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**M.A. Thesis**

**August 2012**

**Removal of antibiotics from contaminated waters using natural zeolite**

**by**

**BooYoung Lee**

**Summer 2012**

**Advisor: Professor Pengfei Zhang**

**Submitted in partial fulfillment of the request for the degree of Master of Arts  
in the College of Liberal Arts and Sciences of the City College of the City  
University of New York**

## **Abstract**

The occurrence of residual antibiotics in the environment has been a worldwide issue, and there is a need to develop methods for antibiotics removal from contaminated water. In this thesis work, the sorption of four antibiotics, namely chlortetracycline (CTC), oxytetracycline (OTC), ofloxacin (OFL), and enrofloxacin (ENR), on natural zeolite was investigated. The impact of pH and natural organic matter (NOM) on the sorption process was examined, and the maximum sorption capacity was calculated using the Langmuir-Freundlich sorption model. The results showed that at a neutral pH the maximum sorption capacity for the antibiotics was up to 8 mg/g. The sorption capacity increased as the solution pH decreased. The presence of NOM reduced the sorption of OTC but enhanced the sorption of the remaining antibiotics.

## **Acknowledgements**

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## 1. Introduction

Antibiotics are an important group of pharmaceuticals. They are used for by humans and animals for the purpose of preventing or treating bacterial infection [1]. Internationally, the use of antibiotics has been estimated at 100,000 to 200,000 tons per year [2]. Due to the extensive use of antibiotics [3], the occurrence of residual antibiotics in the environment is increasing, which is a potential environmental issue. Antibiotics can be discharged into the environment in several different ways (Figure 1). The excretion of poorly metabolized antibiotics by humans and animals is the main source of antibiotics in the environment. Other sources are the disposal of unused or unwanted antibiotics from pharmaceutical manufacturing processes [4, 5]. Several studies have reported that antibiotics are detected in hospital wastewater, wastewater treatment plant (WWTP) influents and effluents, surface waters, groundwater, sediment, and drinking water [1, 4, 6-9]. In aquatic systems, detected antibiotic concentrations were at high  $\mu\text{g/L}$  levels in hospital effluent, at low  $\mu\text{g/L}$  levels in wastewater, and in the low  $\text{ng/L}$  to high  $\mu\text{g/L}$  ranges in various surface and ground waters [1, 6, 8]. In sediments, detection of antibiotics was at low to medium  $\mu\text{g/kg}$  levels [6]. Clearly, antibiotics in hospital effluent and WWTP influent are relatively high compared with other locations [9]. Recently, due to their high toxicity to algae and bacteria at low concentrations and their potential to cause resistance amongst the natural bacterial population, antibiotics have been categorized as a priority risk group [6, 9]. Antibiotics in surface water can potentially disrupt bacteria cycles and processes critical to agriculture (soil fertility) and animal production (rudimentary processes) or to aquatic ecology (nitrification and denitrification) [9, 10].

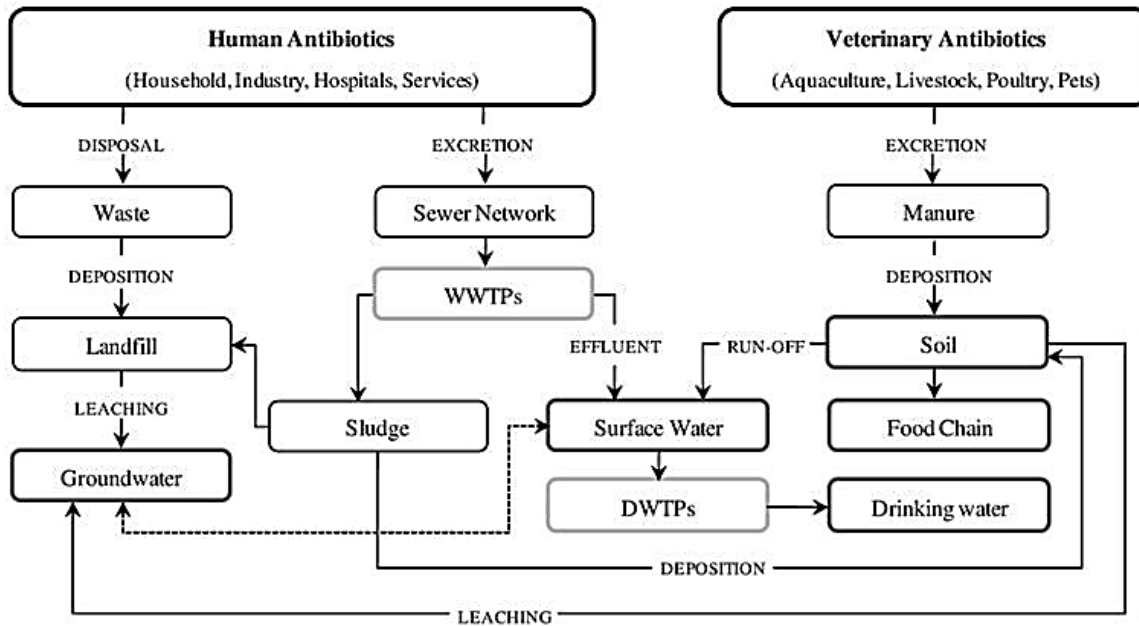


Figure 1. Origins and principal contamination routes of human and veterinary antibiotics. (WWTP: Wastewater treatment plant, DWTP: Drinking water treat plant) [11]

Various methods to treat residual antibiotics have been developed, including ozonation, chlorination, ultraviolet (UV) irradiation, nanofiltration (NF), reverse osmosis (RO) filtration, and adsorption by activated carbons and other materials [12]. These treatment methods have been applied to secondary effluents of WWTPs. Ozonation and chlorination appear to be highly effective for the removal of antibiotics in water and wastewater effluents [13]. However, there is a major concern with using ozone for removing antibiotics due to the potential transformation of antibiotics into products that remain biologically active and resistant to further ozonation [12]. Likewise, there is a concern with using chlorine due to the possible formation of chlorinated byproducts that may be more harmful than the parent compounds [12, 14]. The method of using UV irradiation tends to be effective only with high UV radiation doses, approximately 20 to 100 times higher than the typical disinfection dose, due to existing dissolved organic carbon in wastewater effluent [13, 15]. Dissolved organic carbon also leads to fouling in NF/RO filtration, which in turn can impact rejection of some antibiotics [16]. Adsorption

capacity of 1-2 mmol/g of nitroimidazoles on activated carbon has been reported [17]. In general, adsorption with activated carbon can be effective in removing non-polar antibiotics due to hydrophobic interaction [12, 18]. However, more polar or charged compounds are difficult to remove with activated carbon due to the additional effects of polar interaction and ion exchange [12, 18]. Other methods of antibiotics removal reported in the literature include photodegradation with UV/catalysts or Fenton's reagent [19, 20], adsorption by carbon nanotubes [21] or clays [22], and ion exchange [23], and each has its limitations.

Clearly, there is still a need for inexpensive yet effective sorbents for the removal of antibiotics from various contaminated media. Natural zeolites, hydrated aluminosilicates characterized by high surface areas and high cation exchange capacities (CECs), could be potentially used to remove some antibiotics with positively charged moieties through cation exchange. Like clays, zeolites are negatively surface charged, and internal and external surface areas up to 800 m<sup>2</sup>/g have been reported. Total CECs in natural zeolites vary from 250 to 3000 meq/kg [24], and external cation exchange capacities (ECECs) typically range from 10 to 50 percent of the total cation exchange capacity [25]. Zeolites have rigid three-dimensional crystalline structures free of the shrink-swell behavior typical of smectite clays. Zeolites and clay minerals have a similar composition. They both are hydrated aluminosilicates. However, they have different crystalline structures. Natural zeolite has a frame structure with symmetrically stacked alumina and silica tetrahedrons so that zeolites have an open and stable three-dimensional structure with a negative charge. On the other hand, clay minerals consist of layers of tetrahedral and octahedral sheet structures. Due to substitutions of Al<sup>3+</sup> for Si<sup>4+</sup> in the tetrahedral sheet and Mg<sup>2+</sup> or Fe<sup>2+</sup> for Al<sup>3+</sup> in the octahedral sheets, the clay surface is negatively charged.



Unlike clays that are practically impermeable to flows, natural zeolites can occur as mm- or greater-sized particles and have superior hydraulic characteristics. Natural zeolites are found in geological deposits in many parts of the world and are readily recovered by surface mining techniques. The mined zeolite can be crushed and sieved to any desired aggregate size and permeability, and the final product only costs about \$70/ton. Due to their superior hydraulic properties, high sorption capacities, and low cost, natural zeolites have been used as filter materials in waste treatment to remove ammonium [26] and heavy metals [27, 28]. Zeolites are not digested by animals and can pass through gut with their cation-exchange properties intact and therefore have been used extensively as feed additives to cattle, pigs, and poultry to reduce ammonia emissions from feedlots [29, 30]. Natural zeolites loaded with ammonia and potassium have been used as slow release fertilizer [31, 32].

In this thesis project, the sorption of two tetracyclines (oxytetracycline and chlortetracycline) and two fluoroquinolones (ofloxacin and enrofloxacin, see Table 1 for abbreviations and physicochemical properties) by natural zeolite was examined. All four antibiotics have multiple pKa values and positive moieties at environmentally relevant pH. For instance, OTC has three pKa values (3.22, 7.46, and 8.94) and the dimethylamine group is positively charged at a pH of below 9 (Figure 2). The four antibiotics have their majority of the species (>90%) with at least one positively charged functional group at slightly acidic to neutral pH (5-7, see Table 2 in Results and Discussion). Even at a basic pH of 9, there is still a significant fraction of the OTC, CTC, OFL, and ENR species that possess at least one positively charged functional group (Table 2 in Results and Discussion). Therefore, it was hypothesized that natural zeolite, which has negative surface charges, would be able to retain some of these antibiotics at environmentally relevant pHs via a cation exchange mechanism. Because of the

effect of pH on the protonation/deprotonation of the functional groups in the antibiotics, and possible competition of protons for negative surface sites, it was further hypothesized that the sorption would be impacted by different pH values.

Compound	Enrofloxacin	Ofloxacin	OxytetracyclineHCl	ChlortetracyclineHCl
Abbr.	ENR	OFL	OTC	CTC
Formula	$C_{19}H_{22}FN_3O_3$	$C_{18}H_{20}FN_3O_4$	$C_{22}H_{24}N_2O_9 \cdot HCl$	$C_{22}H_{23}ClN_2O_8 \cdot HCl$
MW	359.4	361.4	496.9	515.3
pKa	3.85 (carboxylic acid group) 6.19/7.59/9.86, assigned in order to 3 basic nitrogen sites starting from ring 1 (nalidixic acid group) to ring 3 (fluoro group) [12, 33]	5.97 (carboxylic acid group) 8.28 (basic piperazinyl group) [34]	3.22 (acidic tricarbonyl group) 7.46 (acidic $\beta$ -diketone group) 8.94 (basic dimethylamine group) [33]	3.33 (acidic tricarbonyl group) 7.55 (acidic $\beta$ -diketone group) 9.33 (basic dimethylamine group) [33]
Solubility (mg/L)	146 [35]	190 [36]	313 [36]	630 [36]
log $K_{ow}$	1.1 [37]	0.35 [37]	-1.12 [38]	-0.62 [36]

Table 1. Abbreviations and physicochemical properties of the four antibiotics studied.

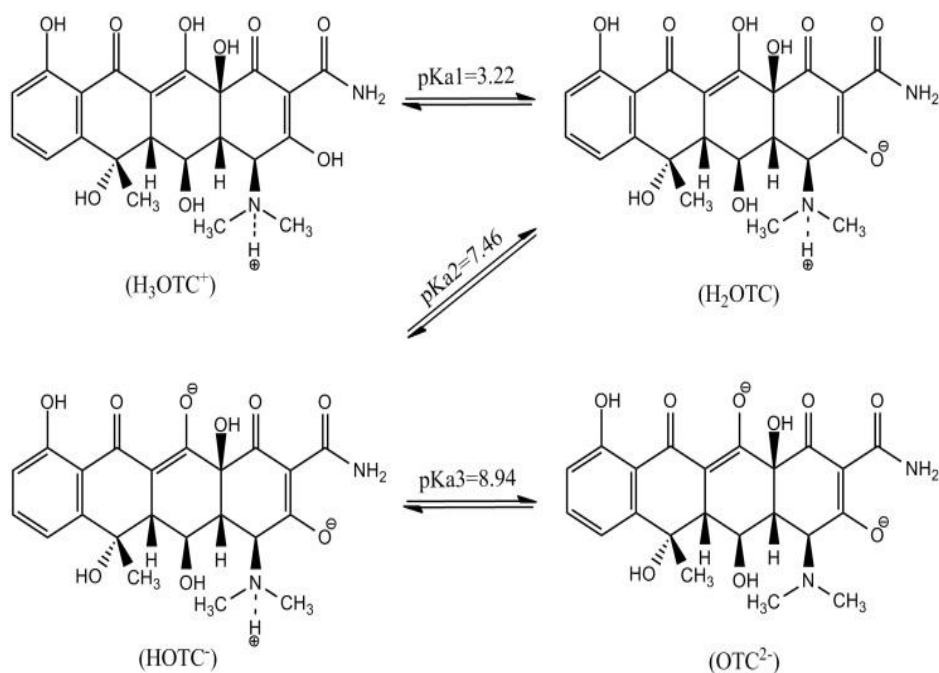


Figure 2. Different OTC species at different pH.

Natural organic matter (NOM), a mixture of organic compounds, presents in surface waters, and it is commonly found in secondary effluents or liquid manure. NOM exists in negatively charged form and in a wide range of chemical compositions and molecular sizes [39]. The acidic groups in NOM would likely interact with the positive moieties in the antibiotics to form pairs or complexes. Therefore, the presence of NOM may affect instrumental analysis and the removal efficiency of antibiotics by natural zeolite.

The objective of this study was therefore to determine the sorption of four antibiotics by natural zeolite at different pHs and with the presence of NOM.

## **2. Materials and Method**

### **2.1 Chemicals**

CTC, ENR and OFL were purchased from Sigma-Aldrich, whereas OTC was acquired from MP Biomedicals. Suwannee River NOM (1R101N) and Nordic Reservoir NOM (1R108N) were supplied by the International Humic Substances Society (IHSS). Sodium acetate ( $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ ) and acetic acid ( $\text{CH}_3\text{COOH}$ ) were used to prepare pH5 buffer solution, and disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and hydrochloric acid (HCl 1N solution) were used to prepare pH7 and pH9 buffer solutions.

### **2.2 Zeolite**

The clinoptilolite rich natural zeolite was obtained from Truth or Consequences, New Mexico. A batch with particle size of 14-40 mesh (0.42-1.41mm) was used for all sorption experiments.

## 2.3 Batch sorption experiment

### 2.3.1 Sorption at different pHs without NOM

To determine the sorption of antibiotics under different pH conditions, three different buffer solutions, pH5, 7, and 9 were prepared. Various concentrations (1, 10, 20, 50, 100, 150, 200 mg/L) of CTC, OTC, and OFL from a stock solution of 200 mg/L were prepared at pH5, 7, and 9. Various concentrations (0.4, 4, 8, 20, 40, 60, 80 mg/L) of ENR from a stock solution of 80 mg/L were prepared at the same pH values. Lower concentrations were used for ENR due to solubility limitations (see Table 1). Natural zeolite (0.2 g) was weighted into glass amber vials and mixed with 20 mL each of the antibiotic solution. This was done in duplicate per concentration for each of the pH values. Samples were shaken on the orbital shaker at room temperature for 24 hours and filtered with 25 mm syringe filter with 0.2  $\mu\text{m}$  polyethersulfone membrane. The filtered samples were analyzed using high-performance liquid chromatography (HPLC).

### 2.3.2. Sorption at pH 7 with NOM

In order to examine whether the presence of NOM had an effect on the sorption behavior of the antibiotics, a 1:1 (w/w) mass mixture of a single antibiotic and one of the two NOMs, Suwannee River NOM (SRNOM) and Nordic Reservoir NOM (NRNOM) in pH7 buffer solution, was prepared. The prepared single antibiotic and single NOM mixture (1:1 w/w) stock solutions (200 mg/L for CTC, OTC, and OFL, 80 mg/L for ENR) were diluted to the following concentrations: 1, 10, 20, 50, 100, 150, and 200 mg/L (CTC, OTC and OFL) and 0.4, 4, 8, 20, 40, 60, and 80 mg/L (ENR). This was done in duplicate per concentration at pH7. Samples were shaken on the orbital shaker at room temperature for 24 hours and filtered with 25 mm syringe filter with 0.2  $\mu\text{m}$  polyethersulfone membrane. The filtered samples were analyzed using

HPLC. Prior to these sorption experiments, quick tests were performed to verify that NOM would not be sorbed onto zeolite. NOM solutions at concentrations of 1, 10, 20, 50, 100, 150, and 200 mg/L were prepared and batch sorption experiments similar to the ones mentioned above were performed.

## 2.4 Methods of analysis

### 2.4.1 HPLC/UV

The initial and equilibrium concentrations of antibiotics were determined using a Waters 2695 separation module HPLC and a Waters 996 photodiode array detector. The analytical column was a Phenomenex Gemini-Nx 5 $\mu$  C18 HPLC column (150 $\times$ 4.60mm). Mobile phase A contained acetonitrile (HPLC grade), whereas mobile phase B contained sulfuric acid buffer at pH2 (500 mL Milli-Q water + 0.1 mL of 98% sulfuric acid). Gradient elution was conducted as follows: 10% A and 90% B from 0 to 1 minute, linear gradient to 30% A and 70% B from 1 to 5 minute, constant at 30%A and 70% B from 5 to 8 minutes, and linear gradient to 10% A and 90% B from 8 to 10 minutes. The injection volume was 10  $\mu$ L and the flow rate of the mobile phase was 1 mL/min. OTC, CTC, ENR, and OFL were detected at 266.7 nm, 268 nm, 294 nm and 278 nm, respectively.

### 2.4.2 UV/Visible

A Varian Cary 50 Bio UV-Vis Spectrophotometer was used to determine NOM concentrations. This was done at an absorbance wavelength of 291.5 nm.

### 2.4.3. Measurement of pH

The pH of all the samples at equilibrium and initial solutions were measured using an IQ125 miniLab pH meter from IQ Scientific.

## 2.5 Data Analysis

### 2.5.1 Sorption isotherm

The equilibrium sorbed concentration was calculated from the equilibrium solution concentration using the equation

$$S = (C_i - C)V / m \quad (1)$$

where S (mg/g) is the sorbed concentration,  $C_i$  and C are the initial and equilibrium concentrations (mg/L) of each antibiotic in the solution, V (L) is the volume of sorbate, and m (g) is the weight of the sorbent.

The sorption data were fitted to the Langmuir-Freundlich (L-F) sorption isotherm to obtain the maximum sorption capacity,

$$S = \frac{S_m (KC)^r}{1 + (KC)^r} \quad (2)$$

where S is the sorbed concentration,  $S_m$  is the maximum sorption capacity (mg/g), K is Langmuir-type equilibrium constant, C is equilibrium concentration and the exponential term r is the heterogeneity parameter of the site energies [40].

### 2.5.2 Calculation of the distribution of different antibiotic species as a function of pH

CTC, OTC, OFL, and ENR are zwitterionic molecules, and the percentages of antibiotic species can be calculated by the following equations:

For CTC and OTC,

$$\alpha(00+) = \frac{100}{1 + 10^{(pH-pK_{a1})} + 10^{(2pH-pK_{a2}-pK_{a1})} + 10^{(3pH-pK_{a3}-pK_{a2}-pK_{a1})}}$$

$$\alpha(-0+) = \frac{100}{1 + 10^{(pK_{a1}-pH)} + 10^{(pH-pK_{a2})} + 10^{(2pH-pK_{a3}-pK_{a2})}}$$

$$\alpha(- - +) = \frac{100}{1 + 10^{(pK_{a2} + pK_{a1} - 2pH)} + 10^{(pK_{a2} - pH)} + 10^{(pH - pK_{a3})}}$$

$$\alpha(- - 0) = \frac{100}{1 + 10^{(pK_{a3} + pK_{a2} + pK_{a1} - 3pH)} + 10^{(pK_{a3} + pK_{a2} - 2pH)} + 10^{(pK_{a3} - pH)}}$$

where  $\alpha$  is the percentage of a certain species, -, 0, and + represent a negatively charged, neutral, or positively charged functional group with an antibiotic molecule.

For OFL,

$$\alpha(0+) = \frac{100}{1 + 10^{(pH - pK_{a1})} + 10^{(2pH - pK_{a1} - pK_{a2})}}$$

$$\alpha(-+) = \frac{100}{1 + 10^{(pK_{a1} - pH)} + 10^{(pH - pK_{a2})}}$$

$$\alpha(-0) = \frac{100}{1 + 10^{(pK_{a1} + pK_{a2} - 2pH)} + 10^{(pK_{a2} - pH)}}$$

Finally, for ENR,

$$\alpha(0+++)= \frac{100}{1 + 10^{(pH - pK_{a1})} + 10^{(2pH - pK_{a2} - pK_{a1})} + 10^{(3pH - pK_{a3} - pK_{a2} - pK_{a1})} + 10^{(4pH - pK_{a4} - pK_{a3} - pK_{a2} - pK_{a1})}}$$

$$\alpha(-+++)= \frac{100}{1 + 10^{(pK_{a1} - pH)} + 10^{(pH - pK_{a2})} + 10^{(2pH - pK_{a2} - pK_{a3})} + 10^{(3pH - pK_{a2} - pK_{a3} - pK_{a3})}}$$

$$\alpha(-0++)= \frac{100}{1 + 10^{(pK_{a1} - pK_{a2} - 2pH)} + 10^{(pK_{a2} - pH)} + 10^{(pH - pK_{a3})} + 10^{(2pH - pK_{a3} - pK_{a4})}}$$

$$\alpha(-00+)= \frac{100}{1 + 10^{(pK_{a1} + pK_{a2} + pK_{a3} - 3pH)} + 10^{(pK_{a2} + pK_{a3} - 2pH)} + 10^{(pK_{a3} - pH)} + 10^{(pH - pK_{a4})}}$$

$$\alpha(-000)= \frac{100}{1 + 10^{(pK_{a1} + pK_{a2} + pK_{a3} + pK_{a4} - 4pH)} + 10^{(pK_{a2} + pK_{a3} + pK_{a4} - 3pH)} + 10^{(pK_{a3} - pK_{a4} - 2pH)} + 10^{(pK_{a4} - pH)}}$$

### 3. Results and Discussion

#### 3.1 Distribution of antibiotic species as a function of pH

The distributions of different species from pH 0 to 14 for the four antibiotics are presented in Figure 3 below. The percent of different species at pH 5, 7, and 9 are listed in Table 2. At pH 5, OTC and CTC are predominated (over 97%) by the (- 0 +) species (Table 2). Even though the overall molecule is neutral, the dimethylamine group is still positively charged. For OFL, the predominate species is the (0 +) species (>90%) at pH 5, whereas for ENR the major species is (- + + +) (>88%).

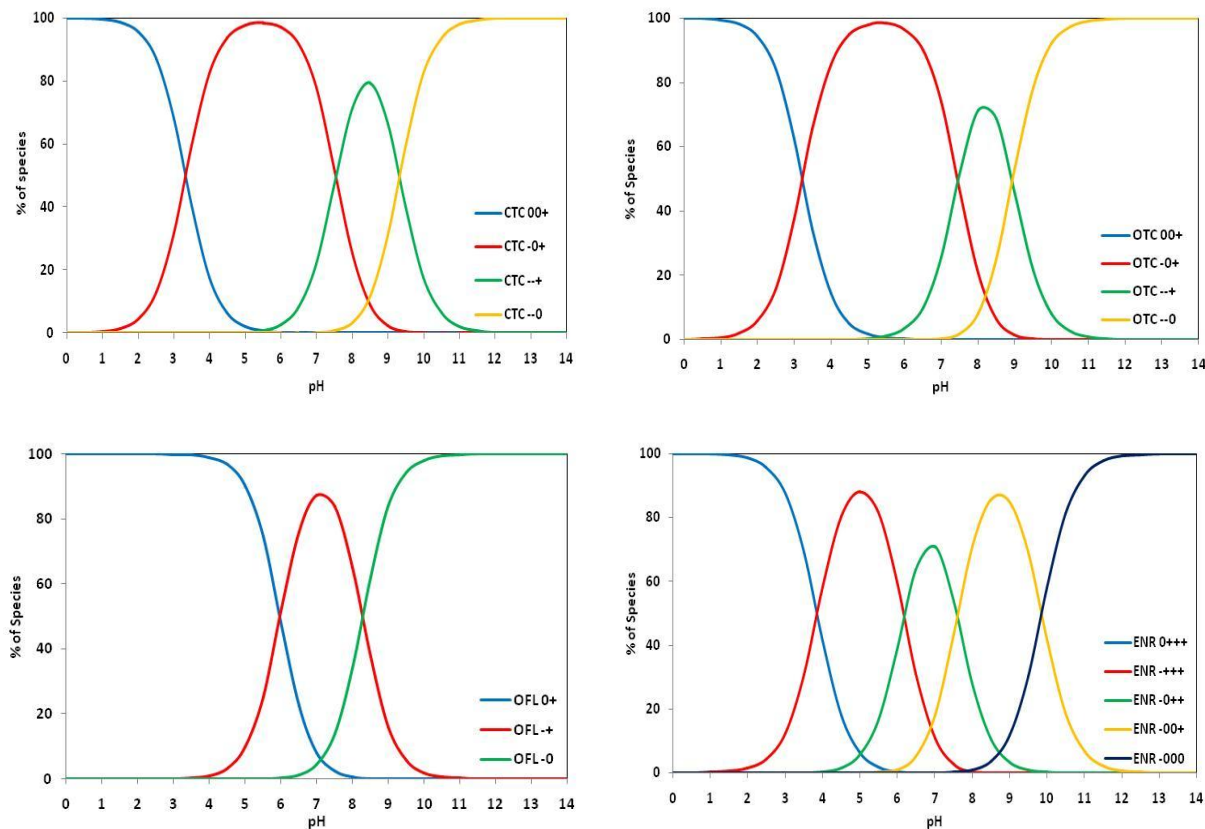


Figure 3. Distribution of antibiotic species as a function of pH.



pH	% of OTC species				% of CTC species			
	00+	-0+	--+	--0	00+	-0+	--+	--0
5	1.63	98.03	0.34	0.00	2.09	97.64	0.28	0.00
7	0.01	74.03	25.67	0.29	0.02	77.92	21.96	0.10
9	0.00	1.32	45.93	52.74	0.00	2.36	66.52	31.12
	% of OFL species				% ENR species			
	0+	-+	-0	0+++	---+	-0++	-00+	-000
5	90.3	9.7	0.0	6.23	88.06	5.69	0.01	0.00
7	8.1	87.3	4.6	0.01	10.97	70.80	18.20	0.03
9	0.0	16.0	84.0	0.00	0.01	3.31	84.96	11.73

Table 2. Distribution of antibiotic species at pH 5, 7, and 9. The symbol -, 0, or + represents a negatively charged, neutral, or positively charged species.

At pH 7, OTC and CTC are still predominated by the (- 0 +) species albeit the percentage is reduced (74% and 78% for OTC and CTC, respectively, Table 2). For OFL, the major species is switched to the (- +) species (87%), whereas for ENR the main species is now the (-0++) species (71%). At pH 9, the main species for OTC and CTC are the (--+) species (46% and 67%, respectively). For OFL, the (-0) species dominates (84%), whereas for ENR, the (-0++) species becomes the major one (85%). Clearly, the amount of the species that possess at least some positively charged functional groups decreases with increasing pH, and their sorption by zeolite would be expected to decrease as pH increases.

### 3.2 Sorption of antibiotics on natural zeolite

As mentioned above, in this study, the sorption characteristics of four different antibiotics on natural zeolite were examined at three different pH values (pH5, 7, and 9) and with the presence of NOM at pH7.

#### 3.2.1 Impact of pH

The sorption isotherms of antibiotics by zeolite at pH 5, 7 and 9 (without NOM) are presented in Figure 4, and the maximum sorption capacities obtained from the L-F model are

listed in Table 3.

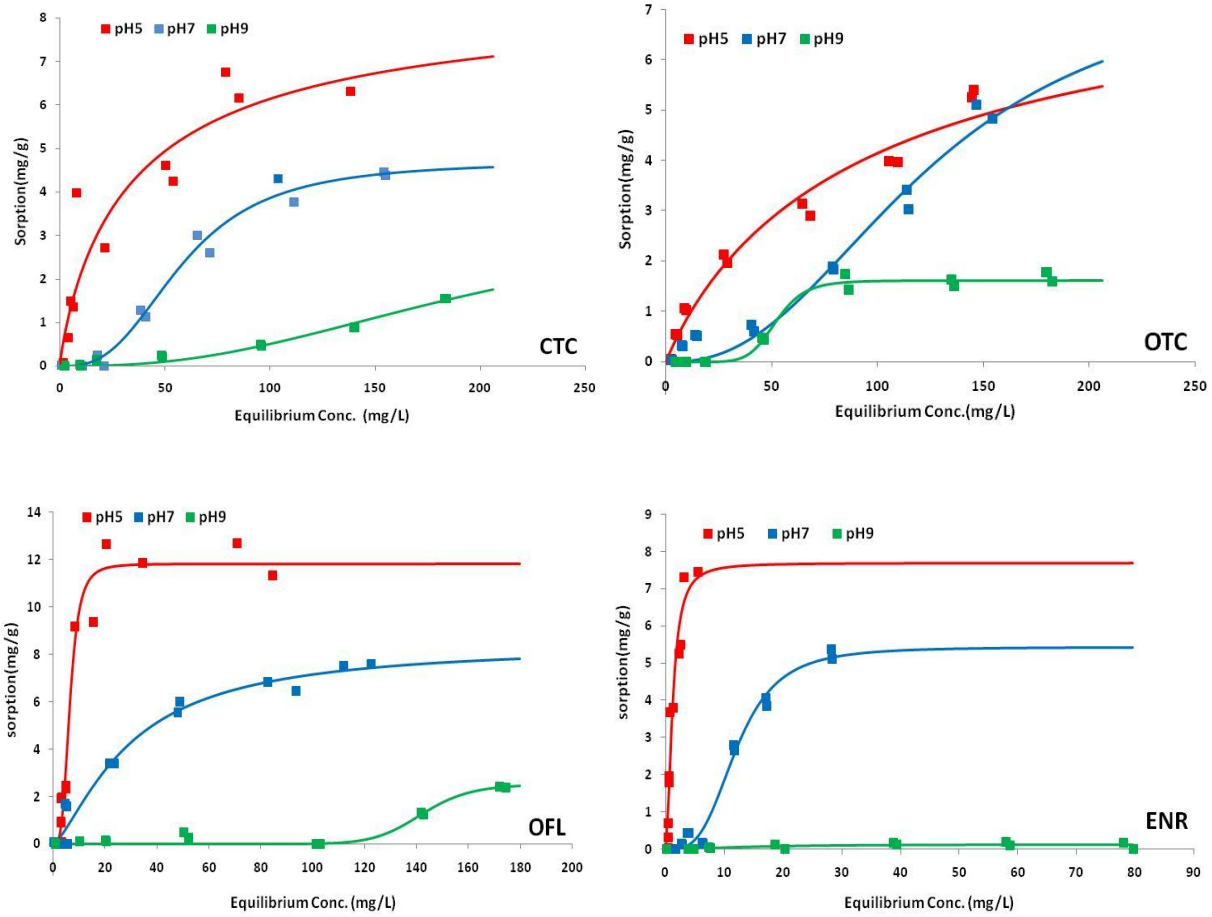


Figure 4. Sorption isotherms for the four antibiotics at different pH. The smooth curves are best-fit curves using the L-F model.

		$S_m(\text{mg/g})$	K	r			$S_m(\text{mg/g})$	K	r
CTC	pH5	$8.8 \pm 0.9$	0.03	0.88	OTC	pH5	$8.2 \pm 0.3$	0.01	0.93
	pH7	$4.7 \pm 0.2$	0.02	2.85		pH7	$7.8 \pm 0.3$	0.01	2.42
	pH9	$3.4 \pm 0.1$	0.005	2.50		pH9	$1.6 \pm 0.1$	0.02	7.74
OFL	pH5	$11.8 \pm 1.0$	0.15	3.68	ENR	pH5	$7.7 \pm 0.8$	0.80	1.97
	pH7	$8.4 \pm 0.6$	0.03	1.41		pH7	$5.4 \pm 0.3$	0.08	3.45
	pH9	$2.5 \pm 0.2$	0.01	15.13		pH9	$0.1 \pm 0.1$	0.07	1.94

Table 3. Parameter values obtained by fitting the sorption isotherm with the L-F model.

At pH5, the highest maximum sorption capacities were observed, approximately 8.8, 8.2, 11.8, and 7.7 mg/g for CTC, OTC, OFL and ENR, respectively. In an acidic condition, the dominant species in the solutions, include zwitterions, are in positive states so that high ionic

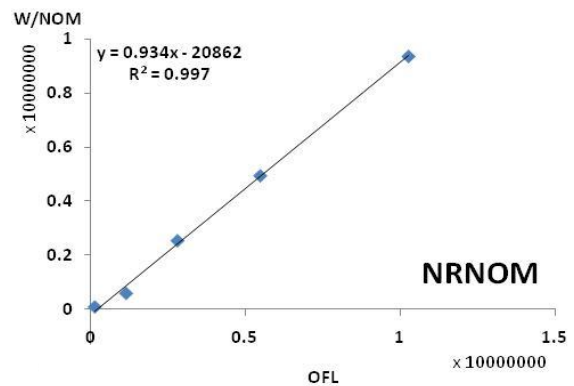
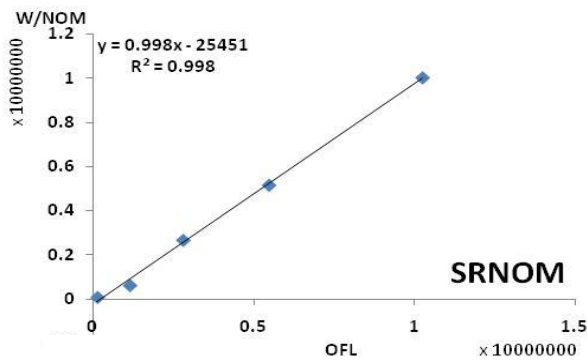
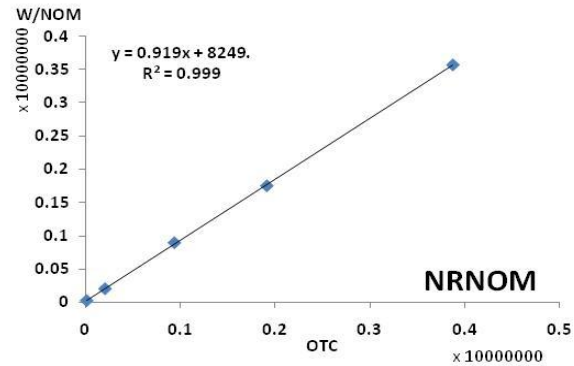
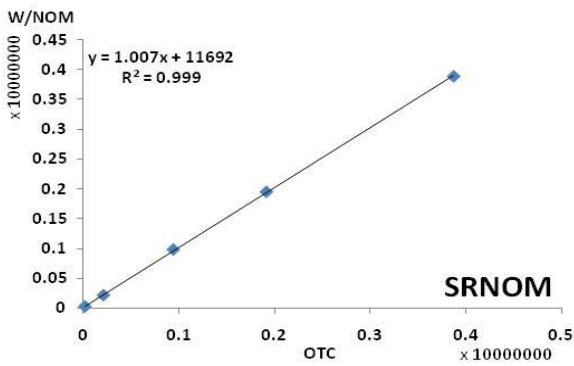
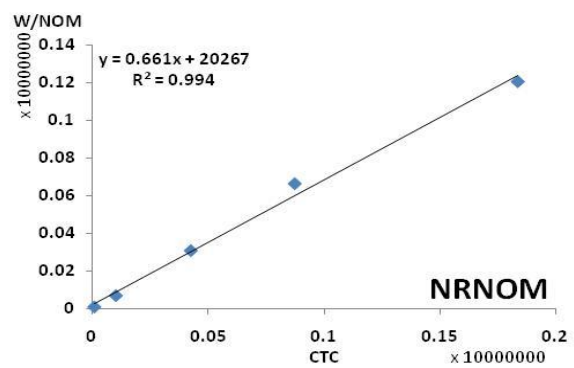
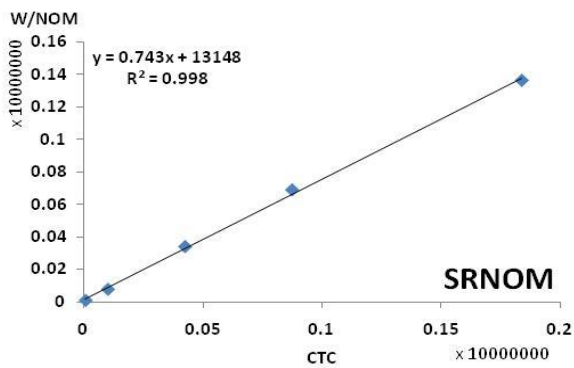
interactions occur between the positively charged antibiotic species and the negatively charged natural zeolite surfaces. At pH7, the sorption capacities decreased to 4.7, 7.8, 8.4, and 5.4 mg/g for CTC, OTC, OFL, and ENR, respectively. At pH 9, the maximum sorption capacities of the antibiotics decreased significantly since negatively charged species are dominant (Table 2). The maximum sorption capacities of CTC and OTC on natural zeolite were 8.8 mg/g and 8.2 mg/g. These values are lower than the 140 mg/g determined for tetracycline sorption onto rectorite [41] and 27 mg/g determined for OTC adsorption on montmorillonite [42]. However, both rectorite and montmorillonite are clay minerals that are not permeable to flow and therefore cannot be used in flow through systems.

### 3.2.2 Impact of NOM

#### 3.2.2.1 Impact of NOM on HPLC analysis of antibiotics

The negatively charged functional groups (e.g.,  $\text{COO}^-$ ) in NOM may interact with the positively charged groups in the antibiotics via ionic interactions to form ion pairs. Alternatively, NOM and antibiotics may share the  $\pi$  electrons on the benzene rings in the molecules to form complexes. The slope of the graphs in Figure 5 represents the interaction between antibiotics and NOM in pH7 solution. A slope of close to 1 indicates that the presence of NOM does not form complexes or pairs between antibiotics and NOM molecules; whereas a slope of less than one suggests that some complexes or pairs are formed and in turn affect HPLC analysis. There are significant interactions between the antibiotics and the two NOMs except for two cases OTC with SRNOM and OFL with SRNOM, where little interaction is evident (Figure 5). In order to avoid artifacts in HPLC analysis caused by NOM, calibration standards with 1:1 (w/w) mass ratio of NOM were used to establish the calibration curves for the sorption experiments with NOM.

If NOM is not retained by natural zeolite, then the formation of ion pairs between antibiotics and NOM may lead to reduced antibiotic removal by natural zeolite as the positively charged functional groups in the antibiotics are no longer available for cation exchange reactions with the negatively charged zeolite surface. In contrast, if antibiotic-NOM complexes are formed via  $\pi$  electron sharing, then the positive charges on the antibiotics are preserved and can still interact with the negative zeolite surface.



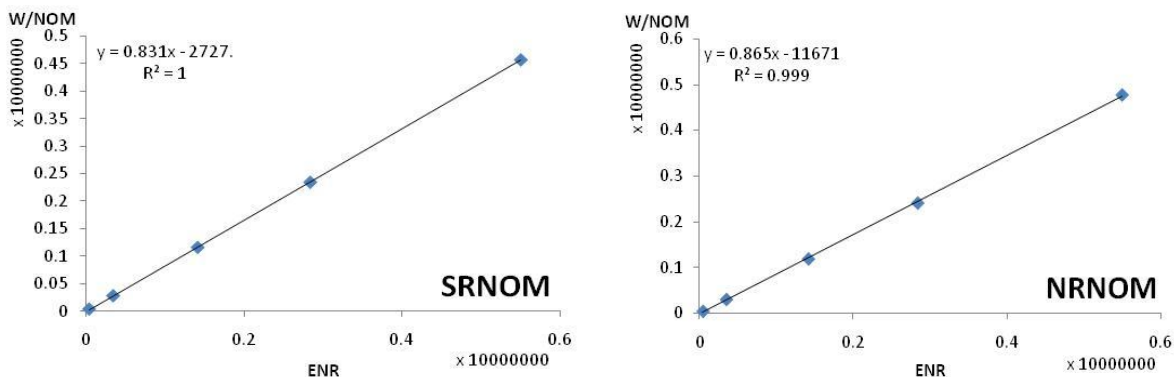


Figure 5. Plots of HPLC signals with and without NOM.

### 3.2.2.2 Impact of NOM on antibiotics sorption onto zeolite

The UV absorbance for the NOM before and after interaction with natural zeolite is presented in Table 4. There was no change in the absorbance and therefore no sorption of NOM by zeolite. This is not surprising since both the NOM and zeolite surface are negatively charged.

		Absorbance				Absorbance	
		before	after			before	after
SRNOM	1(mg/L)	0.04	0.01	NRNOM	1(mg/L)	0.02	0.05
	10(mg/L)	0.10	0.09		10(mg/L)	0.12	0.13
	20(mg/L)	0.15	0.17		20(mg/L)	0.26	0.25
	50(mg/L)	0.41	0.41		50(mg/L)	0.54	0.54
	100(mg/L)	0.81	0.80		100(mg/L)	1.08	1.11
	150(mg/L)	1.25	1.25		150(mg/L)	1.61	1.67
	200(mg/L)	1.67	1.64		200(mg/L)	2.24	2.32

Table 4. UV absorbance at wavelength 291.5 nm for NOM samples before and after interaction with natural zeolite.

The sorption isotherms of the four antibiotics in the presence of NOM are presented in Figure 6 and the maximum sorption capacities are tabulated in Table 5. The amount of sorption of the four antibiotics in the presence of NOM in pH7 were examined and compared with antibiotics without NOM in pH 7 solution. Only the maximum sorption capacity of OTC was

decreased, which could be explained by the formation of ion pairs of OTC and NOM. For the remaining three antibiotics the sorption capacities in the presence of NOM unexpectedly increased (Figure 6 and Table 5). It is hypothesized that in this case antibiotic-NOM complexes were formed via  $\pi$  electron sharing, and charge transfer between the molecules may have shifted the pKa values of the basic groups to higher values. As such, a larger fraction of the basic functional groups would possess positive charges and thereby enhancing cation exchange with zeolite. Further work needs to be done to verify this hypothesis.

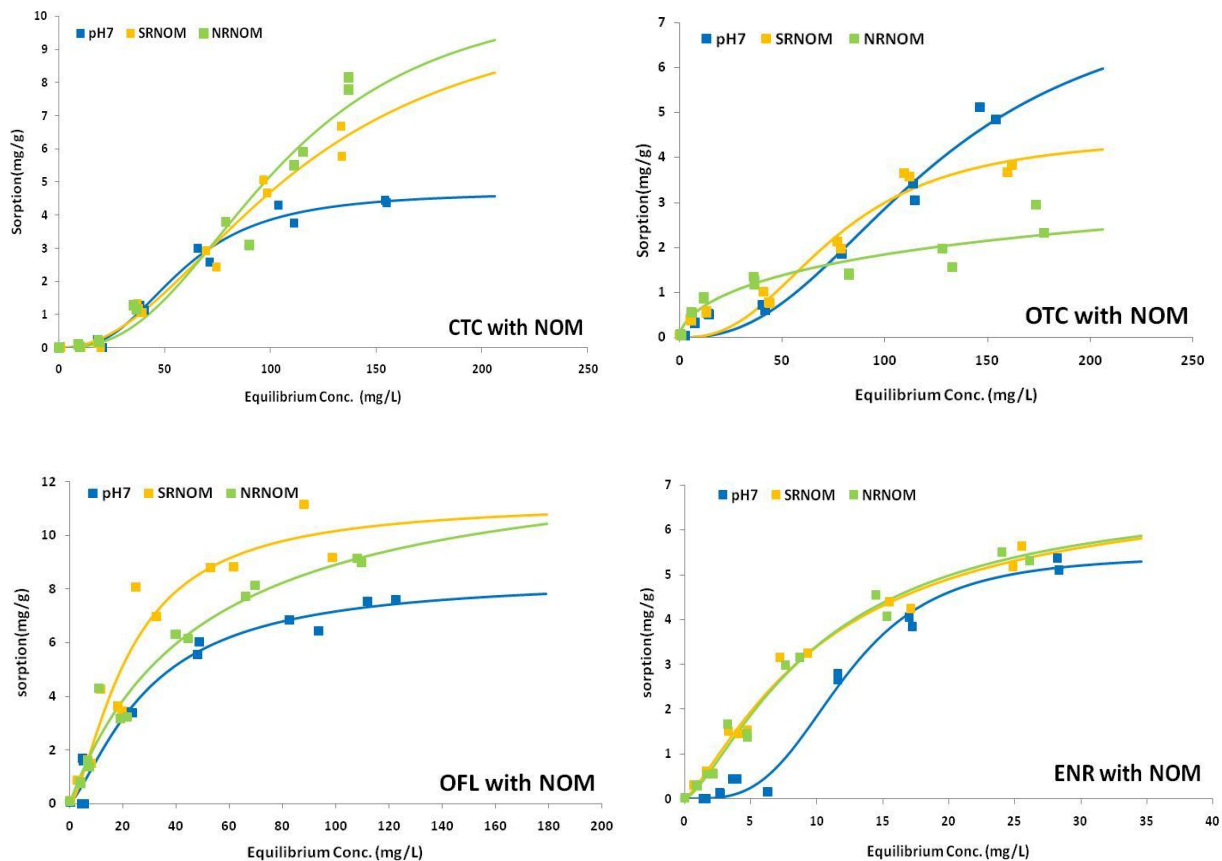


Figure 6. Sorption isotherms of the four antibiotics by zeolite with and without NOM.

		$S_m(\text{mg/g})$	K	r			$S_m(\text{mg/g})$	K	r
CTC	Without NOM	$4.7 \pm 0.2$	0.02	2.85	OTC	Without NOM	$7.8 \pm 0.3$	0.01	2.42
	SRNOM	$10.6 \pm 0.4$	0.01	2.10		SRNOM	$4.5 \pm 0.3$	0.01	2.55
	NRNOM	$10.9 \pm 0.6$	0.01	2.56		NRNOM	$5.5 \pm 0.3$	0.003	0.59
OFL	Without NOM	$8.4 \pm 0.6$	0.03	1.41	ENR	Without NOM	$5.4 \pm 0.3$	0.08	3.45
	SRNOM	$11.3 \pm 1.0$	0.04	1.49		SRNOM	$7.1 \pm 0.2$	0.09	1.29
	NRNOM	$13.3 \pm 0.6$	0.02	1.00		NRNOM	$7.0 \pm 0.3$	0.10	1.40

Table 5. Parameter values obtained by fitting the isotherms with the L-F model.

### 3.3 Environmental Implications

The lab sorption experiments proved that natural zeolite could be an effective and inexpensive adsorbent for antibiotics removal from contaminated water. Natural zeolites could see many applications in removing selected antibiotics. For instance, zeolite could be used as a filter medium in wastewater treatment plants to treat secondary effluent. Zeolite could also be used as the filtration bed in artificial recharge ponds where municipal wastewater is recharged to groundwater (wastewater reclamation and reuse). In addition, zeolite could also be used as a bedding material in animal feedlots or as a feed additive so that antibiotics could be retained before leaching to soils. The low cost and high permeability together with high capacity sorption would make zeolite a very attractive sorbent material.

## 4. Conclusion

The adsorption behavior of the antibiotics on natural zeolite was controlled by pH and affected by NOM. Increased sorption of antibiotics onto natural zeolite was observed as pH decreased. Sorption of OTC decreased in the presence of NOM, presumably due to the formation of ion pairs between OTC and NOM. However, the sorption of CTC, OFL and ENR unexpectedly increased in the presence of NOM. It is hypothesized that ion complexes were formed between antibiotics and NOM via  $\pi$  electron sharing, preserving the positively charged

functional groups on antibiotics. It is further hypothesized that charge transfers between the antibiotics and NOM may shift the pKa of the basic functional groups in antibiotics to higher values. While this result is encouraging from the point of view of antibiotics removal, the mechanism that caused the increased sorption still needs to be explored. Nevertheless, this study demonstrated that sorption by natural zeolite appears to be an economically feasible means of antibiotics removal.



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