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PHARMACEUTICAL REMOVAL BY ION EXCHANGE PROCESS

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การศึกษาปฏิกิริยาระหว่างสารประกอบยา และเรซินแลกเปลี่ยนไอออนที่ใช้กันทั่วไปในกระบวนการผลิตน้ำดื่ม และกระบวนการบำบัดน้ำเสียเพื่อให้เข้าใจเส้นทางและพฤติกรรมของสารเหล่านี้เมื่ออยู่ในแหล่งน้ำ สารประกอบยาที่นำมาใช้ในการศึกษานี้ ได้แก่ อะซิตะมิโนเฟน นาลิดิซิกเอซิด นอฟลอกซาซิน และ 17-แอลฟา-เอทินิลเอสทราไดออล การศึกษานี้จะใช้ระบบแบบแบช ช่วงพีเอชที่เป็นกลาง และเรซินแลกเปลี่ยนประจุลบและประจุบวก การทดสอบเบื้องต้นแสดงให้เห็นว่า อะซิตะมิโนเฟนซึ่งอยู่ในรูปโมเลกุลที่ไม่มีประจุในช่วงพีเอชที่เป็นกลาง และมีค่าการละลายน้ำที่สูงที่สุด(14,000 มิลลิกรัมต่อลิตรที่อุณหภูมิ 25°C) สามารถถูกดูดซับบนเรซินทั้งสองชนิด ขณะที่นาลิดิซิกเอซิดซึ่งไฮโดรเจนไอออนจะแตกตัวออกมาจากโมเลกุล และทำให้นาลิดิซิกเอซิดในรูปประจุลบจะแลกเปลี่ยนกับเรซินแลกเปลี่ยนประจุลบแต่ไม่มีการแลกเปลี่ยนกับเรซินแลกเปลี่ยนประจุบวก ส่วนนอฟลอกซาซินแลกเปลี่ยนกับเรซินทั้งสองชนิด และ17-แอลฟา-เอทินิลเอสทราไดออลจะถูกดูดซับบนเรซินทั้งสองชนิดเช่นกัน สำหรับการศึกษาเวลาเข้าสู่จุดสมดุลพบว่าอะซิตะมิโนเฟนใช้เวลาในการเข้าสู่สมดุลกับเรซินทั้งสองประเภท 3 ชม. นาลิดิซิกเอซิดใช้เวลา 6 ชม. นอฟลอกซาซินกับเรซินทั้งสองชนิดใช้เวลา 1 วัน และ 17-แอลฟา-เอทินิลเอสทราไดออลใช้เวลา 12 ชม. และ 6 ชม. สำหรับสำหรับเรซินแลกเปลี่ยนประจุลบและบวก ตามลำดับ จากผลการศึกษาพบว่าไอโซเทอมแบบแลงมัวสามารถเข้ากับข้อมูลของนาลิดิซิกเอซิดดีที่สุด ส่วนนอฟลอกซาซินและ 17-แอลฟา-เอทินิลเอสทราไดออลเป็นไอโซเทอมแบบเส้นตรง ค่าสัมประสิทธิในการดูดซับ และค่าความจุในการแลกเปลี่ยนสูงสุดของนาลิดิซิกเอซิดกับเรซินแลกเปลี่ยนประจุลบเท่ากับ 94 ลิตรต่อกรัม และ 1.11 มิลลิกรัมต่อกรัม ตามลำดับ ส่วนค่าสัมประสิทธิ์การดูดซับของอะซิตะมิโนเฟนกับเรซินแลกเปลี่ยนประจุลบและบวก เป็น 0.0228 และ 0.0041 ลิตรต่อกรัม ตามลำดับ สำหรับนอฟลอกซาซินกับเรซินแลกเปลี่ยนประจุลบมีค่าสัมประสิทธิ์การดูดซับ และค่าความจุในการแลกเปลี่ยนสูงสุด 42 ลิตรต่อกรัม และ 0.93 มิลลิกรัมต่อกรัม ตามลำดับ ส่วนเรซินแลกเปลี่ยนประจุบวกเป็น 37 ลิตรต่อกรัม และ 27.67 มิลลิกรัมต่อกรัม ตามลำดับ 17-แอลฟา-เอทินิลเอสทราไดออลมีค่าสัมประสิทธิ์การดูดซับกับเรซินแลกเปลี่ยนประจุลบและบวกเท่ากับ 0.8096 และ 0.0510 ลิตรต่อกรัม ตามลำดับ การศึกษาการแข่งขันระหว่างซัลเฟตไออนและไบคาร์บอเนตไอออนกับเรซินแลกเปลี่ยนประจุลบพบว่าซัลเฟตมีผลมากกว่า และจะมีผลเพิ่มขึ้นเมื่อเพิ่มความเข้มข้นของไอออน

สาขาวิชาการจัดการสิ่งแวดล้อม(สหสาขาวิชา) ลายมือชื่อนิสิต.....Ananya Wanitkorkul.....
ปีการศึกษา 2548 ลายมือชื่ออาจารย์ที่ปรึกษา.....
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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KEY WORD: ION EXCHANGE / PHARMACEUTICAL / ANION EXCHANGE RESIN / CATION EXCHANGE RESIN

ANANYA WANITKORKUL: PHARMACEUTICAL REMOVAL BY ION EXCHANGE PROCESS. THESIS ADVISOR: ASST. PROF. KHEMARATH OSATHAPHAN, Ph.D., THESIS CO-ADVISOR: PROF. DAVID A. SABATINI, Ph.D., 70 pp. ISBN 974-53-2619-4.

Understanding the interaction of pharmaceuticals with common ion exchange resin used in drinking water treatment plants and sewage water treatment plants is essential to evaluate their routes and behavior in the aquatic environment. The ion exchange of four pharmaceuticals, acetaminophen (ACE), nalidixic acid (NAL), nofloxacin (NFC), and 17-alpha-ethinyl estradiol (EE2), has been investigated in the laboratory using batch experiments at neutral pH range. Anion exchange and cation exchange resins are used as sorbent materials. The preliminary tests showed that acetaminophen, which is in neutral form and has the highest water solubility (14,000 mg/L at 25°C), was sorbed onto both of ion exchange resins. While nalidixic acid, which has one carboxylic functional group, exchanged with anion exchange resin but no significant ion exchange process with cation exchange resin. Norfloxacin exchanged with both resins. 17 α-ethinyl estradiol, the most hydrophobic molecule, was similar to acetaminophen, it was sorbed onto anion exchange resin and cation exchange resin. For equilibrium time studies, Acetaminophen on anion exchange resin and cation exchange resin showed that equilibrium was reached within 3 hours. While nalidixic acid on anion exchange resin required 6 hours to achieve the equilibrium. Norfloxacin on both resins reached equilibrium at 1 day. 17 α-ethinyl estradiol on anion exchange resin and cation exchange resin were used 12 hours and 6 hours, respectively. A Langmuir isotherm was used to fit to ion exchange data of nalidixic acid and norfloxacin but for acetaminophen and 17 α-ethinyl estradiol were fitted with Linear isotherm. The sorption coefficient and maximum adsorption capacity of nalidixic acid on anion exchange resin were 94 L/g and 1.11 mg/g, respectively. The sorption coefficient of acetaminophen on anion exchange resin and cation exchange resin were 0.0228 L/g and 0.0041 L/g, respectively. The sorption coefficient of norfloxacin on anion exchange resin was 42 L/g and maximum adsorption capacity was 0.93 mg/g, on cation exchange resin, the sorption coefficient was 37 L/g and maximum adsorption capacity was 27.67 mg/g. The sorption coefficient of 17 α-ethinyl estradiol on anion exchange resin was 0.8096 L/g and on cation exchange resin was 0.0510 L/g. For anion competition studies, sulfate ion competed with nalidixic acid and nrofloxacin more than did bicarbonate ion and competition increased with increasing concentration of these two ions.

Field of study: Environmental management Student's signature..Ananya.Wanitkorkul.

(Inter-Department) Advisor's signature..K Osatha.....

Academic year 2005 Co-advisor's signature.....

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NOMENCLATURE

C	=	liquid phase chemical concentration (M/L^3)
C_{ads}	=	concentration in solid phase (M/L)
C_{aq}	=	concentration in aqueous phase (M/L)
C_e	=	equilibrium concentration (M/L)
q	=	mass of chemical sorbed normalized by mass of resin (M/M)
K_d	=	linear isotherm coefficient (L^3/M)
K_F	=	freundlich isotherm coefficient (L^3/M)
K_L	=	langmuir isotherm coefficient (L^3/M)
A_M	=	maximum adsorption capacity (M/M)

CHAPTER I

INTRODUCTION

1.1 Pharmaceuticals in the Environment

Pharmaceutical and personal care products (PPCPs) Phamaceutical Active Compounds (PhACs) are very important in human and animal lives. A large amount of pharmaceutical products are used for therapy, agriculture, and aquaculture. Pharmaceuticals are used for illness treatment, prevention of unwanted pregnancy, and facing stress (Zuccato et al., 2000). They can be applied to stimulate physiological growth in humans, animals, and plants. Many pharmaceuticals are not completely metabolized in humans or animals, and unused medicines are often not disposed in the right way such as they are thrown away in the toilet, water resources, and some areas like a waste. For these reasons, PPCPs and PhACs have been detected in surface water and groundwater up to the µg/L-level around the world, for example, Austria, Brazil, Canada, Croatia, England, Germany, and US through several pathways including from run-off (Heberer 2002). Moreover, pharmaceuticals are not eliminated completely in the municipal sewage treatment plants so they have been detected in the effluent of sewage treatment plants (STPs) (Daughton and Ternes, 1999; Heberer et al., 2000; Ternes et al., 2002). PPCPs and PhACs commonly detected in the environment include antibiotics, endocrine disrupters, and non-prescription analgesic drugs. After the pharmaceuticals enter the environment, they are not biodegraded in the environment and can form complexes with metal ions (Chang-Hwa Song et al., 1999) or conjugated with other chemicals transform into other forms. Some pharmaceuticals can penetrate via aquatic organisms including fish

and shellfish and accumulate in that organism or absorb into organic material in aquifer soil in many countries in Southeast Asia region such as Thailand, Vietnam, and China and there has not been adequate evaluation of PPCPs and PhACs in the environment media (Bruce et al., 2005). Besides, residues of PPCPs and PhACs may also leach into groundwater aquifers. The presence of PPCPs and PhACs from human medical care in groundwater may, however, also be caused by other resources such as landfill leachates or manufacturing residues (Heberer 2002). These criteria are not identified and explored as these interactions are not known but the presence of PPCPs and PhACs are emerging concern in the environmental science community (Drewes et al., 2002; Boxall et al., 2004).

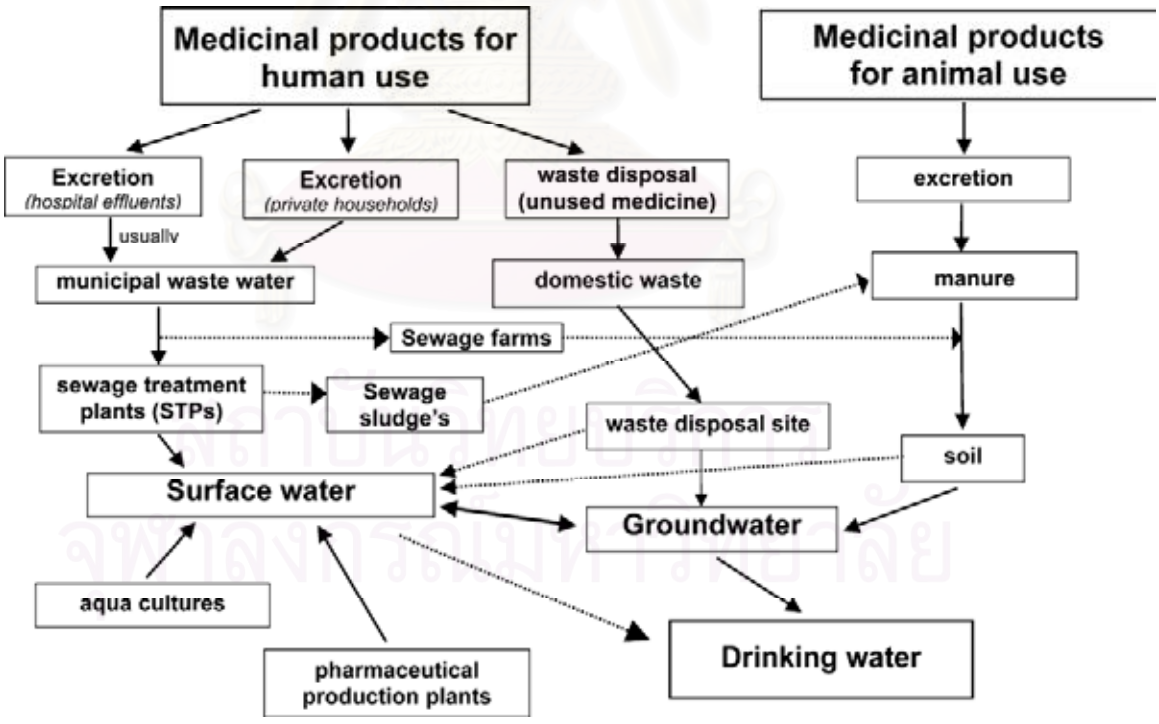


FIGURE 1.1 Possible sources and pathways for the occurrence of pharmaceutical residues in the aquatic environment. (Heberer 2002)

PPCPs and PhACs around 80 compounds have been detected in water resources in countries in Europe region. Some of these pharmaceuticals have the trace level concentration but some have been detected up to µg/L-level.

Table 1.1 Concentrations of PPCPs and PhACs in water resources. (Heberer 2002)

PPCPs and PhACs	Concentration (µg/L)	Location	References
Acetylsalicylic Acid	0.22	Germany	Ternes 1998a
Salicylic Acid	54	Germany	Ternes 1998b
Hydroxyhippuric Acid	6.8	Germany	Ternes 1998b
Gentisic Acid	4.6	Germany	Ternes 1998b
Acetaminophen	Up to 10	Germany	Kolpin et al., 2002
Diclofenac	2.51	Germany	Heberer et al., 2002
Ibuprofen	Up to 2.7	Spain	Farre et al., 2001
Ciprofloxacin	0.25-0.41	Switzerland	Golet et al., 2001
Norfloxacin	0.05-0.12	Switzerland	Golet et al., 2001
Carbamazepine	1.08	Germany	Ternes 1998a
Primodone	Up to 0.64	Germany	Ternes 1998a
Clorofibric Acid	4	Germany	Heberer et al., 1997
17α-ethinylestradiol	0.02	Germany	Stumpf et al., 1996

Several studies have evaluated the effectiveness of different treatment process for removing PPCPs from water. A pilot-scale study by Ternes et al. (2002) found that granular activated carbon and ozonation removed PPCPs to below detection limits, but flocculation with iron chloride and sand filtration were inadequate. Shäfer et al. (2003) concluded that both nanofiltration and reverse osmosis were effective removal methods below the pK_a of the common hormone estrone but not above the pK_a when estrone was in its anionic form. Since many PPCPs molecules have pK_a near neutral pH values, it is important to develop treatment processes for the ionic forms of these species as well.

1.2 Research Aspect

Recently, the appearance of pharmaceuticals in the aquatic environment has become a topic of public interest. Some pharmaceutical compounds cannot be eliminated in wastewater or sewage treatment plants and are not degraded in the environment. They have been detected in surface water, groundwater, and drinking water in the ng/L level up to g/L level (Daughton and Ternes, 1999; Zuccato et al., 2000; Kummerer, 2001; Heberer, 2002).

Although pharmaceuticals have been detected in the environment, sewage treatment plants, and drinking water treatment plants still don't focus on this problem. Therefore, this study will evaluate the behavior of pharmaceutical compounds in water treatment and the competition between pharmaceuticals and ions generally found in surface water and groundwater. The primary objective of this study is to investigate sorption processes of pharmaceuticals onto ion exchange resins. Dowex Marathon A and Dowex HCR-S, which are commercial anion exchange resin and

cation exchange resin, respectively, commonly used in drinking water treatment plants and sewage treatment plants, were selected for this study. Four pharmaceuticals, acetaminophen, nalidixic acid, norfloxacin, and 17-α ethynyl estradiol are frequently detected in water resources and used widely in the world, are used to achieve this research.

1.2.1 Objectives

The main purpose of this study is to evaluate the sorption of acetaminophen, nalidixic acid, 17-α-ethynylestradiol, and norfloxcin on ion exchange resin (cation and anion exchange) and to study the effect of sulfate and bicarbonate competition on nalidixic acid and norfloxacin adsorption on anion exchange resin. The goals of this research were as follows:

1. To evaluate the equilibrium time and sorption characteristic of pharmaceuticals on ion exchange resins.
2. To compare removal efficiency of each ion exchange resin.
3. To evaluate competition of anion to pharmaceuticals on anion exchange resin.

1.2.2 Hypotheses

1. Ion exchange of pharmaceuticals is a function of pharmaceutical properties (e.g. pK_a, K_{ow}) and resin properties (e.g. anion exchange, cation exchange).
2. Background ions can reduce the efficiency of pharmaceutical removal with multivalent ions having a greater effect than monovalent ions.
3. Anions with higher concentration have more competition with nalidixic acid and norfloxacin on anion exchange site.

1.2.3 Scopes of the Study

Except where specified otherwise, all batch experiments will be performed with constant ionic concentration, neutral pH, and controlled room temperature for determining ion exchange equilibria and isotherm of selected pharmaceuticals onto ion exchange resins and anion competition with these pharmaceuticals onto both ion exchange resins.

1.3 Advantages of Research Studies

Even though acetaminophen, nalidixic acid, norfloxacin, and 17-α ethynyl estradiol are detected at low concentration in the environment, the long term effects of these concentrations are unknown. This study will demonstrate the interaction of pharmaceuticals with common ion exchange resins used in drinking water treatment plants and sewage water treatment plants for understanding their routes and behavior in the aquatic environment. The results from this study also make people know and concentrate about use of water resources which have pharmaceuticals in trace level more than in the past and try to find the appropriate method for pharmaceutical removal.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Pharmaceuticals

Acetaminophen (ACE) is a mild analgesic, or pain reliever, which is the most popular painkillers. Its mild pain-relieving property has made it a very useful medication in the treatment of a wild variety of conditions, including migraine headaches, aches and pains due to cold or flu, and fever. However, this drug is a very weak anti-inflammatory agent and it is usually not used to treat stiffness, swelling of joints, or tissue inflammation. Physicians prefer to use this drug for pain relief instead of aspirin because when used appropriately, side effects are rare. The most serious side effect is liver damage due to large doses, chronic use or concomitant use with alcohol or other drugs that also damage the liver. Acetaminophen can be excreted in breast milk. However, use of this drug by a nursing mother appears to be safe. Available in both generic and brand name forms, it is an over-the-counter (OTC) drug that does not require a prescription for purchase.
(www.healthevolution.com/Articles/Acetaminophen.htm)

Nalidixic Acid (NAL) is an antibacterial drug which is used in the treatment of lower urinary tract infections (cystitis) and it is also sometimes given for the prevention of recurrent urinary tract infections. Taken by mouth, it does not accumulate in the body tissue, but it is concentrated in the urine. While it is effective against almost all species of bacteria that commonly infect the urinary tract, because

some organisms rapidly develop resistance, a second course of treatment is less likely to be as effective. This drug is fast acting and usually clears acute outbreaks of infection completely within a few days. Although generally safe, nalidixic acid sometimes causes serious side effects. The drug may interfere with some urine tests and can give a false high reading of urine sugar level. (www.cix.co.uk/~cyberville/medizine/nalidixi.htm)

Norfloxacin (NFC) is used to treat strongly sorbed on the variety of bacterial infections. Norfloxacin belongs to a class of drugs called quinolone antibiotics. It works by stopping the growth of bacteria, but does not work for viral infections (e.g., common cold, flu). Unnecessary use or overuse of any antibiotic can lead to its decreased effectiveness. This drug may pass into breast milk and could have undesirable effects on a nursing infant. (http://my.webmd.com/drugs/drug-11054Norfloxacin+Oral.arpx)

17-α-Ethinyl Estradiol (EE2) is synthetic steroid hormone, which is classified as an endocrine disrupter. This is a powerful synthetic estrogen similar to the natural female sex hormone estradiol and its widest use is in oral contraceptive pill preparations where it is combined with a synthetic progesterone drug (progestogen). Ethynyl estradiol is also used to supplement natural estrogen when the body's production is low, e.g., during menopause. In these conditions, it is often given with progestogen and is occasionally used to control abnormal bleeding from the uterus, and to treat delayed sexual development (hypogonadism) in females. Certain cancers of the prostate respond to this drug and it is sometimes given in high doses for post-coital contraception. In conjunction with cyproterone, it is used to treat severe acne in women. (www.cix.co.uk/~cyberville/medizine/ethinylo.htm)

2.1.2 Ion Exchange Process

An ion exchange reaction is the reversible interchange of ions between a solid phase (the ion exchanger, e.g. resin) and a solution phase, the ion exchanger being insoluble in the solution or chemicals in which the exchange is carried out. An ion exchanger M^-A^+ carries the cation A^+ as the exchanger ion that is replaced by the same charge ion, the cation B^+, in an aqueous solution, an ion exchange reaction takes place which may be represented by following equation (1).

$$M^-A^+ + B^+ \leftrightarrow M^-B^+ + A^+ \quad (1)$$

The equation (1) represents the cation exchange process, where M^- is the insoluble fixed anionic complement of the ion exchanger M^-A^+, often called simply the fixed anion. The cations A^+ and B^+ are referred to as counter-ions, and ions in the solution which bear the same charge as the fixed anion of the exchanger are called co-ions. On the other hand, the anion exchange process will have the fixed cation and anion counter-ions as shown in the equation (2).

$$M^+A^- + B^- \leftrightarrow M^+B^- + A^- \quad (2)$$

The main fact is that electroneutrality is preserved at all times in both the exchanger and solution phases, and this in turn requires that counter-ions are exchange in equivalent amounts. The most important features characterizing an ideal exchanger are (C.E. Harland 2nd Edition, 1994)

1. A hydrophobic structure of regular and reproducible form
2. Controlled and effective ion exchange capacity
3. Rapid rate of exchange
4. Chemical stability
5. Physical stability in terms of mechanical strength and resistance to attrition

6. Consistent particle size and effective surface area compatible with the hydraulic design requirements for large scale plant.

Hydrophobicity, electrostatic force, and affinity of ion exchange resin are important role in ion exchange process. The ions which have high hydrophobicity can have more opportunity to exchange with ion exchange resin. For electrostatic force, the ions have the same charge (positive or negative) as ion sorbed on ion exchange resin are able to exchange with ion exchange resin. There are three rules of affinity for ions shown as follow:

1. Ions of high valence are preferred over ions of low valence or the extent of the exchange reaction increases with increasing ion valence (e.g., $Fe^{3+} > Mg^{2+} > Na^{+}$; $PO_4^{3-} > SO_4^{2-} > NO_3^{-}$). This preference increases with a decrease in the total ionic concentration of the solution
2. For ions of the same valence the extent of the exchange reaction increases with decreasing hydrated radius and increasing atomic number (e.g., $Ca^{2+} > Mg^{2+} > Be^{2+}$; $K^{+} > Na^{+} > Li^{+}$) because of swelling pressure within the resin. Ions of larger hydrated radius increase the swelling pressure within the resin and decrease the affinity of the resin for ions.
3. For a solution with a high total ionic concentration the extent of exchange reaction is often reversed.
4. The relationship between the degree of crosslinking of resin and the size of hydrated ion may affect the extent of the exchange reaction. If the resin has a high degree of crosslinking, the ion may be too large to penetrate into the matrix of the resin.

Table 2.1 Relative affinities of various anions for polystyrene-based strong-base anion exchange resins (after Abrams and Benezra, 1967).

Ions	Relative Affinity	
	Type 1	Type 2
Hydroxide (reference)	1.0	1.0
Benzenesulfonate	500	75
Salicylate	450	65
Citrate	220	23
Iodide	175	17
Phenoxide	110	27
Bisulfate	85	15
Chlorate	74	12
Nitrate	65	8
Bromide	50	6
Bromate	27	3
Nitrite	24	3
Chloride	22	2.3
Iodate	5.5	0.5
Formate	4.6	0.5
Acetate	3.2	0.5
Fluoride	1.6	0.3

Type 1 : Reactive group – $CH_2N(CH_3)_3$

Type 2 : Reactive group – $CH_2N(CH_3)_2C_2H_4OH$

Mechanism of Ion Exchange

Studies of ion exchange reaction on organic exchangers have identified the possible rate controlling steps to be (C.E. Harland 2nd Edition, 1994)

1. Coupled diffusion or transport of counter-ions in the external solution phase
2. Coupled diffusion or transport of counter-ions within the ion exchange resin
3. Chemical reaction at the sites of the functional groups within the exchanger

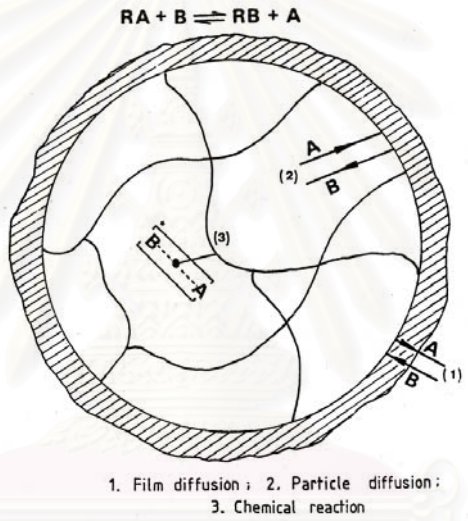


Figure 2.1 Rate determining steps in ion exchange (schematic) (C.E. Harland 2nd Edition, 1994)

1. Coupled diffusion of counter-ions in the external solution

Efficient stirring of the resin with the solution ensures the elimination of concentration gradients in the bulk solution such that mass transfer in this phase is purely by convection and not rate determining. The convective mass transfer is the lowest at close resin bead surface. A stagnant liquid layer or film may be considered to surround the exchanger particles across which ion mass transfer is controlled by

planar or one dimensional diffusion. Ions tries to keep electroneutrality during ion exchange, by whatever mechanism, requires that an equal and opposite counter-ion flux must always apply. Therefore rate control by mass transfer in the external solution is interrupted as *coupled mass transfer* across the hypothetical film or *Nernst layer* surrounding the resin particles by a mechanism of diffusion called *film diffusion*. The driving force for mass transfer is the concentration difference between resin and the solution.

2. Coupled diffusion of counter-ions in the resin

After ions from the solution (ions B) move through the film covered around the resin. They pass into the resin via pores, while ions from the resin (ions A) come out from inside the resin or move in the opposite direction of ions B. This step is called *particle diffusion*. The driving force in this case is the ion concentration gradient between the interior of the resin and the resin-solution interface.

3. Chemical reaction rate control

True chemical reaction at the sites of the functional groups is represented purely schematically in Figure 2.1 by an imaginary transition state complex between ions A, B, and the ionogenic group. Reactions between simple, freely dissociated, aqueous ions are usually very fast and therefore not rate controlling, but chemical reaction rate control for the exchange of transition metal ions or complex ions capable of strong chelate type complex formation with iminodiacetate or phosphonate functional groups.

2.1.3 Ion Exchange Resin

Characterization of Ion Exchange Resins

The ion exchange characteristics of resins available commonly are shown in Table 2.2. These characteristics are divided into two mainly kinds (physical and chemical). Typically, an ion exchange resin is described as being weak or strong, acidic or basic, cationic or anionic. The charge on the counter-ion is important in ion exchange process. While ion exchange resins are in the aqueous solution, they will be hydrated and dissociate to yield equivalent amounts of oppositely charged ions. In conventional aqueous acid or base solutions, resins may be neutralized to give the appropriate salt form. The degree of dissociation is dependent on an apparent equilibrium constant (or pK value) which defines the electrolyte strength of the exchanger and is usually derived from a theoretical treatment of pH titration curves (C.E. Harland 2nd Edition, 1994).

Table 2.2 Classification of terms employed to describe ion exchange resins

General Classification	
Chemical	Physical
matrix (polymer structure) crosslinking (% DVB) functional group ionic form (as supplied) water content ion exchange capacity pH range	appearance (physical form) particle size density

Types of resin

1. Strong Acidic Cationic Resin

This type of resin has sulfonic acid group is a functional group and ionic form may be sodium ion (Na^+) or hydrogen ion (H^+) (e.g. $-SO_3Na$, $-SO_3H$) which are exchanged with cation in the solution. This resin can exchange at any pH. An example of ion exchange process is shown as below :

$$2R\text{-}SO_3Na + Ca^{+2} \longrightarrow (R\text{-}SO_3)_2Ca + 2Na^+$$

2. Weak Acidic Cationic Resin

The functional group of this resin, carboxylic group (e.g. -COOH, -COONa), differs from strong acidic cationic resin. This type has less dissociation than the first type of resin, especially in the acid solution. It can work well when the pH is higher than 4 or 5. An ion exchange process for this resin is expressed by following equation.

$$2RH + Ca(HCO_3)_2 \longrightarrow R_2Ca + 2H_2O + 2CO_2$$

3. Strong Basic Anionic Resin

Strong Basic Anionic Resin commonly has functional group as quaternary amine that is occurred from reaction between polymer and trimethylamine (Type 1) or polymer and dimethyl ethanolamine (Type 2). The structure of both types is as Figure 2.2.

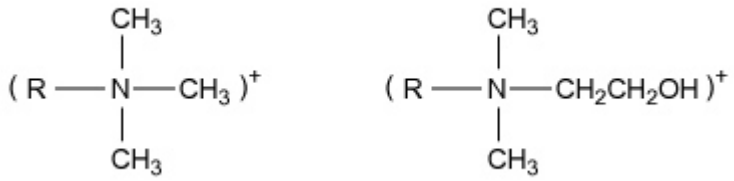


Figure 2.2 The structure of strong basic anionic resin type 1 and type 2

$$2(CH_3)_3CH_2NOH + SO_4^{2-} \longrightarrow [(CH_3)_3CH_2N]_2SO_4^{2-} + 2OH^- \quad (a)$$

$$2(CH_3)_3CH_2NCl + SO_4^{2-} \longrightarrow [(CH_3)_3CH_2N]_2SO_4^{2-} + 2Cl^- \quad (b)$$

Free ion of this resin is usually chloride ion (Cl^-) or hydroxide ion (OH^-). The above equations (a) and (b) demonstrate ion exchange processes of strong basic anionic resin with anion in the solution.

4. Weak Basic Anionic Resin

This is the last type of ion exchange resin that has amine functional group which is divided to two kinds: Secondary Amine $[CH_2NH_2(CH_3)]^+$ and Tertiary Amine $[CH_2NH(CH_3)_2]^+$. This resin can remove only acid from the solution such as HCl, HNO_3, etc. The mechanism of ion removal for this resin is different from the others. It is a sorption process, not ion exchange process.

$$R + HCl \longrightarrow RHCl$$

2.1.4 Sorption Isotherm

When the measured adsorption data are plotted against the concentration value of the adsorbate at equilibrium, the resulting graph is known as an adsorption isotherm (Yaron et al., 1996). Three adsorption models are used to describe three different isotherms.

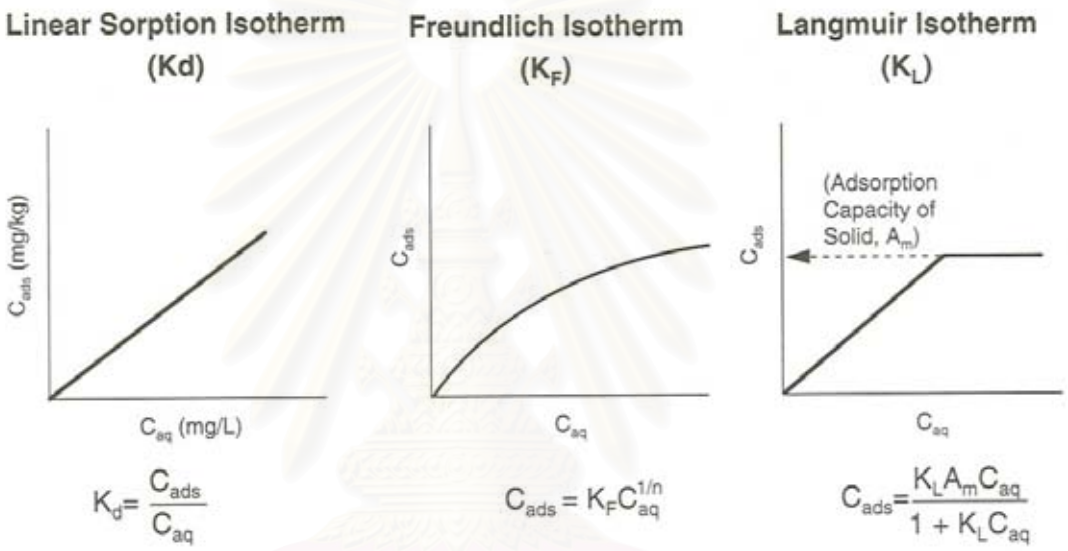


Figure 2.3 Sorption Isotherms

A straight-line plot of adsorption implies that the adsorption affinity is independent of solute concentration and that surface of the solid has unlimited capacity for adsorption. Linear adsorption isotherm is appropriate for many species at low solution concentration, but they are not appropriate at higher concentrations when the surface sites for adsorption become filled. (Deutsch, 1997)

Each of the isotherms is linear at low adsorbate concentration; however, the Freundlich and Langmuir isotherms change slope at higher concentrations. Both of

these isotherms can be applied to fit with ion exchange data. The Freundlich isotherm becomes a curve at higher concentration reflecting lower adsorption at these values as the adsorption sites become filled. However, there is no total capacity term in the Freundlich isotherm equation, so there is no upper limit on adsorption. The Langmuir isotherm has a capacity term (A_m) in its definition. Once the concentration of adsorbed species reaches this capacity term, adsorption decrease to zero and any additional increase in species solution concentration remains in solution (Deutsch, 1997).

2.2 Literature Reviews

2.2.1 Occurrence of Pharmaceuticals in the Aquatic Environment

Buser and Müller (1998) illustrated clofibric acid (CA) and the herbicide mecoprop (MCPP) were presented in Swiss lakes from populated areas and in the North sea at concentrations similar to pesticides. CA appears to be highly mobile and persistent in the aquatic environment. The presence of CA in the environment points to inputs from the therapeutic use of this compound via wastewater treatment plants. The study showed that not only agricultural but also certain pharmaceutical compounds have to be considered as environmental contaminants.

Daughton and Ternes (1999) documented the occurrence of pharmaceuticals and personal care products (PPCPs) in the environment. PPCPs, which are used in large amounts throughout the world, discharged into the environment via sewage treatment facilities and wet weather runoff. The literature showed some PPCPs were extreamly persistent and introduced to the environment in very high quantities and perhaps have already gained ubiquity worldwide, others could act as if they were

persistent; simply because their continual infusion into aquatic environment serves to sustain perpetual life-cycle exposure for aquatic organisms.

Kümmerer (2001) investigated emission of drugs, diagnostic aids, and disinfectants into wastewater by hospitals and other sources. A brief summary of input by different sources, occurrence, and elimination of different pharmaceutical groups such as antibiotics, anti-tumor drugs, anaesthetics, and adsorbable organic halogen compounds (AOX) resulting from hospital effluent into sewage water and surface water is presented. The literature showed that pharmaceuticals which are excreted by patients enter into wastewater. Furthermore, unused drugs are disposed of down the drain. Disposed of antibiotic drugs can disturb wastewater treatment processes and the microbial ecology in surface water.

Heberer (2002) showed some pharmaceutically active compounds (PhACs) are not eliminated completely in the municipal sewagetreatment plants (STPs) and they are discharged as contaminants into the receiving waters. This study carried out in Berlin showed that PhACs such as clofibric acid, diclofenac, ibuprofen, propyphenazone, primidone and carbonnazepine were detected at individual concentrations up to the μg/1-level in influent and effluent samples from STPs. In addition, their presence in groundwater so there is a potential risk of drinking water contamination when groundwater recharge was used in drinking water production.

Ternes et al. (2002) studied the efficiency of different treatment steps to remove the antiphlogistic diclofenac, the antiepileptic carbamazepine, and the lipid regulators clofibric acid and bezafibrate during drinking water treatment. This research used flocculation using iron (III) chloride, ozonation, and filtration with granular activated carbon (GAC) for pharmaceuticals removal. The study showed

flocculation was no significant elimination of the selected target pharmaceuticals. Ozone can reduce the concentrations of diclofenac and carbamazepine more than 90%, while bezafibrate was eliminated by 50%. But this method cannot remove clofibric acid. GAC was very effective in removing pharmaceuticals except for clofibric acid.

Hohenblum et al. (2004) monitored endocrine disrupting substances (EDS) in groundwater and surface water in Austria. Studies and risk assessments reveqled that among other compounds, steroidal hormones and industrial chemicals. Results indicated hormones estrone and 17β-estradiol were detected in the majority of all investigated surface water samples. In groundwater, 17β-estradiol was mostly detected when compared with other substances.

2.2.2 Ion Exchange Process

Storm et al. (1985) studied cytostatic drug removal by using cation exchange resin Dowex 50W-X4. The results indicated that hydrophobic and electrostatic (ion exchange) effects play a role in adsorption process of drugs onto resin. Moreover, hydrophobic contributions to the interaction were responsible for the high resistance offered by the binding forces against desorption of adsorbed drugs.

Hänninen et al. (2003) demonstrated the impact of compound lipophilicity, valence, aqueous solubility and hydrogen bonding into and release from a strong anion-exchange fiber (Smopex DS-218v) by using ten salicylate anions as model compounds. An increase in the molar amount of external chloride-ions resulted in a more effective release of all salicylates from the fiber. Hydrophobic interactions decreased the rate and amount of drug release from the fiber with the most lipophilic salicylates. Hydrogen bonding between the fiber and the compound restricted also the

rate and extent of ion-exchange process of the hydrophilic 5-aminosalicylic acid and 5-hydroxysalicylic acid. The release of the divalent salicylates is smaller than the monovalent.

Lee et al. (2004) illustrated recovery of the dichloromethane which was dissolved in wastewater by using a hydrophobic polymeric resin (XAD-1600), hydrophilic polymer resin (XAD-7) and activated carbon (DY-GAC). The results were the adsorption amount at high concentration was in the order of XAD-1600>XAD-7>DY-GAC on a mass basis. A hybrid model Langmuir and BET equations was used to fit the adsorption equilibrium data of two polymer resins. Langmuir isotherm has been found to adequately describe the adsorption on DY-GAC activated carbon.

Otero et al. (2004) showed salicylic acid removal by polymeric resins (sephabeads SP206 and SP207) and activated charcoal (Filtrasorb F400). Salicylic acid is a drug responsible for many medications and prescription drugs such as aspirin. In this paper, activated charcoal had the higher adsorption than two polymeric resins. The adsorption of all adsorbents decreased with increasing temperature because the adsorption was favored by lowering temperature.

Yilmax et al. (2004) studied boron removal from boron containing wastewater by ion exchange process. Amberlite IRA-743,which is a weak-base anion exchange resin, was used as an anion-exchanger. A continuous system was used in this experiment. The results of study were the boron removal increased with increasing bed volume of resin, boron removal rate increased with decreasing boron concentration in wastewater, and boron removal increased with increasing temperature up to 313 K.

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Ion Exchange Resin

Two ion exchange resins were studied in this research: Dowex HCR-S (cation exchange resins) and Dowex Marathon A (anion exchange resins). Both of them were obtained from Dowex Chemical Company and their properties were given in table 3.1.

Table 3.1 Ion exchange resin properties

Resin	Free Ion Form	Total Exchange Capacity (eq/l)	Water Content (%)	Mean Particle Size (μm)	Particle Density (g/ml)
HCR-S	Na^+	2.0	44-48	N/A	1.28
Marathon A	Cl^-	1.3	50-60	575±50	1.08

N/A : Not Available

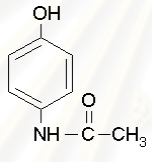
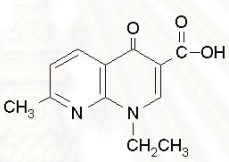
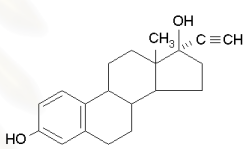
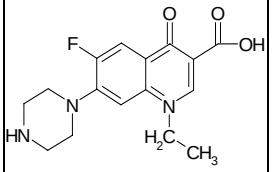
Referrences : Dowex Chemical Co.

3.1.2 Pharmaceutical Compounds

Four pharmaceutical compounds, acetaminophen (analgesic, paracetamon), nalidixic acid (antibiotic), norfloxacin (anti-bacterial infection), and 17-α-ethinyl estradiol (oral contraceptive), were used in this study. Acetaminophen has a water solubility of 14,000 mg/L, log K_{ow} of 0.46, and pK_a of 9.38 was purchased from Sigma Chemical Co. Nalidixic acid, with a water solubility of 100 mg/L, log K_{ow} of

1.59, and pK_a of 6.33 was purchased from Sigma Chemical Co. Norfloxacin, with a water solubility of 280 mg/L, log K_{ow} of -1.0, and pK_a of 6.34 and 8.75 was purchased from Sigma Chemical Co. 17-α-ethinyl estradiol, with water solubility of 11.3 mg/L, log K_{ow} 3.67, and pK_a of 10.4 was obtained from Aldrich Chemical Co. The properties of these pharmaceuticals were given in Table 3.2.

Table 3.2 Pharmaceuticals properties

Chem. Name	Acetaminophen	Nalidixic acid	17-α-ethinylestradiol	Norfloxacin
Structure				
CAS Number	103-90-2	389-08-2	57-63-6	70458-96-7
Mol formula	$C_8H_9NO_2$	$C_{12}H_{12}N_2O_3$	$C_{20}H_{24}O_2$	$C_{16}H_{18}FN_3O_3$
Mol weight	151.17	232.24	296.41	319.33
Melting point	170°C	229.5°C	183°C	227-228°C
Water solubility at 25°C (mg/L)	14000	100	11.3	280
Log K_{ow}	0.46	1.59	3.67	-1.0 (a)
Vapor Pressure at 25°C (mm Hg)	7×10^{-6}	3.56×10^{-7}	2.67×10^{-9}	6.77×10^{-13}
pKa	9.38	6.33	10.4	6.34, 8.75
Henry's constant (atm-m3/mole)	6.42×10^{-13}	5.12×10^{-16}	7.94×10^{-12}	8.7×10^{-19}

Reference: SRC PhysProp Database (http://esc.syrres.com)
(a) www.ecn.nl/docs/society/horizontal/hor_desk_26_pharmaceuticals.pdf

3.1.3 Chemicals

Reagent grade MeOH (99% purity) used as a solvent for preparing pharmaceutical stock solution was purchased from Aldrich Chemical Co. Calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) used as background ionic strength of sample solutions was purchased from Fisher Scientific Co. In study of anion competition with pharmaceuticals, sodium sulfate (Na_2SO_4) and sodium bicarbonate ($NaHCO_3$) were used and they are purchased from Fisher Scientific Co.

3.2 Experimental Methods

Acetaminophen was prepared in nanopure water. Nalidixic acid, norfloxacin and 17 α-ethinyl estradiol were prepared in stock solutions of MeOH to aid in dissolution. All batch experiments were conducted at room temperature (~25°C). Calcium chloride was added to maintain a constant ionic strength (0.01 M $CaCl_2 \cdot 2H_2O$) for all tests. Triplicate samples were evaluated for each set of conditions. When pH values were not externally altered, they remained in the neutral range. Most sorption studies were conducted using a constant volume of solution. For nalidixic acid with anion exchange resin, a sorbent to solution ratio of 1:80 g/ml was used. For acetaminophen with both ion exchange resins, ratio of 1:20 g/ml was used. For norfloxacin with anion exchange resin, ratio of 1:40 g/ml was used, while norfloxacin with cation exchange resin, ratio of 1:800 g/ml was used. For 17 α-ethinyl estradiol with anion exchange resin, ratio of 1:1600 g/ml was used but for 17 α-ethinyl estradiol with cation exchange resin, ratio of 1:40 g/ml was used.

Acetaminophen, nalidixic acid, norfloxacin, and 17 α-ethinyl estradiol concentrations were varied in a series of 20 ml vials and shaken until equilibrium was

achieved (predetermined to be within 24 hours and 48 hours for anion exchange resin and cation exchange resin in equilibrium time studies). The supernatant from each vial was transferred into a 20 ml vial for subsequent analysis.

For study competition of anion in water resources to nalidixic acid and norfloxacin, sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) at concentration of 10 mg/l and 100 mg/l were used. Na_2SO_4 and $NaHCO_3$ were used in this study while NaOH 0.001 M. was used to adjust pH of samples added with $NaHCO_3$. All of experiments will be conducted at room temperature and neutral pH.

Triplicates are evaluated for each set of conditions. Pharmaceuticals and media blanks are conducted for each isotherm study to account for loss/gains during the experimental procedure. Initial pH value was not externally controlled.

3.3 Analytical Instruments

For determination of pharmaceuticals at mg/l concentrations, a UV spectrometer was used. A SHIMADZU UV-1601 spectrophotometer was used to analyze acetaminophen and nalidixic acid. A wavelength of 242 nm was used to analyze acetaminophen; a wavelength of 258 nm was used to analyze nalidixic acid, and a wavelength of 272 nm. was used to analyze norfloxacin.

At first, 17-∝-ethinyl estradiol was analyzed using the SHIMADZU UV-1601 spectrophotometer together with 1 cm UV cell but absorbent peak was very small. Thus, 17-∝-ethinylestradiol was determined by HP 8452A Diode Array Spectrophotometer together with 4 cm cell in order to increase the adsorbent peak by increasing path length. A wavelength of 280 nm was used to analyze 17-∝-ethinyl estradiol.

Table 3.3 Maximum wavelength absorption (λ_{max}) of acetaminophen, nalidixic acid, norfloxacin, and 17-∝-ethinyl estradiol.

Pharmaceuticals	λ_{max} (nm)
Acetaminophen	242
Nalidixic Acid	258
Norfloxacin	272
17-∝-ethinyl estradiol	280

A pH meter model 12, Scientific Instrument connected with glass pH probe, was used to measure pH of samples. Ion Selective Electrode (ISE) meter 710A and atomic absorption (AA) was used to measure chloride ions and sodium ions in samples after reaching equilibrium, respectively.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Equilibrium Time of Pharmaceuticals with Ion Exchange Resins

The preliminary tests of four pharmaceuticals (acetaminophane, nalidixic acid, norfloxacin, and 17 α-ethinyl estradiol) with anion exchange resin and cation exchange resin showed that acetaminophen was sorbed onto both of ion exchange resins. While nalidixic acid exchanged with anion exchange resin but no significant ion exchange process with cation exchange resin. Norfloxacin exchanged with both resins. 17 α-ethinyl estradiol was similar to acetaminophen, it was sorbed onto anion exchange resin and cation exchange resin.

Equilibrium time was evaluated for these pharmaceuticals onto anion exchange resin and cation exchange resin. Acetaminophen on anion exchange resin and cation exchange resin showed that equilibrium was reached within 3 hours (Figure 4.1). While nalidixic acid on anion exchange resin required 6 hours to achieve the equilibrium (Figure 4.2). Norfloxacin on both resins reached equilibrium at 1 day (Figure 4.3). 17 α-ethinyl estradiol on anion exchange resin and cation exchange resin were used 12 hours and 6 hours, respectively (Figure 4.4).

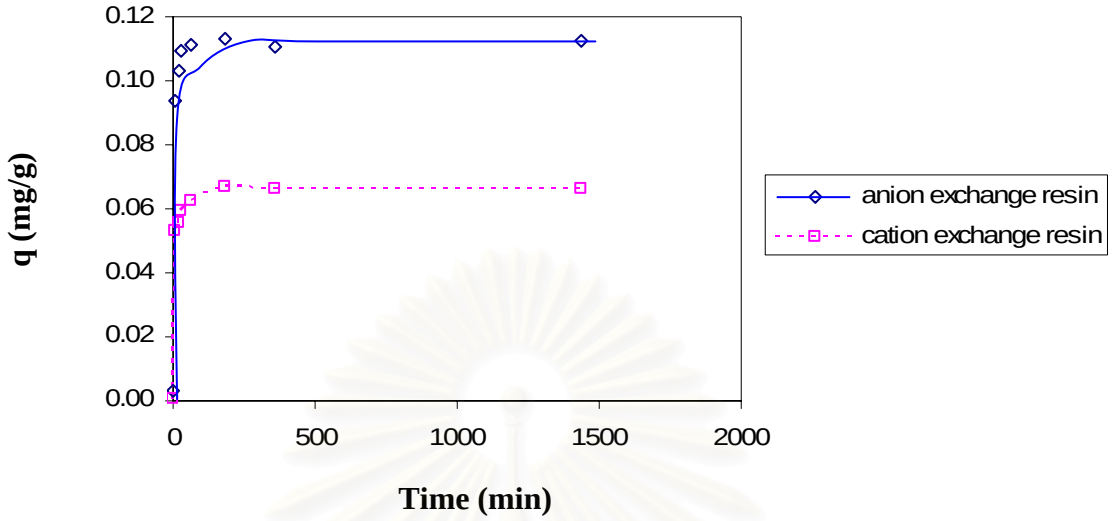


Figure 4.1 The equilibrium time of acetaminophen on anion exchange and cation exchange resins.

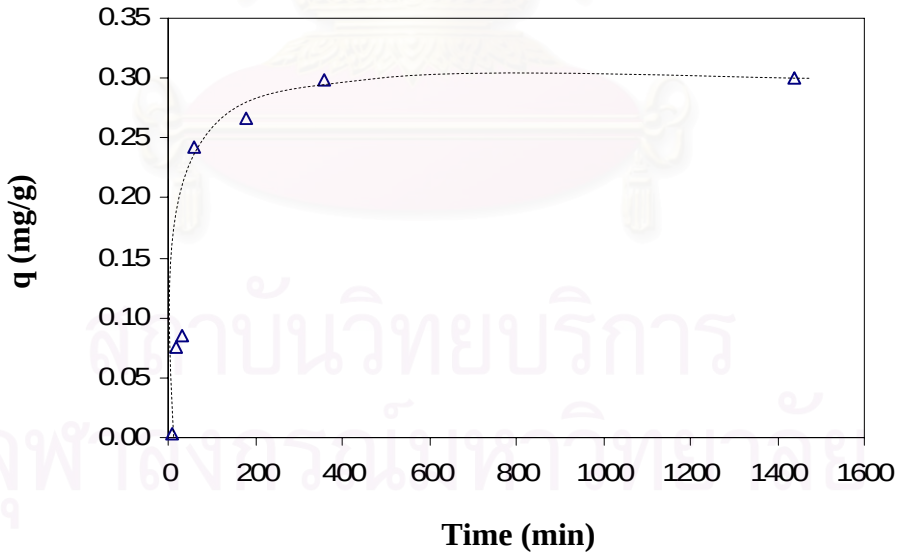


Figure 4.2 The equilibrium time of nalidixic acid on anion exchange resin.

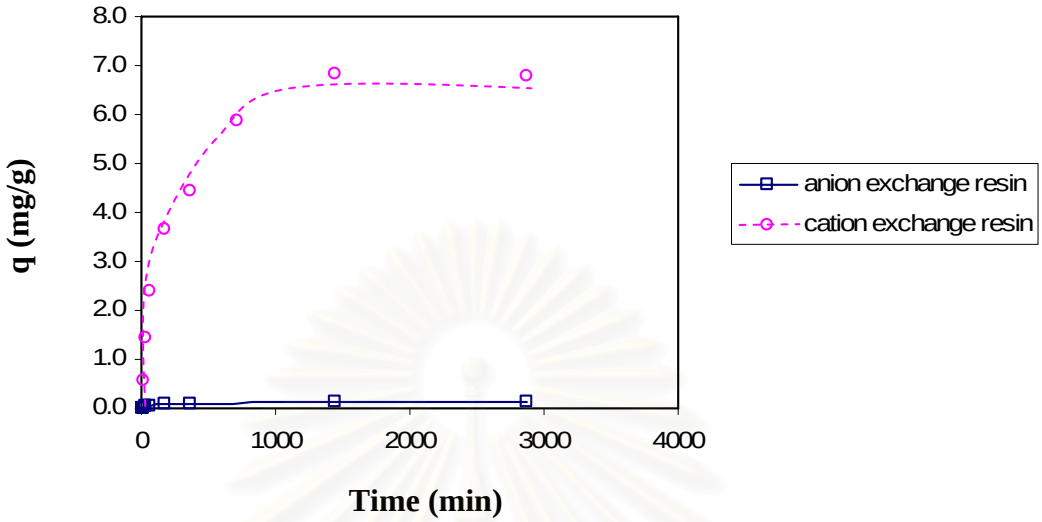


Figure 4.3 The equilibrium time of norfloxacin on anion exchange and cation exchange resins.

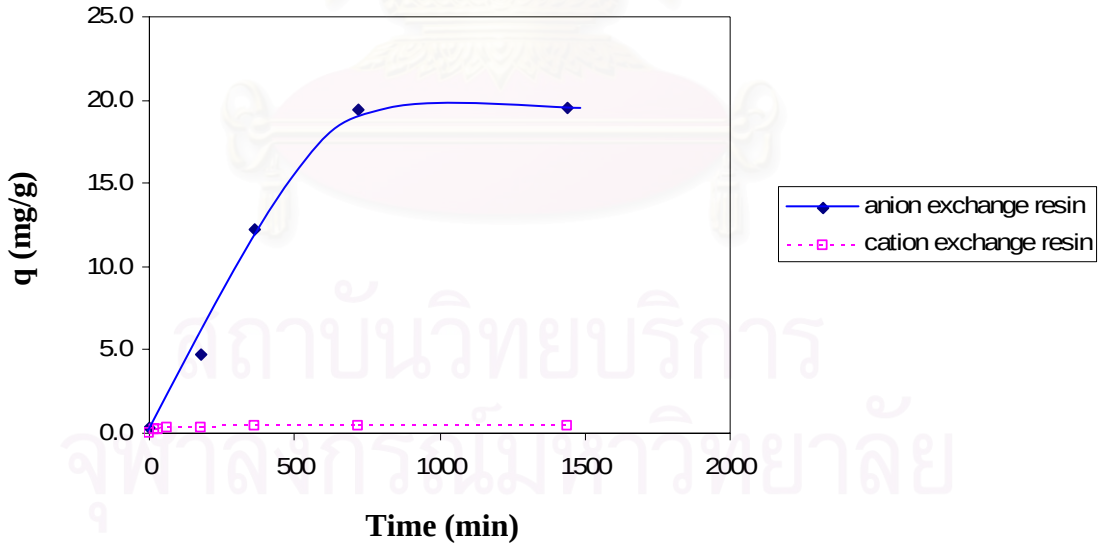


Figure 4.4 The equilibrium time of 17 α-ethinyl estradiol on anion exchange and cation exchange resins.

4.2 Ion Exchange Studies

Ion exchange studies were conducted with the four pharmaceuticals (acetaminophane, nalidixic acid, norfloxacin, and 17 α-ethinyl estradiol) and two ion exchange resins (anion and cation exchange resin). The experiments were conducted at neutral pH. In this pH range, nalidixic acid and norfloxacin existed mainly in ionized form, while acetaminophen and 17 α-ethinyl estradiol existed mainly in their neutral form.

The isotherms of nalidixic acid on anion and cation exchange resin were shown in **Figure 4.5.** While Langmuir plateau adsorption was observed between nalidixic acid on anion exchange resin, no significant sorption was observed on cation exchange resin. The sorption coefficient on anion exchange resin (pH = 6.75 ± 0.06) was 94 L/g and maximum adsorption capacity was 1.11 mg/g (Table 4.1). Due to its pKa of 6.33, nalidixic acid will be in anionic form at neutral pH. Therefore, both hydrophobic and electrostatic sorption mechanisms were expected to be important. Because nalidixic did not have ion exchange on cation exchange resin, it can be shown that the electrostatic attraction had a greater influence on the sorption than hydrophobic interaction. The ratio between nalidixic acid exchanged with anion exchange resin and chloride released from anion exchange resin was approximate to 1:13 (molar/molar).

The Linear isotherms of acetaminophen on anion and cation exchange resin were shown in **Figure 4.6**. The sorption coefficient on anion exchange resin (pH 7.47±0.05) was 0.0228 L/g and on cation exchange resin (pH 7.50±0.00) was 0.0041 L/g (Table 4.1). With a pKa of 9.38, acetaminophen existed almost exclusively in the neutral form at neutral pH. Thus, attractive force between the benzene ring of

acetaminophen and the resin were expected as the main sorption mechanism. However, acetaminophen has much adsorption on anion exchange resin. This shows that anion exchange resin has more affinity for acetaminophen than cation exchange resin. The reason for this is not known and should be further studied in future research.

The isotherms of norfloxacin on anion and cation exchange resin were shown in **Figure 4.7.** The sorption coefficient of norfloxacin on anion exchange resin (pH = 7.13±0.18) was 42 L/g, maximum adsorption capacity was 0.93 mg/g, and the ratio between norfloxacin exchange with resin and chloride released from resin was approximate to 1:9 (molar/molar), on cation exchange resin (pH = 7.47±0.14), the sorption coefficient was 37 L/g, maximum adsorption capacity was 27.67 mg/g and the ratio between norfloxacin exchange with resin and sodium released from resin was approximate to 1: 16 (molar/molar). The norfloxacin isotherm was Langmuir for both resins. Norfloxacin has two proton-binding sites (carboxyl and piperazinyl group) with reported pKa values of 6.34 and 8.75, respectively, and has an isoelectric point of 7.4. With these two pKa values, norfloxacin can exist in four forms (neutral, zwitterionic, anionic and cationic), at neutral pH range (pH 6.2-8.5) the zwitterionic form dominates, ion exchange process on anion and cation exchange resin was expected. However, ion exchange on cation exchange resin was significantly greater than on anion exchange resin, suggesting that the cationic functional groups of the zwitterionic norfloxacin have a greater ion exchange on cation exchange resin than the anionic functional groups on anion exchange resin. The exact reasons for this are not clear at this time and should be further evaluated in the future research.

The isotherms of 17 α-ethinyl estradiol on anion and cation exchange resin were shown in **Figure 4.8.** Linear sorption was observed for 17 α-ethinyl estradiol and both resins. The sorption coefficient on anion exchange resin (pH 7.40±0.02) was 0.8096 L/g and on cation exchange resin (pH 7.50±0.01) was 0.0510 L/g **(Table 3).** Due to its pK_a of 10.4, 17 α-ethinyl estradiol existed in neutral form at neutral pH. Therefore, attractive force between bezene ring of 17 α-ethinyl estradiol and resin and hydrophobic (log K_{ow} of 3.67) were important mechanism.

Figures 4.9 and 4.10 showed the adsorption isotherms for all four PhACs with anion and cation exchange resins, respectively. These results showed that 17 α-ethinyl estradiol, the least water solubility and the most log K_{ow}, had the most sorption on anion exchange resin. This meant that the anion exchange resin had more affinity for 17 α-ethinyl estradiol than other pharmaceuticals. In contrast, the cation exchange resin had more affinity for norfloxacin which is the hydrophobic compound.

Table 4.1 Summary of the sorption coefficients and maximum adsorption capacity of acetaminophen, 17 α-ethinyl estradiol, nalidixic acid, and norfloxacin on cation (sodium form) exchange and anion (chloride form) exchange resins.

Pharmaceuticals	resin	pH	K_d (L/g)	K_L (L/g)	A_M (mg/g)	R^2
Acetaminophen	Cl	7.47±0.05	0.0228±0.0002	N/A	N/A	0.99
	Na	7.50±0.00	0.0041±0.0000	N/A	N/A	0.99
17 α-ethinyl estradiol	Cl	7.40±0.02	0.8096±0.0016	N/A	N/A	0.97
	Na	7.50±0.01	0.0510±0.0002	N/A	N/A	0.97
nalidixic acid	Cl	6.75±0.06	N/A	94±7.1	1.11±0.04	0.95
	Na	6.72±0.10	N/A	N/A	N/A	N/A
norfloxacin	Cl	7.13±0.18	N/A	42±1.5	0.93±0.01	1
	Na	7.47±0.14	N/A	37±0.6	27.67±0.40	0.99

N/A : Not Available

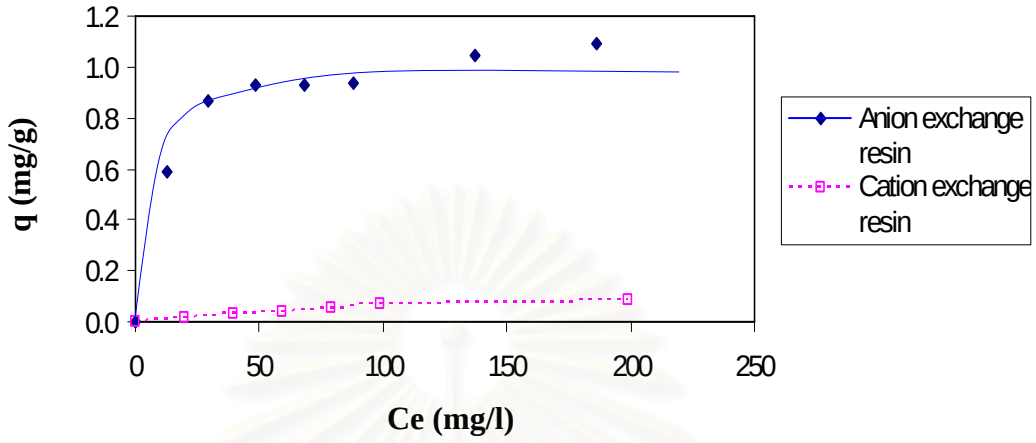


Figure 4.5 The isotherms of nalidixic acid on anion exchange and cation exchange resins.

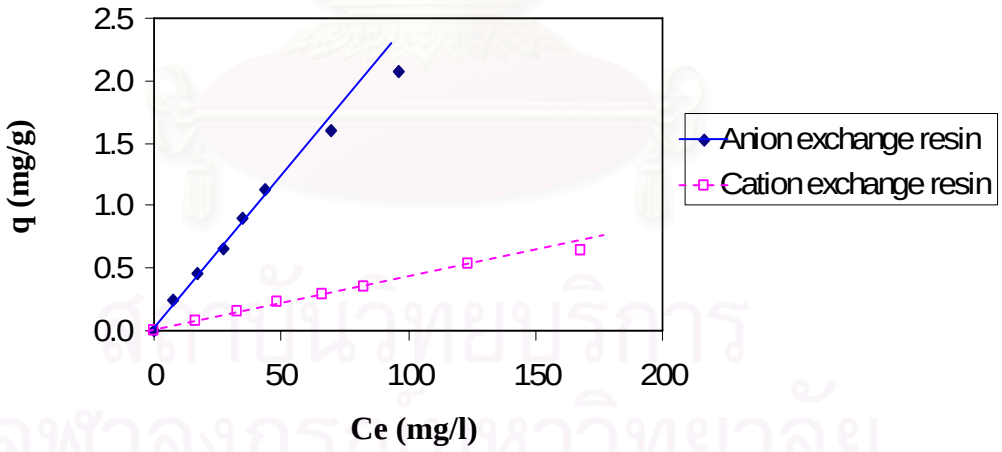


Figure 4.6 The isotherms of acetaminophen on anion exchange and cation exchange resins.

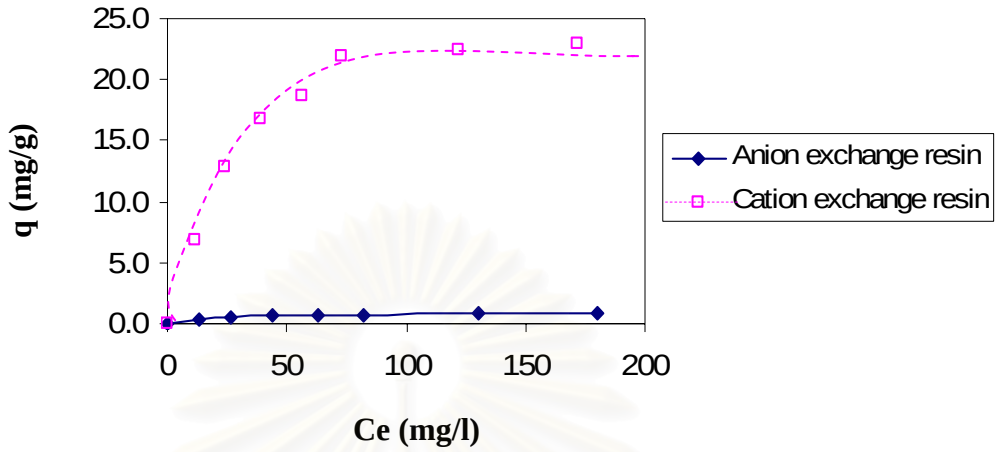


Figure 4.7 The isotherms of norfloxacin on anion exchange and cation exchange resins.

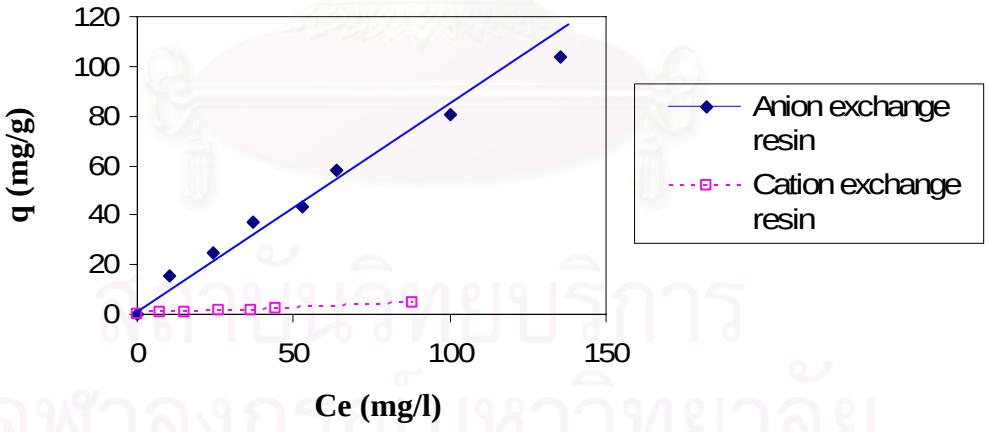


Figure 4.8 The isotherms of 17 α-ethinyl estradiol on anion exchange and cation exchange resins.

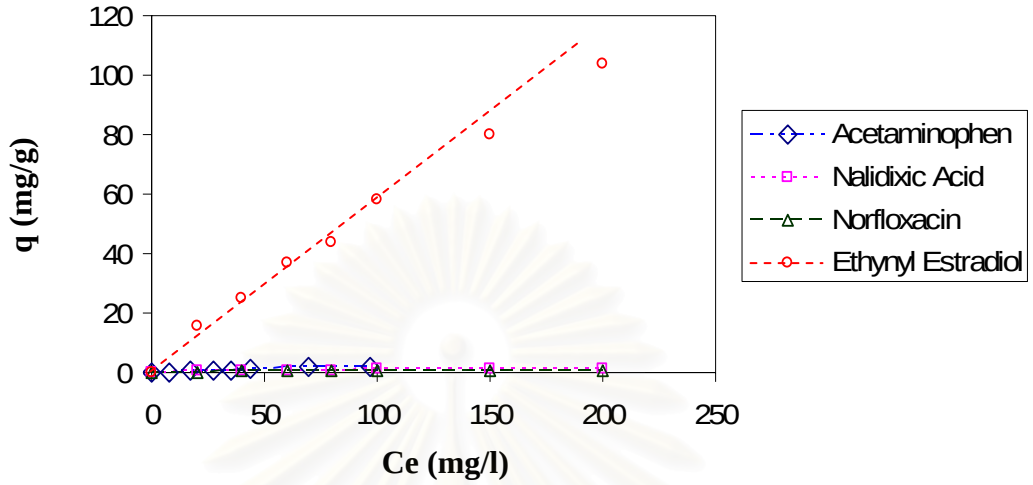


Figure 4.9 The isotherms of nalidixic acid, acetaminophen, norfloxacin, and 17 α-ethinyl estradiol on anion exchange resin.

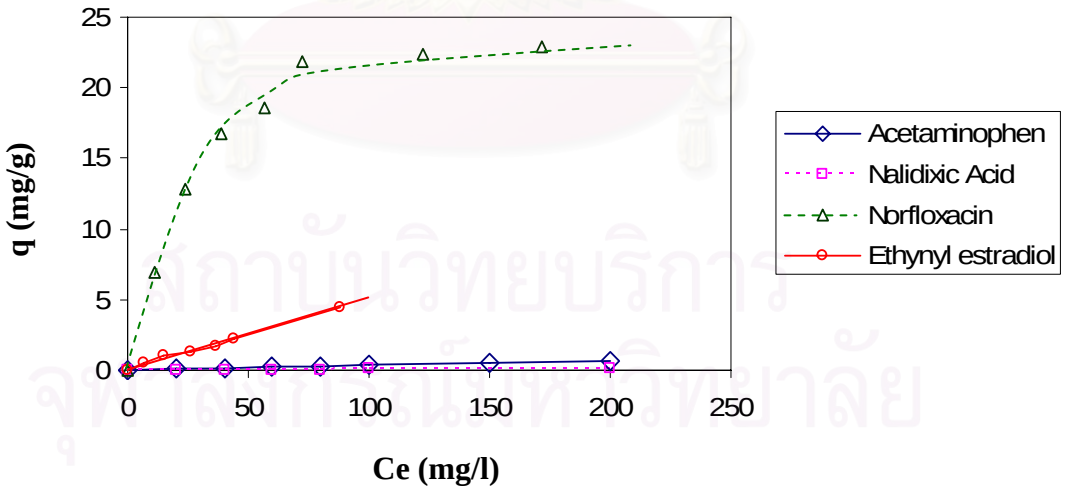


Figure 4.10 The isotherms of nalidixic acid, acetaminophen, norfloxacin, and 17 α-ethinyl estradiol on cation exchange resin.

4.3 Anion Competition Studies

Competition studies were conducted with the two pharmaceuticals (nalidixic acid and norfloxacin) that demonstrated adsorption by ion exchange process. All experiments were still conducted at neutral pH as sorption studies.

The sorption isotherm of nalidixic acid added with Na_2SO_4 at concentration of 10 mg/L (pH 6.68±0.03) and 100 mg/L (pH 6.62±0.05) compared with nalidixic acid with ionic strength of $CaCl_2$ 0.01 M. are shown in **Figure 4.11**. The sorption coefficient and maximum adsorption capacity at concentration of 10 mg/L were 45 L/g and 1 mg/g, respectively. While at concentration of 100 mg/l were 28 L/g and 0.60 mg/g, respectively **(Table 4.2)**. Sulfate can compete with nalidixic acid on anion exchange resin because it had more valence (more charge) than nalidixic acid. At the same concentration in the unit of molar, sulfate can reduce 50 percent exchange of nalidixic acid with anion exchange resin and the competition increased with increasing sulfate concentration. For calcium ion and sodium ion, it was shown in **Figure 4.12 and 4.13** respectively, both of these ions did not have significant effect to nalidixic acid because even though concentration of $CaCl_2$ and NaCl were changed but isotherms were still the same.

The sorption isotherm of nalidixic acid added with $NaHCO_3$ at concentration of 10 mg/L (8.28±0.08) and 100 mg/L (pH 8.22±0.05) compared with nalidixic acid with ionic strength of $CaCl_2$ 0.01 M. and Na_2SO_4 at concentration of 10 mg/L and 100 mg/L were shown in **Figure 4.14**. The sorption coefficient and maximum adsorption capacity of $NaHCO_3$ 10 mg/l were 89 L/g and 1.04 mg/g, respectively, while $NaHCO_3$ 100 mg/l were 77 L/g and 0.97 mg/g, respectively **(Table 4.3)**. Bicarbonate had less effect with nalidixic acid than sulfate because it had less valence (less charge).

Bicarbonate can reduce 20 percent exchange of norfloxacin with anion exchange resin and the higher bicarbonate concentration made more competition.

The sorption isotherm of norfloxacin added with Na_2SO_4 at concentration of 10 mg/L (pH 7.01±0.12) and 100 mg/L (pH 6.98±0.11) compared with norfloxacin with ionic strength of $CaCl_2$ 0.01 M. were shown in **Figure 4.15**. The sorption coefficient and maximum adsorption capacity at concentration of 10 mg/L were 40 L/g and 0.74 mg/g, respectively. While at concentration of 100 mg/L were 23 L/g and 0.50 mg/g, respectively **(Table 4.2)**. Sulfate can compete with norfloxacin on anion exchange resin because it had more valence (more charge) than norfloxacin. And it can reduce 50 percent exchange of norfloxacin with anion exchange resin. Moreover, from experiments, calcium ion had a little bit competition with norfloxacin on anion exchange resin. From **Figure 4.16 and 4.17,** it is shown that calcium and sodium ion did not have significant effect to norfloxacin because even though concentration of $CaCl_2$ and NaCl were changed but isotherms were still the same.

The sorption isotherm of norfloxacin added with $NaHCO_3$ at concentration of 10 mg/L and 100 mg/L (pH 8.32±0.13) compared with norfloxacin with ionic strength of $CaCl_2$ 0.01 M. and Na_2SO_4 at concentration of 10 mg/L and 100 mg/L were shown in **Figure 4.18**. The sorption coefficient and maximum adsorption capacity of $NaHCO_3$ 10 mg/L were 41 L/g and 0.87 mg/g, respectively, while $NaHCO_3$ 100 mg/L were 40 L/g and 0.81 mg/g, respectively **(Table 4.3)**. Bicarbonate has less effect with norfloxacin than sulfate because it has less valence (less charge) and it can reduce 20 percent exchange of norfloxacin with anion exchange resin.

Table 4.2 Summary of the sorption coefficients and maximum adsorption capacity of nalidixic acid and norfloxacin added with Na_2SO_4 at concentration of 10 mg/L and 100 mg/L on anion exchange resins.

Pharmaceuticals	Na_2SO_4 Concentration (mg/L)	pH	K_L (L/g)	A_M (mg/g)	R^2
nalidixic acid	10	6.68±0.03	45±4.0	1.00±0.03	1
	100	6.62±0.05	28±0.6	0.60±0.003	0.99
norfloxacin	10	7.01±0.12	40±1.5	0.74±0.004	0.94
	100	6.98±0.11	23±2.0	0.50±0.010	1

Table 4.3 Summary of the sorption coefficients and maximum adsorption capacity of nalidixic acid and norfloxacin added with $NaHCO_3$ at concentration of 10 mg/L and 100 mg/L on anion exchange resins.

Pharmaceuticals	$NaHCO_3$ Concentration (mg/L)	pH	K_L (L/g)	A_M (mg/g)	R^2
nalidixic acid	10	8.28±0.08	89±1.1	1.04±0.01	0.95
	100	8.22±0.05	77±4.9	0.97±0.01	0.99
norfloxacin	10	8.34±0.11	41±1.0	0.87±0.002	0.97
	100	8.32±0.13	40±1.2	0.81±0.006	0.98

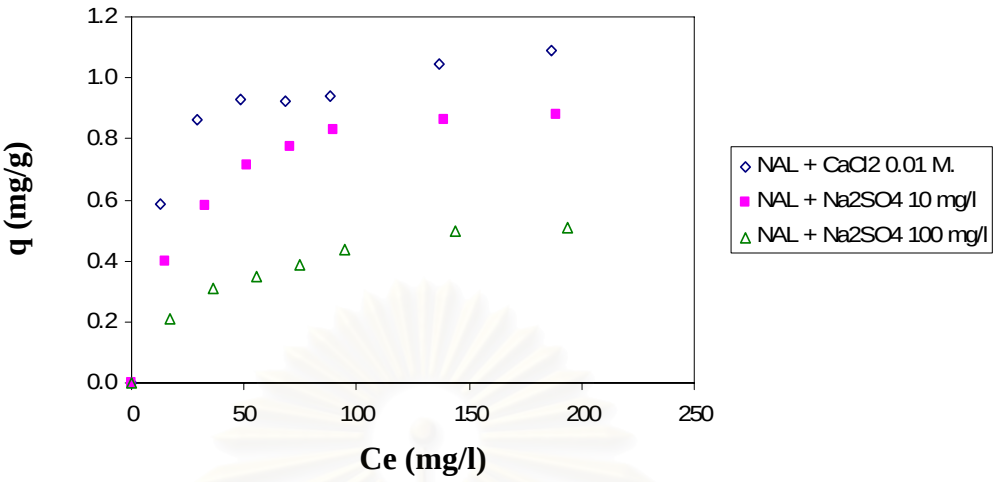


Figure 4.11 Sorption isotherm of nalidixic acid added with $CaCl_2$ 0.01 M., Na_2SO_4 10 mg/L, and Na_2SO_4 100 mg/L (Note : 0.01 M. $CaCl_2$ = 1,110 mg/l).

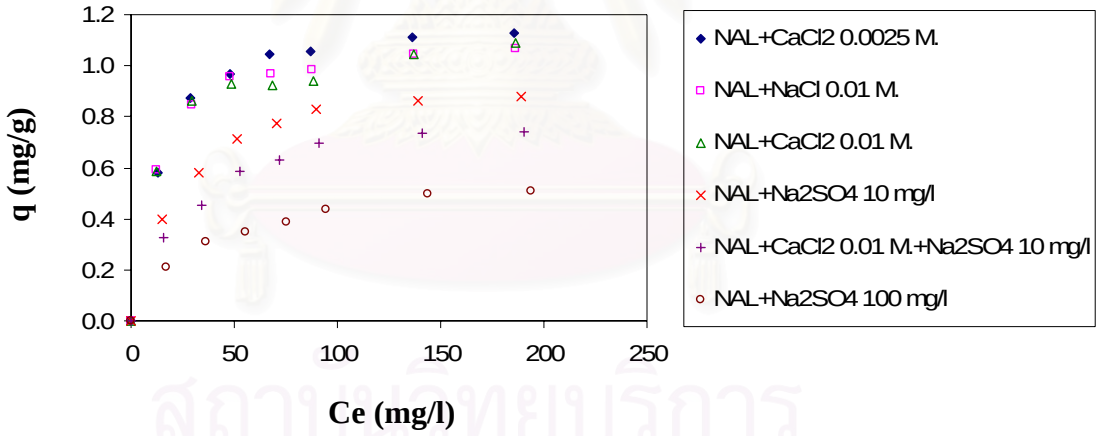


Figure 4.12 Sorption isotherm of nalidixic acid added with sulfate at concentration of 10 mg/L and 100 mg/L on anion exchange resin (Note : 0.01 M. NaCl = 585 mg/L, 0.01 M. $CaCl_2$ = 1,110 mg/L).

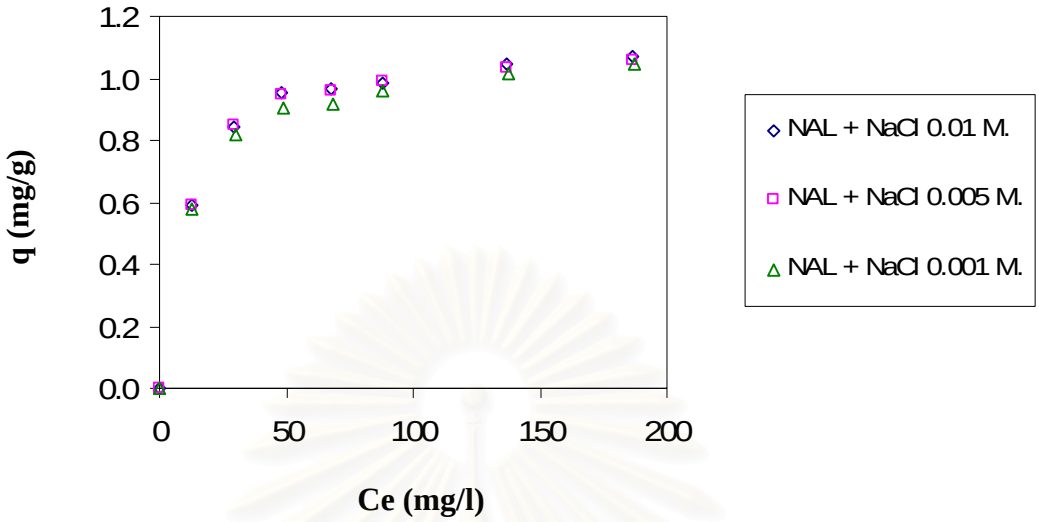


Figure 4.13 Sorption isotherm of nalidixic acid added with NaCl at concentration of 0.01 M., 0.005 M., and 0.001 M.

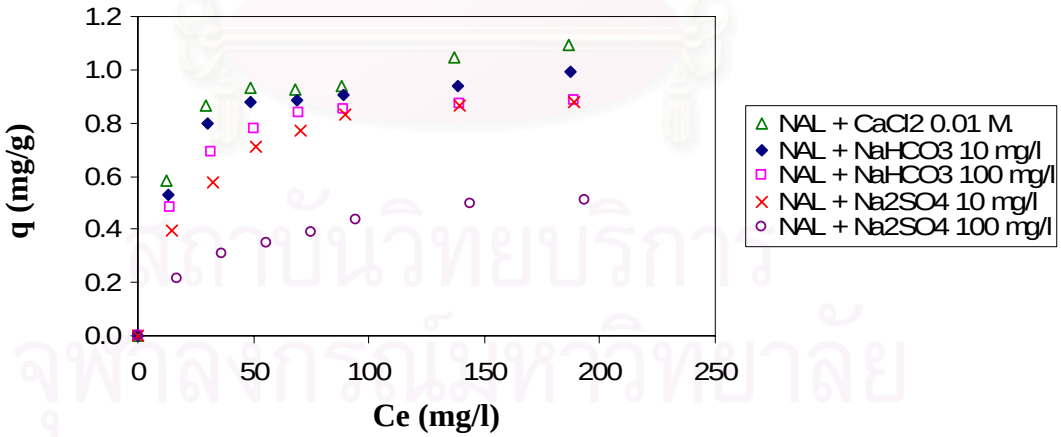


Figure 4.14 Sorption isotherm of nalidixic acid added with $CaCl_2$ 0.01 M., Na_2SO_4 10 mg/L, Na_2SO_4 100 mg/L, $NaHCO_3$ 10 mg/L, and $NaHCO_3$ 100 mg/L.

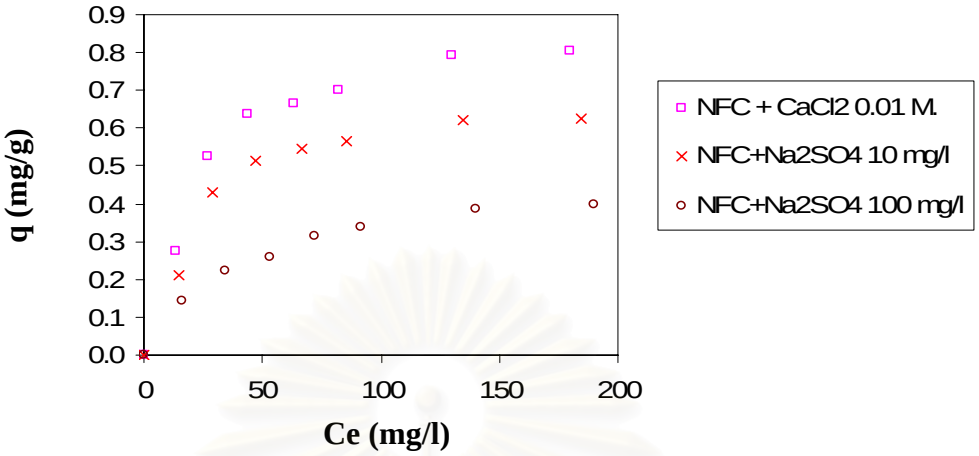


Figure 4.15 Sorption isotherm of norfloxacin added with $CaCl_2$ 0.01 M., Na_2SO_4 10 mg/L, and Na_2SO_4 100 mg/L (Note : 0.01 M. $CaCl_2$ = 1,110 mg/L).

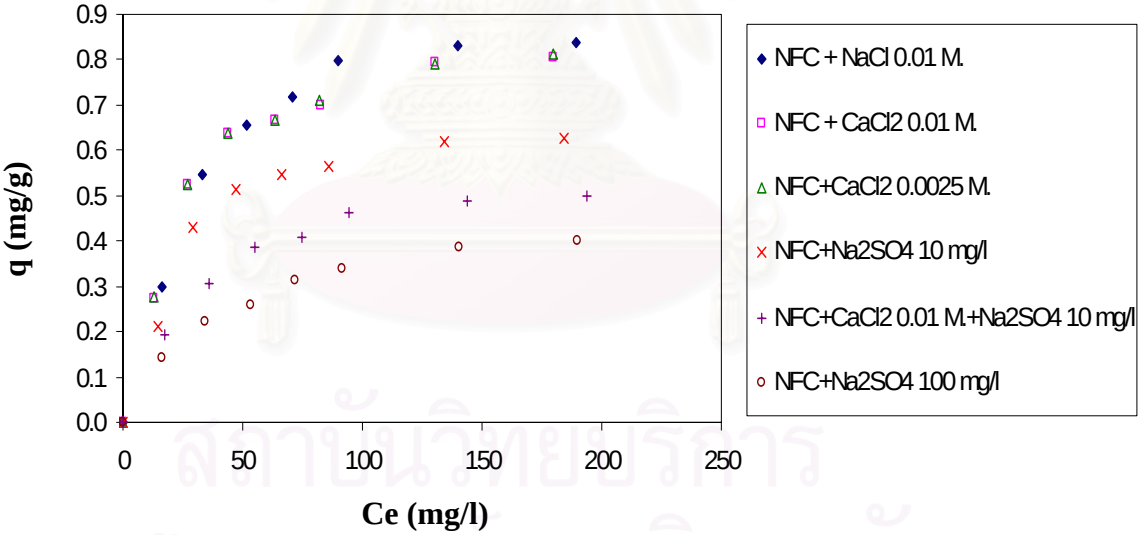


Figure 4.16 Sorption isotherm of norfloxacin added with sulfate at concentration of 10 mg/L and 100 mg/L on anion exchange resin (Note : 0.01 M. NaCl = 585 mg/L, 0.01 M. $CaCl_2$ = 1,110 mg/L).

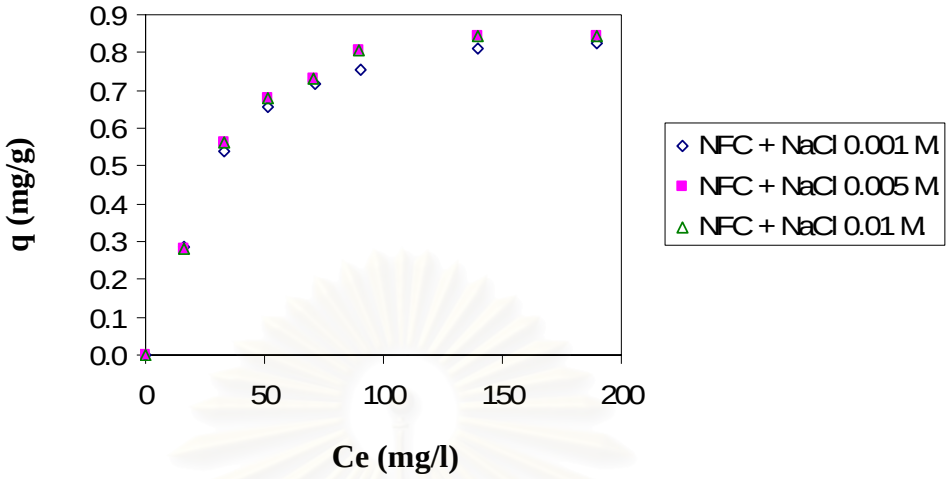


Figure 4.17 Sorption isotherm of norfloxacin added with NaCl at concentration of 0.01 M., 0.005 M., and 0.001 M.

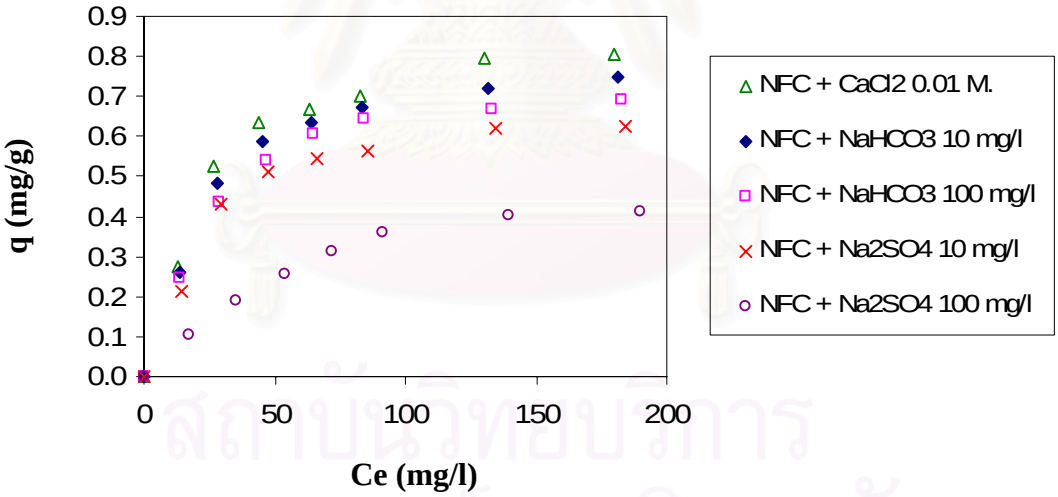


Figure 4.18 Sorption isotherm of norfloxacin added with $CaCl_2$ 0.01 M., Na_2SO_4 10 mg/L, Na_2SO_4 100 mg/L, $NaHCO_3$ 10 mg/L, and $NaHCO_3$ 100 mg/L.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Strong-base anion exchange resin and strong-acid cation exchange resin were studied as representative of the major ion exchange resin used in drinking water treatment plant. The pharmaceuticals studied in this research were acetaminophen, nalidixic acid, 17 α-ethinyl estradiol, and norfloxacin. Equilibrium sorption kinetic for acetaminophen on anion exchange resin and cation exchange resin showed that equilibrium was reached within 3 hours. While nalidixic acid (monoprotic acid) on anion exchange resin required 6 hours to achieve the equilibrium. 17 α-ethinyl estradiol on anion exchange resin and cation exchange resin were used 12 hours and 6 hours, respectively. Norfloxacin on both resins reached equilibrium at 1 day. (All sorption kinetic data are shown in appendix A)

For ion exchange studies, nalidixic acid was removed by anion exchange resin but there was no significant ion exchange on cation exchange resin. While acetaminophen, norfloxacin, and 17 α-ethinyl estradiol, they were exchanged with anion exchange resin better than did with cation exchange resin.

For anion competition studies, sulfate ions have more competition with nalidixic acid and norfloxacin than bicarbonate ion because sulfate has more valences or more charges. Therefore, nalidixic acid and norfloxacin added with sulfate and bicarbonate were exchanged with anion exchange resin less than added with calcium chloride. Moreover, the competition increased with increasing anion concentration.

At neutral pH, nalidixic acid, hydrophobic and ionizing pharmaceutical, was exchange with chloride ion from anion exchange resin and showed no significant sorption on cation exchange resin. While norfloxacin, zwitterionic compound, was exchange with chloride ion and sodium ion from anion and cation exchange resin, respectively. Acetaminophen (non hydrophobic and non-ionizing pharmaceutical) and 17 α-ethinyl estradiol (hydrophobic and non-ionizing pharmaceutical) strongly sorbed on both resin.

This research demonstrates that the ion exchange process of ionizing pharmaceuticals depends on the system of pH, the pharmaceuticals property (pKa), and surface charges of ion exchange resins. For non-ionizing pharmaceuticals (at pH is lower than their pKa), main ion exchange factors are solubility or hydrophobicity and log K_{ow}. Besides, ion exchange process was inadequate for high concentration ionic pharmaceutical removal and should find the appropriate way to remove in the future.

5.2 Recommendations

These pharmaceuticals should be conducted in column study with anion exchange resin and cation exchange resin. They may be added with common surfactants to study effect and also applied in groundwater modeling to predict transport of them. Furthermore, it should have more study of anion and cation or competition in water resource with these pharmaceuticals. In addition, the study of other pharmaceuticals which have big molecules should be studied for proving whether or not ion exchange process depends on molecular size of pharmaceuticals. Moreover, nowadays countries in Southeast Asia including Thailand still don’t

concentrate about PPCPs and PhACs in water resources. Even though the concentration of these pharmaceuticals is trace-level but these pharmaceuticals are tended to use widely and increasingly for human, plant, and animal lives. Therefore, countries in this region should collaborate to handle, observe, and protect these drugs contaminate to surface water and groundwater. Additionally, Thailand should improve existing laws and punishments or create the standard about pharmaceuticals removal, for example, unused drugs should be separated from common trashes in household and sent to plants for removal, e.g. landfill, incinerator.

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APPENDICES

APPENDIX A

TABLE A-1 Concentrations of different drugs (µg/L) as measure in wastewater, surface water, groundwater, and drinking water. (Kümmerer, 2001)

Active substance/ Group	Wastewater	Surface water	Groundwater (GW), Drinking water (DW)	References
Analgesics/	2.4	Up to 0.5		UBA (1997)
Anti-rheumatic agent	20	Up to 0.5	0.006 (DW)	Ternes et al. (1997)
		Up to 0.5		Heberer et al. (1997)
Antibiotic		Up to 1.7		Hirsch et al. (1999)
	Approx. 1	Up to 6[a]		UBA (1997)
	0.1-1.7			Ternes et al. (1997)
	Up to 1	Up to 1		Richardson and Bowron (1985)
Lipid lowering agent	1-1.7		0.17 (DW)	Stan et al. (1994)
		0.55		Ternes et al. (1997)
			7.5 (GW)	Heberer et al. (1997)
			0.07 (DW)	Heberer et al. (1997)
Psychopharmacological	<1			UBA (1997)
agents	Up to 6.1			Ternes et al. (1997)
Cytostatic agents	Up to 5	Up to 0.02		Aherne et al. (1990)
		Up to 4[a]		Kümmerer et al. (1997)
X-ray contrast media				Steger-Hartmann et al. (1997)
				Kümmerer et al. (1998)
		9[a]		Steger-Hartmann et al. (1998)
		Up to 3.1[a]	Up to 0.07	Hirsch et al. (2000)
		0.01-0.15		

[a] STP-effluent (diluted by surface water)

TABLE A-2 Amount of pharmaceuticals sold (antibiotic and hormone) in Thailand during 1999-2001.

Custom Code	Name	1999		2000		2001		Total	
		Kgs.	Baht (Million)	Kgs	Baht (Million)	Kgs	Baht (Million)	Kgs	Baht (Million)
	Antibiotic								
2941.100-008	Penicilin and derivatives	546,027	768.2	700,899	900.2	N/A	1,122.8	1,246,926	2,791.2
2941.200-004	Steptomycin	18,708	19.3	14,155	11.8	16,816	15.2	49,679	46.4
2941.300-102	Aureomycin	13,217	13.8	10,424	10.3	7,858	6.4	31,499	30.5
2941.300-203	Terramycin (oxytetracycline)	253,615	124.7	239,000	92.5	220,275	70.0	712,890	287.3
2941.300-904	Tetracycline and derivatives	115,225	40.1	64,523	51.7	59,962	44.1	239,710	135.9
2941.400-003	Chloramphenical and derivatives	84,436	62.0	71,250	60.0	56,290	57.5	211,976	179.5
2941.500-005	Erythromycin and derivatives	119,653	230.9	161,999	338.6	176,346	436.9	457,998	1,006.4
	Hormone								
2937.21.006	Cortisone, Hydrocortisone, Predisone, and Prenisolone	952	23.4	1,084	25.5	N/A	N/A	2,036	48.9
2937.21.006	Halogenated derivatives of Corticosteroid hormones	457	87.7	9,440	91.8	10,495	102.7	20,392	282.2
2937.21.006	Other steroid hormones and derivatives	167	5.6	2,318	7.9	267	13.5	2,752	27.0
2937.21.006	Ostrogen and Progestogen	1,682	135.5	1,250	56.9	2,326	98.2	5,258	290.6
2937.21.006	Pituitang and derivatives (and similar hormones)	165	4.7	187	5.3	155	5.6	507	15.7

N/A : Not Available

APPENDIX B

TABLE B-1 Equilibrium time data for acetaminophen onto anion exchange resin.

Initial concentration 10 mg/l

Time (min)	A1	A2	A3	Aavg	Ce (mg/l)	q (mg/g)
0	0.732	0.713	0.709	0.718	9.852	0.003
5	0.439	0.428	0.419	0.429	5.882	0.082
10	0.393	0.390	0.378	0.387	5.310	0.094
20	0.340	0.341	0.378	0.353	4.844	0.103
30	0.329	0.321	0.340	0.330	4.528	0.109
60	0.321	0.327	0.323	0.324	4.441	0.111
180	0.318	0.319	0.315	0.317	4.354	0.113
360	0.333	0.327	0.319	0.326	4.478	0.110
1440	0.315	0.314	0.325	0.318	4.364	0.113

TABLE B-2 Equilibrium time data for acetaminophen onto cation exchange resin.

Initial concentration 10 mg/l

Time (min)	A1	A2	A3	Aavg	Ce (mg/l)	q (mg/g)
0	0.730	0.724	0.728	0.727	9.980	0.000
10	0.533	0.543	0.527	0.534	7.332	0.053
20	0.517	0.541	0.522	0.527	7.227	0.055
30	0.504	0.504	0.529	0.512	7.030	0.059
60	0.475	0.522	0.506	0.501	6.875	0.063
180	0.477	0.492	0.486	0.485	6.655	0.067
360	0.487	0.485	0.488	0.487	6.678	0.066
1440	0.486	0.485	0.489	0.487	6.678	0.066

TABLE B-3 Equilibrium time data for nalidixic acid onto anion exchange resin.

Initial concentration 10 mg/l

Time (min)	A1	A2	A3	Aavg	Ce (mg/l)	q (mg/g)
0	1.331	1.259	1.187	1.259	10.619	-0.050
5	1.297	1.223	1.273	1.264	10.664	-0.053
10	1.100	1.253	1.189	1.181	9.958	0.003
20	1.078	1.069	1.072	1.073	9.050	0.076
30	1.056	1.041	1.081	1.059	8.935	0.085
60	0.808	0.833	0.839	0.827	6.973	0.242
180	0.819	0.777	0.773	0.790	6.660	0.267
360	0.74	0.753	0.734	0.742	6.261	0.299
1440	0.777	0.746	0.700	0.741	6.250	0.300

TABLE B-4 Equilibrium time data for nalidixic acid onto cation exchange resin.

Initial concentration 10 mg/l

Time (min)	A1	A2	A3	Aavg	Ce (mg/l)	q (mg/g)
0	1.295	1.298	1.296	1.296	9.911	0.007
10	1.294	1.293	1.293	1.293	9.888	0.009
20	1.289	1.287	1.285	1.287	9.840	0.013
30	1.286	1.285	1.286	1.286	9.830	0.014
60	1.284	1.283	1.281	1.283	9.807	0.015
180	1.282	1.284	1.282	1.283	9.807	0.015
360	1.283	1.283	1.283	1.283	9.809	0.015
1440	1.281	1.282	1.282	1.282	9.799	0.016
2880	1.282	1.280	1.281	1.281	9.794	0.016

TABLE B-5 Equilibrium time data for norfloxacin onto anion exchange resin.

Initial concentration 10 mg/l

Time (min)	A1	A2	A3	Aavg	Ce (mg/l)	q (mg/g)
0	1.130	1.135	1.132	1.132	10.313	-0.013
5	1.048	1.106	1.082	1.079	9.824	0.007
10	1.056	1.05	1.052	1.053	9.587	0.017
20	1.046	1.053	1.049	1.049	9.557	0.018
30	1.063	0.969	1.079	1.037	9.445	0.022
60	0.907	0.973	0.956	0.945	8.610	0.056
180	0.815	0.936	0.922	0.891	8.115	0.075
360	0.801	0.805	0.809	0.805	7.332	0.107
1440	0.750	0.695	0.860	0.768	6.998	0.120
2880	0.770	0.760	0.766	0.765	6.971	0.121

TABLE B-6 Equilibrium time data for norfloxacin onto cation exchange resin.

Initial concentration 10 mg/l

Time (min)	A1	A2	A3	A avg	Ce (mg/l)	q (mg/g)
0	1.245	1.139	1.231	1.205	10.466	-0.373
10	1.060	1.089	1.054	1.068	9.274	0.581
30	0.957	0.890	0.990	0.946	8.214	1.429
60	0.867	0.774	0.786	0.809	7.027	2.379
180	0.625	0.628	0.624	0.626	5.434	3.652
360	0.522	0.498	0.511	0.510	4.433	4.454
720	0.381	0.207	0.329	0.306	2.655	5.876
1440	0.246	0.120	0.149	0.172	1.491	6.807
2880	0.177	0.173	0.172	0.174	1.511	6.791

TABLE B-7 Equilibrium time data for 17 α-ethynyl estradiol onto anion exchange resin.

Initial concentration 20 mg/l

Time (min.)	A1	A2	A3	Aavg	Ce (mg/l)	q (mg/g)
0	0.941	0.939	0.948	0.943	19.781	0.351
180	0.805	0.817	0.814	0.812	17.039	4.738
360	0.595	0.584	0.587	0.589	12.353	12.236
720	0.397	0.310	0.421	0.376	7.890	19.376
1440	0.438	0.354	0.319	0.370	7.771	19.566

TABLE B-8 Equilibrium time data for 17 α-ethynyl estradiol onto cation exchange resin.

Initial concentration 20 mg/l

Time (min)	A1	A2	A3	Aavg	Ce (mg/l)	q (mg/g)
0	0.797	0.799	0.794	0.797	19.805	0.008
20	0.600	0.653	0.621	0.625	15.529	0.179
30	0.609	0.598	0.588	0.598	14.875	0.205
60	0.491	0.475	0.482	0.483	11.999	0.320
180	0.463	0.457	0.444	0.455	11.303	0.348
360	0.421	0.401	0.433	0.418	10.400	0.384
720	0.425	0.418	0.411	0.418	10.391	0.384
1440	0.419	0.417	0.42	0.419	10.408	0.384
2880	0.415	0.423	0.416	0.418	10.391	0.384

APPENDIX C

TABLE C-1 Ion exchange data of acetaminophen onto anion exchange resin: ratio 1 : 20 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/l)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	0.049	0.041	0.053	7.813	6.537	8.450	7.600	0.244	0.269	0.231	0.248	0.019
40	0.109	0.107	0.111	17.379	17.060	17.698	17.379	0.452	0.459	0.446	0.452	0.006
60	0.179	0.176	0.163	28.540	28.061	25.989	27.530	0.629	0.639	0.680	0.649	0.027
80	0.219	0.221	0.219	34.917	35.236	34.917	35.024	0.902	0.895	0.902	0.900	0.004
100	0.281	0.267	0.270	44.803	42.570	43.049	43.474	1.104	1.149	1.139	1.131	0.024
150	0.433	0.441	0.439	69.038	70.313	69.994	69.782	1.619	1.594	1.600	1.604	0.013
200	0.602	0.610	0.605	95.983	97.258	96.461	96.567	2.080	2.055	2.071	2.069	0.013

TABLE C-2 Ion exchange data of acetaminophen onto cation exchange resin: ratio 1 : 20 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.090	1.070	1.030	16.715	16.408	15.795	16.306	0.066	0.072	0.084	0.074	0.009
40	2.110	2.120	2.140	32.357	32.510	32.817	32.561	0.153	0.150	0.144	0.149	0.005
60	3.140	3.150	3.170	48.152	48.305	48.612	48.356	0.237	0.234	0.228	0.233	0.005
80	4.300	4.310	4.280	65.941	66.094	65.634	65.889	0.281	0.278	0.287	0.282	0.005
100	5.380	5.410	5.350	82.502	82.962	82.042	82.502	0.350	0.341	0.359	0.350	0.009
150	8.050	8.080	8.070	123.447	123.907	123.753	123.702	0.531	0.522	0.525	0.526	0.005
200	10.910	10.930	10.950	167.305	167.612	167.918	167.612	0.654	0.648	0.642	0.648	0.006

TABLE C-3 Ion exchange data of nalidixic acid onto anion exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	0.131	0.134	0.142	12.234	12.515	13.262	12.670	0.621	0.599	0.539	0.586	0.042
40	0.317	0.310	0.311	29.606	28.952	29.045	29.201	0.832	0.884	0.876	0.864	0.028
60	0.518	0.514	0.522	48.378	48.004	48.751	48.378	0.930	0.960	0.900	0.930	0.030
80	0.708	0.754	0.736	66.122	70.418	68.737	68.426	1.110	0.767	0.901	0.926	0.173
100	0.945	0.941	0.949	88.256	87.883	88.630	88.256	0.939	0.969	0.910	0.939	0.030
150	1.455	1.467	1.477	135.887	137.008	137.941	136.945	1.129	1.039	0.965	1.044	0.082
200	1.999	1.992	1.995	186.693	186.039	186.319	186.350	1.065	1.117	1.094	1.092	0.026

TABLE C-4 Ion exchange data of nalidixic acid onto cation exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	2.590	2.600	2.580	19.802	19.879	19.726	19.802	0.016	0.010	0.022	0.016	0.006
40	5.180	5.190	5.170	39.605	39.681	39.528	39.605	0.032	0.026	0.038	0.032	0.006
60	7.780	7.790	7.770	59.484	59.560	59.407	59.484	0.041	0.035	0.047	0.041	0.006
80	10.370	10.390	10.380	79.286	79.439	79.362	79.362	0.057	0.045	0.051	0.051	0.006
100	12.980	12.970	12.960	99.241	99.165	99.088	99.165	0.061	0.067	0.073	0.067	0.006
200	26.030	26.020	26.010	199.018	198.941	198.865	198.941	0.079	0.085	0.091	0.085	0.006

TABLE C-5 Ion exchange data of norfloxacin onto anion exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	0.150	0.163	0.171	12.218	13.277	13.928	13.141	0.311	0.269	0.243	0.274	0.035
40	0.335	0.329	0.327	27.287	26.798	26.635	26.907	0.509	0.528	0.535	0.524	0.014
60	0.538	0.541	0.544	43.822	44.066	44.310	44.066	0.647	0.637	0.628	0.637	0.010
80	0.793	0.768	0.771	64.592	62.556	62.800	63.316	0.616	0.698	0.688	0.667	0.044
100	1.005	1.011	1.022	81.860	82.349	83.245	82.485	0.726	0.706	0.670	0.701	0.028
150	1.587	1.595	1.612	129.266	129.918	131.302	130.162	0.829	0.803	0.748	0.794	0.042
200	2.209	2.211	2.204	179.930	180.093	179.522	179.848	0.803	0.796	0.819	0.806	0.012

TABLE C-6 Ion exchange data of norfloxacin onto cation exchange resin: ratio 1 : 800 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	0.125	0.123	0.126	11.415	11.232	11.506	11.385	6.868	7.014	6.795	6.892	0.112
40	0.261	0.263	0.262	23.835	24.017	23.926	23.926	12.932	12.786	12.859	12.859	0.073
60	0.425	0.429	0.427	38.811	39.177	38.994	38.994	16.951	16.659	16.805	16.805	0.146
80	0.620	0.624	0.621	56.619	56.984	56.710	56.771	18.705	18.413	18.632	18.583	0.152
100	0.790	0.795	0.801	72.144	72.600	73.148	72.631	22.285	21.920	21.482	21.895	0.402
150	1.330	1.340	1.340	121.457	122.370	122.370	122.066	22.834	22.104	22.104	22.347	0.422
200	1.875	1.877	1.878	171.227	171.410	171.501	171.379	23.019	22.872	22.799	22.897	0.112

TABLE C-7 Ion exchange data of 17-α ethinyl estradiol onto anion exchange resin: ratio 1 : 1,600 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	0.433	0.391	0.412	10.812	9.763	10.287	10.287	14.701	16.379	15.540	15.540	0.839
40	0.971	0.977	0.974	24.245	24.395	24.320	24.320	25.208	24.968	25.088	25.088	0.120
60	1.481	1.479	1.483	36.979	36.929	37.029	36.979	36.833	36.913	36.754	36.833	0.080
80	2.115	2.111	2.114	52.809	52.710	52.784	52.768	43.505	43.665	43.545	43.571	0.083
100	2.559	2.556	2.553	63.896	63.821	63.746	63.821	57.767	57.887	58.007	57.887	0.120
150	4.005	4.002	3.998	100.001	99.926	99.826	99.918	79.9986	80.118	80.278	80.132	0.140
200	5.423	5.419	5.418	135.407	135.307	135.282	135.332	103.349	103.509	103.549	103.469	0.106

TABLE C-8 Ion exchange data of 17-α ethinyl estradiol onto cation exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	0.370	0.324	0.312	7.764	6.799	6.547	7.037	0.489	0.528	0.538	0.519	0.026
40	0.711	0.721	0.733	14.920	15.129	15.381	15.143	1.003	0.995	0.985	0.994	0.009
60	1.229	1.236	1.232	25.789	25.936	25.852	25.859	1.368	1.363	1.366	1.366	0.003
80	1.722	1.735	1.737	36.134	36.407	36.449	36.330	1.755	1.744	1.742	1.747	0.007
100	2.112	2.115	2.117	44.318	44.381	44.423	44.374	2.227	2.225	2.223	2.225	0.002
200	4.185	4.187	4.189	87.818	87.860	87.902	87.860	4.487	4.486	4.484	4.486	0.002

APPENDIX D

TABLE D-1 Ion exchange data of nalidixic acid with Na_2SO_4 10 mg/L onto anion exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.890	1.870	1.860	15.160	15.000	14.920	15.027	0.387	0.400	0.406	0.398	0.010
40	4.100	4.090	4.070	32.888	32.808	32.647	32.781	0.569	0.575	0.588	0.578	0.010
60	6.350	6.390	6.370	50.936	51.257	51.096	51.096	0.725	0.699	0.712	0.712	0.013
80	8.770	8.760	8.780	70.348	70.267	70.428	70.348	0.772	0.779	0.766	0.772	0.006
100	11.180	11.170	11.180	89.679	89.599	89.679	89.653	0.826	0.832	0.826	0.828	0.004
150	17.330	17.360	17.380	139.011	139.252	139.412	139.225	0.879	0.860	0.847	0.862	0.016
200	23.540	23.570	23.590	188.824	189.064	189.225	189.038	0.894	0.875	0.862	0.877	0.016

TABLE D-2 Ion exchange data of nalidixic acid with Na_2SO_4 100 mg/L onto anion exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.850	1.840	1.860	17.354	17.260	17.448	17.354	0.212	0.219	0.204	0.212	0.008
40	3.860	3.840	3.850	36.210	36.022	36.116	36.116	0.303	0.318	0.311	0.311	0.008
60	5.930	5.940	5.930	55.628	55.721	55.628	55.659	0.350	0.342	0.350	0.347	0.004
80	8.010	8.000	8.020	75.139	75.046	75.233	75.139	0.389	0.396	0.381	0.389	0.008
100	10.090	10.080	10.070	94.651	94.557	94.464	94.557	0.428	0.435	0.443	0.435	0.008
150	15.330	15.320	15.330	143.806	143.712	143.806	143.775	0.496	0.503	0.496	0.498	0.004
200	20.640	20.630	20.650	193.618	193.524	193.711	193.618	0.511	0.518	0.503	0.511	0.008

TABLE D-3 Ion exchange data of nalidixic acid with $NaHCO_3$ 10 mg/L onto anion exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	0.143	0.141	0.145	13.414	13.227	13.602	13.414	0.527	0.542	0.512	0.527	0.015
40	0.319	0.320	0.321	29.924	30.018	30.112	30.018	0.806	0.799	0.791	0.799	0.008
60	0.525	0.520	0.523	49.249	48.780	49.061	49.030	0.860	0.898	0.875	0.878	0.019
80	0.733	0.735	0.736	68.761	68.948	69.042	68.917	0.899	0.884	0.877	0.887	0.011
100	0.946	0.944	0.947	88.741	88.554	88.835	88.710	0.901	0.916	0.893	0.903	0.011
150	1.474	1.473	1.476	138.272	138.178	138.459	138.303	0.938	0.946	0.923	0.936	0.011
200	1.999	1.997	2.003	187.520	187.333	187.895	187.583	0.998	1.013	0.968	0.993	0.023

TABLE D-4 Ion exchange data of nalidixic acid with $NaHCO_3$ 100 mg/L onto anion exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.500	1.490	1.470	14.071	13.977	13.790	13.946	0.474	0.482	0.497	0.484	0.011
40	3.350	3.340	3.350	31.425	31.332	31.425	31.394	0.686	0.693	0.686	0.688	0.004
60	5.370	5.360	5.350	50.374	50.281	50.187	50.281	0.770	0.778	0.785	0.778	0.008
80	7.410	7.400	7.420	69.511	69.417	69.605	69.511	0.839	0.847	0.832	0.839	0.008
100	9.520	9.510	9.540	89.304	89.210	89.492	89.336	0.856	0.863	0.841	0.853	0.011
150	14.830	14.820	14.830	139.116	139.022	139.116	139.085	0.871	0.878	0.871	0.873	0.004
200	20.140	20.130	20.150	188.927	188.833	189.021	188.927	0.886	0.893	0.878	0.886	0.008

TABLE D-5 Ion exchange data of norfloxacin with Na_2SO_4 10 mg/L onto anion exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.630	1.650	1.640	14.646	14.826	14.736	14.736	0.214	0.207	0.211	0.211	0.004
40	3.230	3.290	3.250	29.022	29.561	29.202	29.262	0.439	0.418	0.432	0.430	0.011
60	5.250	5.270	5.240	47.172	47.352	47.082	47.202	0.513	0.506	0.517	0.512	0.005
80	7.380	7.370	7.410	66.311	66.221	66.580	66.371	0.548	0.551	0.537	0.545	0.007
100	9.540	9.550	9.570	85.719	85.809	85.988	85.839	0.571	0.568	0.560	0.566	0.005
150	14.980	14.970	14.950	134.598	134.508	134.329	134.478	0.616	0.620	0.627	0.621	0.005
200	20.510	20.530	20.520	184.286	184.466	184.376	184.376	0.629	0.621	0.625	0.625	0.004

TABLE D-6 Ion exchange data of norfloxacin with Na_2SO_4 100 mg/L onto anion exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.830	1.840	1.820	16.443	16.533	16.353	16.443	0.142	0.139	0.146	0.142	0.004
40	3.830	3.820	3.840	34.413	34.323	34.503	34.413	0.223	0.227	0.220	0.223	0.004
60	5.950	5.940	5.970	53.462	53.372	53.642	53.492	0.262	0.265	0.254	0.260	0.005
80	8.010	8.030	8.050	71.971	72.151	72.331	72.151	0.321	0.314	0.307	0.314	0.007
100	10.190	10.180	10.200	91.559	91.469	91.649	91.559	0.338	0.341	0.334	0.338	0.004
150	15.630	15.610	15.600	140.439	140.259	140.169	140.289	0.382	0.390	0.393	0.388	0.005
200	21.170	21.150	21.120	190.217	190.037	189.767	190.007	0.391	0.399	0.409	0.400	0.009

TABLE D-7 Ion exchange data of norfloxacin with $NaHCO_3$ 10 mg/L onto anion exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	0.150	0.151	0.149	13.478	13.568	13.388	13.478	0.261	0.257	0.264	0.261	0.004
40	0.309	0.311	0.312	27.764	27.944	28.034	27.914	0.489	0.482	0.479	0.483	0.005
60	0.503	0.504	0.506	45.196	45.285	45.465	45.315	0.592	0.589	0.581	0.587	0.005
80	0.712	0.714	0.716	63.975	64.154	64.334	64.154	0.641	0.634	0.627	0.634	0.007
100	0.927	0.925	0.924	83.293	83.113	83.023	83.143	0.668	0.675	0.679	0.674	0.005
150	1.469	1.470	1.468	131.993	132.082	131.903	131.993	0.720	0.717	0.724	0.720	0.004
200	2.016	2.019	2.018	181.142	181.411	181.321	181.291	0.754	0.744	0.747	0.748	0.005

TABLE D-8 Ion exchange data of norfloxacin with $NaHCO_3$ 100 mg/L onto anion exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.530	1.550	1.540	13.747	13.927	13.837	13.837	0.250	0.243	0.247	0.247	0.004
40	3.250	3.240	3.210	29.202	29.112	28.842	29.052	0.432	0.436	0.446	0.438	0.007
60	5.180	5.170	5.160	46.543	46.453	46.364	46.453	0.538	0.542	0.545	0.542	0.004
80	7.220	7.210	7.220	64.873	64.783	64.873	64.843	0.605	0.609	0.605	0.606	0.002
100	9.320	9.330	9.350	83.742	83.832	84.012	83.862	0.650	0.647	0.640	0.646	0.005
150	14.830	14.840	14.850	133.251	133.340	133.430	133.340	0.670	0.666	0.663	0.666	0.004
200	20.350	20.330	20.340	182.849	182.669	182.759	182.759	0.686	0.693	0.690	0.690	0.004

TABLE D-9 Ion exchange data of nalidixic acid with NaCl 0.001 M. onto anion exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.680	1.690	1.680	12.730	12.805	12.730	12.755	0.582	0.576	0.582	0.580	0.003
40	3.910	3.930	3.950	29.627	29.778	29.930	29.778	0.830	0.818	0.806	0.818	0.012
60	6.410	6.440	6.430	48.570	48.797	48.721	48.696	0.914	0.896	0.902	0.904	0.009
80	9.010	9.050	9.070	68.271	68.574	68.725	68.523	0.938	0.914	0.902	0.918	0.019
100	11.590	11.610	11.630	87.820	87.971	88.123	87.971	0.974	0.962	0.950	0.962	0.012
150	18.110	18.120	18.120	137.223	137.299	137.299	137.274	1.022	1.016	1.016	1.018	0.003
200	24.670	24.680	24.660	186.930	187.005	186.854	186.930	1.046	1.040	1.052	1.046	0.006

TABLE D-10 Ion exchange data of nalidixic acid with NaCl 0.005 M. onto anion exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.680	1.660	1.660	12.730	12.578	12.578	12.629	0.582	0.594	0.594	0.590	0.007
40	3.870	3.880	3.890	29.324	29.400	29.475	29.400	0.854	0.848	0.842	0.848	0.006
60	6.350	6.370	6.360	48.115	48.267	48.191	48.191	0.951	0.939	0.945	0.945	0.006
80	8.960	8.990	8.980	67.892	68.119	68.043	68.018	0.969	0.950	0.957	0.959	0.009
100	11.580	11.580	11.540	87.744	87.744	87.441	87.643	0.980	0.980	1.005	0.989	0.014
150	18.110	18.080	18.090	137.223	136.996	137.072	137.097	1.022	1.040	1.034	1.032	0.009
200	24.640	24.660	24.650	186.702	186.854	186.778	186.778	1.064	1.052	1.058	1.058	0.006

TABLE D-11 Ion exchange data of nalidixic acid with NaCl 0.01 M. onto anion exchange resin: ratio 1 : 80 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	1.660	1.670	1.660	12.578	12.654	12.578	12.603	0.594	0.588	0.594	0.592	0.003
40	3.880	3.890	3.890	29.400	29.475	29.475	29.450	0.848	0.842	0.842	0.844	0.003
60	6.360	6.340	6.330	48.191	48.039	47.964	48.065	0.945	0.957	0.963	0.955	0.009
80	8.980	8.950	8.970	68.043	67.816	67.967	67.942	0.957	0.975	0.963	0.965	0.009
100	11.570	11.560	11.580	87.668	87.592	87.744	87.668	0.987	0.993	0.980	0.987	0.006
150	18.090	18.070	18.060	137.072	136.920	136.844	136.945	1.034	1.046	1.052	1.044	0.009
200	24.610	24.650	24.630	186.475	186.778	186.626	186.626	1.082	1.058	1.070	1.070	0.012

TABLE D-12 Ion exchange data of norfloxacin with NaCl 0.001 M. onto anion exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	2.180	2.160	2.170	16.518	16.367	16.443	16.443	0.279	0.291	0.285	0.285	0.006
40	4.410	4.390	4.370	33.415	33.264	33.112	33.264	0.527	0.539	0.551	0.539	0.012
60	6.830	6.820	6.870	51.752	51.677	52.055	51.828	0.660	0.666	0.636	0.654	0.016
80	9.390	9.370	9.360	71.150	70.998	70.923	71.024	0.708	0.720	0.726	0.718	0.009
100	11.950	11.960	11.940	90.548	90.623	90.472	90.548	0.756	0.750	0.762	0.756	0.006
150	18.470	18.460	18.440	139.951	139.875	139.724	139.850	0.804	0.810	0.822	0.812	0.009
200	25.050	25.030	25.010	189.809	189.657	189.506	189.657	0.815	0.827	0.840	0.827	0.012

TABLE D-13 Ion exchange data of norfloxacin with NaCl 0.005 M. onto anion exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	2.190	2.170	2.160	16.594	16.443	16.367	16.468	0.272	0.285	0.291	0.283	0.009
40	4.340	4.360	4.350	32.885	33.037	32.961	32.961	0.569	0.557	0.563	0.563	0.006
60	6.800	6.790	6.810	51.525	51.449	51.601	51.525	0.678	0.684	0.672	0.678	0.006
80	9.350	9.340	9.370	70.847	70.771	70.998	70.872	0.732	0.738	0.720	0.730	0.009
100	11.850	11.870	11.880	89.790	89.941	90.017	89.916	0.817	0.805	0.799	0.807	0.009
150	18.400	18.420	18.390	139.420	139.572	139.345	139.446	0.846	0.834	0.852	0.844	0.009
200	25.010	25.020	24.990	189.506	189.582	189.354	189.481	0.840	0.833	0.852	0.842	0.009

TABLE D-14 Ion exchange data of norfloxacin with NaCl 0.01 M. onto anion exchange resin: ratio 1 : 40 g/mL.

Conc. (mg/l)	A1	A2	A3	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Ceavg (mg/l)	q1 (mg/g)	q2 (mg/g)	q3 (mg/g)	qavg (mg/g)	STDEV q
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	2.150	2.130	2.170	16.291	16.139	16.443	16.291	0.297	0.309	0.285	0.297	0.012
40	4.400	4.390	4.350	33.340	33.264	32.961	33.188	0.533	0.539	0.563	0.545	0.016
60	6.810	6.830	6.870	51.601	51.752	52.055	51.803	0.672	0.660	0.636	0.656	0.019
80	9.390	9.370	9.360	71.150	70.998	70.923	71.024	0.708	0.720	0.726	0.718	0.009
100	11.890	11.880	11.870	90.093	90.017	89.941	90.017	0.793	0.799	0.805	0.799	0.006
150	18.430	18.410	18.440	139.648	139.496	139.724	139.623	0.828	0.840	0.822	0.830	0.009
200	25.030	25.010	25.000	189.657	189.506	189.430	189.531	0.827	0.840	0.846	0.838	0.009

APPENDIX E

TABLE E-1 Chloride measurement in sample of acetaminophen onto anion exchange resin. (dilute 20x)

Sample	Value 1 (mg/l)	Value 2 (mg/l)	Value3 (mg/l)	Avg. (mg/l)
Blank	32.7	32.7	33.3	32.9
ACE	33.1	33.3	31.4	32.6

Chloride concentration in sample = (32.6 - 32.9)*20 = - 6 mg/l

TABLE E-2 Chloride measurement in sample of nalidixic acid onto anion exchange resin. (dilute 20x)

Sample	Value 1 (mg/l)	Value 2 (mg/l)	Value 3 (mg/l)	Avg. (mg/l)
Blank	35.2	34.9	35.2	35.1
NAL	35.5	35.5	35.5	35.5

Chloride concentration in sample = (35.5 – 35.1)*20 = 8 mg/l

TABLE E-3 Chloride measurement in sample of norfloxacin onto anion exchange resin. (dilute 20x)

Sample	Value 1 (mg/l)	Value 2 (mg/l)	Value 3 (mg/l)	Avg. (mg/l)
Blank	33.4	34.2	33.6	33.7
NFC	33.9	33.8	34.1	33.9

Chloride concentration in sample = (33.9 – 33.7)*20 = 4 mg/l

TABLE E-4 Chloride measurement in sample of 17-α ethinyl estradiol onto anion exchange resin. (dilute 20x)

Sample	Value 1 (mg/l)	Value 2 (mg/l)	Value3 (mg/l)	Avg. (mg/l)
Blank	34.7	34.7	33.9	34.4
EE2	34.1	34.3	34.4	34.3

Chloride concentration in sample = (34.3 – 34.4)*20 = - 2 mg/l

TABLE E-5 Sodium measurement in sample of acetaminophen onto cation exchange resin. (dilute 1,000x)

Sample	Absorbance	Conc. (mg/l)	True Conc. (mg/l)	Avg. Conc. (mg/l)
Blank 1	0.130	0.599	598.64	
Blank 2	0.128	0.589	589.43	595.57
Blank 3	0.130	0.599	598.64	
ACE 1	0.131	0.603	603.24	
ACE 2	0.126	0.580	580.22	594.03
ACE 3	0.130	0.599	598.64	

Sodium concentration in sample = 594.03 - 595.57 = - 1.54 mg/l

TABLE E-6 Sodium measurement in sample of nalidixic acid onto cation exchange resin. (dilute 1,000x)

Sample	Absorbance	Conc. (mg/l)	True Conc. (mg/l)	Avg. Conc. (mg/l)
Blank 1	0.112	0.320	319.68	
Blank 2	0.110	0.314	313.97	314.90
Blank 3	0.109	0.311	311.12	
NAL 1	0.107	0.305	305.41	
NAL 2	0.103	0.294	293.99	299.70
NAL 3	0.105	0.300	299.70	

Sodium concentration in sample = 299.70 - 314.92 = - 15.22 mg/l

TABLE E-7 Sodium measurement in sample of norfloxacin onto cation exchange resin. (dilute 1,000x)

Sample	Absorbance	Conc. (mg/l)	True Conc. (mg/l)	Avg. Conc. (mg/l)
Blank 1	0.015	0.043	42.82	
Blank 2	0.014	0.040	39.96	48.52
Blank 3	0.022	0.063	62.80	
NFC 1	0.019	0.054	54.23	
NFC 2	0.021	0.060	59.94	55.18
NFC 3	0.018	0.051	51.38	

Sodium concentration in sample = 55.18 - 48.52 = 6.66 mg/l

TABLE E-8 Sodium measurement in sample of 17-α ethinyl estradiol onto cation exchange resin. (dilute 1,000x)

Sample	Absorbance	Conc. (mg/l)	True Conc. (mg/l)	Avg. Conc. (mg/l)
Blank 1	0.112	0.320	319.68	
Blank 2	0.113	0.323	322.54	319.68
Blank 3	0.111	0.317	316.83	
EE2 1	0.109	0.311	311.12	
EE2 2	0.110	0.314	313.97	311.12
EE2 3	0.108	0.308	308.26	

Sodium concentration in sample = 311.12 – 319.68 = - 8.56 mg/l

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