

Research Article

Sorption of Tetracycline, Oxytetracycline, and Chlortetracycline in Illite and Kaolinite Suspensions

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The sorption interaction of three widely used tetracycline antibiotics, namely, tetracycline, chlortetracycline, and oxytetracycline, under various conditions of time, pH, temperature, ionic strength, and exchangeable cations on illites and kaolinites was examined. First-order reaction indicated diffusion-controlled adsorption, maximum adsorption occurring at pH values of 3.5, 3, and 4 for tetracycline, oxytetracycline, and chlortetracycline, respectively. Adsorption isotherms of "L" type showed that the adsorption of antibiotics was in the order of chlortetracycline > oxytetracycline > tetracycline. Adsorption was maximum for Al-saturated complexes and followed the order of Al- > Na- > K- Ca. The adsorption varied inversely with changes in temperature and ionic strength up to 0.6 after which it became constant. Free energy changes (ΔG) were negative signifying a spontaneous reaction; the values of ΔG suggest a partial physical adsorption. Enthalpy changes showed that the process is exothermic. The positive values of entropy change suggest that adsorption of tetracyclines molecules is in disordered arrangement on clay surfaces. The data of these parameters with IR and X-ray studies revealed the existence of protonation and/or coordination between exchangeable cation and oxygen of >C=O group of antibiotics. The amount of cations desorbed indicated that cation exchange phenomena played an important role during adsorption.

1. Introduction

The use of antibiotics as veterinary pharmaceuticals has become the integral part of the animal food industry because of their valuable contributions in treating diseases [1], as growth promoters [2], and in improving feed efficiency [3]. The tetracyclines (tetracycline (TC), oxytetracycline (OTC), and chlortetracycline (CTC)) are broad spectrum antibiotics widely used in animal food industry. Tetracyclines contribute approximately 50% of total antibiotics production. Antibiotics may appear in the environment when manure, sewage sludge, and wastewater effluents are used up in different agricultural applications. Thus, a genuine concern arises that residual concentration of antibiotics in agricultural soils may lead to the development of bacterial resistance which may disperse in the environment or, alternatively, highly mobile antibiotics will accumulate in the soil and leach into groundwater. So, efforts towards their removal from wastewater and manure have been stimulated. Parolo et al. [4] found that Patagonian montmorillonite appeared as a good adsorbent of TC. Barbooti et al. [5] reported that Iraqi montmorillonite can remove 94%–96% of OTC. The partitioning behavior of pharmaceuticals in aquatic environments is likely to be dictated by a number of physicochemical parameters such as pH, ionic strength, and organic content present [6].

As Indian saline soil mainly contains illite and kaolinite clays, the purpose of this work is to study the sorption of tetracycline, oxytetracycline, and chlortetracycline on Morris illite and Bath kaolinite under different physical and chemical conditions along with X-ray diffraction, IR analyses, and thermodynamic parameters in order to evaluate the feasibility of clays to remove tetracyclines from wastewater.

2. Materials and Methods

The minerals used in these studies were an illite from Morris, IL, USA, and monomineralic standard kaolinite from Bath, SC, USA. Through treatment with 1N NaCl, a <2 um fraction of clay samples was purified by sedimentation



FIGURE 1: Sorption of tetracyclines on illite and kaolinite at different pH values.

and centrifugation and converted into Cl⁻ free Na-saturated clay. Homoionic suspensions of K-, Ca-, and Al-illite and kaolinite were obtained from the Na form by the ion exchange technique. The CEC of illite was 20.8 C mol (p⁺) kg⁻¹ for the illite and 11 C mol (p⁺) kg⁻¹ for the kaolinite.

The effect of the equilibrium pH on adsorption of tetracycline, oxytetracycline, and chlortetracycline was investigated at pH values ranging between 2 and 11 with a 0.5 increment obtained by adding 0.1 M HCl or 0.1 M NaOH as required on Na-illite and Na-kaolinite. A 10 mL of clay suspension (containing 0.1 g of clay) was mixed with a 15 mL of tetracycline solution ($100 \,\mu g \, mL^{-1}$ for illite and 50 $\mu g \, mL^{-1}$ for kaolinite), making the volume up to 25 mL (the initial concentration of antibiotics was 60 mg/L for illite and 30 mg/L for kaolinite). The suspensions were shaken for 24 h in a constant-temperature water bath at 20 ± 1°C. The amount of tetracycline adsorbed was calculated.

Batch sorption experiments were conducted using 10 mL of the appropriate illite or kaolinite suspensions in a large number of glass stoppered tubes, adding 0 to 15 mL of standard tetracyclines solution (concentration $100 \,\mu \text{g mL}^{-1}$ for illite and $50 \,\mu \text{g mL}^{-1}$ for kaolinite) and making the volume up to 25 mL with distilled water (the initial concentration of antibiotics was 0 to 60 mg/L for illite and 0 to 30 mg/L for kaolinite). The suspensions were shaken for 24 h in a constant-temperature water bath at 293 ± 1 K, 308 ± 1 K, and 323 ± 1 K (preliminary studies indicated that equilibrium was attained within 24 h) followed by centrifugation for 15 min at 13000 rpm. The concentration of tetracycline, oxytetracycline, and chlortetracycline in supernatants was estimated.

The amount of tetracycline adsorbed was obtained from the amount added minus that remaining in the supernatants.

For ionic strength experiment, 10 mL of appropriate illite or kaolinite suspensions (containing 0.1 g of clay) were mixed with a 15 mL of tetracyclines solution (100 μ g mL⁻¹ for illite and 50 μ g mL⁻¹ for kaolinite), which was initially prepared in appropriate solution of different electrolytes ranging from 0.00166 to 0.3 N at constant volume of 25 mL (the initial concentration of antibiotics was 60 mg/L for illite and 30 mg/L for kaolinite). The suspensions were shaken for 24 h in a constant-temperature water bath at 20 ± 1°C. The amount of tetracycline adsorbed was calculated.

The concentrations of TC, OTC, and CTC in extracts were analyzed by HPLC using an Agillent 1100 system with an octadecylsilane column (50 mm × 4 mm × 3 μ m, AQ-YMC), and TC, OTC, and CTC were analyzed simultaneously. A gradient elution was carried out over 20 min with 0.1% formic acid in acetonitrile (Solvent A) and 0.1% formic acid in water (Solvent B). The initial percent of Solvent A was 5%, which then increased to 30% from 0 to 7 min and remained at 30% from 7 to 8.5 min. The percentage of Solvent A returned to 5% from 8.5 to 10 min and remained at 5% from 10 to 12 min. The flow rate was maintained 0.70 mL min⁻¹ throughout the analysis and simultaneous detection of TC, OTC, and CTC was performed at 360 nm. Retention times of OTC, CTC, and TC were 6.4, 17.3, and 9.6 min, respectively. The minimum limit of detection was 0.5 μ gkg⁻¹ soil.

Metal cations desorbed were estimated in the supernatant solution by atomic absorption spectrophotometer/flame photometer.

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TABLE 1: Adsorption of tetracycline, oxytetracycline, and chlortetracycline on illite and kaolinite saturated with different cations at several ionic strengths (of appropriate salt) at 293 K.

Ionic strength	Saturating cation	Amount of tet (m	racycline sorbed ng/g)	Amount of oxy (tetracycline sorbed mg/g)	Amount of chlortetracycline sorbed (mg/g)		
strength		Illite	Kaolinite	Illite	Kaolinite	Illite	Kaolinite	
I = 0.000	Al ³⁺	8.62	4.65	8.85	4.78	9.03	4.92	
	Na^+	8.41	4.54	8.67	4.65	8.82	4.78	
	K^+	8.29	4.41	8.52	4.52	8.65	4.65	
	Ca ²⁺	8.15	4.25	8.41	4.40	8.49	4.52	
	Al ³⁺	8.23	4.32	17.10	4.52	17.32	4.74	
I = 0.006	Na ⁺	8.04	4.18	16.84	4.38	17.10	4.50	
1 0.000	K^+	7.95	4.07	16.66	4.25	16.90	4.40	
	Ca ²⁺	7.77	3.96	16.40	4.14	16.62	4.25	
	Al ³⁺	7.96	4.02	16.70	4.26	16.85	4.45	
I = 0.018	Na^+	7.84	3.90	16.44	4.12	16.62	4.26	
1 - 0.010	K^+	7.68	3.75	16.25	3.92	16.40	4.10	
	Ca ²⁺	7.52	3.58	16.08	3.78	16.22	3.88	
	Al ³⁺	7.15	3.76	16.35	3.90	16.55	4.12	
I = 0.054	Na ⁺	6.95	3.62	16.12	3.75	16.28	3.88	
1 0.051	K^+	6.74	3.45	15.90	3.55	16.04	3.65	
	Ca ²⁺	6.50	3.32	15.68	3.45	15.84	3.54	
	Al ³⁺	6.75	3.58	15.75	3.70	15.94	3.88	
I = 0.09	Na^+	6.44	3.46	15.62	3.55	15.80	3.65	
1 - 0.07	K^+	6.32	3.28	15.54	3.40	15.65	3.43	
	Ca ²⁺	6.18	3.14	15.38	3.22	15.50	3.38	
	Al ³⁺	6.24	3.44	15.18	3.54	15.32	3.62	
I = 0.27	Na ⁺	5.92	3.28	15.06	3.36	15.20	3.55	
1 - 0.27	K^+	5.78	3.14	14.92	3.24	15.06	3.34	
	Ca ²⁺	5.58	3.07	14.80	3.12	14.92	3.26	
I = 0.54, 1.08, 1.62	Al ³⁺	6.14	3.32	6.36	3.38	6.48	3.47	
	Na^+	5.86	3.15	6.02	3.20	6.10	3.29	
	K^+	5.74	3.07	5.84	3.10	5.98	3.16	
	Ca ²⁺	5.56	2.95	5.72	3.02	5.86	3.10	

The results of adsorption were correlated with X-ray and IR studies. For X-ray analysis, the clay samples and clayantibiotics complexes were orientated on glass slides and allowed to dry at room temperature. The X-ray patterns were recorded on a General Electric XRD 6 diffraction unit at 2θ 0.4°/min, Ni-filtered CuK_{α} radiation was used. The IR spectra of samples were also recorded in the range of 4000–400 cm⁻¹ on a Beckman IR-20 double beam spectrophotometer.

All the chemicals used were of analytical grade and all the experiments were done in three replicates.

3. Results and Discussion

The first-order kinetics model was best fitted for the sorption of tetracycline, oxytetracycline, and chlortetracycline on illites and kaolinites. The first-order kinetics model is given by the following expression:

$$\log Y = \log \left(a - x \right) \left(\log b \right), \tag{1}$$

where *Y* = residue, *x* = time, and log *a* = logarithm of residue at time *x* = 0. From the slope of the straight line (log *b*), the time elapsed till a certain percentage of the initial reached can be calculated. The rate constants for sorption were 0.112 to 0.123 h^{-1} and the equilibrium was attained within 24 h so, in subsequent experiments, the equilibrium time was set for 24 h.

The influence of pH on the adsorption of tetracyclines on illite (Figure 1) indicated a strong correlation between pH and adsorption, the maximum adsorption of tetracycline occurs at pH 3.5, at pH 3 for oxytetracycline, and at pH 4 for chlortetracycline, and thereafter a decrease in adsorption (for illite 9.2 to 6, 9.75 to 6.15, and 9.95 to 6.25 mg/g and for kaolinite 6.05 to 3.45, 6.25 to 3.45, and 6.55 to 3.55 mg/g for tetracycline, oxytetracycline, and chlortetracycline, resp.) occurs with the increase in pH values. As expected, maximum adsorption occurs at pH values near the pka₁values of appropriate tetracyclines. As the tetracyclines molecules can undergo protonation-deprotonation reactions and adopt

TABLE 2: Freundlich adsorption isotherm constants of three antibiotics adsorption on illite and kaolinite, saturated with Na-, K-, Ca-, and Al-cations.

	Tetracycline						Oxytetracycline					Chlortetracycline						
Sorbent		Κ			1/n			Κ			1/n			Κ			1/n	
	293	308	323 K	293	308	323 K	293	308	323 K	293	308	323 K	293	308	323 K	293	308	323 K
Al-illite	108	100	94	0.880	0.855	0.825	113	105	99	0.895	0.865	0.840	117	109	103	0.915	0.885	0.865
Na-illite	103	97	90	0.865	0.835	0.800	106	101	96	0.880	0.850	0.820	111	104	99	0.895	0.865	0.840
K-illite	98	93	85	0.845	0.820	0.795	102	98	93	0.860	0.830	0.805	106	100	95	0.875	0.855	0.830
Ca-illite	93	88	80	0.835	0.805	0.785	96	92	85	0.845	0.820	0.805	102	96	90	0.860	0.835	0.815
Al-kaolinite	105	98	92	0.865	0.850	0.820	109	103	97	0.885	0.860	0.835	115	107	102	0.890	0.865	0.845
Na-kaolinite	101	95	88	0.855	0.830	0.810	103	98	93	0.875	0.850	0.820	110	103	97	0.880	0.850	0.835
K-kaolinite	96	91	86	0.840	0.810	0.790	101	95	90	0.860	0.835	0.805	105	99	93	0.865	0.845	0.820
Ca-kaolinite	91	86	79	0.830	0.800	0.775	95	90	86	0.845	0.820	0.795	99	93	89	0.855	0.830	0.810



FIGURE 2: Adsorption isotherms for sorption of tetracycline, oxytetracycline, and chlortetracycline on illite and kaolinite saturated with different cations.



FIGURE 3: Effect of temperature on adsorption of tetracyclines on Na-saturated illites and kaolinites.

different ionic species depending on the pH of solution, the maximum adsorption at pH 3.5, 3, or 4 may be attributed to the cationic exchange interactions that are dominant at lower pH values when tetracyclines are positively charged [7, 8].

The data showing the effect of solution ionic strength on sorption of tetracyclines (Table 1) indicated that adsorption of tetracyclines decreases with the increase in the ionic strength of the solute. The adsorption of tetracycline, oxytetracycline, and chlortetracycline decreases from 32% to 29% for illites and from 33% to 31% for kaolinites of initial input (Table 1) with increasing ionic strength (0.0–0.6). Also the data showed that part of tetracyclines sorption on illite and kaolinite was due to ion exchange mechanism. Decrease in adsorption with increasing ionic strength may be due to (i) competition of tetracycline with increasing amount of cations for sites [7], and (ii) formation of nonadsorbable metaltetracycline complex in solution [9].

The experimental data of sorption of studied tetracyclines on illite and kaolinite at pH 5-6 in the studied range were best fitted ($R^2 > 0.96$) to Freundlich isotherm. The linear form of this equation is $\log C_s = \log K_f + (1/n) \log C_e$, where C_s (mg/kg) is the amount of antibiotics adsorbed by soil, C_e (mg L⁻¹) is the equilibrium concentration in solution, and $\log K_f$ and 1/n all empirical coefficients representing the intercepts and slope of isotherm, respectively. The data are given in Table 2. The values of 1/n during tetracyclines adsorption on Al-, Na-, K-, and Ca-saturated illites and kaolinites were less than unity indicating an L type of



FIGURE 4: Amount of total metal cations desorbed as affected by tetracycline sorption on illite and kaolinite.

isotherms (Figure 2). Such isotherms have been observed where adsorption was either concentration dependent or where factors other than those related to the structural status of the clay-water system were involved. According to Giles et al. [10, 11], the L type of isotherms may arise because of minimum competition of solvent for sites on the adsorbing surface. The slope of the isotherm decreases steadily with the increase in solute concentration, because vacant sites become less accessible with the progressive covering of the surface. The curvilinear isotherm suggests that the number of available sites for the sorption become a limiting factor.

Figure 2 shows that adsorption of tetracyclines follows the order Al-clay > Na-clay > K-clay > Ca-clay, indicating that the adsorption decreases as the polarizing power of exchangeable cation decreases. Highest adsorption during Al-clay suspension may be attributed to its polarizing ability by increasing the acidity of innerlayer water. An increase in temperature from 293 to 323 K results in decrease of adsorption (Figure 3). A decrease in adsorption with temperature may be attributed to change in the energy of adsorption or weakening (or both) of the van der Waals forces of attraction between tetracycline and clay surface, causing a decrease in physical adsorption.

The amount of metal cations desorbed (Figure 4) was positively correlated to the amount of tetracyclines adsorbed, and the amount of cation desorbed was lesser than the amount of tetracyclines adsorbed suggesting that cation exchange played an important part during adsorption of tetracyclines on clay minerals.

The thermodynamic parameters of sorption were calculated using following relationship:

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R},\tag{2}$$

where K_d is the ratio of amount sorbed to equilibrium concentration, ΔH is the change in enthalpy, ΔS is the change in entropy, *R* is gas constant, and *T* is the reaction temperature. The free energy change of sorption can be obtained by

$$\Delta G = \Delta H - T \Delta S. \tag{3}$$

					(a) Illite				
nН		$\ln K_d$ (L/kg)			ΔG (kJ/mole)		AH (kI/mole)	AS (I/mole V)	
PII	293 K	308 K	323 K	293 K	308 K	323 K	$\Delta \Pi (\mathbf{K})/\Pi O(\mathbf{C})$	23 ()/mole-R)	
				Te	etracycline				
3.5	5.32	5.17	5.02	-12.97	-13.23	-13.48	-8.02	16.97	
6	5.764	5.696	5.643	-14.10	-14.66	-15.21	-3.23	36.35	
8.5	5.83	5.70	5.57	-14.27	-14.64	-15.01	-7.03	24.71	
11	5.30	5.17	5.04	-12.92	-13.22	-13.53	-6.93	20.43	
				Oxy	rtetracycline				
3.5	5.36	5.20	5.04	-13.06	-13.32	-13.54	-8.47	15.67	
6	5.835	5.764	5.696	-14.21	-14.76	-15.30	-3.65	36.06	
8.5	5.89	5.73	5.58	-14.41	-14.66	-14.97	-7.81	20.89	
11	5.33	5.19	5.06	-12.99	-13.28	-13.56	-7.40	19.08	
				Chlo	ortetracycline				
3.5	5.40	5.22	5.05	-13.06	-13.38	-13.59	-9.08	13.92	
6	5.873	5.791	5.723	-14.30	-14.84	-15.37	-7.33	35.41	
8.5	5.94	5.76	5.59	-14.48	-14.74	-15.03	-9.20	17.89	
11	5.36	5.21	5.06	-13.06	-13.32	-13.59	-7.99	17.31	
				(b)) Kaolinite				
рН		$\ln K_d$ (L/kg)			ΔG (kJ/mole)		ΔH (kI/mole)	AS (I/mole-K)	
P11	293 K	308 K	323 K	293 K	308 K	323 K	(i),)	20 ()/11010 10)	
				Те	etracycline				
3.5	5.32	5.17	5.02	-12.97	-13.23	-13.48	-8.02	16.97	
6	5.950	5.863	5.764	-14.49	-14.99	-15.48	-4.89	32.78	
8.5	5.83	5.70	5.57	-14.27	-14.64	-15.01	-7.03	24.71	
11	5.30	5.17	5.04	-12.92	-13.22	-13.53	-6.93	20.43	
				Oxy	rtetracycline				
3.5	5.36	5.20	5.04	-13.06	-13.32	-13.54	-8.47	15.67	
6	6.022	5.928	5.839	-14.67	-15.18	-15.68	-4.81	33.66	
8.5	5.89	5.73	5.58	-14.41	-14.66	-14.97	-7.81	20.89	
11	5.33	5.19	5.06	-12.99	-13.28	-13.56	-7.40	19.08	
				Chlo	rtetracycline				
3.5	5.40	5.22	5.05	-13.06	-13.38	-13.59	-9.08	13.92	
6	6.086	5.967	5.867	-14.83	-15.29	-15.76	-5.74	31.41	
8.5	5.94	5.76	5.59	-14.48	-14.74	-15.03	-9.20	17.89	
11	5.36	5.21	5.06	-13.06	-13.32	-13.59	-7.99	17.31	

The values of K_d (Table 3) have been found to be higher than unity pointing towards a higher preference of antibiotics for clay. Table 3 also denotes that the values of K_d were maximum for chlortetracycline followed by oxytetracycline and tetracycline. The values of K_d for all the studies decrease as the temperature increases. The values of K_d were slightly higher for kaolinite than for illite. The values of ΔG for all the studies at all the three temperatures were negative and increased with a rise in temperature, pointing towards spontaneity of reaction. The values of ΔG suggest a physical adsorption [12]. The data of Table 3 denote that affinity of studied antibiotics was more for kaolinite than for illite and followed the order chlortetracycline > oxytetracycline > tetracycline.

The negative values of overall adsorption heat (ΔH) (which is the net result of enthalpy change, molecular diffusion, and repulsion between adsorbed molecules and desorption of solvent) indicate the exothermic nature of reaction with a strong binding of antibiotics molecules on the adsorbent surface. The values of ΔH also denote that the adsorption occurs through covalent bonding mechanism. The small positive values of entropy (ΔS) changes during the studies indicate that sorption process is spontaneous as randomness of the system increases. It may also suggest that the adsorbed tetracycline molecules might be arranged in randomly oriented manner instead of arranging in orderly pattern on external surface of clay particles.

An examination of IR spectra showed a shift of bands at 1620 cm⁻¹ ($\Delta v = -25$ to -15 cm⁻¹) and 1380 cm⁻¹ ($\Delta v =$ +10 to +15 cm⁻¹) attributed to a >C=O stretching vibration and to C–N stretching of CONH₂ group, respectively. These shifts indicate the coordination or protonation (or both) of the antibiotics molecule to metal ion with oxygen with or without water bridge [13]. X-ray data show an expansion of 0.15 to 0.30 nm in the basal thickness for Na, K-, Ca-, and Al-saturated illites and kaolinites for three tetracycline antibiotics, indicating a flat orientation of the intercalated antibiotics in monomolecular layers with formation of complexes at the basal surface.

4. Conclusions

The present study reveals that adsorption of three tetracycline antibiotics on illite and kaolinite is influenced by solution pH and solution ionic strength. The sorption obeyed first-order kinetics and equilibrium is attained within 24 h. Sorption of tetracyclines on illite and kaolinite followed Freundlich sorption isotherm. From the thermodynamic parameters, it may be inferred that adsorption of all the studied antibiotics on clay minerals occurs via protonation and/or coordination in between cations of clay and oxygen of >C=O group of tetracyclines. The adsorption is correlated directly with the polarizing power of exchangeable cation and inversely with the temperature and solution ionic strength. The adsorption was in the order CTC > OTC > TC. XRD and IR data showed that the sorption is restricted to the external surfaces of clay.

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