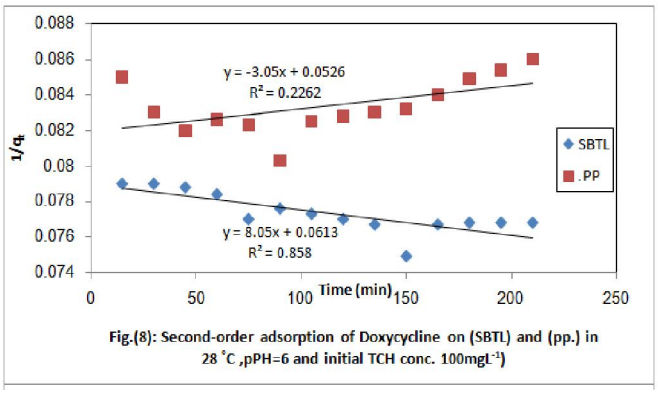


Fig.(8): Second-order adsorption of Doxycycline on (SBTL) and (pp.) in 28 °C ,pPH=6 and initial TCH conc. 100mgL-1)

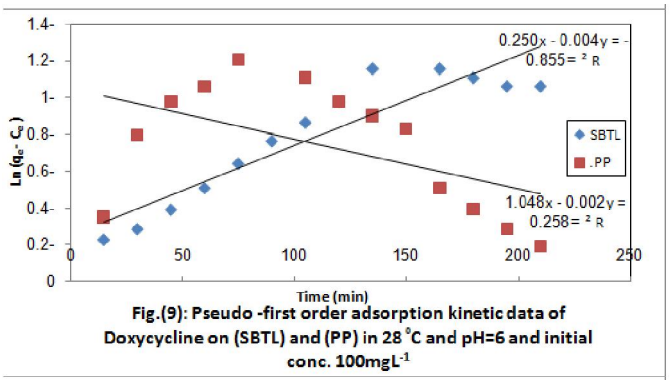


Fig.(9): Pseudo -first order adsorption kinetic data of Doxycycline on (SBTL) and (PP) in 28 °C and pH=6 and initial conc. 100mgL-1

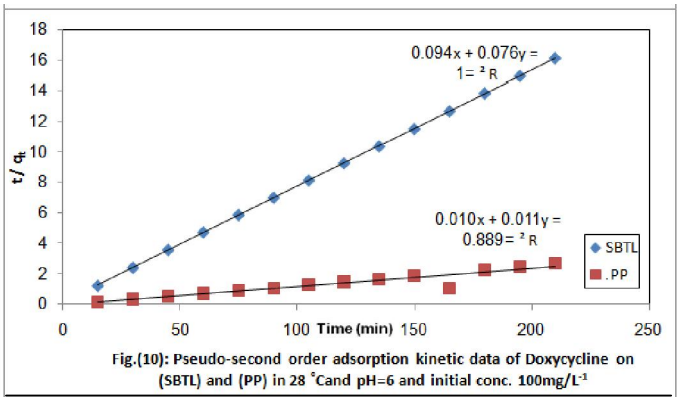


Fig.(10): Pseudo-second order adsorption kinetic data of Doxycycline on (SBTL) and (PP) in 28 °Cand pH=6 and initial conc. 100mg/L-1

competing with cations group of the DOC. At pH 6 the concentration of the H^+ is lowered and the adsorption of DOC 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 DOC and the surface of both wastes and so the adsorption of DOC will be reduced.

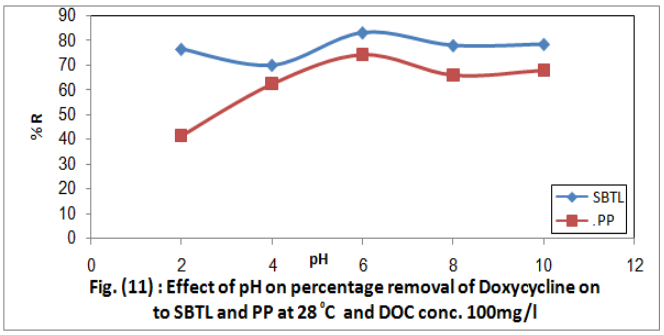


Fig. (11) : Effect of pH on percentage removal of Doxycycline on to SBTL and PP at 28 °C and DOC conc. 100mg/l

Temperature dependence

The data of DOC 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 DOC on to both wastes was increased by decreasing the temperature, indicating that the adsorption process is an exothermic and favourable at low temperature, 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 equation (Liangliang et al., 2010):

$$S = (1 - \Theta) \exp(- Ea / RT)$$

$$\Theta = 1 - C_e / C_o$$

Where Θ is the surface coverage, C_o and C_e are the initial and equilibrium DOC 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 negative value of

Table 2. Isotherms parameters of 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	q_o mg/g	K_1 Min^{-1}	R^2	qe mg/g	K_{1p} Min^{-1}	R^2	q_o mg/g	K_2 mgg^{-1} Min^{-1}	R^2	qe mg/g	K_{2p} mgg^{-1} Min^{-1}	R^2
SBTL	12.531	-2×10^{-4}	0.724	0.779	0.004	0.855	16.313	8.05	0.858	13.106	0.061	1
PP.	18.113	1×10^{-4}	0.225	0.35	-0.002	0.258	19.011	-3.05	0.226	84.033	0.013	0.889

pH Dependence

The infleunce of pH on the adsorption of DOC 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 DOC 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 DOC solution till pH 6 then decreased with increasing in pH value. This observation attributed to the DOC antibiotic, which are amphoteric molecules having multiple ionizable functional groups, acquire tricarbonyl amide, phenolic diketon and dimethyl amine moieties, in addition, DOC is characterized by three dissociation constants and exists as cationic, Zwitterionic and ionic species under acidic, neutral and alkaline conditions (Sassman and Lee, 2005; Gu *et al*., 2007). At low pH value the presence of H^+ ions which

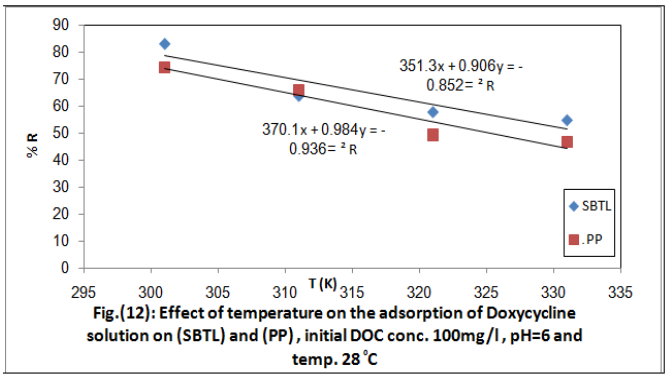


Fig.(12): Effect of temperature on the adsorption of Doxycycline solution on (SBTL) and (PP), initial DOC conc. 100mg/l, pH=6 and temp. 28 °C

activation energy (Ea) indicates that the adsorption mechanism is a diffusion controlled - process such result have been reported (Jnr and Spiff, 2005). The value of sticking

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

		SBTL				PP			
T(K)	1000/T(K^{-1})	ΔG $kJmol^{-1}$	ΔH $kJmol^{-1}$	ΔS $Jmo1k^{-1}$	E_a $KJmol^{-1}$	ΔG $kJmol^{-1}$	ΔH $kJmol^{-1}$	ΔS $Jmo1^{-1}$ k^{-1}	E_a $KJmol^{-1}$
301	3.322	+36.877	- 0.037	- 122.639	- 0.023	+38.28	-0.035	-127.29	-0.021
311	3.215	+38.103	-	-	-	+39.623	-	-	-
321	3.115	+39.33	-	-	-	+40.826	-	-	-
331	3.021	+40.556	-	-	-	+42.099	-	-	-

probability for DOX sorption on to (SBTL) and (PP)

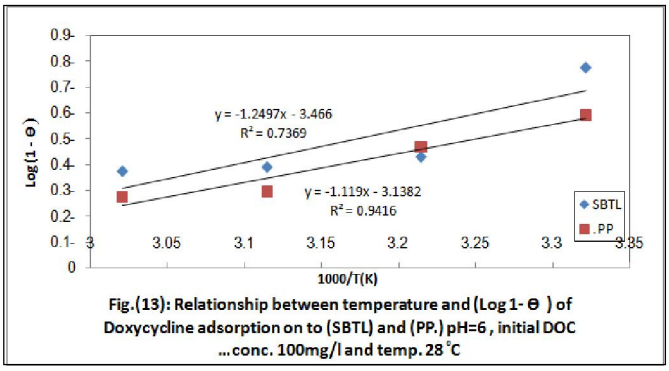


Fig.(13): Relationship between temperature and (Log 1- Θ) of Doxycycline adsorption on to (SBTL) and (PP.) pH=6 , initial DOC ...conc. 100mg/l and temp. 28 °C

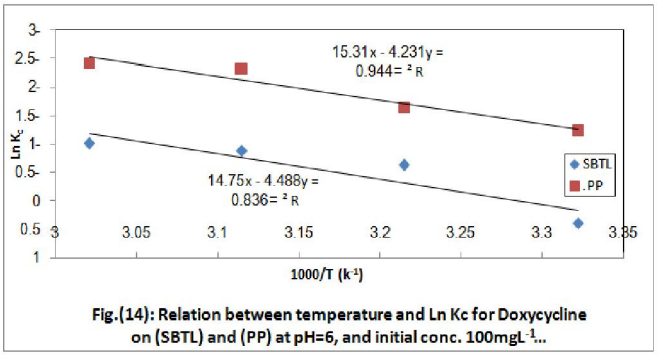


Fig.(14): Relation between temperature and Ln Kc for Doxycycline on (SBTL) and (PP) at pH=6, and initial conc. 100mgL^{-1}...

probability is S<<1 which indicate that the adsorption process is physisorption. Thermodynamic parameters were calculated to evaluate the thermodynamic feasibility of the DOC adsorption. Thermodynamic considrations necessary to conclude wether the process is spontaneous or not, the Gibbs, free energy change, ΔG°, is an important criterion for non-spontaneity. Both enthalpy ΔH° and entropy ΔS° parameters must be considered in order to determine the Gibbs free energy of the process, the following equation had been used to calculate these parameters:

$$\text{Ln } k_c = - \Delta H/RT + \Delta S/R$$

$$\Delta G^o = \Delta H° - T \Delta S°$$

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 in K_c and temperature, the positive values of ΔG° indicate the adsorption process is non-spontaneous in nature, furthermore, the nagative value of ΔS° suggests the decreased randomness at the solid solution interface during the adsorption of DOC. Table 4 show the thermodynamic parameters, activation energy and surface coverage of DOC adsorption on to (SBTL) and (PP) at the temperature range (28 - 58° C) and pH=6.

Conclusion

The adsorption of DOX onto wastes of (SBTL) and (PP) has been studied. Adsorption experiments were tested at various parameters such as sorbent dosage, contact time, pH, DOC concentration and temperature. The equilibrium data were analyzed by using Freundlich, Langmui, Tempkin and D- R isotherm models and the results are well fitted to D-R and Freundlich equations. It was found that the equilibrium was reached within 150 and 90 min. for (SBTL) and (PP) wastes respectively, also it was found that the optimum pH value of the DOC adsorption was 6. The kinetic studies follow the pseudo-second-order model, effect of temperature on adsorption process shows that adsorption is an exothermic, non-spontaneous and the mechanism is physisorption because of low activation energy. The present work concludes that (SBTL) and (PP) agricultural wastes are effective adsorbents in removing DOC from aqueous solutions.

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