Equilibrium Adsorption of Antibiotics at Solid Liquid Interface

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ABSTRACT

Background and Objectives: The presence of pharmaceuticals in the environment is an emerging concern in the environmental community. Sorption interactions of three high – use antibiotics [Cefotaxime (CEF), Ciprofloxacin (CIP), and Oxytetracycline (OTC)] with soils from Erbil governorate were investigated. This study was aimed to find out the fate and the behavior of antibiotics in our local environment, no such study has been done in Kurdistan.

Methods: Adsorption of the selected antibiotics on the studied soil samples were conducted using batch equilibrium techniques. The samples were analyzed by HPLC and UV visible spectrophotometer.

Results: Adsorption data were correlated with linear distribution, Freundlich and Langmuir models. Freundlich model being found to provide the best fit of the experimental data (R^2 ≥0.856). The results showed that the three studied antibiotics were found to adsorb strongly to the soils with 50- 76% adsorbed under all experimental conditions. Values of equilibrium constant were increased with temperature. Values of standard Free energy change were in the range -10.412 to -2.089, -14.102 to -2.721, and -25.952 to - 1.414 KJmol^{-1}, for CEF, CIP and OTC respectively. Values of standard enthalpy change followed the range 51.043-74.081, 38.535-85.476, and 52.561- 73.512 Kjmol^{-1}, for Cef, Cip and OTC respectively.

Conclusions: : Values of standard Free energy change were negative and increased with temperature, indicating that at all experimental temperatures: the interactions of antibiotics with soils were spontaneous with a high preference of the soil surface and the adsorption occurred through a bonding mechanism. The results of effect of temperature and thermodynamic parameters confirm the adsorption process to be endothermic in nature.

Key words: Sorption equilibria, antibiotics, thermodynamic, soil, equilibrium constant, Freundlich isotherm.

INTRODUCTION:

Application of liquid manure in agricultural land from livestock and sewage sludge from waste water treatment plants is a general practice on internationally encourage the contamination of different environmental compartments through the entry of hazardous material. The behavior of antibiotics in soil greatly depends on their adsorption-desorption characteristics, and the knowledge of these processes are important to predict their bioavailability, fate and transport mechanism through soil into ground water or surface water[1-3]. The dissipation of OTC in soils have been studied under different redox condition[4], which was influenced by many factors including soil properties(pH, organic matter and metal ions) and chemical nature of OTC as well as redox conditions. The study of Cip sorption to 30 soils from the eastern United States revealed a statistically significant effect of pH on the

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distribution coefficient. To date, the behavior and the effects of pharmaceuticals in the environment are widely unknown and very little information is available on the environmental fate and transport of antibiotics. No such study has been done in Kurdistan. Thus this study was proposed to know about the adsorptions of antibiotics onto solid matrices and may accumulate in the environment. The primary aim of this study was to evaluate thermodynamic adsorption behavior of three commonly used antibiotics Cef, CIP and OTC on selected

MATERIALS AND METHODS

soils from Erbil governorate.
Adsorbents and Reagents
The soil samples (S_1-S_4) selected for this study were collected from four different locations in Erbil governorates (Minara, Runaki, Sorbash, and Havalan respectively) in August 2008 and defined by GPS system. Standard soil characterization methods were followed, to provide information on some of the physical and chemical nature of the soils. The samples were chosen for their similar pH (7.62, 7.26, 7.45& 7.5) and low soil organic matter[2-4] (SOM% 1.4, 0.82, 1.3&0.62). Cef powder and Cip were obtained from the Copran, Ajanta-India, while OTC was obtained from Fluka AG, Buchs SG. All the chemical compounds used to prepare the reagent solutions were of analytical grade and used without further purification and all solutions and standards were prepared using de-ionized water. Concentration analysis of Cip were performed on High performance liquid chromatography (HPLC), Advanced scientific instruments (KNAUER, Germany) with Smart line manager (5~000), pump (1000) and UV detector (2500) at 278nm. The chromatographic separation was carried out in an Atlantis™ dC18 HPLC column (150 mm × 3.0 mm, 3 μm) using injection volume of 100 μl and linear elution as follows: from 50% A (diluted formic acid,

detected UV Visible spactrometer at 235, and 370 nm respsctively.
Adsorption Equilibrium Procedure
A preliminary sorption experiments were conducted for each antibiotics to determine contact times, soil: solution ratio and initial concentration required to attain sorption equilibrium. Sorption experiments were conducted in accordance with OECD test guideline no. 106 using the batch procedure described previously[5-7]. The experiments were done by equilibrating 10 ml of antibiotic/ soil suspensions at 288, 298 and 308 K in an initial concentration of 4,6,8 and 10 μg ml^{-1}, 10,20,40 and 50 μg ml^{-1}, and 20,40,50, and 70 μg ml^{-1} for OTC, Cip and Cef, respectively. The suspension was shaken at temperature controlled water bath shaker (185 rpm) for 12 h, and then centrifuged for 45 min at 3500 rpm. Control samples (without soil), blank samples (without antibiotic) were prepared and analyzed by identical procedures as the adsorption samples to avoid any interfering from the equipments and the soil. Two replicates were used for collecting each data point.

RESULT:

Equilibrium Adsorption
Several models have been used in the adsorption studies to describe the experimental data adsorption isotherms for antibiotic including, Linear, Freundlich and Langmuir models.

Freundlich Adsorption Isotherm:
Freundlich model is an empirical equation based on sorption on heterogeneous surfaces or surfaces supporting sites of varied affinities. The Freundlich equation can be expressed as follows[8-9]:

$$\log q_e = \log K_f + n \log C_e \ldots\ldots\ldots[1]$$

Where K_f is Freundlic adsorption constant, n is the Freundlich exponent, q_e and C_e are the equilibrium concentration of antibiotic adsorbed on solid ($\mu g g^{-1}$) and in the liquid phase ($\mu g ml^{-1}$) respectively. From the plot of $\log q_e$ *vs*. $\log C_e$ (Figure 1), values of K_f and n can be estimated from the intercept and slope, respectively. Values of K_f

(Table 1) for CEF varied between 1.448-43.822 ml g^{-1}), for CIP 3.742- 52.601 ml g^{-1} and for OTC between 2.884-14.709 ml g^{-1}.

Equilibrium adsorption thermodynamics

The adsorption isotherm is the most important parameter, which indicates how adsorbate molecules are distributed between the liquid and solid phases when the adsorption process reaches equilibrium[15]. Adsorption experiments were conducted at 15, 25, and 35 °C to study the thermodynamic (equilibrium) parameters, associated with the adsorption of the studied antibiotics on the selected soil samples.

Thermodynamic equilibrium constant

The thermodynamic parameters associated with the adsorption processes can be calculated from the variation of thermodynamic equilibrium constant (K_o) with temperature, during the adsorption reaction[16].Values of lin K_o were obtained from the plot of lin (q_e / Ce) vs. q_e, the lin K_o was obtained at q_e=0, as described by Biggar et al [17]. Values of lin K_o (Table 3) were in the range 0.872-4.066, 1.136-5.507, and 0.590-10.135 for Cef, CIP and OTC respectively.

Standard Free energy change

The standard free energy change (ΔG^o) for sorption is computed using adsorption equilibrium constant[16].

$$\Delta G^o = -RT \, lin \, K_o \ldots\ldots\ldots\ldots\ldots\ldots\ldots[2]$$

The values of ΔG^o for adsorption of the studied antibiotics on the selected soil samples at 288.15, 298.15 and 309.15 °k were summarized in Table 2.. The ΔG^o values were in the range -10.412 to -2.089, -14.102 to -2.721, and -25.952 to -1.414 KJmol^{-1}, for Cef, CIP and OTC, respectively. At constant temperature a more negative of ΔG^o implied a greater driving force of sorption, resulting in a higher sorption capacity. The results obtained in the present study are similar to those obtained by other researchers[18-19].

Enthalpy and entropy changes

The change in enthalpy (ΔH^o) and entropy (ΔS^o) were estimated from the

$$Lin \, ko = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

The values of ΔH^o and ΔS^o were calculated from the slope and intercept of the plot of the lin K_o versus 1/T respectively and were summarized in Table 3. The values of ΔH^o followed the range 51.043-74.081, 38.535-85.476, and 52.561- 73.512 KJmol^{-1}, for Cef, CIP and OTC, respectively. The over all adsorption process seems to be endothermic.. The values of ΔS^o were in the range 258.291-190.506, 306.186-142.568 and 340.907- 185.718 Jmol^{-1}K^{-1}, for Cef, CIP and OTC, respectively.
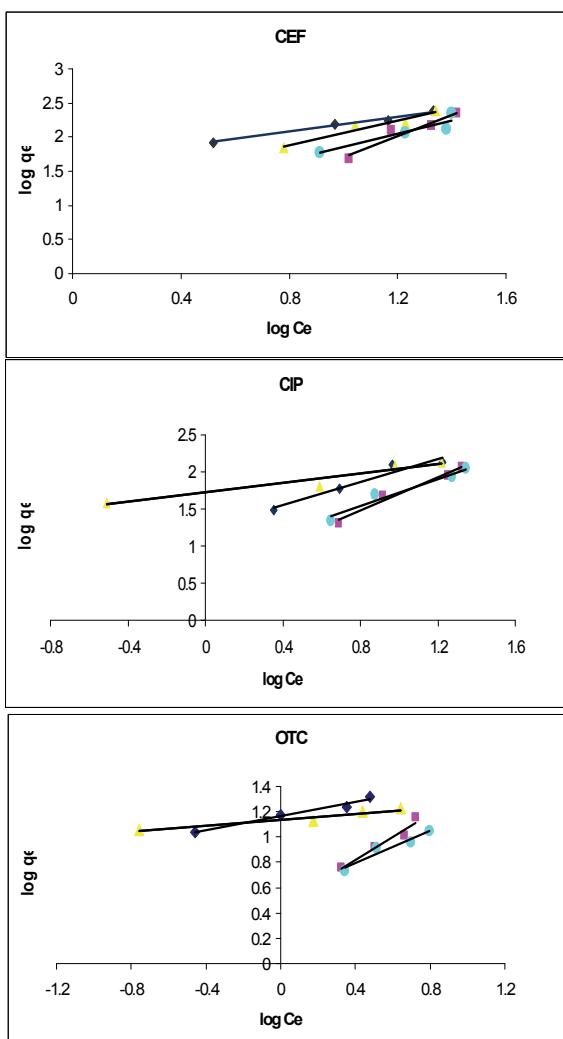

Figure 1: Freundlich adsorption isotherm for (a) Cef, (b) Cip and (c) OTC (♦ S$_1$, ■ S$_2$, ▲ S$_3$ ● S$_4$).

Table 1: Adsorption isotherm parameters for the linear, Freundlich and Langmuir models for CEF, CIP and OTC.

antibiotics	Adsorption models	parameter	S_1	S_2	S_3	S_4
Cefotaxime	Dist.Coeff.	Kd(cal)	12.297	7.615	10.898	7.181
		R^2	0.696	0.879	0.927	0.725
	Freundlich	Kf (ml g^{-1})	43.822	1.448	15.187	7.271
		n	0.546	1.545	0.8805	0.9855
		R^2	0.987	0.914	0.943	0.856
	Longmiur.	KL	0.083	-0.020	84.444	0.002
		Qm	-357.14	-200	1111.100	3333.33
		R^2	0.927	0.513	0.277	0.006
Ciprofloxacin	Dist. Coeff	Kd(cal)	9.477	5.299	9.548	4.917
		R^2	0.699	0.982	0.417	0.950
	Freundlich	K_f(ml g^{-1})	17.676	3.741	52.601	6.513
		n	0.779	1.125	0.317	0.908
		R^2	0.944	0.978	0.926	0.954
	Longmiur.	KL	0.058	-0.008	0.358	0.010
		Qm	285.714	-500	153.840	555.500
		R^2	0.790	0.285	0.935	0.266
Oxytetracycline	Dist. Coeff	Kd(cal)	7.948	2.535	4.810	1.938
		R^2	-1.351	0.914	-9.183	0.815
	Freundlich	Kf(ml g^{-1})	14.709	2.884	13.775	3.466
		n	0.280	0.9059	0.116	0.636
		R^2	0.968	0.946	0.930	0.921
	Longmiur	KL	0.494	0.027	4.090	0.157
		Qm	23.090	101	17.450	22.020
		R^2	0.972	0.126	0.992	0.833

Table 2: Equilibrium constant and standard free energy change for adsorption of CEF, CIP and OTC

Antibiotics	soil	288.15 °K		298.15 °K		309.15 °K	
		ln k_o	ΔG° (kj mol^{-1})	ln ko	ΔG° (kj mol^{-1})	ln k_o	ΔG° (kj mol^{-1})
Cefotaxime	S1	2.458	-5.886	3.615	-8.957	4.066	-10.412
	S2	0.872	-2.089	1.460	-3.618	2.654	-6.798
	S3	2.057	-4.925	2.618	-6.486	3.284	-8.411
	S4	1.179	-2.824	1.734	-4.298	2.755	-7.056
Ciprofloxacin	S1	1.963	-4.701	2.729	-6.762	4.019	-10.293
	S2	1.136	-2.721	1.486	-3.683	2.528	-6.475
	S3	3.623	-8.676	5.132	-12.716	5.507	-14.102
	S4	1.439	-3.445	1.753	-4.344	2.366	-6.058
ytetracycline	S1	4.108	-9.836	5.053	-12.521	5.872	-15.038
	S2	0.590	-1.414	0.957	-2.372	1.944	-4.979
	S3	8.211	-19.661	9.451	-23.417	10.135	-25.952
	S4	0.955	-2.287	1.251	-3.100	2.219	-5.683
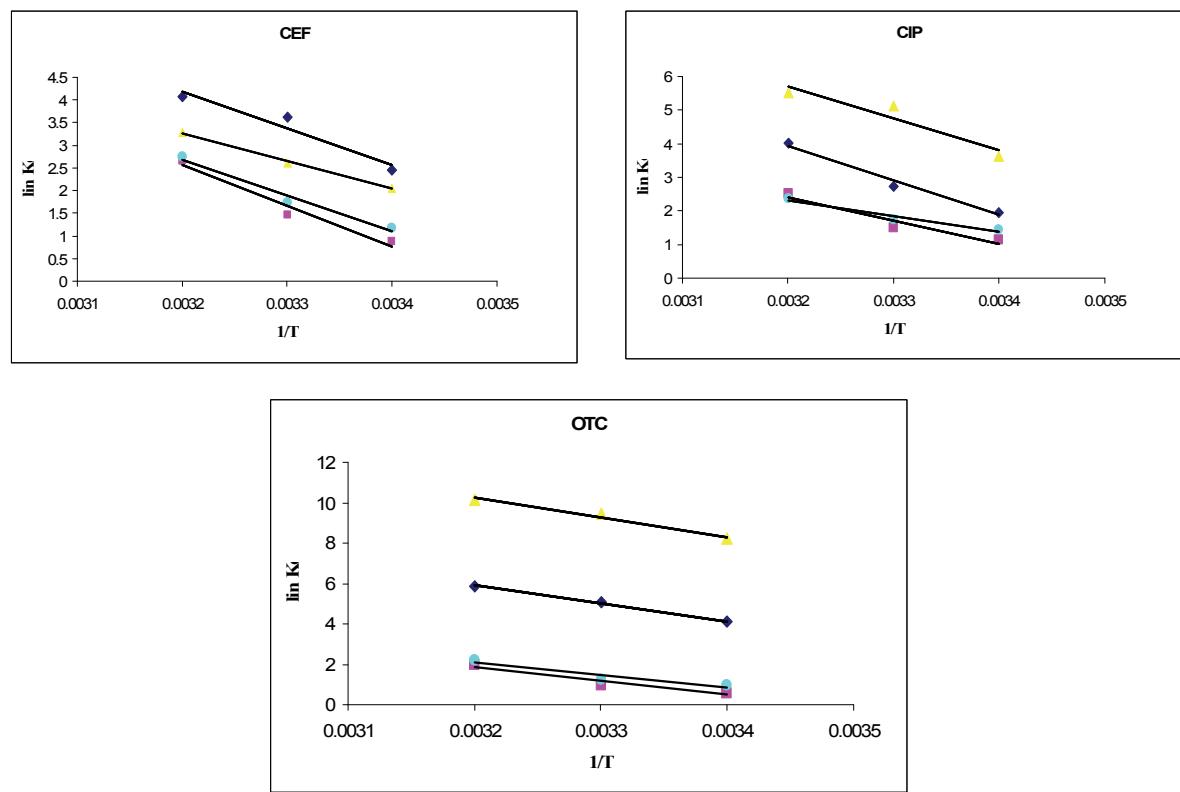
Figure 2: variation of lin K_o with 1/T for adsorption of, (a) Cef, (b) CIP and(c) OTC.
(◆ S$_1$, ■ S$_2$, ▲ S$_3$ ● S$_4$).

Table 3: Standard enthalpy change and entropy change (determined graphically) for adsorption of Cef, CIP, and OTC on the selected soil samples.

Soil	Cefotaxime			Ciprofloxacin			Oxytetracycline		
	$\Delta H°$ (kJ mol^{-1})	R^2	$\Delta S°$ (J mol^{-1} k)	$\Delta H°$ (kJ mol^{-1})	R^2	$\Delta S°$ (J mol^{-1} k)	$\Delta H°$ (kJ mol^{-1})	R^2	$\Delta S°$ (J mol^{-1} k)
S1	66.840	0.939	248.670	85.467	0.978	306.186	73.512	0.998	284.247
S2	74.081	0.962	258.291	57.873	0.924	205.264	56.264	0.934	195.35
S3	51.043	0.997	190.506	78.313	0.8922	297.965	79.959	0.972	340.907
S4	65.506	0.971	231.885	38.535	0.966	142.568	52.561	0.913	185.718

DISCUSSION :

The results of Adsorption isotherm parameters for the Linear, Langmuire and Freundlich models (Table 1) indicated that the experimental data showed good agreement and fit with Freundlich mathematical model (R^2 >0.914)**.** The differences in the behavior of the antibiotics toward the same soil sample are due to the difference in the type of interaction of the antibiotic and the characteristics of the studied soil samples. The interaction between antibiotic and soil was related to the surface charge of the soil particle and functional groups of antibiotic [10-11]. It reveals that adsorption is a complex phenomenon involving different types of adsorption sites with different surface energies and the process has a multilayer character [12]. Our results were in good agreement with those obtained by other researchers[13-14]. Considering that the values of n (parameter indicating the variation in the adsorption with concentration) depart from unity the adsorption values will vary with concentration of antibiotic in the solution. The adsorptivity of the soils for antibiotics (Table 2) was in order OTC >CIP> CEF in the soil with a highest organic mater (S_3) , and this order may be due to the characteristics of each antibiotic and their

temperature and the position of equilibrium depends only on thermodynamic quantities and is independent of any consideration of kinetics or mechanism. Results in Table 2 showed that K_o values were increased by increasing temperature, confirming that the antibiotics had a high preference for adsorption at high temperature. The values of $\Delta G°$ of adsorption(Table2) were negative and increased with increasing temperature, indicating that, at all experimental temperatures the interaction of antibiotics on soils was spontaneous and the degree of spontaneity increases with increasing temperature with a high preference of the soil surface and the adsorption occurred through a bonding mechanism[18]**.** At constant temperature a more negative of $\Delta G°$ implied a greater driving force of sorption, resulting in a higher sorption capacity. The results obtained in the present study are similar to those obtained by other researchers[18-19]. The over all adsorption process seems to be endothermic. Results in table 3 shows The different values of $\Delta H°$ for adsorption of the same antibiotic on the selected soil samples may be correlated to difference in soil components. High values of $\Delta H°$ pointed towered chemisorption mechanism, it may be through the coordination and /or protonation, hydrogen bonding and dipole association or Van der

between the soil and organic molecules occur with or with out a water bridge[19]. The positive values ΔS^o (Table 3) indicates the entropy increases as a result of adsorption. This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs the antibiotic near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free molecules to molecules interacting with the adsorbent will be higher in the adsorbed state. As a result the randomness will increase at the solid solution interface.

CONCLUSION:

For every solute- sorbent system tested, Freundlich model fits well the data obtained and Freundlich constants were calculated. Thermodynamic studies of adsorption of tested antibiotics were carried out, the values of the thermodynamic parameters namely K_o, ΔG^o, ΔH^o, ΔS^o were determined. The interaction of antibiotics on soils was endothermic, spontaneous and the degree of spontaneity increases with increasing temperature. The higher positive values of ΔH^o indicate stronger binding.

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