Application of adsorption on activated carbon for the removal of antibiotics from wastewater of livestock production facilities

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ABSTRACT

Antibiotics are used for treatment of both human and livestock. Due to incomplete metabolization, a considerable amount of consumed antibiotics may be excreted from the body. Even at low concentration, this pharmaceutical compound can have an adverse effect on the environment and promote development of antibiotic resistance in bacteria. Lincomycin and tetracycline are the two most common antibiotics that are used in the swine industry in Canada. A practical solution should be developed to remove these antibiotics from wastewater.

This research dealt with the evaluation of activated carbon (Cabot Norit 1240) performance in removal of tetracycline and lincomycin as individual and in a binary mixture. Initial concentration variations at different temperature on adsorption capacity in the single-solute and binary adsorption were explored.

In single-solute adsorption both lincomycin and tetracycline were adsorbed more effectively at 32 °C compared to other temperatures (5, 12, 22 °C). The effect of initial concentration on the adsorption process indicated that the adsorption for both individual antibiotics were greater at higher initial concentrations. The thermodynamic parameters for both individual adsorption processes were calculated. Enthalpy values were 29400 and 28000 J mol^{-1} for tetracycline and lincomycin adsorption processes, respectively which demonstrated individual antibiotic adsorption are endothermic. Additionally, entropy values, 122 and 123 J mol^{-1} K^{-1} for tetracycline and lincomycin, respectively show that randomness in the system increased.

Effect of temperature on binary adsorption was studied. The results showed that at 32 °C, lincomycin and tetracycline antibiotics as a binary system could be adsorbed more effectively compared to lower temperatures. Moreover, increasing initial concentration of antibiotics resulted in higher adsorption.

Enthalpy values for the adsorption of tetracycline (38000 J mol^{-1}) and lincomycin (36230 J mol^{-1}) in the mixture show that the binary process was also an endothermic process. Also, determination of entropy for binary process (150 J mol^{-1} K^{-1} for tetracycline and 149 J mol^{-1} K^{-1} for lincomycin) demonstrate that randomness in the binary system increased.

Monitoring the concentration of tetracycline in manure showed that tetracycline concentration fluctuated with time and reached a relatively constant value after 10 days. Evaluating the effect of adsorbent dosage on adsorption of tetracycline in manure solution showed that the required dosage of activated carbon to remove tetracycline in the manure was 1.5 g L^{-1}.

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NOMENCLATURE

ΔG	Gibbs free energy change of adsorption (J mol^{-1})
$\Delta H°$	Standard enthalpy change of adsorption (J mol^{-1})
$\Delta S°$	Standard entropy change of adsorption (J $mol^{-1}K^{-1}$)
C_e	Concentration of adsorbate in solution (mg L^{-1})
K_c	Thermodynamic equilibrium constant
K_L	Langmuir isotherm model constant (L mg^{-1})
K_S	Sips isotherm model constant
K_F	Freundlich isotherm model constant (mg g^{-1}) (L $mg^{-1})^{1/n}$
pKa	Acid dissociation constant
q_e	Adsorption capacity (mg adsorbate mg $adsorbent^{-1}$)
Q_{max}	Monolayer maximum adsorption capacity in Langmuir and Sip isotherm model (mg adsorbate mg $adsorbent^{-1}$)
R	Universal gas constant (8.314 J K^{-1} mol^{-1})
rpm	Revolutions per minute
T	Absolute temperature (K)
V	Volume of the solution (L)
W	Weight of adsorbent (g)
n	Freundlich adsorption affinity parameter

ABBREVIATIONS

CN1240	Cabot Norit 1240 granular activated carbon
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
HPLC	High-performance liquid chromatography
IAST	Ideal adsorbed solution theory
PZC	Point of zero charge
IEP	Isoelectric point

Chapter 1

INTRODUCTION

The existence of emerging pollutants, even at low concentration, in the natural environment can have irrecoverable effects on human and aquatic life. Emerging pollutants are relatively broad class of unregulated compounds including pharmaceuticals, personal care products, endocrine disrupting compounds and hormones [1]. Among emerging pollutants, pharmaceutical compounds have attracted attention due to their negative impacts on the environment [2].

Among different pharmaceutical compounds, special attention has been placed on the antibiotics due to their high usage for both humans and animals. Based on the European Animal Health Association, in 2000 around 10,000 tons of antibiotics were used, of this amount around 5,000 tons of antibiotics were used in European animal production industries [3]. In veterinary medicine, antibiotics are used mostly for disease treatment [3]. In Canada, according to the reports in 2014 around 1.5 million kg of antibiotics were used in the livestock production industry [4]. Recent studies have shown that up to 90% of antibiotics are excreted from the body due to incomplete metabolization [5].

The occurrence of antibiotics in environment may influence the environment negatively specially by considering that antibiotics in the environment even at low concentration can lead to development of anti- bacterial resistance [5]. Among different antibiotics, tetracycline and lincomycin are two widely used antibiotics in Canadian swine industries [4].

Tetracyclines are broad-spectrum antibiotics, which are generally utilized against infectious diseases in both animals and humans. In the environment, tetracycline usually is not detected at high concentrations due to its precipitation with cations including calcium and its accumulation in the sludge [6]. Tetracycline was detected at concentrations between 0.15-0.97 $\mu g\ L^{-1}$ in the final wastewater effluent of 5 different cities in Canada [7]. In another study, Dargnat et al. reported that 0.2 $\mu g\ L^{-1}$ of tetracycline was detected in the final effluent of wastewater treatment plant in Marne, France [8].

Lincosamide is a group of antimicrobials and based on its molecular structure lincomycin belongs to this group. Lincomycin is most effective against anaerobic and gram-positive bacteria [9]. Lincomycin cannot be metabolized in the body completely and it is excreted through feces and urine. In pork industry, based on the oral administration, 79 to 86% of the given lincomycin dose is excreted in feces [10].

Concerns related to the environmental problems and health issues because of the presence of antibiotic in the environment have provoked attention in order to find efficient and practical methods to remove this class of emerging pollutants from wastewater. Different methods such as advanced oxidation, membrane separation, coagulation-flocculation treatment have been studied to eliminate antibiotics from wastewater. These methods either are inefficient or expensive [11]. Adsorption is an alternative method which does not have the above problems. However, because of using adsorbent in this method and transferring pollutant from liquid to the solid, post treatment of the loaded adsorbents is still needed [12].

Activated carbon has been generally used to eliminate pollutants from wastewater. This adsorbent has high surface area as well as high capacity for removing contaminates. According to the reports, in some cases, this adsorbent has close to 100% removal efficiency [13].

In this work, commercial activated carbon was used to remove tetracycline and lincomycin either as an individual antibiotic or as mixture in different media including water and manure slurry supernatant. The effects of concentration and temperature were investigated. Finally, an appropriate adsorption isotherm model was identified and used for adsorption of both individual antibiotics and mixture of two antibiotics. Thermodynamics parameters of adsorption were also determined.

The present thesis consists of six chapters including introduction, literature review and research objectives, materials and methods, results regarding the adsorption of lincomycin and tetracycline in deionized water for both individual and mixture experiments, results of the adsorption of lincomycin and tetracycline from real manure solution for both individual and mixture of two antibiotics, and conclusions and recommendations for future work.

Chapter 2
LITERATURE REVIEW

This chapter briefly provides information related to the occurrence of antibiotics in the environment in section 2.1. In section 2.2, common treatment methods for removal of antibiotics from water are explained and the obtained results through using each method are mentioned. Finally, in section 2.3 mathematical equations required for isotherm fitting and thermodynamic analysis is provided.

2.1. Occurrence of pharmaceuticals in water

Emerging contaminants (ECs) are mainly synthetic organic chemicals and have been recently found in the environment. Although these relatively new contaminants include a large number of harmful compounds, no regulation controls their use [1]. ECs concentration in the environment can be between a few ng L^{-1} to almost 100 g L^{-1} [1]. The most well-known ECs are hormones, personal care products, pesticides, and pharmaceutical compounds [1]. Pharmaceutical compounds have received a great deal of attention because they biodegrade poorly in wastewater. However, the long-term effects of these compounds in water are not clear [14].

Among pharmaceutical compounds, antibiotics have received more attention due to their high selectivity that allows them to act on particular bacteria while other tissues in the body are unaffected [15]. According to reports, in 2000, about 23 million kg of antibiotics were produced in the United States [16]. Another study related to antibiotic consumption was done on 79 countries from 2000 to 2015. The results obtained through this study indicated that the global antibiotic usage increased by 39% [17].

Antibiotics are used not only in human medicine but also, in animal production industry. There are two reasons for using antibiotics for animals. First, antibiotics are used to treat or prevent diseases. Second, in some cases, antibiotics are used for enhancing growth [18]. In China, around 8,000 tons of antibiotics were used as growth promoter in the animal production industry in 2009 [6]. In Canada, most antimicrobials in the animal production industry are used to treat or prevent diseases, and there is a legal action to disallow companies to use antibiotics as a growth promoter [19]. According to reports, in 2016, approximately 1 million kg of antibiotics were distributed in animal production industry in Canada and of that amount around 39,976 kg of antibiotics were used in Saskatchewan [19].

After antibiotics are administered to humans and animals, up to 90% is excreted from the body through urine and feces either in an unchanged form or as active metabolites due to partial metabolization [5]. For this reason, different concentrations of antibiotics have been found in surface waters. For example, the concentration of oxytetracycline was investigated in sediments under a marine salmon farm in Ireland, and the results showed about 0.1-0.11 $\mu g\, g^{-1}$ of this antibiotic in soil [16].

The existence of antibiotics in environment can cause serious problems, such as aquatic toxicity, and bacteria resistance. Bacteria resistance can reduce the effectiveness of the original antibiotic to fight a particular bacterium, requiring additional antibiotics to be developed [20]. It has been shown that more than 90% of bacteria in water could develop resistance to antibiotics [21]. As a result, the World Health Organization has identified this issue as a critical public health concern [22]. Lincomycin and tetracycline are the two most dominant antibiotics used in Canadian swine production industry [19].

2.1.1 Tetracycline

Tetracycline antibiotics contain four different compounds: Tetracycline (TC), Chlorotetracycline (CTC), Oxytetracycline (OTC), and Doxycycline (DC). Tetracycline is a wide usage antibiotic that acts against both gram-positive and gram-negative bacteria.

Figure 2.1 shows the molecular structure of tetracycline. Tetracycline has a number of ionizable functional groups and because of these groups, this antibiotic can have different forms including anion, zwitterion, and cation at different pH conditions. According to Figure 2.4, tetracycline has three different pKa including, 3.3 because of the tricarbonyl system, 7.68 because of the phenolic diketone system, and 9.69 due to the dimethylammonium group [23].

Tetracycline acts as a cation if the pH of the solution is below 3.30, it will be zwitterion if the pH of the solution is between 3.30 and 7.7, and it may act as anion when the pH of the solution is between 7.68 and 9.7 [24].

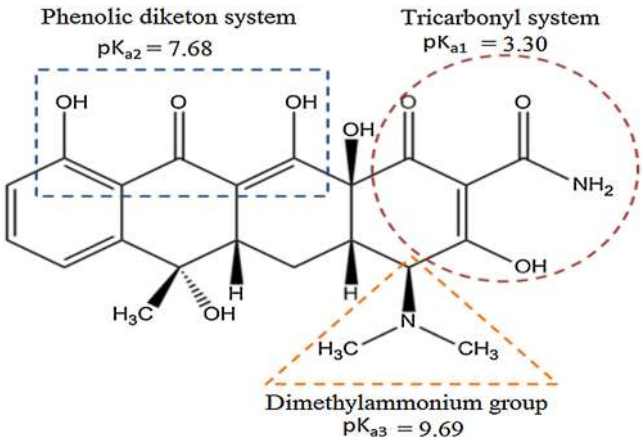

Figure 2.1 Molecular structure of tetracycline [24]

Tetracycline is mostly used for treatment of infectious diseases in the animal production industry as well as in human medicine [6]. According to reports, the annual consumption of tetracycline in swine production industry has reached approximately 2.3 million kilograms in the United States [25]. In Canada, approximately 600,000 kg of tetracycline was distributed for animal usage in 2016 [19].

Due to incomplete metabolization, only a small fraction of tetracycline is digested in the body, and most of this compound (around 50-80%) is excreted from the body through urine and feces [23]. Tetracycline is not usually found in high concentrations in the environment because of precipitation with cations such as calcium or accumulating in the sediments [6]. Based on a report which studied the final wastewater effluent in five different Canadian cities – Vancouver, Calgary, Burlington, Peterborough, and Windsor – tetracycline was detected in quantities between 0.15-0.97 $\mu g\ L^{-1}$ [7]. In a later study, Dargnat et al. [8] reported that 0.2 $\mu g\ L^{-1}$ of tetracycline was detected in the final wastewater plant effluent in Marne, France.

2.1.2. Lincomycin

Another popular antibiotic used in the Canadian animal production industry is lincomycin. Lincomycin is classified as a lincosamides antibiotic. Based on its activity, this antibiotic is similar to macrolide antibiotics. Lincomycin is predominantly effective against anaerobic and gram-positive bacteria but it is ineffective against gram-negative bacteria.

Figure 2.5 shows the structure of lincomycin. Lincomycin contains three major groups including one N-methyl, two C-methyl, and one basic function [26]. Lincomycin can be cation or zwitterion based on the solution pH because lincomycin has a pyrrolidine ring and this ring has pKa=7.8. According to this number, lincomycin can be found as a cation if the solution pH is below 7.8, and it can act as zwitterion if the solution pH is above 7.8.

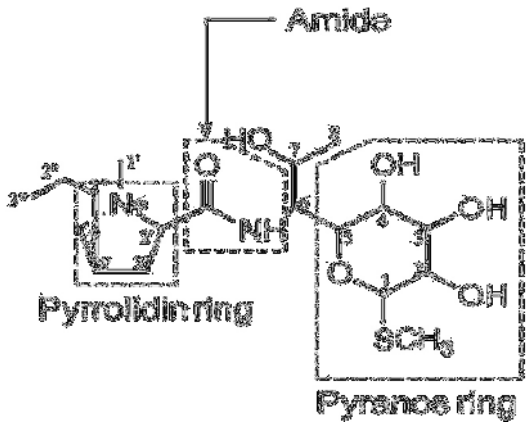

Figure 2.2 Molecular structure of lincomycin [26]

To act effectively and fast, this antibiotic is used together with spectinomycin. In the Canadian swine industry, 22 g of lincomycin per ton of complete food can be added to reduce the severity of Mycoplasmal Pneumonia in growing swine [27]. In 2016, less than 200,000 kg of lincomycin was distributed in the animal production industry in Canada [19].

Lincomycin cannot be consumed in the body completely and it is excreted through feces and urine. In the pork industry, based on oral administration, 79 to 86% of lincomycin doses is excreted in feces, and between 14 to 21% is excreted in urine [10]. In a study carried out in the Grand River in Canada lincomycin was found as well. According to this study, in 91% of 125 collected samples from Grand River, lincomycin had concentration from 0.2 to 355 ng L^{-1} [28]. Kutcha et al. investigated lincomycin concentration in liquid swine manure and found that concentration of lincomycin in fresh manure is around 9.78 ppm while after 5 weeks of storage, this number decreased to 2.52 ppm [29].

2.2. Wastewater treatment methods

Due to serious problems that the presence of antibiotics even at low concentration can cause in the environment, different treatment methods have been evaluated in order to remove these pharmaceuticals from wastewater. Some of these methods are described in the following sections.

2.2.1. Coagulation/flocculation

Coagulation is a process used to neutralize the charged particles and flocculation is a follow-up procedure in which low-speed mixing promotes the formation of larger aggregates [12]. This method was employed to treat wastewaters containing antibiotics; however, the efficiency is low. Treatment of wastewater which contained fluoroquinolones, quinoxaline derivatives, and trimethoprim was studied using this method but the removal efficiency was less than 30% [30].

2.2.2. Advanced oxidation process

This is a highly efficient method in which pollutants are degraded using active oxygenated species. For instance, degradation of enrofloxacin in wastewater was investigated using heterogeneous catalysis (CuO encapsulated CuY zeolite) by semiconductors and more than 90% of this antibiotic was oxidized [31]. Although this method has high efficiency for removal of antibiotics from wastewater it is not feasible to be used in industry mainly because of its high cost [31].

2.2.3. Membrane processes

Over the past decades, this separation process has received a lot of attention. This technology is a separation process that employs semipermeable membranes.

In order to remove tetracycline from wastewater, nano-filtration was applied, and 95% removal was obtained [32]. In addition, the same outcome was observed for treatment of wastewater containing enrofloxacin [33]. Reverse osmosis was employed for treatment and 95% removal was obtained. Similar to the advanced oxidation process, this method is expensive and as a result, it is not considered a feasible option for large-scale industrial applications [32].

2.2.4. Adsorption

The methods that are mentioned before having inherent shortcomings regarding removing antibiotics from wastewater. They either have low efficiency or are expensive. Therefore, in order to treat wastewater containing antibiotics, another technique should be considered. Adsorption, which has been used for over 100 years, not only is a low cost method but also it has reasonable efficiency [22,23].

In this process, the reaction happens between two phases: one is a solid phase and the other one is fluid either gas or liquid. The solid phase is known as an adsorbent and the adsorbate is in the fluid phase [36]. Figure 2.6 shows the fundamental elements in the adsorption process. Based on Figure 2.6, molecules in fluid phase (liquid or gas) move toward the solid phase (adsorbent) and because of physical or chemical properties of adsorbent, they interact with the adsorbent and accumulate on it. In essence, adsorption involves mass transfer between gas or a liquid and a solid surface [36].

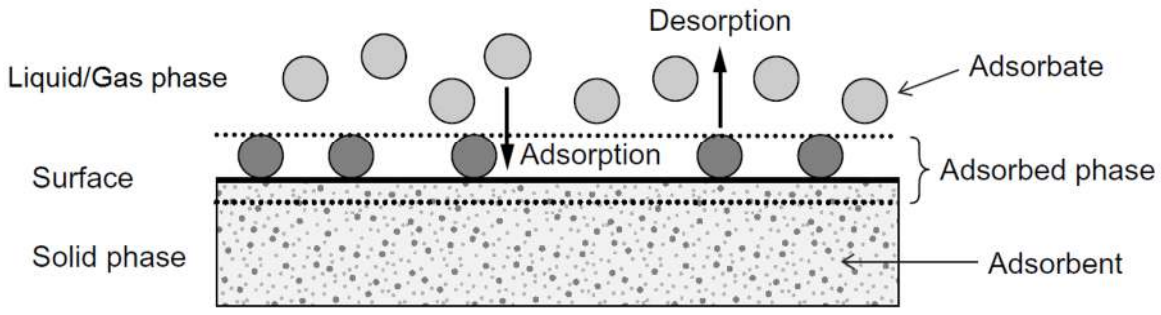

Figure 2.3 Fundamental elements of an adsorption process [25]

Activated carbon is a commercial adsorbent that is commonly used in adsorption process. Using granular activated carbon with 1112 $m^2\ g^{-1}$surface area and powdered activated carbon with 882 $m^2 g^{-1}$ surface area, Kim et al. [37] studied adsorption of trimethoprim at different pH ranging from 4 to 10 at 25 ℃. With these adsorbents, 90% of trimethoprim was removed at pH=4. Adams et al. [38] evaluated removal of sulfathiazole from deionized water and Missouri River water using powdered activated carbon. They found that this adsorbent could remove more than 90% of sulfathiazole antibiotic from deionized water; however, the adsorption efficiency in Missouri River water was less than that in deionized water and it was about 73% [38]. In another study, powdered activated carbon derived from coal with 1054 $m^2\ g^{-1}$ surface area was used to remove tetracycline from water. The results showed that this adsorbent was able to remove 97% of tetracycline in water when the antibiotic concentration and adsorbent dosage in water was 489 $mg\ L^{-1}$and 24 $mg\ L^{-1}$ respectively [39].

Biochar is a type of adsorbent that is made from heating biomass including wood and manure with little or no oxygen. Biochars contain a large amount of carbon [40]. Due to their low cost, they have received a lot of attention in recent years. Generally, biochars have lower surface area compared to other adsorbents and they need to be treated before use. Wang et al. [41] investigated the feasibility of the adsorption process in synthetic wastewater and found that bamboo biochar adsorbent which was prepared at 500 ℃ could remove more than 90% fluoroquinolone antibiotics (enrofloxacin and ofloxacin) [41]. Pouretedal et al. [42] used biochar adsorbent prepared from vine wood and explored the efficiency of this adsorbent for antibiotic removal. They found that at pH=2, 0.4 $g\ L^{-1}$ of adsorbent could remove 20 $mg\ L^{-1}$of tetracycline [42]. In another study, lincomycin adsorption was investigated in water. In this study, removal of lincomycin in water was investigated using manure-derived biochar. The results demonstrated that adsorption of lincomycin was better at pH 6 to 7.5 than pH 9.9 to 10.4 due to electrostatic interactions [28].

Clay is another adsorbent that has been used in order to remove antibiotics from wastewater. Kaolinite is one of the most important components in soil. Li et al. [34] used kaolinite to remove ciprofloxacin from water. It was found that the adsorption was pH dependent and increasing pH had a negative effect on the adsorption effectiveness [43]. Montmorillonite is another type of clay that has been used as an adsorbent. Essington et al. [35] used montmorillonite to eliminate chlortetracycline from water. The results showed that

adsorption of chlortetracycline would decrease with increasing pH and ionic strength due to the fact that the cation exchange was the predominant retention process [44].

Another type of adsorbent, which has a reasonable capability to remove antibiotics from wastewater, is carbon nanotubes. Ji et al. [36] investigated the mechanism of tetracycline adsorption on single-wall carbon nanotubes and activated carbon [45]. They found that tetracycline affinity in adsorption process is better for the single-wall carbon nanotubes compared to activated carbon. The weaker TC adsorption on activated carbon was the result of AC having less available adsorption sites compared to the single-wall carbon nanotubes [25]. Removal of lincomycin and sulfamethoxazole using single-walled and multi-walled carbon nanotubes was investigated by Kim et al. [46] and the results were compared with powdered activated carbon. The results demonstrated that the adsorption process followed the following order: SWCNTs> PAC> MWCNTs. A possible reason for less adsorption on MWCNTs was its low surface area compared to the other two adsorbents [46].

2.3. Factors affecting adsorption

2.3.1. Effect of antibiotic initial concentration

Adsorption capacity may be affected by initial antibiotic concentration variations. Huang et al. [47] investigated the removal of tetracycline from the water at room temperature using biochar prepared from lignin treated with H_3PO_4 . According to the authors, increasing the initial concentration of tetracycline from 200 to 600 mg L^{-1} increased adsorption capacity from 200 to 475 mg g^{-1}.

2.3.2. Effect of temperature

Temperature can affect adsorption capacity favorably or adversely. This depends on the nature of adsorption. During an exothermic process, increasing temperature affects adsorption capacity adversely while the increasing temperature in an endothermic process can affect adsorption capacity positively. Pouretedal et al. [42] studied the removal of tetracycline from water using activated carbon prepared from vine wood. Based on this report, in the case of activated carbon prepared from vine wood, adsorption of tetracycline showed to be an endothermic process and increasing temperature from 35 °C to 45 °C, adsorption capacity increases. Huang et al. [47] studied thermodynamic parameters for ciprofloxacin adsorption using activated carbon prepared from lignin treated with H_3PO_4. According to authors, during the increase of temperature from 25 °C to 40 °C, adsorption capacity decreased from 420 to 380 mg g^{-1}.

2.4. Adsorption isotherms

Adsorption process can be studied through equilibrium data. Equilibrium data is useful in order to describe the distribution of molecules that are adsorbed on the adsorbent [48]. Two factors can affect the adsorption process: concentration of adsorbate and temperature. For simplicity, adsorption process will be studied under a single temperature and, subsequently, the concentration of adsorbate in the solution will be changed [49]. The relation between adsorbate concentration and adsorption capacity at a specific temperature is identified as adsorption isotherm [49].

An adsorption isotherm is a curve that describes the pattern of transferring molecules from liquid phase to solid one. Different models have been developed to describe adsorption isotherm including one-parameter models, two-parameter models, and so on.

2.4.1. Single solute isotherm

2.4.1.1. Langmuir model

This model for the first time was developed in order to describe the gas-solid adsorption process using activated carbon as an adsorbent. This model assumes monolayer adsorption [49]. In the case of energy distribution, this model assumes that energy distribution is homogeneous which means that adsorption of each molecule has constant enthalpy change and activation energy [49].

Langmuir model equation is described as below:

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \qquad (2.1)$$

, where K_L (L mg^{-1}) is Langmuir constant which describes the affinity between adsorbate and adsorbent. Also, Q_{max} (mg g^{-1}) is the monolayer maximum capacity. The parameter q_e represents adsorption capacity measured in mg g^{-1}. C_e is the equilibrium concentration of adsorbate in solution measured in mg L^{-1}.

Also, Langmuir isotherm can be linearized. Eq. (2.2) represents the linear form of the Langmuir isotherm.

$$\frac{1}{q_e} = \left(\frac{1}{Q_{max}K_L}\right)\frac{1}{C_e} + \frac{1}{Q_{max}} \qquad (2.2)$$

In the case of a system with low adsorbate concentration, the Langmuir model reduces to linear form and obeys Henry's law, which can be identified as a strong point for this model compared to other models. However, this model is only valid for the single-layer adsorption system due to the monolayer assumption, and in the case of multilayer adsorption because of high adsorbate concentration, it does not perform well [49].

Separation factor is a dimensionless constant that can be derived from Langmuir isotherm [50]. To describe essential features of Langmuir model, determination of separation factor is indispensable. Eq. (2.3) describes separation factor:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (2.3)$$

, where C_0 (mg L^{-1}) is the initial concentration of adsorbate in solution and K_L (L mg^{-1}) is Langmuir equilibrium constant. R_L (dimensionless) represents the separation factor of the solid-liquid system.

If R_L value changes between zero and unity, this indicates that favorable adsorption occurs. When R_L value approaches to unity, this means that unfavorable adsorption occurs. If K_L value is high, then R_L value becomes zero which demonstrates irreversible adsorption [50].

2.4.1.2.Freundlich model

Freundlich isotherm is the earliest model which was developed in order to describe the non-ideal process [48]. This empirical model also considers the multilayer and non-uniform distribution of adsorbate on the heterogeneous surface. Freundlich equation is presented below:

$$q_e = K_F C_e^n \quad (2.4)$$

$K_F\ (mg\ g^{-1})(L\ mg^{-1})^{-n}$ is Freundlich constant and n indicates surface heterogeneity for the Freundlich model. Therefore, the greater value of n represents a more heterogeneous distribution of adsorbate on the adsorbent. The parameter q_e represents adsorption capacity measured in mg L^{-1}. C_e is the equilibrium concentration of adsorbate in solution measured in mg L^{-1}.

Eq. (2.5) shows the linear form of Freundlich isotherm.

$$\text{Log}\ (q_e) = n\log(C_e) + \log K_F \quad (2.5)$$

Mostly this model is applicable for organic compound adsorption on activated carbon and molecular sieves. However, at low solute concentration levels because of not obeying Henry law, this model is not appropriate [48].

2.4.1.3.Sip model

Sip model is a three-coefficient isotherm. This model is a combination of Langmuir and Freundlich models [51]. Therefore, this model overcomes Langmuir and Freundlich limitations. The below equation describes Sip isotherm:

$$q_e = \frac{Q_{max} K_s C_e^{n_s}}{1 + K_s C_e^{n_s}} \quad (2.6)$$

, where K_s is Sip constant, which describes the affinity between adsorbate and adsorbent. Also, Q_{max} (mg g^{-1}) is the maximum adsorption capacity. Value of n_s describes surface heterogeneity. The parameter q_e represents adsorption capacity measured in mg g^{-1}. C_e is the equilibrium concentration of adsorbate in solution measured in mg L^{-1}.

In contrast to the Freundlich model, at low concentration Sip isotherm obeys Henry's law. Additionally, this model is able to predict the maximum adsorption capacity for adsorbent [51].

2.4.2. Multicomponent adsorption isotherm

To predict the experimental data obtained through binary adsorption, it is possible to treat the system as a single-solute adsorption. However, in this situation, the interaction between adsorbate and adsorbent is not considered [52]. To consider the interactions between adsorbate and adsorbent, two extended isotherms models were used to predict the mixture adsorption experimental data.

2.4.2.1.Extended Langmuir model

This model describes competitive adsorption. Eq. (2.7) describes extended Langmuir model for component j in an N-component adsorbate solution.

$$q_e = \frac{Q_{max,j} K_{L,j} C_{e,j}}{1 + \sum_{j=1}^{N} K_{L,j} C_{e,j}} \qquad (2.7)$$

Here in Eq. (2.7), Q_{max} and K_L have the same meaning similar to Langmuir single-solute isotherm as explained in section 2.4.1.

The extended Langmuir isotherm can be used when all adsorbates in the solution have the same value of maximum adsorption capacity [52]. However, this assumption is not satisfied in competitive adsorption system. Therefore, extended Langmuir isotherm was modified by Jain and Snoeyink in 1937. The new extension Langmuir was described as below:

$$q_{e,1} = \frac{(Q_{max,1} - Q_{max,2}) K_{L,1} C_{e,1}}{1 + K_{L,1} C_{e,1}} + \frac{Q_{max,2} K_{L,2} C_{e,2}}{1 + K_{L,2} C_{e,2} + K_{L,1} C_{e,1}} \qquad (2.8)$$

$$q_{e,2} = \frac{Q_{max,2} K_{L,2} C_{e,2}}{1 + K_{L,2} C_{e,2} + K_{L,1} C_{e,1}}$$

Here in Eq. (2.8), Q_{max} and K_L have the same meaning similar to Langmuir single-solute isotherm as explained in section 2.4.1. Eq. (2.8) was proposed based on the assumption that only the fraction of adsorbing sites that are available for component one could be occupied by component two [52].

2.4.2.2.Extended Sip model

Single solute sip isotherm can be extended to a binary system as well [53]. Eq. (2.9) indicates extended sip model for j component in an N-component system.

$$q_e = \frac{Q_{max,j} K_{s,j} C_{e,j}{}^{n_{s,j}}}{1 + \sum_{j=1}^{N} K_{s,j} C_{e,j}{}^{n_{s,j}}} \qquad (2.9)$$

, where Q_{max}, K_s, and n_s have the same meaning similar to Sip single-solute isotherm as explained in section 2.4.1.

2.5. Adsorption thermodynamic characterization

The equilibrium state is invaluable in order to understand the adsorbent capacity for a specific adsorbate and in addition, it describes the interaction between adsorbate and adsorbent [48]. In the equilibrium state, besides using isotherm to understand the adsorption capacity, it is necessary to explore thermodynamics properties of the process. In order to describe the mechanism of adsorption, it is necessary to investigate the temperature effects on the adsorption process and develop thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy change [54].

The investigation of thermodynamic parameters mostly relies on the equilibrium constant value and isotherm model. The significance of thermodynamic parameters will be presented in the following section. Then, methods that can be applied to determine equilibrium constant will be discussed.

2.5.1. Fundamental of thermodynamic

In order to understand the thermodynamic characteristics of an adsorption process, three parameters namely Gibbs free energy, enthalpy, and entropy change should be determined [50]. The following equations indicate the relation between each parameter:

$$\Delta G = -RT\ln K_c \qquad (2.10)$$

$$\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (2.11)$$

$$\Delta G = \Delta H^0 - T\Delta S^0 \qquad (2.12)$$

, here K_c (dimensionless) is the equilibrium constant, R is universal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$), and T is the temperature in Kelvin. Enthalpy and entropy variation can be obtained by determination of slope and intercept of the linear graph between $\ln K_c$ and T^{-1}.

Gibbs free energy change exhibits weather an adsorption process is spontaneous or not [55]. In order to have a spontaneous adsorption process, this value should be negative. The greater negative value of this parameter indicates that the process is more favorable and if this value is positive, the process does not happen spontaneously [56].

Another important parameter that its value determines the type of the adsorption process is enthalpy change. According to the thermodynamic point of view, enthalpy change indicates the amount of heat that is required for the process and this heat could be released or absorbed. The magnitude of enthalpy change provides useful information for understanding the type of adsorption. The magnitude of this value indicates that either the adsorption is physisorption or chemisorption. When the value of enthalpy change is less than 80 kJ mol^{-1}, the bonds between adsorbate and adsorbent are weak and physisorption occurs [54]. However, if the value of enthalpy change is higher than 80 kJ mol^{-1}, then chemisorption happens and bonds between adsorbate and adsorbent are strong [54]. The differences between physisorption and chemisorption are listed in Table 2.1 [54].

Table 2.1 Characteristics of physical and chemical adsorption [54]

Property	Physical adsorption	Chemical adsorption
Type of bonding forces	Van der Waals	Similar to a chemical bond
Adsorption heat	Low, 10-80 kJ mol^{-1}	High, 80-200 kJ mol^{-1}
Reversibility	Fully reversible	Irreversible
Formation of multilayer	Yes	No

Another interpretation of enthalpy changes in the system is related to its sign. The negative value of this parameter indicates that the adsorption process is exothermic and heat is released from the system, while a positive value shows that the system absorbs heat and it is endothermic [57].

Entropy indicates randomness in the system. The positive value of entropy change represents that randomness in the solid-liquid system increases; however, the negative value for entropy change describes that randomness in the adsorption system decreases. Based on Eq. (2.12), in a spontaneous system, it is expected that Gibbs free energy should be negative. If an endothermic process occurs, the sign of entropy change should be positive. While during an exothermic process, the sign of entropy change is negative [57].

2.6. Determination of thermodynamic parameters

2.6.1. Equilibrium Constant

According to Eqs. (2.10) and (2.11), to develop thermodynamic parameters and discuss the thermodynamic characteristics, finding equilibrium constant is essential. This constant depends strongly on the isotherm model that is developed for modeling the equilibrium state [50]. The concerns related to this constant are that first, this parameter should be dimensionless and second, ln K_L vs T^{-1} should have high regression coefficient [50]. To find the equilibrium constant, different procedures were proposed.

The first method for finding this parameter is considering the value of equilibrium constant equal to the Langmuir constant. This method is the easiest procedure. However, this method is not accurate because the Langmuir constant has unit (L mg^{-1}) while, thermodynamic equilibrium constant should dimensionless [50].

The second method was proposed by Khan and Singh [58] for the first time and then this method was modified by Milonjic' [59]. In this method, the distribution coefficient is used in order to find the equilibrium constant. Distribution coefficient can be identified through the following equation:

$$K_d = \frac{q_e}{C_e} \quad (2.13)$$

Here is this equation, K_d (L g^{-1}) represents distribution coefficient, q_e (mg g^{-1}) and C_e (mg L^{-1}) are the adsorption capacity at equilibrium and adsorbate concentration in the solution, respectively [50].

Distribution coefficient value can be found by plotting ln (q_e/C_e) vs C_e. Intersection of the plot with the vertical axis provides distribution coefficient value. This method was proposed based on Henry's law [50].

However, the same problem discussed for the first method is associated with this method. The thermodynamic equilibrium constant determined by this method has a dimension (L g^{-1}). In order to solve this problem, Milonjic' proposed a procedure [59]. According to Milonjic'[59], the equilibrium constant may become dimensionless if the value is multiplied by the density of water (1000 g L^{-1}) at 25 °C. Therefore, the equation for the equilibrium constant will become:

$$\Delta G = -RT\ln K_L = \Delta G = -RT\ln(1000 * K_d) \quad (2.14)$$

2.6.2. Non-isothermal fitting

To find the value of enthalpy and entropy change, experimental data can be fitted non-isothermally with an isotherm, which is incorporated with van't Hoff equation (Eq. (2.11)). In this research, Sip isotherm incorporated with van't Hoff equation was used to predict experimental data non-isothermally. Non-isothermal Sip can be identified as the following equation:

$$q_e = \frac{Q_{max}\exp(-\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R})C_e^{n_s}}{1 + \exp(-\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R})C_e^{n_s}} \quad (2.15)$$

2.7. Knowledge gaps and research objectives

Knowledge Gaps

Even though much research has been done on the adsorption of antibiotics, the focus of these earlier studies has been on removing antibiotics from water. Overall reviewing the literature, a number of areas are identified as the knowledge gaps that justifies the need for further work. These include:

- Most of the earlier works have been conducted with a single antibiotic and the possibility of using the adsorption process in order to remove lincomycin and tetracycline in a mixture in water has not been explored.
- Thermodynamic characterization of lincomycin and tetracycline as a mixture in water has not been conducted.
- Despite the fact that a lot of research has been conducted in order to remove antibiotics from water using adsorption, the feasibility of adsorption in removal of lincomycin and tetracycline from liquid manure has not been studied.

Objectives

In this study, the adsorption process with activated carbon as an adsorbent was used in order to remove two important antibiotics, tetracycline and lincomycin. This study was conducted in order to address the above-mentioned gaps; therefore, the specific objectives of this research are as follows:

1. Evaluate the performance of activated carbon in removal of lincomycin and tetracycline either as an individual or as mixture in water medium. Investigate the effect of antibiotic initial concentration on the adsorption process. Develop an appropriate isotherm to study the adsorption process. The obtained results from single solute adsorption and from binary solution adsorption need to be compared with each other.
2. Effect of temperature on single-solute and binary solution adsorption needs to be studied. Thermodynamic parameters should be determined. A comparison between the results from a single solute and binary solution need to be carried out.
3. The capability of activated carbon in removal of lincomycin and tetracycline in manure slurry needs to be evaluated.

Chapter 3

MATERIALS AND METHODS

This chapter describes materials that were used in all experiments, as well as experimental procedures and analytical methods.

3.1. Materials

Analytical grade monohydrochloride lincomycin ($C_{18}H_{34}N_2O_6S$•HCl) and tetracycline ($C_{22}H_{24}N_2O_8$) were obtained from Alfa Aesar, Canada. Important specifications for these antibiotics are listed in Table 3.1 [60].

Table 3.1 Physiochemical properties of the selected antibiotics [60]

	Tetracycline	**Lincomycin hydrochloride**
Form	Crystalline powder	Crystalline powder
Molecular Weight	444.43	443
pKa	3.3, 7.7, 9.7	7.8
Melting Point	172-174 ℃	156-158 ℃
Solubility in water at (25°C)	12×10^3 mg L^{-1}	50×10^3 mg L^{-1}

Deionized water (18.2 MΩ.cm at 25 °C) was used to prepare antibiotic solutions with concentrations of 20, 40, 60, 100, 200, 300 mg L^{-1}.

Commercial Cabot Norit 1240 that was used as the adsorbent was purchased from Cabot Corporation, Canada.

Manure slurry was collected from the swine barn of the Prairie Swine Center Inc. in Saskatoon, SK. Within the barn, manure was collected from the manure pit of a production room with grower pigs weighing between 25-28 kg, which were not treated with antibiotics. Six 10-L containers were filled with manure screened using a commercial wire mesh with 120 μm pore size. The containers were brought to the laboratory at University of Saskatchewan, and then the contents of six containers were transferred into a 60-L barrel and kept in refrigerator at 4 ℃.

3.2. Experimental Procedures

3.2.1. Adsorbent preparation

Before using adsorbent in adsorption experiments, it was grounded and sieved to 60-120 mesh size. It was then washed with deionized water several times to make sure that dust was removed. Finally, it was dried at 110 ℃ in an oven and after cooling stored in a desiccator.

3.2.2. Equilibrium time determination

Equilibrium time is an important component of adsorption processes. At first, it is required to determine equilibrium time before starting other experiments. To find the equilibrium time, the following experiment at room temperature (22 ℃) was done:

Solutions of 60 and 100 mg L^{-1} of each antibiotic, lincomycin and tetracycline, were prepared. Then, 100 ml of each solution was added to flasks. Each flask contained 0.01% (0.1 g L^{-1}) of activated carbon, based on the earlier study done by Balladares [52].

All flasks were shaken at 130 rpm for 8 days. Samples were taken from each flask on a daily basis and analyzed for antibiotic concentration using an HPLC. The time at which the difference in concentration of antibiotic in two consecutive days was less than 1 mg L^{-1} was selected as the adsorption equilibrium time.

3.2.3. Adsorption experiments in water

3.2.3.1. Investigating the effect of antibiotic initial concentration at different temperatures on adsorption capacity

Adsorption experiments at different initial concentrations were done to see how initial concentrations of individual antibiotic could affect activated carbon adsorption capacity. To satisfy this objective, different initial concentrations were chosen including 20, 40, 60, 100, 200, and 300 mg L^{-1}. These concentrations are above practical levels, but they were chosen to assess the ultimate capability of the activated carbon to remove tetracycline and lincomycin. Additionally, to investigate whether temperature could affect activated carbon adsorption, adsorption experiments were carried out at different temperatures of 5, 12, 22, and 32 ℃. The highest temperature was chosen based on the average temperature of Saskatoon during spring and summer and the lowest temperature was set at 5 ℃ because it represented a low temperature above the freezing point.

To prepare the solutions with the designated initial concentrations, the required amount of either tetracycline or lincomycin was weighted and dissolved in deionized water. Then 100 ml of each prepared solution was poured into the flask. To avoid photodegradation of tetracycline, amber flasks were used. Each flask contained 0.01% (0.1 g L^{-1}) of activated carbon based on the earlier work done by Balladares [52]. To study the effect of temperature on activated carbon adsorption capacity Chemviron environmental chamber was used.

In order to ensure accurate temperature was used at the beginning of experiments, preparation of various flask with different antibiotic concentrations were conducted inside the chamber and solutions was kept in the chamber. As part of experiments, flasks were shaken at 130 rpm for 7 days to reach equilibrium time, as determined by the procedure described in section 3.2.2. Every two days, samples were taken from each flask and analyzed with HPLC to determine lincomycin and tetracycline concentrations. All experimental data were fitted into Langmuir, Freundlich and Sip model, using nonlinear fitting and Excel software as explained in section 2.4.1.

3.2.3.2.Studying the effect of initial concentrations of antibiotics in a binary mixture at different temperatures on adsorption capacity

To assess the capability of activated carbon to remove binary components, adsorption of lincomycin and tetracycline in the mixture was studied. Furthermore, to study whether initial concentration variation might affect adsorption capacity for the antibiotic mixture, different initial concentrations were evaluated. The value of initial concentrations was similar to those used in the experiments with individual antibiotics (50% of each antibiotic in the mixture solutions) to facilitate the comparison. These concentrations included 20, 40, 60, 100, 200, and 300 mg L^{-1} of each antibiotic in mixture. The effect of temperature was assessed conducting the experiments at 5, 12, 22, and 32 ℃.

Adsorption experiments were carried out following the procedure indicated in the previous section. Based on initial concentration, required amount of each antibiotic, lincomycin or tetracycline was weighed and dissolved in deionized water with specification mentioned in section 3.1. Finally, 100 ml of each concentration solution was poured into flask. To avoid photodegradation of tetracycline, dark flasks were used. Each flask contained 0.01% (0.1 g L^{-1}) of activated carbon based on the earlier work done by Balladares [52].

In order to study binary adsorption at different temperature, Chemviron environmental chamber was used. To ensure that accurate temperature was used at the beginning of experiments, preparation of various flask with different antibiotic concentrations were conducted inside the chamber and solutions were kept in the chamber. As part of experiments, flasks were shaken at 130 rpm for 7 days to reach equilibrium time, as determined by the procedure described in section 3.2.2. Every two days, samples were taken from each flask and analyzed with HPLC to determine lincomycin and tetracycline concentrations. All experimental data were fitted with extended Langmuir and extended Sip isotherm, using nonlinear fitting and Excel software as explained in section 2.4.1.

3.2.4. Adsorption experiments in manure

3.2.4.1.Manure preparation

Before each experiment, first manure in the main container was shaken for 30 second. Second, 1 L of manure was collected from the container and poured into an Erlenmeyer. Manure in the Erlenmeyer was kept in the refrigerator at 4 ℃ for 24 hours to let particulates settle down. Finally, 500 mL of the supernatant manure was removed and centrifuged. The resulting liquid was then used in the adsorption experiments.

3.2.4.2. Tetracycline stability in manure

In order to study adsorption in liquid manure, it is important to investigate whether the antibiotic concentration remains stable in manure or decreases with time. Therefore, an experiment was carried out to observe tetracycline concentration in manure over time. To run the experiment, different concentrations were chosen, namely 20, 40, 60, 80, and 100 mg L^{-1}. Before, preparation of tetracycline solution, manure slurry was pretreated based on procedure explained in previous section. The required amounts of tetracycline to prepare different concentrations were weighted. Then, it was added to an Erlenmeyer, which contained

centrifuged manure. The manure solution with tetracycline was then stirred for 2 hours to make sure that all tetracycline was dissolved in manure.

Finally, 100 ml of each mixture was poured to flasks. Each flask was shaken at 130 rpm and sampled daily. Samples were kept in freezer at -80 ℃ to make sure that tetracycline degradation could not happen in samples until analysis by HPLC. The required time at which the difference in concentration of antibiotic in two consecutive days was insignificant was selected as the equilibrium time.

3.2.4.3.Adsorbent dosage and adsorption process

To determine the capability of activated carbon to remove tetracycline in manure, adsorption experiments were carried out. To accomplish this objective, two concentrations were chosen, 40 and 100 mg L^{-1}. Before, preparation of tetracycline solution, manure slurry was pretreated based on procedure explained in section 3.2.4.1. For preparation of tetracycline in manure, the procedure explained in the previous section was used.

Flasks were shaken at 130 rpm. The first sample was taken from each flask immediately after preparation and it was analyzed with HPLC to measure the initial tetracycline concentration. Then again, samples were taken from each flask on 8^{th} and 9^{th} day after preparation as explained in the previous section and were analyzed with HPLC to measure tetracycline concentration to make sure that tetracycline concentration became stable. Finally, into the remaining solutions, tetracycline was added again and the flasks were stirred for two hours to let tetracycline dissolve in solution and reach the selected concentration. Then, the new tetracycline solutions were poured into the flask which contained different amounts of activated carbon namely 50, 80, 150, 200, 300, and 500 mg of activated carbon.

3.3. Analytical methods

3.3.1. Determination of lincomycin and tetracycline concentration using HPLC

An Agilent HPLC (1200 Series) with a ZORBAX SB-C18 column (4.6 x 150 mm, 5 µm) was used to determine the concentration of tetracycline and lincomycin in deionized water. The mobile phase was 50 mM KH_2PO_4 and acetonitrile (80:20 ratio) at a flow rate of 1 mL min^{-1} with a sample injection volume of 20 µL. Tetracycline and lincomycin peaks were detected at wavelengths of 360 and 200 nm, respectively. Retention time was 3.12 ± 0.5 minutes for tetracycline and 4.43 ± 0.5 minutes for lincomycin.

A calibration curve was developed for each antibiotic using standard concentrations in the range 1 to 100 mg L^{-1} . The correlations coefficinets were 99.69% for lincomycin and 99.98% for tetarcycline. Figure A.1 in Appendix I shows tetracycline and lincomycin caliberation curves.

The same HPLC column with a slightly modified mobile phase (1 mmolar formic acid and acetonitrile; 85:15 ratio) was used for analysis of tetracycline concentration in manure solution. The flow rate of mobile phase was 1 $\mathrm{mL\ min^{-1}}$ and a sample with an injection volume of 20 µL was used. Retention time for tetracycline was 7 ± 0.5 min. A calibration curve was developed for tetracycline detection in manure using standard concentrations in the range 1 to 100 mg L^{-1}. The correlation coefficient was 90.54%. Figure A.2 in Appendix A shows tetracycline calibration curve in manure.

3.3.2. Reproducibility and uncertainty analysis

During experiments, the average values of lincomycin and tetracycline concentration were calculated from duplicate samples. Reported data was the average of analysis for duplicate sampling and error bars represent standard deviation.

3.4. Adsorbent characterization

3.4.1. Surface area and pore size distribution measurement

Adsorbent surface area and porosity were determined based on Brunauer-Emmert-Teller (BET) method using an Accelerated Surface Area and Porosimeter system (ASAP 2020, Micromeritics).

3.4.2. Scanning electron microscopy

Surface morphology of activated carbon was investigated using high-resolution field emission scanning electron microscope (FE-SEM, Hitachi SU8000), with a voltage of 3keV.

3.4.3. Zeta potential determination

Zeta potential was determined using Malvern zetasizer nano series (Nano ZS). To obtain zeta potential, 0.01 M NaCl solution was prepared at different pH ranging from 2-10. Then, 0.1 g L^{-1} of the adsorbent was added to each solution. Then, each solution was sonicated for 20 min using VWR Symphony ultrasonic. Finally, the obtained zeta potential for each sample was plotted versus pH.

3.5. Analysis of Adsorption data

3.5.1. Determination of adsorption capacity

Eq. (3.1) was used to determine the adsorption capacity.

$$q_e = \frac{(C_0 - C_{e)}V}{M} \qquad (3.1)$$

, where C_0 (mg L^{-1}) is the initial concentration of adsorbate in solution, C_e (mg L^{-1}) is the equilibrium concentration of adsorbate in solution, V (L) is the volume of solution, M (g) indicates the quantity of used adsorbent (dry weight) and q_e (mg L^{-1}) represents the amount of adsorbate adsorbed by adsorbent at equilibrium [50].

3.5.2. Adsorption isotherms for single solute

In this research, Langmuir, Freundlich, and Sip isotherm models were used to model the experimental data based on Eqs. (2.1), (2.4), and (2.6), respectively as explained in section 2.4.1. Sip model is considered as a combination of Langmuir and Freundlich models.

3.5.3. Adsorption isotherm for binary system

To model the experimental data obtained through binary adsorption, it is possible to treat the system like a single-solute adsorption. However, in this situation, the interaction between adsorbate and adsorbent is not being considered. To consider the interactions between adsorbate and adsorbent, two extended isotherm models were also used to predict the mixture adsorption experimental data.

Extended Langmuir isotherm was used to predict the experimental data for lincomycin and tetracycline in the mixture based on Eq. (2.8) as explained in section 2.4.2. Furthermore, extended Sip model was used according to Eq. (2.9) as explained in section 2.4.2 to study more on obtained experimental data.

In addition, the binary adsorption experimental data were fitted with single-solute isotherms.

3.5.4. Adsorption equilibrium fitting

In this research, Excel software was used to fit the experimental data nonlinearly with Langmuir, Freundlich, and Sip isotherm equations. GRC nonlinear function was used. This was carried out by minimizing the objective function (Eq. (3.2)), defined as the sum of squares of differences between the experimental data and predicted adsorption capacities.

$$f = \sum_{i} \left(q_{e,i} - q_{cal,i}\right)^2 \qquad (3.2)$$

, where q_e represents the experimental data calculated from Eq. (3.1) mentioned in section 3.5.1. Parameter q_{cal} demonstrates the calculated adsorption capacity. i indicates the data point at each initial concentration (20, 40, 60, 100, 200, and 300 mg L^{-1}) [50].

It is important to distinguish which isotherm model can predict the experimental data well compared to other ones. To identify the most suitable isotherm, Chi-squared (Eq. (3.3)) and R-squared (Eq. (3.4)) parameters were used.

$$x^2 = \sum_{i} \frac{\left(q_{e,i} - q_{cal,i}\right)^2}{q_{cal,i}} \qquad (3.3)$$

$$R^2 = 1 - \frac{\sum_i \left(q_{e,i} - q_{cal,i}\right)^2}{\sum_i \left(q_{e,i} - q_{e,mean}\right)^2} \qquad (3.4)$$

, where q_{mean} is the average value of all experimental adsorption capacities [50].

3.5.5. Adsorption thermodynamic characterization

Equilibrium state is an invaluable state in order to determine the adsorption capacity for a specific adsorbent and in addition, it describes the interaction between adsorbate and adsorbent. At equilibrium state, besides using isotherm models to determine the adsorption capacity, it is necessary to explore thermodynamic properties of the process. In order to describe the mechanism of adsorption, it is necessary to investigate the temperature effects on the adsorption process and develop thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy change in adsorption process.

In this research, thermodynamic parameters were determined through linearization using distribution coefficient based on Eq. (2.11) as explained in section 2.5.1. Furthermore, experimental data were fitted non-isothermally into sip model incorporated with van't Hoff equation Eq. (2.15) as explained in section 2.6.2. The objective function Eq. (3.2) was minimized through GRC method in Excel software.

Chapter 4

RESULTS AND DISCUSSIONS

The following chapter presents all the results obtained through characterization of adsorbents and the adsorption experiments in water. Section 4.1 presents the results of activated carbon characterization including zeta potential and surface area determination and SEM spectroscopy. In sections 4.3.1 and 4.3.2 adsorption of individual tetracycline and lincomycin, as representative antibiotics, are presented and discussed. Effect of different parameters on the adsorption as well as the results of modeling the experimental data with different isotherm models are explained. Thermodynamic parameters, determined for adsorption of tetracycline and lincomycin in water, are presented. In section 4.3.3, the results of binary adsorption and how different parameters affected the adsorption of antibiotics in a mixture are discussed. The results obtained through modeling with different isotherms are explained and thermodynamic parameters for the adsorption are presented. In the last section, adsorption results in the manure slurry are presented.

4.1. Adsorbent Characterization

4.1.1. Isoelectric point determination

Adsorbents particles can have positive or negative surface charge in water. This depends on the solution pH and adsorbent characteristics. Electrical state of an adsorbent's surface can be assessed through determination of either point of zero charge (PZC) or isoelectric point (IEP).

Isoelectric point value demonstrates the external surface charge of adsorbent, while point of zero charge indicates the total surface charge (external and internal) [61]. The difference between IEP and PCZ value may be interpreted as an adsorbent's surface charge distribution [61]. The value greater than zero represents an external surface that is negatively charged more than internal surface; however, the value closes to zero represents the homogenous surface charge distribution [61].

IEP point of activated carbon was determined at room temperature. NaCl solutions with different range of pH (2-10) were prepared as previously explained in section 3.4.3. The activated carbon zeta potential as a function of pH is demonstrated in Figure 4.1.

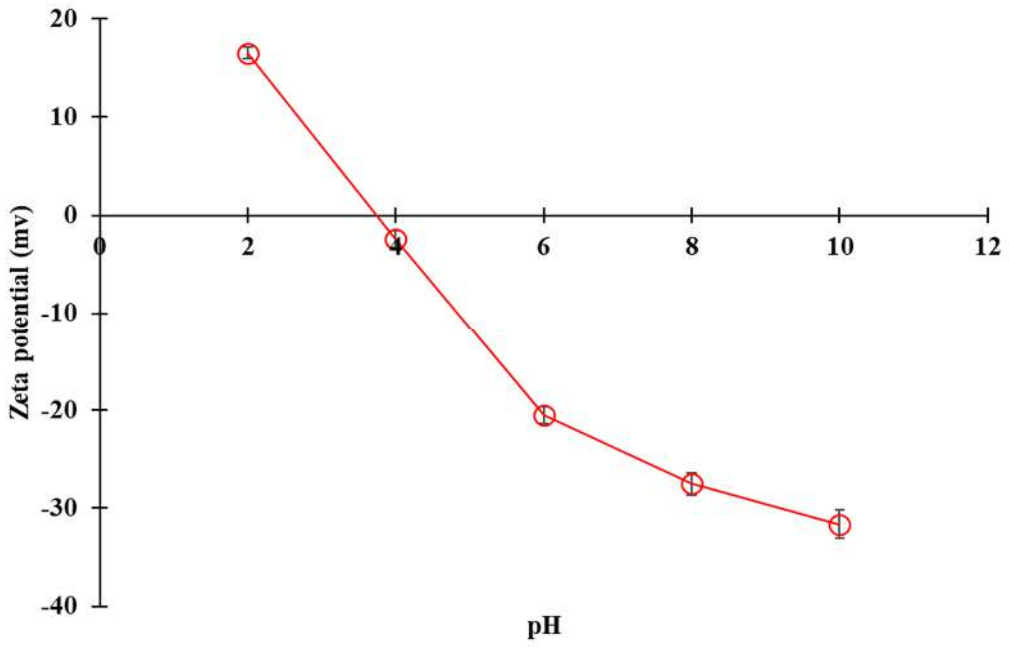

Figure 4.1 Activated carbon zeta potential as a function of pH

According to Figure 4.1 zeta potential for activated carbon decreases from 16.53 mv to 31.63 mv when solution pH is increased from 2 to 10. Isoelectric point for activated carbon is determined around 3.7. This means that at pH values above 3.7, activated carbon has negative external surface charge, while at pH values below 3.7, external surface of activated carbon is positively charged.

PZC was determined for the chosen activated carbon in an earlier study by Balladares [62]. The value of PZC for the activated carbon used in current study was determined as 10.3. The difference between IEP and PZC, indicates that external surface of activated carbon is more negatively charged compared to its internal surface.

4.1.2. Adsorbent surface area and pore size distribution

Activated carbon porosity was characterized by physical adsorption of nitrogen at -196 ℃ using Accelerated Surface Area and Porosimeter system (ASAP 2020, Micromeritics). Surface area was determined using Brunauer, Emmet and Teller (BET) isotherm model. Activated carbon pore size distribution was determined using Barrrett–Joyner–Halenda (BJH) method.

Figure 4.2 shows the N_2 adsorption-desorption isotherms acquired for the activated carbon.

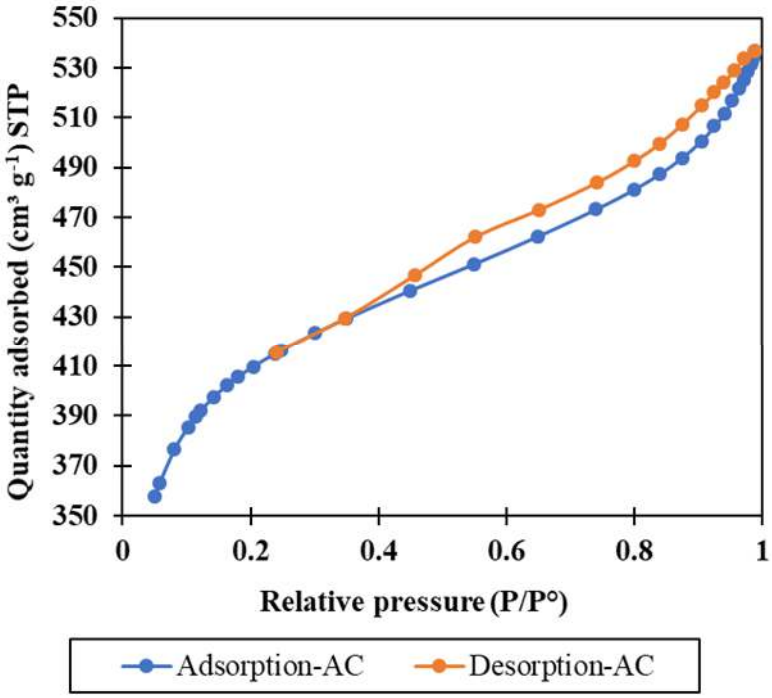

Figure 4.2 N_2 Adsorption-desorption isotherms of activated carbon at 77 K

According to Figure 4.2 activated carbon exhibits a combination of Type I and Type II adsorption-desorption isotherms based on the IUPAC (International Union of Pure and Applied Chemistry) adsorption isotherms classification [63]. This implies that activated carbon has a combination of micropores (pore size < 2 nm) and mesopores (2 nm<pore size<50 nm). The hysteresis loops in the isotherm is assigned to type H4 (in agreement with IUPAC classifications), indicative of the presence of slit-shaped pores characteristic of activated carbons [63].

The pore size distribution of AC is shown in Figure 4.3. According to Figure 4.3, pore size concentration of activated carbon is between 2 and 10 nm and D_p the average pore diameter (4V/A) calculated by BJH adsorption for AC is 5.12 nm.

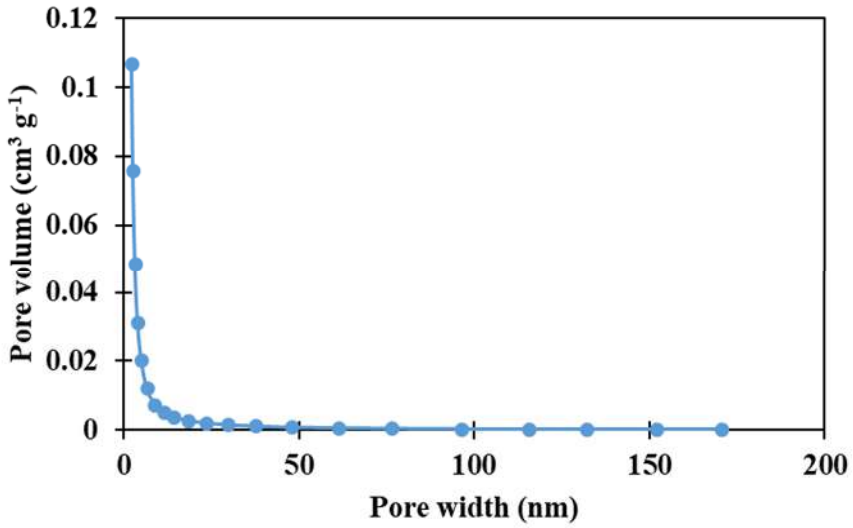

Figure 4.3 Pore size distribution of activated carbon

Total pore volume for activated carbon was determined based on nitrogen volume that adsorbed. Activated carbon surface area was determined from summation of microporous surface area (S_{micro}) and external surface area (S_{ext}). Mesoporous volume (V_{meso}) was calculated by subtraction of total pore volume (V_t) and microporous pore volume (V_{micro}). The textural parameters of AC are presented in Table 4.1.

Table 4.1 Textural parameters obtained from nitrogen adsorption isotherms of activated carbon

Sample	S_{BET} ($m^2\ g^{-1}$)	S_{ext} ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)	V_t ($cm^3\ g^{-1}$)	$(D_p)_{avg}$ (nm)
AC	1302	587	715	0.38	0.45	0.83	5.12

4.1.3. Scanning electron microscopy (SEM)

Figure 4.3 represents the results obtained through SEM analysis for activated carbon.

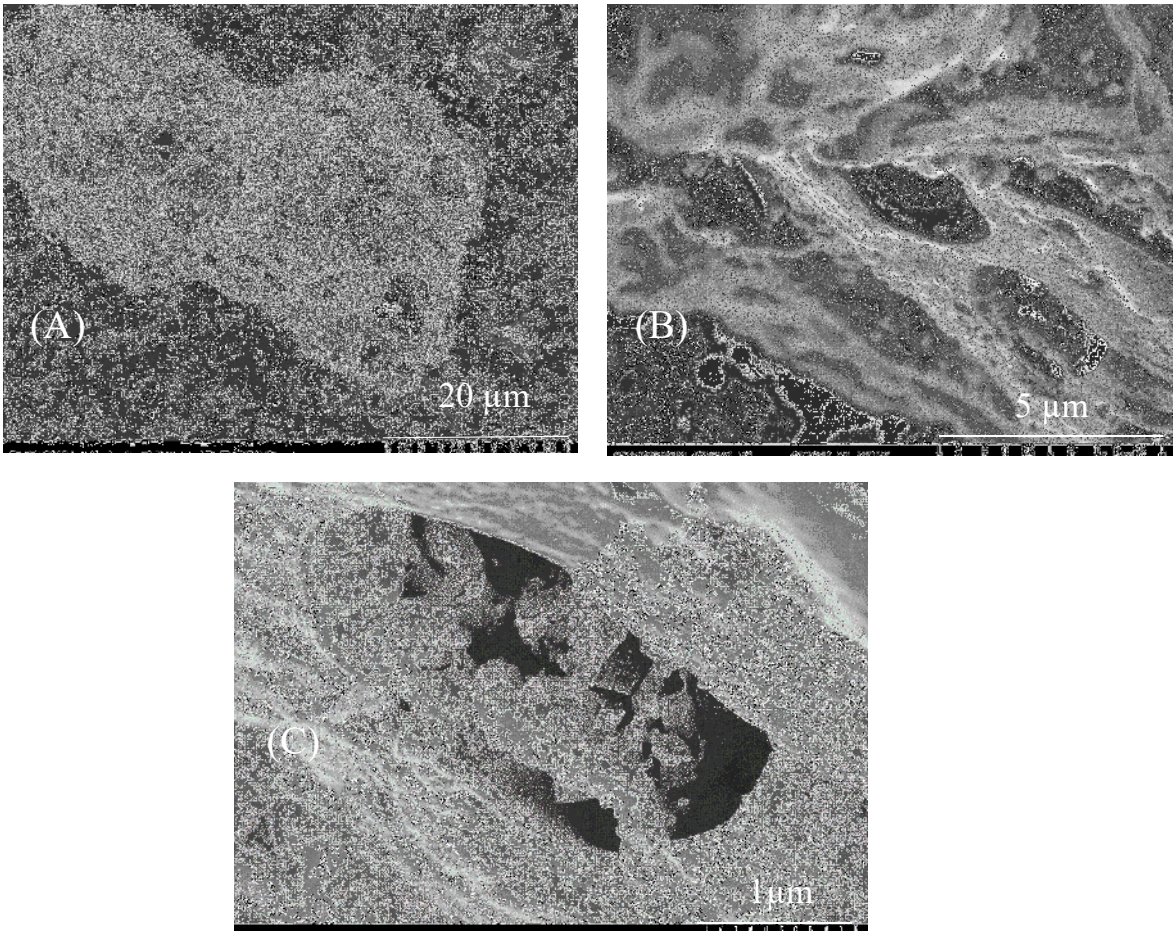

Figure 4.4 SEM images for activated carbon at different magnifications (A) 20 µm, (B) 5 µm, and (C) 1 µm

4.2. Determination of Adsorption Equilibrium time

To study the adsorption process, it is essential to determine equilibrium time. A procedure as mentioned in section 3.1.3 was used to determine equilibrium time for lincomycin and tetracycline adsorption. Figure 4.5 demonstrates the profile of concentration of lincomycin and tetracycline as a function of time. The average values of lincomycin and tetracycline concentration were calculated from duplicate samples. Reported data was the average of analysis for duplicate sampling and error bars represent standard deviation.

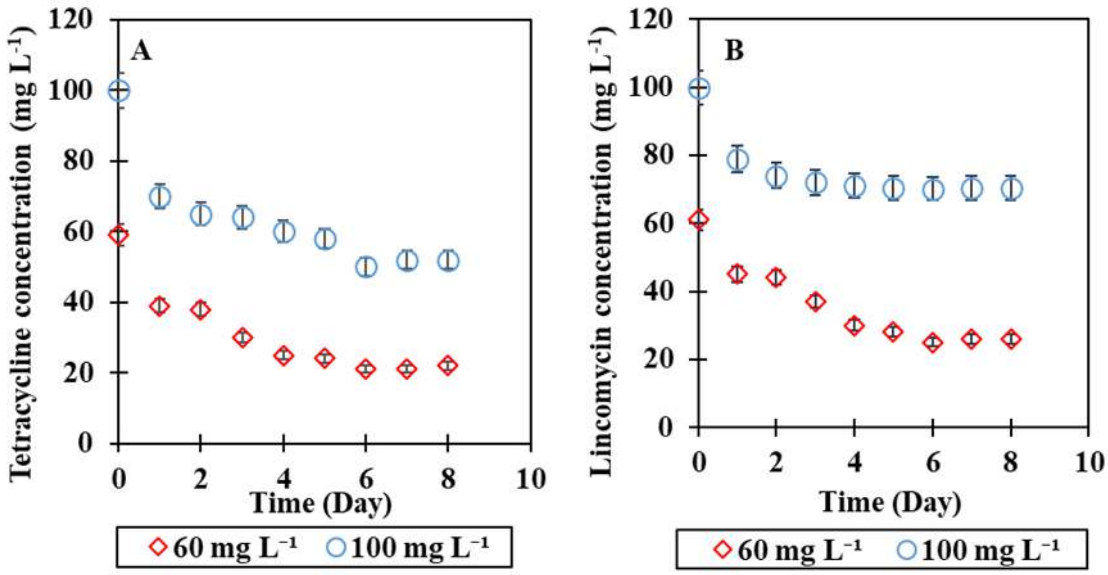

Figure 4.5 Profile of concentration of tetracycline (Panel A) and lincomycin (Panel B) as function of time for two initial concentrations of 60 and 100 mg L^{-1}. Error bars are standard deviation for duplicate sampling.

As seen in Figure 4.5, tetracycline concentration (with the initial concentration of 60 and 100 mg L^{-1}) does not change significantly after 6 days. For the initial concentration of 100 mg L^{-1}, after 6 days the solution concentration becomes 58 mg L^{-1}, while in 7 and 8 days this value are 57.5 and 57.1 mg L^{-1}, respectively. This trend is observed for lincomycin as well. Therefore, the equilibrium time for both tetracycline and lincomycin adsorption corresponded to 7 days. This result is comparable with a similar study which reported an equilibrium time of 7 days using activated carbon made from biochar in order to remove tetracycline from water at room temperature and pH=7 [64].

4.3. Adsorption equilibrium

4.3.1.Tetracycline

4.3.1.1. Effect of concentration and temperature

To develop adsorption isotherms for tetracycline, experiments were carried out based on the procedure explained in section 3.2.1. Figure 4.6 shows how different initial concentrations at different temperatures could affect the tetracycline adsorption.

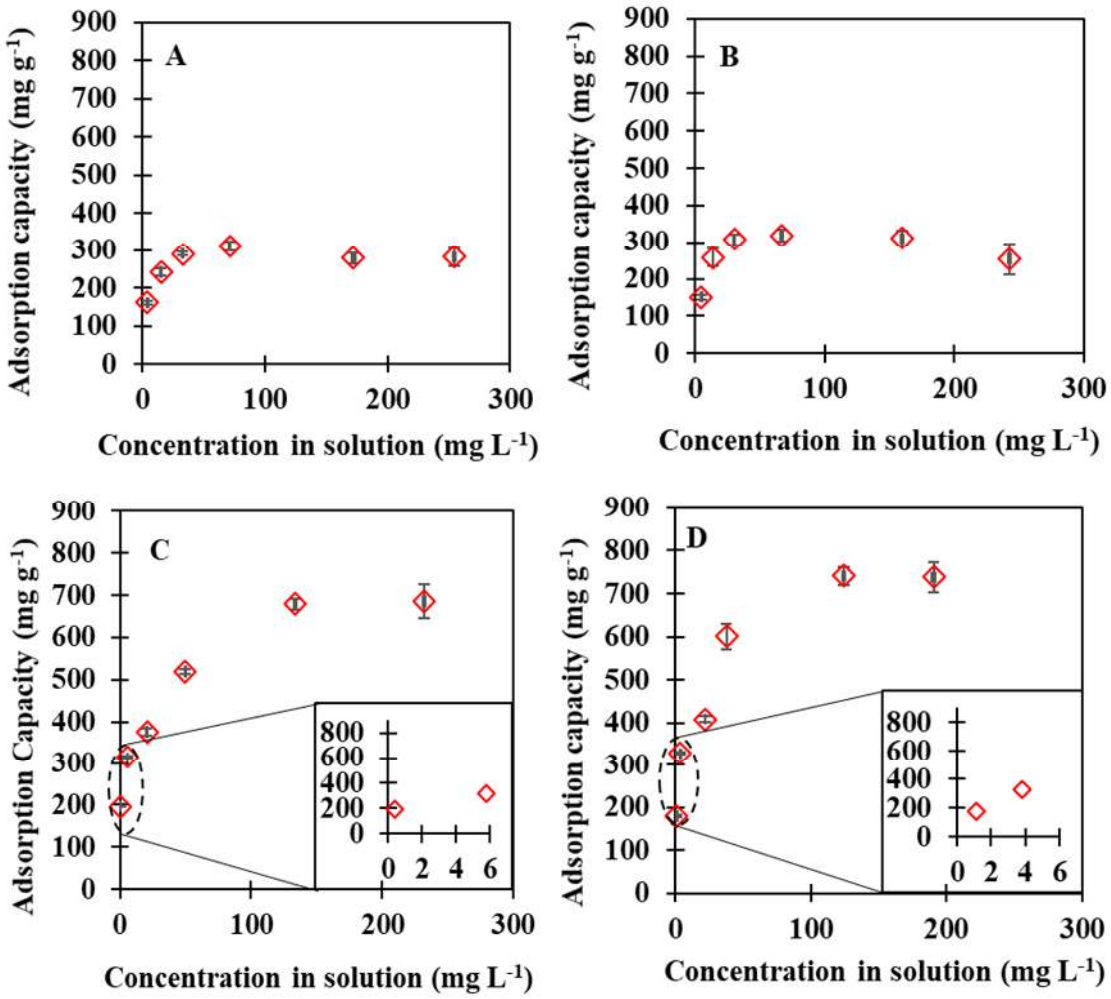

Figure 4.6 Effect of initial concentration and temperature on tetracycline adsorption process. (A) 5 ℃, (B) 12 ℃, (C) 22 ℃, and (D) 32 ℃ on. Error bars are standard deviation for duplicate sampling.

According to Figure 4.6, regardless of temperatures, increasing the tetracycline initial concentration from 20 to 100 mg L^{-1} increased the adsorption capacity. This is possibly happening because the higher initial concentration means a higher mass transfer driving force [65]. However, further increase in concentration beyond 100 mg L^{-1}, the adsorption capacity does not increase. Less increase of adsorption capacity at higher concentrations than 100 mg L^{-1} may indicate that available active sites of activated carbon are saturated [66]. Similar results were obtained by Jiang et al. [66] who investigated the removal of 17 β-Estradiol from water using graphene oxide nanosheets at pH=7 and room temperature. According to these authors adsorption capacity for graphene oxide increased when the initial concentration of pollutant increased from 20 to 60 mg L^{-1}. However, by increasing initial concentration from

60 to 80 mg L^{-1}, adsorption capacity did not change anymore. This was ascribed to the point that graphene oxide available actives sites were saturated.

Results also showed that temperature could affect tetracycline uptake positively. According to Figure 4.6, adsorption capacity at an initial concentration of 300 mg L^{-1} increases from 300 mg g^{-1} to 800 mg g^{-1} when the temperature is elevated from 5 ℃ to 32 ℃, respectively. This increase can be attributed to the mobility of adsorbate which increases when the temperature rises. As a result, a number of molecules that could across the boundary layer between adsorbate and adsorbent increases [67]. Therefore, increasing the mobility of tetracycline in water could increase the interaction between tetracycline and activated carbon. Additionally, an increase in adsorption capacity due to increase of temperature could be a sign of an endothermic process [68]. Ghaedi et al. [67] investigated the feasibility of adsorption process to remove a dye, Direct Yellow 12, from water using magnetic graphene oxide. According to these authors, the adsorption capacity increased when the temperature rose from 10 ℃ to 60 ℃ [67]. This increase was ascribed to increasing number of molecules that could cross the boundary layer at higher temperature [67].

4.3.1.2. Fitting the tetracycline adsorption data in isotherms

Tetracycline adsorption results obtained at different temperatures were fitted into three isotherm models, namely Langmuir, Freundlich, and Sip. Excel software was used to nonlinearly fit the experimental data to Eqs. (2.1), (2.4), and (2.6) as explained in section 2.4.1 and to determine the associated parameters. This was carried out by minimizing the sum of squares of differences between experimental and theoretical results for adsorption capacities as explained in section 3.5.4 using GRC nonlinear function of Excel software. To identify the most suitable isotherm, a procedure explained in section 3.5.4 was used.

Figure 4.7 represents the quality of fit of different isotherms for tetracycline adsorption at 5 ℃ and Table 4.2 summarizes the associated coefficients related to each model. The results obtained at other temperatures followed similar patterns and are presented in appendix B.

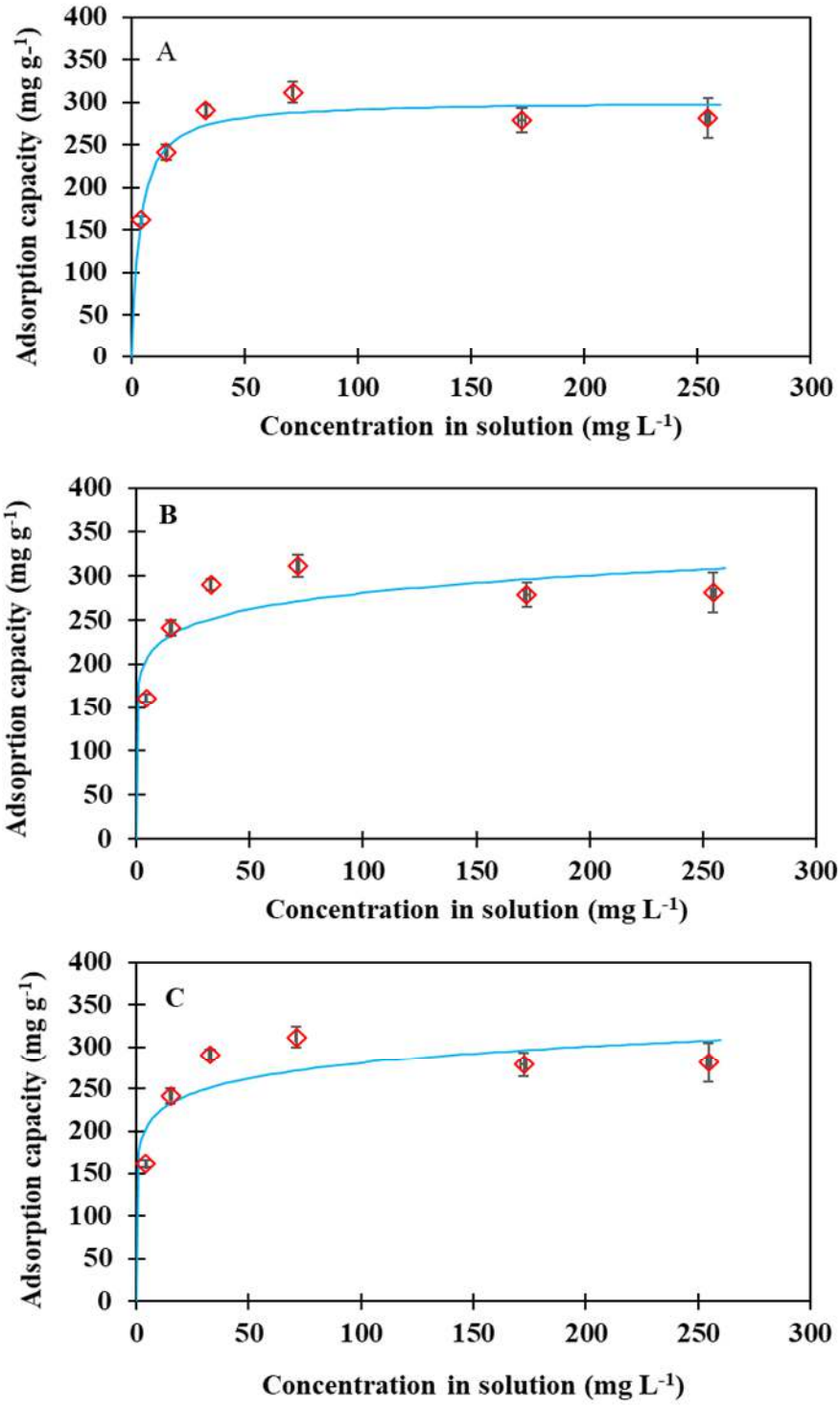

Figure 4.7 Tetracycline adsorption experimental results (symbols) and model predictions (lines) for (A) Langmuir, (B) Freundlich, (C) Sip isotherms. Error bars are standard deviation for duplicate sampling.

Table 4.2 Calculated parameters for different isotherms for tetracycline adsorption

Langmuir				
Temperature (℃)	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_L}$ ($L\ mg^{-1}$)	$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	301	0.29	0.897	5.29
12	312	0.26	0.971	19.14
22	684	0.10	0.772	126.1
32	723	0.15	0.872	111.18

Freundlich				
Temperature (℃)	$\mathbf{K_F}$ ($mg\ g^{-1}$)($L\ mg^{-1}$)$^{1/n}$	**n**	$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	178	0.10	0.573	25.16
12	187	0.09	0.368	49.89
22	216	0.20	0.974	11.19
32	218	0.39	0.947	31.90

Sip					
Temperature (℃)	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_s}$ ($L\ mg^{-1}$)	$\mathbf{n_s}$	$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	294	0.17	0.76	0.918	4.22
12	302	0.15	0.73	0.851	10.81
22	1100	0.21	0.37	0.955	11.22
32	1249	0.17	0.42	0.965	23.86

According to Table 4.2, based on R^2 and χ^2 (Chi-square) Sip model could predict the experimental data with higher accuracy when compared to Langmuir and Freundlich isotherms. Langmuir model is often inappropriate to predict the experimental data because of its assumptions of monolayer adsorption which might not apply at high concentrations [69]. Freundlich isotherm is an empirical model [69]. The lack of thermodynamic basis is a problem for Freundlich isotherm because, this model at low concentration does not follow Henry's law ($q_e=K_H*C_e$) [70].

According to Table 4.2, the value of maximum adsorption capacity increased from 294 mg g^{-1} at 5 ℃ to 1294 mg g^{-1} at 32 ℃ which indicates that higher temperature is more favorable for adsorption process. During temperature increase, tetracycline molecules' mobility increases as well [67]. Therefore, the number of molecules that could pass the boundary layer between adsorbent and adsorbate increase. This means that the interaction between adsorbent and adsorbate increases and this results in higher adsorption [71]. Similar

results were reported by Chen et al. [72] who studied the removal of a dye at different temperatures using treated biochar prepared from rice husks. According to these authors, adsorption capacity increased from 543.5 to 600.1 mg g^{-1} when temperature increased from 20 ℃ to 30 ℃. This increase was attributed to the increase in the number of molecules that could pass the external boundary layer into internal pores. Also, the obtained results for maximum adsorption capacity are different from the ones calculated from the Langmuir model. Because during fitting in Sip model, experimental data approches to saturation point slowly because of n_s term.

Value of coefficient n_s, indicates the surface heterogeneity. The range of values for n_s is between 0 and 1. If n_s value approches to zero, the surface is more heterogenous, while the value closes to 1, represents the more homogenous adsorption. If the value of n_s equals to unity, Sip model becomes equivalent to the Langmuir model and it describes a purely homogenous surface. Based on Table 4.2, n_s values are far from unity. This means that in tetracycline adsorption heterogenous adsorption is more dominant.

Whether the experimental conditions are favorable for adsorption can be investigated using separation factor (R_L) [73]. R_L (dimensionless) values at different initial concentrations and different temperatures were calculated according to Eq. (2.3) as mentioned in section 2.4.1. A value of separation factor between 0-1, indicates that the examined condition is favorable for adsorption process [73]. Figure 4.8 shows the value of R_L values versus different operating conditions (changes in temperature and initial concentration). According to Figure 4.8, the value of R_L is between 0-1 which indicates that at all operating conditions tetracycline adsorption on activated carbon is favorable. However, at higher initial concentration, the value of R_L approaches to zero which points out that the adsorption process is more favorable at this condition. Saygih et al. [74] Studied the removal of tetracycline (200-400 mg L^{-1}) from water using activated carbon prepared from tomato at different temperatures (15 and 5 ℃). According to these authors, R_L values were between 0.054 and 0.059 for all operating conditions which indicated that adsorption process was favorable.

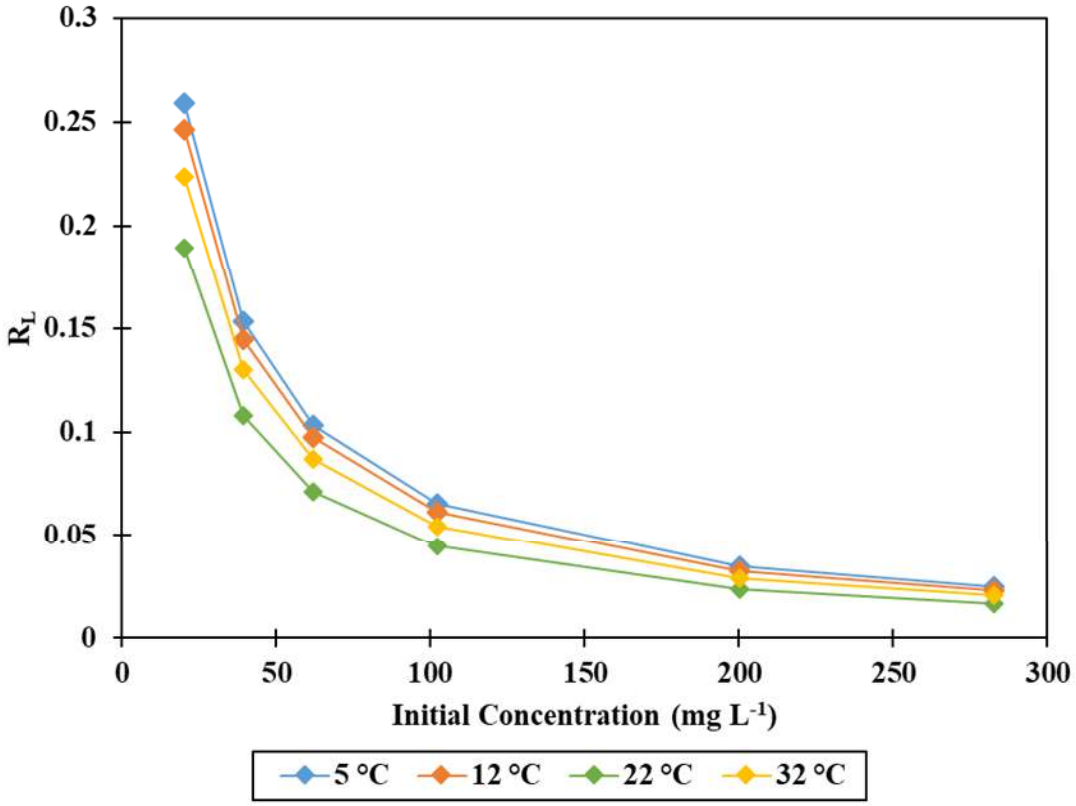

Figure 4.8 R_L values at different initial concentrations and temperatures for tetracycline adsorption

The obtained results were also fitted with Langmuir and Freundlich isotherm models through linearization according to Eq. (2.2) and (2.5) as mentioned in section 2.4.1. All associated coefficients are summarized in Table B.1 in Appendix B.

4.3.1.3. Determination of thermodynamic parameters for tetracycline adsorption

Thermodynamic parameters can help to explain the mechanism of adsorption. Excel software was used to fit all experimental data non-isothermally into Sip model that incorporated van't Hoff expression (Eq. (2.15)) as described in section 2.6.2. Gibbs free energy change was calculated based on Eq. (2.12). The values of thermodynamic parameters were determined using GRC nonlinear function of Excel software by minimizing Eq. (3.2) as described in section 3.5.4.

Table 4.3 represents enthalpy and entropy changes for tetracycline adsorption. Gibbs free energy change values at different temperatures are also listed in Table 4.3.

Table 4.3 Thermodynamic parameters determined through fitting non-isothermally Sip model incorporated with van't Hoff expression for tetracycline adsorption

$\Delta \mathbf{H}$=29400 ($\mathbf{J\ mol^{-1}}$)	
$\Delta \mathbf{S}$=122 ($\mathbf{J\ mol^{-1}\ K^{-1}}$)	
Temperature (℃)	$\Delta \mathbf{G}$ ($J\ mol^{-1}$)
5	-4534
12	-5388
22	-6608
32	-7828

spontaneously, while a positive value shows the nonspontaneous process. According to Table 4.3, Gibbs free energy change values are between -4534 and -7828 J mol^{-1} when temperature increases from 5 ℃ to 32 ℃. Gibbs free energy values are negative at all temperatures which means that the adsorption process is spontaneous at all temperatures. Moreover, Gibbs free energy value increases due to temperature increase. This can indicate that a higher temperature is more thermodynamically favorable [75]. This pattern was expected as previous results show that at higher temperature activated carbon adsorption capacity increases. Similar results were obtained by Acosta et al. [76] who investigated the removal of tetracycline in water using treated biochar prepared from tyre char. According to authors, Gibbs free energy values changed between -19 and -4900 J mol^{-1} when temperature increased from 15 ℃ to 35 ℃.

Sign of enthalpy change determines the endothermic or exothermic nature of the adsorption process. If the change in enthalpy is positive, the process is endothermic, while a negative value shows the exothermic process. According to Table 4.3, enthalpy of adsorption is positive which indicates that an endothermic process occurs. This pattern was expected as previous results demonstrate increasing temperature brings in higher adsorption capacity values. This means that in this solid-liquid system, tetracycline molecules have to displace more than two adsorbed water molecules [77]. Guzel et al. [78] studied the removal of tetracycline from water at pH=7 using biochar prepared from grape pulps. According to the

authors, the adsorption process was endothermic and the value of enthalpy change was 42 kJ mol^{-1}.

Based on the value of enthalpy of adsorption, it is possible to distinguish the type of adsorption as either physisorption or chemisorption. When the value of enthalpy is less than 80 kJ mol^{-1}, the bonds between adsorbate and adsorbent are weak and physisorption is dominant [54]. However, if the value of enthalpy is between 80 and 200 kJ mol^{-1}, then chemisorption happens and bonds between adsorbate and adsorbent are strong [54]. In this system, the value of enthalpy of adsorption is close to 40 kJ $mole^{-1}$ which indicates that physisorption is predominant.

Values of the entropy change of adsorption indicate increased randomness in the system. The positive value of entropy change indicates that randomness increases in the system, while a negative value shows decreasing in the system randomness [57]. Based on Table 4.3, entropy increases during the adsorption process which demonstrates that randomness at solid-solution surface increases [74].

The increase in randomness may occur because of affinity between tetracycline and activated carbon. Because of affinity between tetracycline and activated carbon, the replacement on the activated carbon surface between water molecules and tetracycline might occur. This affinity could cause disruption for reorienting of water molecules at activated carbon surface [79]. Similar results were obtained by Pouretedal et al. [42] who investigated the removal of tetracycline from water at different temperatures using biochar adsorbent prepared from vine wood. According to these authors, the entropy value was 260 J mol^{-1} K^{-1}. The positive entorpy was ascribed to that affinity between tetracycline and adsorbent could cause an increases in randomness at the solid surface.

Thermodynamic parameters for tetracycline adsorption were also determined using distribution coefficient Eq. (2.11) as explained and discussed in section 3.5.1. Table D.1 in Appendix D summarizes thermodynamics parameter values determined based on the distribution coefficient through linearization.

4.3.2. Lincomycin

4.3.2.1. Effects of concentration and temperature

Effect of different initial concentrations at different temperatures on lincomycin adsorption capacity was investigated according to the procedure explained in section 3.2.1. Figure 4.9 represents how different initial concentrations at different temperature affect lincomycin adsorption capacity.

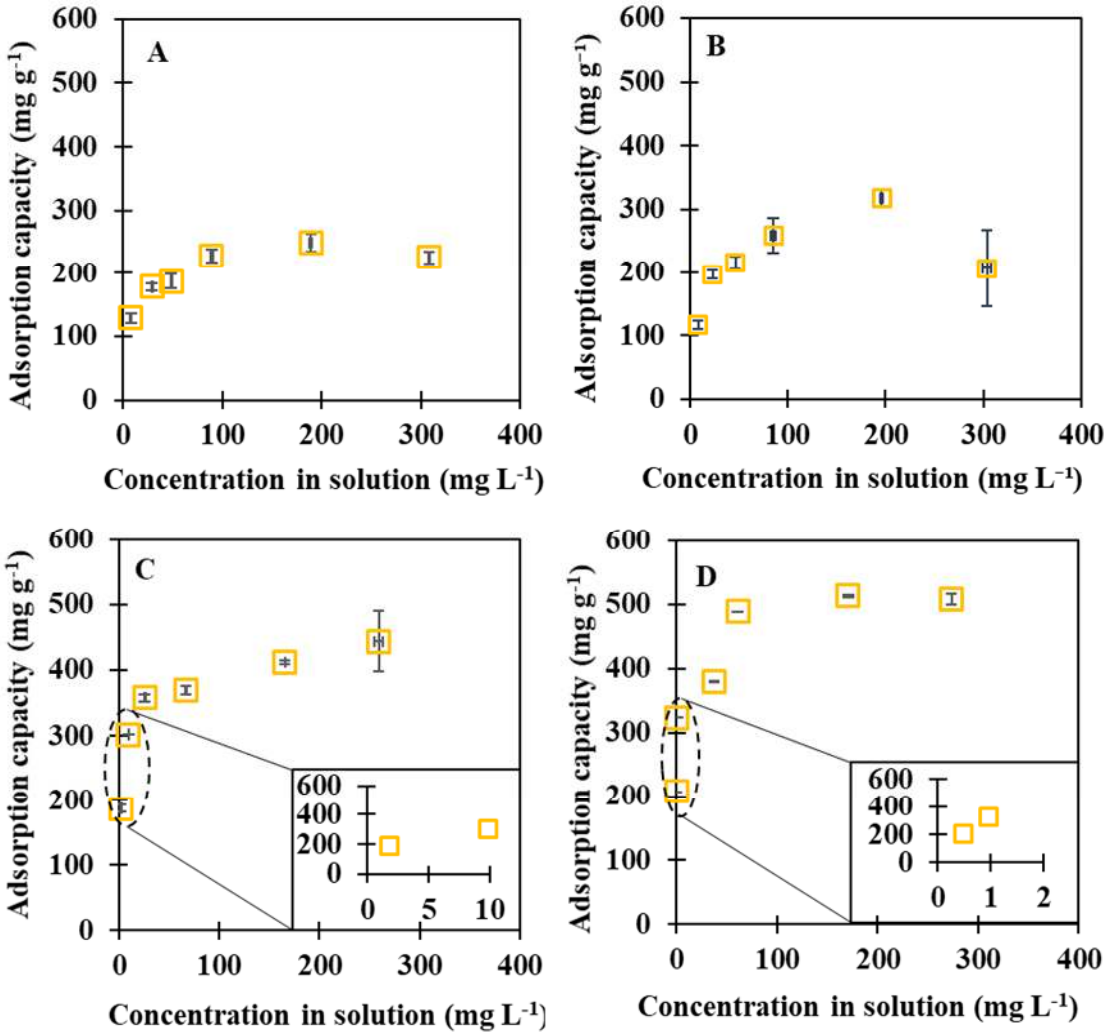

Figure 4.9 Effects of initial concentration and temperature on lincomycin adsorption process. (A) 5 ℃, (B) 12 ℃, (C) 22 ℃, and (D) 32 ℃. Error bars are standard deviation for duplicate sampling.

According to Figure 4.9, the change in the initial concentration of lincomycin affects the adsorption process. Increasing lincomycin initial concentration from 20 mg L^{-1} to 100 mg L^{-1} increases the adsorption capacity from 129 mg g^{-1} to 228 mg g^{-1} at 5 ℃. This could occur because increasing lincomycin initial concentration in solution, increases driving force and this increases the possibility of interaction between lincomycin and activated carbon and leads to higher uptake [65]. However, after 100 mg L^{-1}, by increasing lincomycin initial concentration the adsorption capacity does not change crucially at all temperatures. This could indicate that active sites on the activated carbon surface become saturated [66]. Rahmi et al. [80] investigated the removal of methyl blue using eggshell as an adsorbent. According to authors, adsorption capacity increased from 48 to 60 mg g^{-1} when the initial concentration

of methyl blue increased from 5 to 40 mg L^{-1}. However, after increasing initial concentration to 60 mg L^{-1}, adsorption capacity did not increase.

Temperature is another factor that affects lincomycin adsorption capacity. According to Figure 4.9, adsorption capacity increases when temperature increases from 5 ℃ to 32 ℃. Adsorption capacity for 100 mg L^{-1} at 5 ℃ is 228 mg g^{-1} while this number at 32 ℃ is 488 mg g^{-1}. At high temperature, lincomycin molecules mobility increases. This increase in mobility can increase the number of molecules that can overcome the external boundary layer between adsorbent and adsorbate. Thus, because of passing the boundary layer, more adsorption can occur [66]. Also, adsorption capacity increase due to temperature increase can be sign of endothermic adsorption process [66]. Wang et al. [75] studied the removal of vinyl alcohol from water using bentonite. According to the authors, adsorption capacity increased when the temperature rose from 30 ℃ to 50 ℃. This increase was attributed to some new active sites that was create at high temperature and increase in the number of molecules that could pass the boundary layer.

4.3.2.2. Adsorption isotherm fitting for lincomycin

Experimental data obtained through lincomycin adsorption were modeled using different isotherm models of Langmuir, Freundlich, and Sip. Excel software was implemented to fit the obtained results nonlinearly into Eqs. (2.1), (2.4), and (2.6) as explained earlier in section 2.4.1 and all coefficients were determined. GRC nonlinear function was used to minimize the sum of squares of differences between the experimental and theoretical results of lincomycin adsorption capacities, which were explained in section 3.5.4. To identify the most suitable isotherm, a procedure explained in section 3.5.4 was used.

Figure 4.10 represents the goodness fit of different isotherms for lincomycin adsorption at 5 ℃. Table 4.4 summarizes all associated coefficients related to each model.

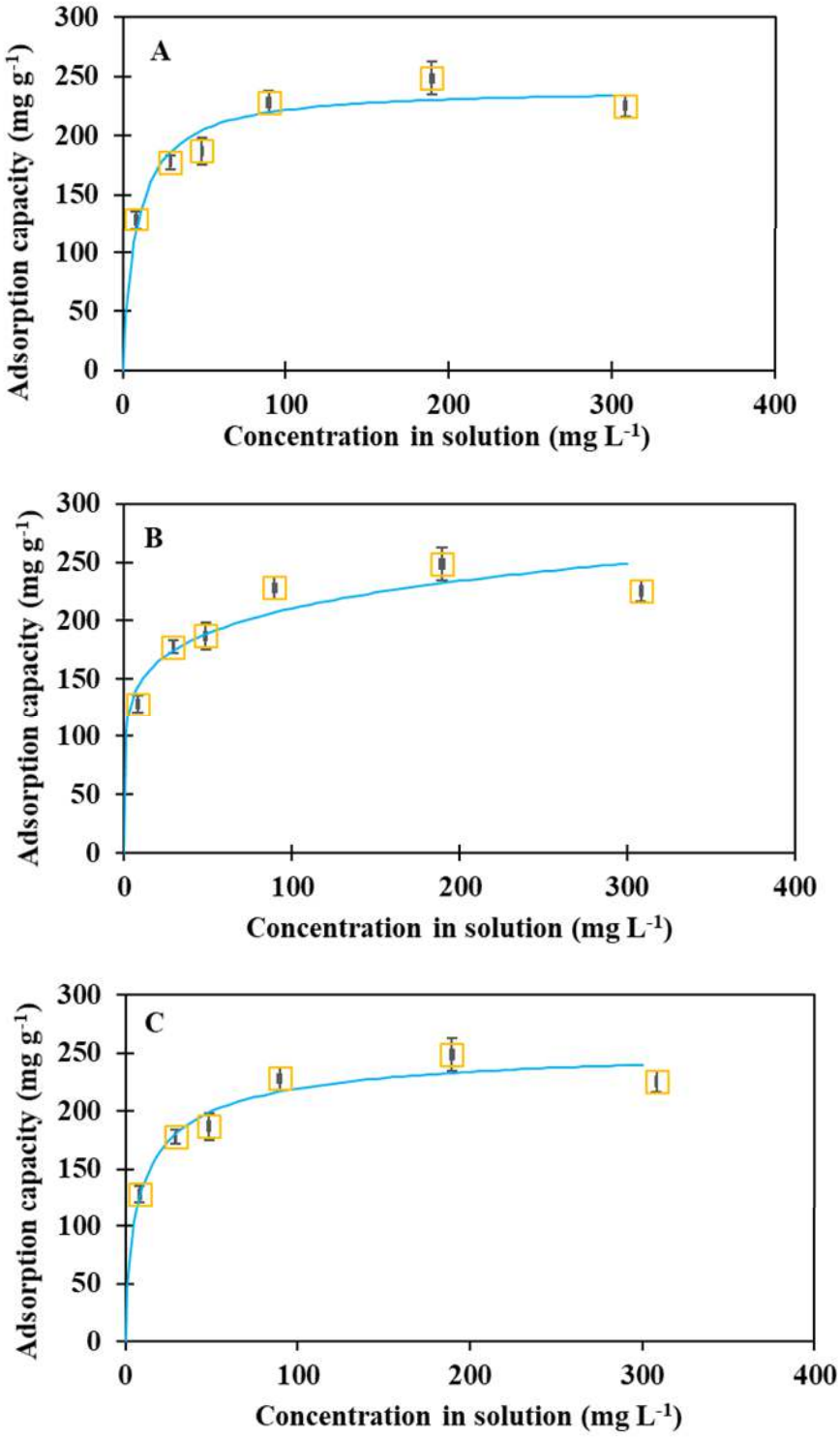

Figure 4.10 Lincomycin adsorption experimental data (symbols) fitted nonlinearly with different isotherm models (lines): (A) Langmuir, (B) Freundlich, and (C) Sip at 5 ℃. Error bars are standard deviation for duplicate sampling.

Table 4.4 Langmuir, Freundlich, and Sip model coefficients determined using Excel software for lincomycin adsorption

Langmuir				
Temperature (℃)	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_L}$ ($L\ mg^{-1}$)	$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	240	0.12	0.897	4.94
12	275	0.10	0.997	27.42
22	412	0.34	0.927	9.4
32	477	1.80	0.847	25.65

Freundlich				
Temperature (℃)	$\mathbf{K_F}$ $(mg\ g^{-1})(L\ mg^{-1})^{1/n}$	**n**	$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	104	0.15	0.836	7.38
12	113	0.15	0.531	48.14
22	204	0.14	0.929	10.94
32	276	0.11	0.946	26.82

Sip					
Temperature (℃)	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_s}$ ($L\ mg^{-1}$)	$\mathbf{n_s}$	$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	261	0.22	0.79	0.921	3.39
12	283	0.20	0.74	0.701	26.32
22	476	0.49	0.53	0.997	2.09
32	843	0.48	0.21	0.899	25.53

According to Table 4.4, Sip isotherm could predict the obtained results for lincomycin adsorption well when compared with Langmuir and Freundlich model based on R^2 and χ^2. Langmuir assumptions do not fulfill in all adsorption cases especially at high concentrations [70]. Moreover, Freundlich isotherm is not able to predict maximum adsorption capacity and at low concentrations this isotherm does not follow Henry's law [70].

According to Table 4.4, lincomycin maximum adsorption capacity is affected directly by temperature. When the temperature increases from 5 ℃ to 32 ℃, the maximum adsorption capacity increases from 261 mg g^{-1} to 843 mg g^{-1}. This indicates that a higher temperature is more favorable for adsorption process. Increasing adsorption capacity due to temperature increase is a sign of an endothermic process [68]. The reason behind increasing adsorption capacity due to temperature increase can be explained through mobility [67]. At high temperature, mobility of lincomycin molecules increases. As a result, the number of

molecules that could pass the layer between adsorbate and adsorbent increases as well. Therefore, at high temperature, more lincomycin molecules can attach to activated carbon. Similar results were observed in previous studies. Gupta et al. [81] studied the removal of bisphenol A from water at different temperatures using synthesized graphene oxide. According to the authors, the uptake increased from 70 to 90 mg g^{-1} when temperature increased from 25 ℃ to 55 ℃.

Based on Table 4.4, K_L coefficient increases with temperature. This parameter describes the affinity between adsorbate and adsorbent [70]. Therefore, the increasing temperature could increase the affinity between lincomycin and activated carbon. This could be another reason to explain why at high temperature more lincomycin can be adsorbed.

To investigate that adsorption is monolayer or multilayer, determination of n_s is crucial [70]. If n_s value approaches to unity, this indicates that monolayer homogenous adsorption occurs while the value above unity indicates non-uniform distribution on heterogeneous surface [70]. According to Table 4.4, n_s values are different from unity. This indicates that lincomycin adsorption is a heterogeneous process [51].

To explore whether the operational parameters are favorable or not, R_L (dimensionless) values were calculated based on Eq. (2.3) as mentioned in section 2.4.1 [73]. Figure 4.11 shows R_L changes as a function of temperature and initial concentration. According to Figure 4.11, R_L values are less at a high initial concentration, which indicates that high initial concentration is more favorable.

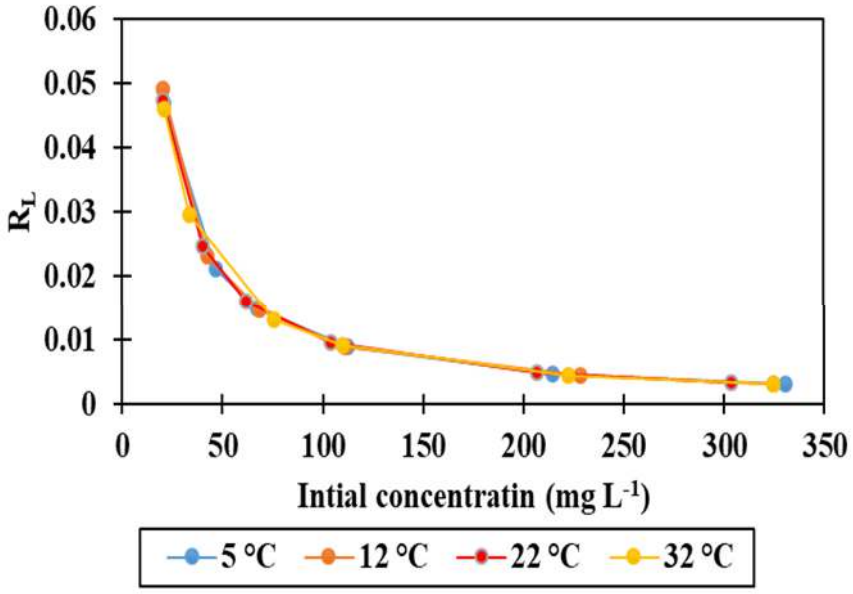

Figure 4.11 R_L values as function of initial concentration and temperature for lincomycin adsorption

Also, lincomycin adsorption data were fitted with Langmuir and Freundlich isotherm models using the linearization method using Eqs. (2.2) and (2.5) as mentioned in section 2.4.1. All associated coefficients are summarized in Table B.1 in Appendix B.

4.3.2.3. Determination of thermodynamic parameters for lincomycin adsorption

To predict the adsorption mechanism, it is important to study the thermodynamics of adsorption. Lincomycin adsorption experimental data were thermodynamically studied to identify the adsorption mechanism. Excel software was used to fit all experimental data non-isothermally into Sip model that incorporated van't Hoff expression (Eq. (2.15)) as described in section 2.6.2. Gibbs free energy change was calculated based on Eq. (2.12). The values of thermodynamic parameters were determined using GRC nonlinear function of Excel software by minimizing Eq. (3.2) as described in section 3.5.4.

Table 4.5 represents enthalpy and entropy change for tetracycline adsorption. All Gibbs free energy change values at different temperatures are listed in Table 4.5.

Table 4.5 Thermodynamic coefficients determined based on non-isothermally fitting into Sip model incorporated with van't Hoff expression using Excel software

$\Delta \mathbf{H}$=28000 $(\mathbf{J\ mol^{-1}})$	
$\Delta \mathbf{S}$=123 $(\mathbf{J\ mol^{-1}\ K^{-1}})$	
Temperature (℃)	$\Delta \mathbf{G}$ ($J\ mol^{-1}$)
5	-6212
12	-7073
22	-8303
32	-9533

According to Table 4.5, Gibbs free energy value is negative at all temperatures which means that the adsorption process is spontaneous. Moreover, the values of this parameter increase when the temperature increases. This could suggest that a higher temperature is more thermodynamically favorable for lincomycin adsorption. This result was expected as the previous disccusion regarding lincomycin adsorption shows that at a higher temperature, more adsorption occurs. Sun et al. [82] investigated the removal of ciprofloxacin using activated carbon treated with H_3PO_4. According to authors, the absolute value of free Gibbs free energy change increased from 24 to 28 kJ mol^{-1} when temperature increased from 30 ℃ to 50 ℃.

To understand whether the adsorption process is endothermic or exothermic, determination of enthalpy sign is an indispensable component. Based on Table 4.5, the enthalpy value is positive. This indicates that lincomycin adsorption on activated carbon is an endothermic process. This result is in good agreement with the results that demonstrate increasing temperature brings in higher adsorption capacity values. Peng et al. [68] studied ciprofloxacin removal from water using graphitic ordered mesoporous carbon. According to the authors, the value of enthalpy for the adsorption process was 21 kJ mol^{-1} which shows that an endothermic process occurred. Additionally, the value of enthalpy determines the mechanisms of adsorption. According to Table 4.5, enthalpy value is 28 kJ mol^{-1} which

shows that physisorption process should be more dominant as previously discussed in section 4.3.1.

Based on Table 4.5, entropy change is positive which demonstrates that randomness increases in the process. During the adsorption process, activated carbon has an affinity to adsorb lincomycin molecules. Therefore, the adsorption of lincomycin on the activated carbon surface can cause disruption for water molecules reorientation which increases the randomness at a solid surface [83]. Sun et al. [82] studied the removal of ciprofloxacin from water using two different adsorbents activated carbon treated with H_3PO_4 and activated carbon treated with $H_4P_2O_3$. According to the authors, the obtained results demonstrated that entropy change values for both the adsorption system were positive which indicated an increase occurred in randomness.

Also, thermodynamic coefficients for lincomycin adsorption were determined using linearization based on Eq. (2.11). Table D.1 in Appendix D summarizes the results.

4.3.3. Comparison of lincomycin and tetracycline adsorption

The experimental data demonstrate that higher concentration could increase adsorption capacity for lincomycin and tetracycline. However, by comparison, the results obtained through the adsorption of these two antibiotics at the specific temperature demonstrates that for activated carbon tetracycline adsorption capacity is higher than lincomycin. For instance, lincomycin adsorption capacity at 5 ℃ for 300 mg L^{-1} concentration is 240 mg g^{-1}, while for tetracycline at the same condition the corresponding value is 301 mg g^{-1}. This implies that activated carbon has higher affinity for tetracycline when compared to lincomycin. This could be explained through tetarcycline and lincomycin molecular structures. Both antibiotics are able to attach to activated carbon through creation of hydrogen bonds. However, the difference between these two structures is the number of aromatic ring. Tetracycline structure has more aromatic rings compared to lincomycin structure which ables tetracyline molecules to attach to activated carbon through $\pi - \pi$ interaction . Ji et al. [84] studied the feasibility of tetracycline adsorption on carbon nanotubes, activated carbon and graphite. According to these authors, tetracycline could attach to activated carbon surface through the creation of different bonds including $\pi - \pi$ interaction, cation$-\pi$ bonding, and hydrogen bond. Among these bonds, the creation of $\pi - \pi$ interaction was proposed to be dominant because of a number of aromatic rings that exist in tetracycline structure. Kim et al. [46] investigated the removal of lincomycin and sulfamethoxazole from water using powder

activated carbon with 1130 m^2 g^{-1} surface area and single-walled carbon nanotubes with 1020 m^2 g^{-1} surface area. According to the authors, the unexpected result occurred for the adsorption capacity because PAC adsorbed less lincomycin compared to SWCNT while PAC surface area was much higher than SWCNT. It was suggested that other factors such as the type of interaction could affect the adsorption process. Since lincomycin is a hydrophilic compound, it was recommended that lincomycin could be adsorbed by SWCNT through hydrogen bonds.

The results obtained through the adsorption process at different temperatures indicate that temperature could affect adsorption of both lincomycin and tetracycline. The experimental data indicate that tetracycline and lincomycin adsorption capacities increase at higher temperature. However, this increase is more significant in the case of tetracycline adsorption. The difference could be justified through lincomycin and tetracycline's structures. Number of aromatic rings in lincomycin is less than tetracycline. Therefore lincomycin molecules can be adsorbed by activated carbon through hydrogen bond while tetracycline has ability to be adsorbed through $\pi - \pi$ interaction, cation$-\pi$ bonding, and hydrogen bond.

R_L value indicate whether the experimental conditions are favorable for adsorption or not. If the value of R_L approches zero, this means that the operational condition of process is favorable while when this value is close to unity this means that operational condition is unfavorable. As previously discussed, R_L values for both lincomycin and tetracycline adsorption are close to zero induicating that higher initial concentration is more favorable for adsorption of both lincomycin and tetracycline. Moreover, obtained R_L values demonstrate that running adsorption at higher temperature results in higher adsorption capacity.

Regarding regression, Sip model could predict the experimental data well for both adsorption processes compared to other isotherms based on R^2 and Chi-square. In the case of Sip coefficient, tetracycline adsorption shows higher value in maximum adsorption capacity compared to lincomycin. This could occur because number of aromatic rings in tetracycline structure enables this antibiotic to attach to activated carbon through $\pi - \pi$ interaction as well as hydrogen bonds and cation$-\pi$ bonding. While lincomycin only could attach to activated carbon surface through hydrogen bonds. n_s value in Sip model determines how adsorbate distributes over adsorbent surface. As ealier discussed, values of n_s at different temperature are far from unity for both lincomycin and tetracycline which represent that both adsorptions are heterogenous process.

Thermodynamic parameters for both adsorption experiments were determined. The sign of Gibbs free energy change is negative for lincomycin and tetracycline adsorption which suggests that the adsorption process for both antibiotics is spontaneous. Also, increase in the value of Gibbs free energy due to increase of temperature in both cases indicates that higher temperature is more thermodynamically favorable for adsorption process. Enthalpy change sign for lincomycin and tetracycline adsorption processes are positive. This means that lincomycin and tetracycline adsorption is an endothermic process. The value of enthalpy change in two adsorption processes is less than 80 kJ mol^{-1} which indicates that physisorption is more dominant in two processes. The difference between the enthalpy change value of tetracycline adsorption and lincomycin adsorption shows that stronger adsorption occurs in the case of tetracycline. Entropy change value also is positive in two processes which points out increasing in randomness. During the adosprtion process, both lincomycin and tetracycline have affinity to activated carbon which disables water molecules to reorientate on the activated carbon surface [77].

4.3.4. Antibiotics mixture

4.3.4.1. Effects of initial concentration and temperature

The mixture of lincomycin and tetracycline was prepared according to Table 3.2 as mentioned in section 3.2.3. Effect of different initial concentrations on the adsorption capacity at different temperatures of 5 ℃, 12 ℃, 22 ℃, and 32 ℃ was investigated. Figure 4.12 represents the results for adsorption of antibiotics in the mixture at different temperatures.

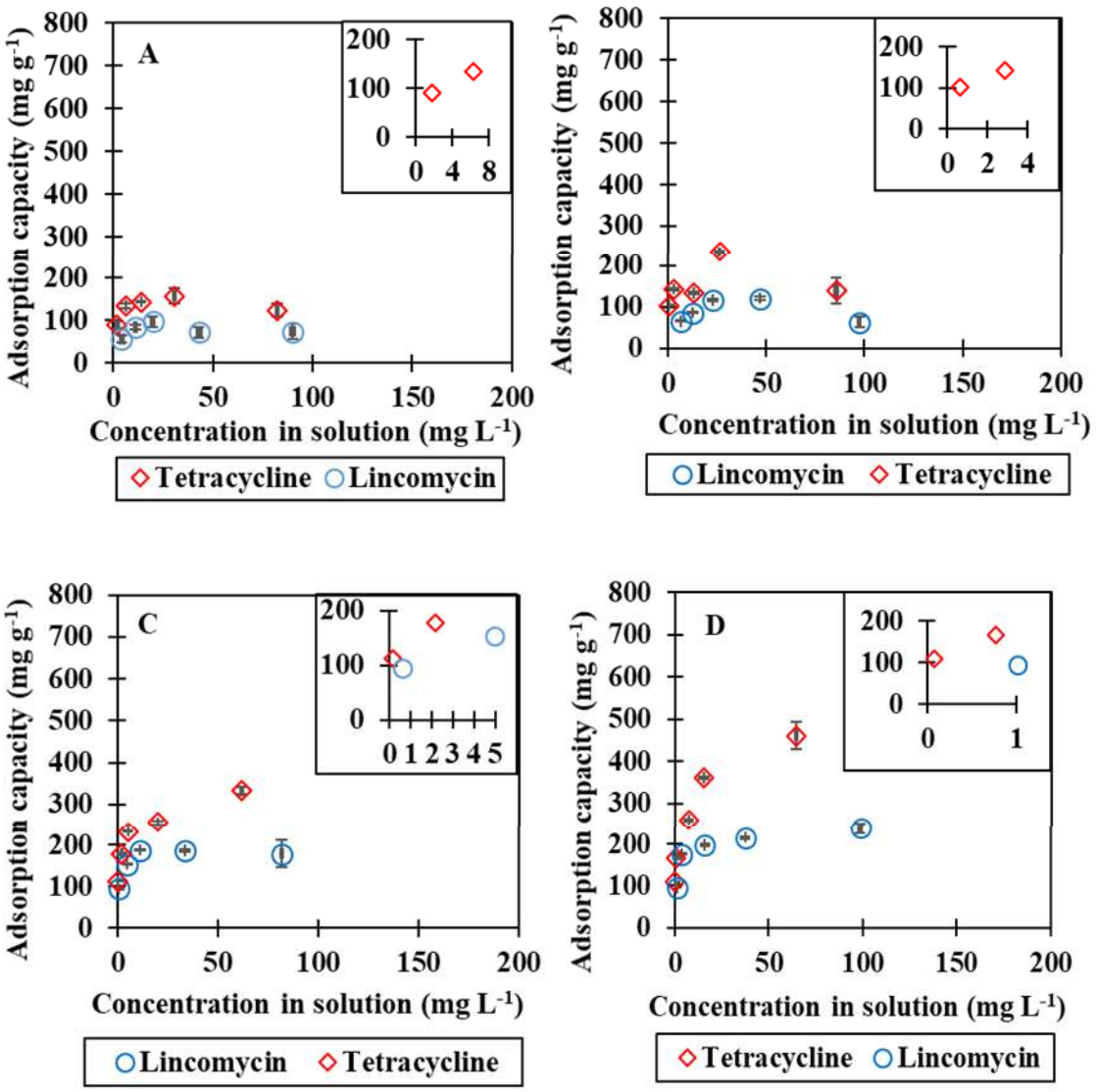

Figure 4.12 Effect of initial concentrations on adsorption of tetracycline and lincomycin at (A) 5 ℃, (B) 12 ℃, (C) 22 ℃, and (D) 32 ℃. Error bars are standard deviation for duplicate sampling.

According to Figure 4.12, similar to patterns observed with individual antibiotics, at a specific temperature, the increase in initial concentration of lincomycin and tetracycline in the mixture increases their respective adsorption capacity. At 5 ℃ lincomycin adsorption capacity increases from 55 to 71 mg g^{-1}, respectively by increase of initial concentration from 20 to 100 mg L^{-1}. A similar pattern is also observed for tetracycline. Specifically, tetracycline adsorption capacity increases from 89 to 156 mg L^{-1}, respectively when the initial concentration of tetracycline in the mixture increases from 20 to 100 mg L^{-1}. This increase occurred because the higher initial concentration means a higher driving force. Thus, this could lead to higher uptake [75]. The difference between lincomycin and tetracycline adsorption capacity can be because of their structure. As mentioned in the previous section, tetracycline can attach to activated carbon through different bonds including $\pi - \pi$ interaction, cation$-\pi$ bonding, and hydrogen bond while lincomycin can be adsorbed by activated carbon through hydrogen bonds [19,20]. By continuing the increase in initial concentration after 100 mg g^{-1}, adsorption capacity does not change crucially and in some cases, it decreases for both antibiotics. This could occur because accessible and available active sites are saturated [65]. Dogan et al. [85] studied the performance of cryogel in removing methylene blue from water. According to the authors, increasing the initial concentration of methyl blue from 100 to 1000 mg L^{-1} increased the adsorption capacity of adsorbent from 5 to 38 mg g^{-1}. However, by increasing the initial concentration, adsorption capacity remained constant. This was attributed to the fact that available active sites of the adsorbent were saturated.

Based on Figure 4.12 increase of temperature could lead to an increase in the adsorption capacity of both antibiotics in the mixture. Thus, a higher temperature is more favorable for the adsorption process. Also, adsorption capacity enhancement due to rising temperature indicates that an endothermic process occurs. As mentioned before, during a temperature increase, molecules' mobility increases as well. Therefore, more molecules can pass the boundary layer between adsorbent and adsorbate. As a result, more adsorption occurs when temperature increases [71]. Abdulsalam K. A. et al. [86] studied the adsorption of Rhodamine B in binary solution on sawdust of *Parkia biglobosa* at different temperatures. According to the authors, adsorption capacity increased from 16 to 22 mg g^{-1} when temperature increased from 30 ℃ to 60 ℃. This was attributed to the point that at high temperature, more molecules could acquire sufficient energy to pass the boundary layer between adsorbent and adsorbate and undergo interaction with active sites of adsorbent.

4.3.4.2. Analysis of lincomycin and tetracycline adsorption data in the mixture

Experimental data obtained through adsorption of antibiotics in the mixture at different temperatures were fitted nonlinearly into Extended Langmuir and Extended Sip based on Eqs. (2.8) and (2.9) that describe the adsorption in a multi-substrate system as mentioned earlier in section 2.4.2. Excel software was used to fit the experimental data nonlinearly and to determine all coefficients using GRC nonlinear function. GRC nonlinear function was used to minimize the sum of squares of differences between experimental and theoretical results of mixture adsorption capacities, which were explained earlier in section 3.5.4. To distinguish the goodness of fitting R-square and Chi-square were used according to Eqs. (3.3) and (3.4) as mentioned earlier in section 3.5.4.

Figure 4.13 represents the goodness of fit of different isotherms for lincomycin adsorption at 5 ℃. Table 4.6 summarizes all associated coefficients related to each model.

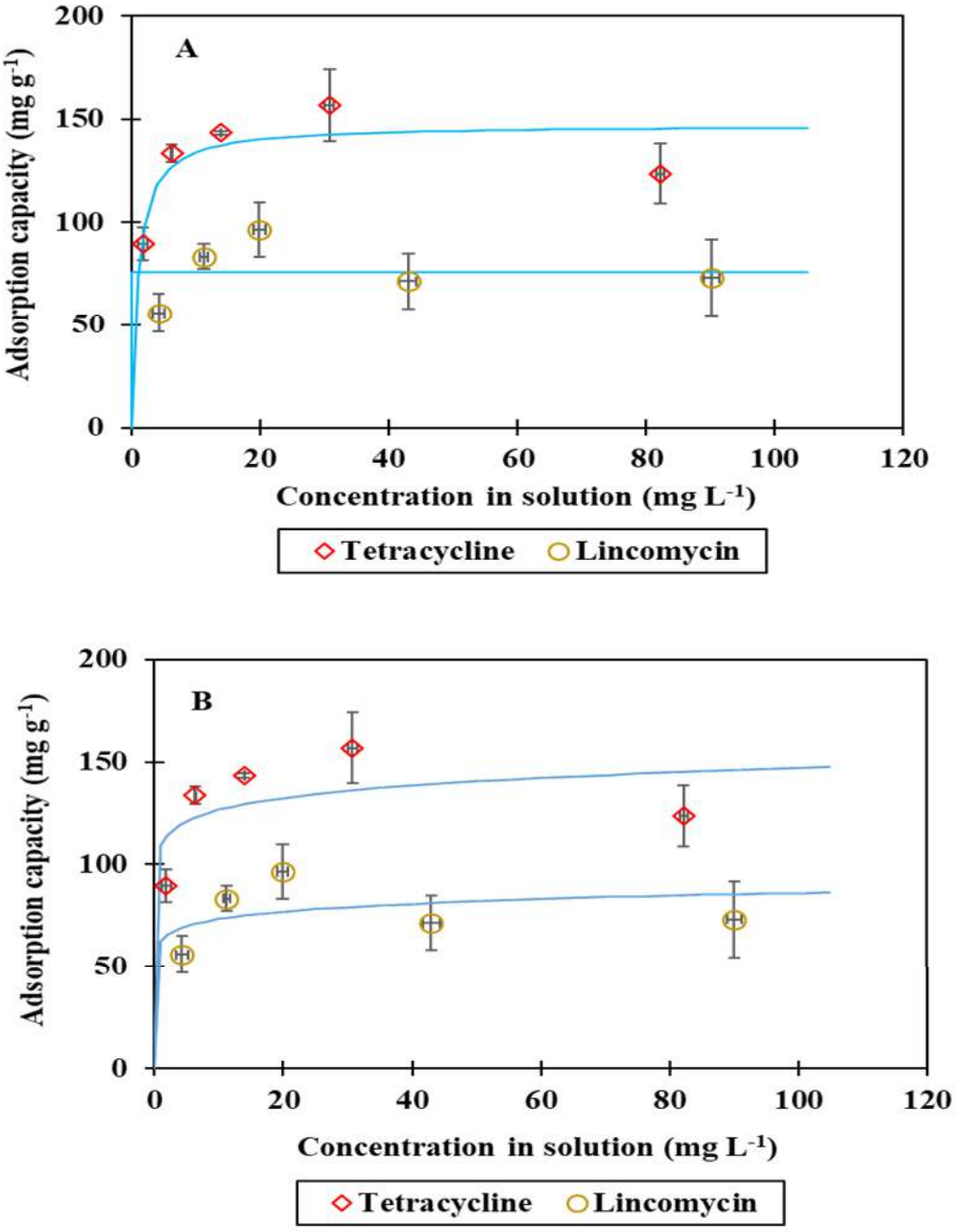

Figure 4.13 Antibiotic mixture adsorption experimental results (symbols) and model predictions (lines) for (A) extended Langmuir and (B) extended Sip isotherms at 5 °C. Error bars are standard deviation for duplicate sampling.

Table 4.6 Calculated parameters for extended Langmuir and extended Sip models at different temperatures for the mixture adsorption

Extended Langmuir					
Tetracycline					
Temperature (℃)	$\mathbf{q_{max}}$ (mg g^{-1})	$\mathbf{K_L}$ (L mg^{-1})		$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	223	1.01		0.514	17.56
12	271	2.11		0.255	71.47
22	468	0.74		0.805	160.66
32	628	0.67		0.662	472.84
Lincomycin					
Temperature (℃)	$\mathbf{q_{max}}$ (mg g^{-1})	$\mathbf{K_L}$ (L mg^{-1})		$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	76	26662.62		0.514	17.56
12	93	161158.5		0.255	71.47
22	200	2.35		0.805	160.66
32	220	5075.06		0.661	472.84
Extended Sip					
Tetracycline					
Temperature (℃)	$\mathbf{q_{max}}$ (mg g^{-1})	$\mathbf{K_s}$ (L mg^{-1})	$\mathbf{n_s}$	$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	273	0.18	0.06	0.605	14.23
12	300	0.20	0.07	0.381	65.12
22	1025	0.06	0.18	0.902	19.35
32	1131	0.06	0.24	0.957	22.42
Lincomycin					
Temperature (℃)	$\mathbf{q_{max}}$ (mg g^{-1})	$\mathbf{K_s}$ (L mg^{-1})	$\mathbf{n_s}$	$\mathbf{R^2}$	$\boldsymbol{\chi^2}$
5	251	0.02	0.10	0.605	14.23
12	260	0.02	0.10	0.381	65.12
22	450	0.06	0.01	0.902	19.35
32	802	0.04	0.01	0.957	22.42

According to Figure 4.13, extended Sip model could predict the experimental data well when compared to the extended Langmuir model based on R-square and Chi-square. Extended Langmuir considers that only a fraction of adsorption sites that are occupied by component 1 can also be used by component 2 [52]. This assumption cannot be satisfied, when two components have affinity to the adsorbent. Based on the earlier discussion in single-solute adsorption, lincomycin and tetracycline both have affinity to attach to activated carbon.

Based on Table 4.6, in case of tetracycline increase of temperature from 5 ℃ to 32 ℃, increases the maximum adsorption capacity from 273 to 1131 mg g^{-1}, respectively. Also, for lincomycin, the maximum adsorption capacity increases from 251 to 802 mg g^{-1}, respectively when the temperature rises from 5 ℃ to 32 ℃. This pattern was expected as previous result indicates that increasing temperature can increase adsorption capacities of both antibiotics. This could indicate that increasing mobility of molecules due to temperature increase, enhances the number of molecules that could pass the boundary layer and attach to activated carbon. Bentaher et al. [87] investigated the adsorption feasibility of methylene blue and crystal violet in a binary solution on natural clay. According to these authors, by increasing temperature from 20 ℃ to 50 ℃, adsorption capacity for methylene blue and crystal violet increased from 203 to 225 mg g^{-1} and from 177 to 199 mg g^{-1} respectively. This was ascribed to the point that at high temperature, lincomycin and tetracycline molecules acquired sufficient energy to pass the external boundary layer and interact with active sites.

K_L parameter determines the affinity between adsorbate and adsorbent. According to Table 4.6, tetracycline affinity is approximately constant at different temperatures. While for lincomycin, similar to individual adsorption, affinity increases with increasing temperature.

According to Table 4.6, n_s values for both lincomycin and tetracycline are far from unity, which indicates that heterogeneous process occurs.

Also, lincomycin and tetracycline experimental data in binary solution was fitted with single-solute isotherm separately. Table B.2 in Appendix B summarizes all coefficients related to each isotherm.

4.3.4.3. Determination of thermodynamic parameters for mixture adsorption

Thermodynamic parameters were determined through linearization using distribution coefficient based on Eq. (2.15) as explained earlier in section 2.6.2. All thermodynamic parameters are listed in Table 4.7.

Table 4.7 Thermodynamic parameters determined through linearization based on distribution coefficient

Tetracycline	
ΔH=38000 **($J\ mol^{-1}$)**	
ΔS=150 **($J\ mol^{-1}\ K^{-1}$)**	
Temperature (℃)	**ΔG** ($J\ mol^{-1}$)
5	-3722
12	-4772
22	-6272
32	-7772
Lincomycin	
ΔH =36233 **($J\ mole^{-1}$)**	
ΔS=149 **($J\ mole^{-1}\ K^{-1}$)**	
Temperature (℃)	**ΔG** ($J\ mol^{-1}$)
5	-5211
12	-6254
22	-7744
32	-9234

According to Table 4.7, Gibbs free energy change for tetracycline and lincomycin is negative at all temperatures which can indicate that the adsorption process is spontaneous [52]. Additionally, based on Table 4.7, Gibbs free energy change value increases when temperature increases from 5 ℃ to 32 ℃. This could mean that temperature is thermodynamically favorable for adsorption. Bentaher et al. [87] studied the removal of methylene blue and crystal violet in binary solution at different temperatures using natural clay. According to authors, Gibbs free energy change was negative at all temperatures and the value of Gibbs free energy change increased from 20 to 24 kJ mol^{-1} when the temperature increased from 22 ℃ to 50 ℃.

Enthalpy sign for both tetracycline and lincomycin is positive which shows that the adsorption process is endothermic. This is in good agreement with previous results, which indicated that temperature increase could result in increasing adsorption capacity. This could mean that lincomycin and tetracycline molecules have to displace more than two water molecules. Abdulsalam K.A et al. [86] studied the adsorption of Rhodamine B in binary solution on sawdust of *Parkia biglobosa* at different temperatures and determined the value of enthalpy change for the adsorption process. According to the authors, enthalpy change value for the adsorption process was 35 kJ mol^{-1}. According to Table 4.7, the value of enthalpy change for lincomycin and tetracycline are below 80 kJ mol^{-1} which shows that a physisorption process occurs [54].

Based on Table 4.7, entropy change value is positive for both antibiotics which demonstrates that randomness increases in the system [57]. As previously mentioned, in the adsorption process, lincomycin and tetracycline molecules cause disruption for water molecules to reorientate at the solid surface [57]. Abdulsalam K.A et al. [86]investigated the removal of Rhodamine B in binary solution on sawdust of *Parkia biglobosa* at different temperatures and determined the value of entropy change. According to the authors, entropy change value for the adsorption process was 122 J mol^{-1} K^{-1}. The positive value of entropy change was attributed to that the randomness increased at the solid surface.

Also, thermodynamic coefficients for binary adsorption were determined using linearization based on Eq. (2.11). Table D.1 in Appendix D summarizes the results.

4.3.5. Comparison of adsorption of individual antibiotics and adsorption of antibiotics in the mixture

Sip parameters calculated for single-solute and binary adsorption are listed in Table 4.8. Thermodynamic parameters for both individual antibiotic adsorption and multicomponent adsorption are summarized in Table 4.9. Different values of q_{max}, ΔH, and ΔS reported in literature for lincomycin and tetracycline adsorption are listed in Table 4.8. Also, operating condition for each study is described in Table 4.10.

Table 4.8 Sip and extended parameters for both single-solute and binary adsorption

Single-solute adsorption						
	Tetracycline			**Lincomycin**		
Temperature (°C)	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_s}$ ($L\ mg^{-1}$)	$\mathbf{n_s}$	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_s}$ ($L\ mg^{-1}$)	$\mathbf{n_s}$
5	294	0.17	0.76	261	0.22	0.79
12	302	0.15	0.73	283	0.20	0.74
22	1100	0.21	0.37	476	0.49	0.53
32	1249	0.17	0.42	843	0.48	0.21
Binary adsorption						
	Tetracycline			**Lincomycin**		
Temperature (°C)	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_s}$ ($L\ mg^{-1}$)	$\mathbf{n_s}$	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_s}$ ($L\ mg^{-1}$)	$\mathbf{n_s}$
5	273	0.18	0.06	251	0.02	0.1
12	300	0.20	0.07	260	0.02	0.1
22	1025	0.06	0.18	450	0.06	0.01
32	1131	0.06	0.24	802	0.04	0.01

Table 4.9 Thermodynamic parameters calculated for single-solute and binary adsorption

Sing-solute adsorption			
Tetracycline		**Lincomycin**	
$\mathbf{\Delta H}$ ($J\ mol^{-1}$)	$\mathbf{\Delta S}$ ($J\ mol^{-1}\ K^{-1}$)	$\mathbf{\Delta H}$ ($J\ mol^{-1}$)	$\mathbf{\Delta S}$ ($J\ mol^{-1}\ K^{-1}$)
29400	122	28000	123
Binary adsorption			
Tetracycline		**Lincomycin**	
$\mathbf{\Delta H}$ ($J\ mol^{-1}$)	$\mathbf{\Delta S}$ ($J\ mol^{-1}\ K^{-1}$)	$\mathbf{\Delta H}$ ($J\ mol^{-1}$)	$\mathbf{\Delta S}$ ($J\ mol^{-1}\ K^{-1}$)
38000	150	36230	149

Table 4.10 Different values for maximum adsorption capacity, enthalpy and entropy for tetracycline and lincomycin adsorption at different operating condition

Adsorbate	Adsorbent	C_0 (mg L^{-1})	T (°C)	q_{max} (Mg g^{-1})	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})	Ref
Tetracycline	Activated carbon[1]	200-400	15-35	550	21000	105	[74]
Tetracycline	Activated carbon[2]	200-400	15-35	625	42000	165	[91]
Tetracycline	Activated carbon[3]	20-200	35-55	200	79000	268	[42]
Tetracycline	Petroleum coke	60-200	30-50	1121	-	-	[92]
Lincomycin	Activated carbon[4]	0.2-0.8	22	0.5	-	-	[93]
Lincomycin (Present work)	Activated carbon	20-300	5-32	802	28000	123	
Tetracycline (Present work)	Activated carbon	20-300	5-32	1249	29400	122	

[1] Prepared from tomato waste [2] Prepared from Grape pulp [3] Prepared from Vinewood
[4] Prepared from biochar

By comparison between the calculated maximum adsorption capacity for tetracycline and lincomycin and the reported values in different articles, the used activated carbon shows promising result to uptake these antibiotics from the water.

Effect of initial concentration variation is a parameter that was studied in the adsorption process. The results of the present study show that initial concentration can affect the adsorption of individual antibiotics, as well as those for antibiotics in mixture. The results demonstrate that during individual antibiotic adsorption, if the initial concentration of antibiotic increases, adsorption capacity will increase as well. This trend can be observed in binary adsorption as well. More important, adsorption capacity in the binary mixture is lower compared to that of individual antibiotics. According to Tables 4.9, in single solute adsorption, tetracycline maximum adsorption capacity is 294 mg g^{-1} at 5 ℃ and lincomycin maximum adsorption capacity is 261 mg g^{-1} at 5 ℃. While, in the binary adsorption, at 5 ℃, tetracycline and lincomycin maximum adsorption capacity are 273 mg g^{-1} and 251 mg g^{-1} respectively. During the individual adsorption process, all of the adsorption sites on the activated carbon are available to one antibiotic, lincomycin or tetracycline while in binary

mixture adsorption, there is a competition between the antibiotics to be adsorbed on the same number of sites. Hence, the adsorption is less. Allan et al. [88] studied the removal of three basic dyes namely Basic blue 3, Basic yellow 21, and Basic red 22 in multi-component solution from water using peat at room temperature. According to the authors, the maximum adsorption capacity for Basic blue 3 in a single system was 660 mg g^{-1}. While this number for Basic blue 3 in a tertiary system with other dyes was 310 mg g^{-1}. This decrease in maximum adsorption capacity was attributed to the competitive adsorption between them.

Experimental data from either binary or single-solute adsorption suggest that at a specific temperature, uptake for tetracycline is higher than lincomycin. This could occur because of the difference between lincomycin and tetracycline structure. As previously discussed, the existence of aromatic rings in tetracycline structure cause difference between tetracycline and lincomycin adsorption. Tetracycline is able to attach to activated carbon through different bonds including $\pi - \pi$ interaction, cation$-\pi$ bonding, and hydrogen bond while lincomycin is adsorbed by hydrogen bond [18,19].

Experimental data trend from the mixture and individual antibiotic adsorption shows that temperature could affect the adsorption process. For individual antibiotics, temperature increase leads to adsorption capacity enhancement. Also, the mixture experimental data shows that the adsorption capacity for both antibiotics is higher at a higher temperature. This can occur because at high-temperature adsorbate mobility increases [67]. As a result, more molecules acquire sufficient energy to pass the external boundary layer between adsorbate and adsorbent. Thus, the interaction between adsorbate and adsorbent increases and this could lead to more uptake [67].

The results obtained through adsorption isotherm regression show that Sip model could predict the individual antibiotic experimental data well compared to other isotherms based on R-square and Chi-square. Langmuir and Freundlich's limitations do not match the characteristics the lincomycin and tetracycline adsorption. Furthermore, mixture experimental data could be predicted well with extended Sip model. Extended Langmuir model as discussed in section 2.4.2 does not consider the possibility of competition between adsorbents during adsorption. In all experiments activated carbon shows the affinity to adsorb both lincomycin and tetracycline which means during mixture adsorption, there should be a competition between them to be adsorbed by activated carbon [52].

Maximum adsorption capacity results show a direct relation with temperature increase. For individual antibiotic, this value increases for both lincomycin and tetracycline when the temperature increases. Also, in the mixture adsorption, the results obtained through nonlinear regression demonstrate that adsorption at higher temperature results in higher maximum adsorption capacity for both antibiotics. However, this value in mixture adsorption is lower for two antibiotics when compared to individual antibiotics adsorption results. During the individual adsorption process all the adsorption sites on the activated carbon are available to one antibiotic, Lincomycin or Tetracycline while in binary mixture adsorption, there is a competition between the antibiotics to be adsorbed on the same number of sites. Hence the adsorption is less.

It can be observed that tetracycline maximum adsorption capacity is higher than lincomycin either in individual adsorption or adsorption of the mixture. This implies that activated carbon can adsorb more tetracycline. This result can be explained through tetracycline structure. Tetracycline structure enables this antibiotic to attach to activated carbon surface through different bonds including $\pi - \pi$ interaction, cation$-\pi$ bonding, and hydrogen bond [84] bonding while based on lincomycin structure, this antibiotic could be adsorbed by activated carbon through hydrogen bonds [46].

To understand the type of adsorbate distribution on the adsorbent surface, n_s value was determined for both single-solute or binary adsorption. An n_s value close to zero indicates heterogeneous adsorption while a value close to unity represents homogenous adsorption. According to Table 4.9, either in single-solute adsorption or in binary adsorption, n_s values for lincomycin and tetracycline are far from unity, which represents that in all experiment, heterogeneous adsorption should be considered.

Gibbs free energy change for both individual and mixture adsorption experiment is negative at all temperatures. This means that the adsorption process is spontaneous. Additionally, either in individual adsorption or in the mixture adsorption, it can be seen that the absolute Gibbs free energy change value increases when temperature increases from 5 ℃ to 32 ℃. Thus, the temperature increase is thermodynamically favorable.

Lincomycin and tetracycline adsorption as an individual antibiotic have positive enthalpy change. This means that for both individual adsorptions endothermic process occurs. Additionally, for the mixture adsorption, enthalpy change is positive which means that the mixture adsorption is an endothermic process. The value for enthalpy either in individual

antibiotic or in the mixture is less than 80 kJ mol^{-1} which indicates that the physisorption process is more dominant.

The results obtained through thermodynamic calculation demonstrate that entropy change has a positive value for both lincomycin and tetracycline either as an individual antibiotic or in the mixture. This means that in all experiment, randomness increases in the process. This means that during the adsorption process, activated carbon has an affinity to adsorb lincomycin and tetracycline which causes disruption for water molecules reorientation on the solid surface.

4.3.6. Adsorption in manure

4.3.6.1. Stability of tetracycline in manure

To investigate whether tetracycline could degrade in the manure or not, an experiment was carried out based on the procedure explained in 3.2.4. Figure 4.14 shows tetracycline profile of concentration in manure solution as a function of time for different initial concentration.

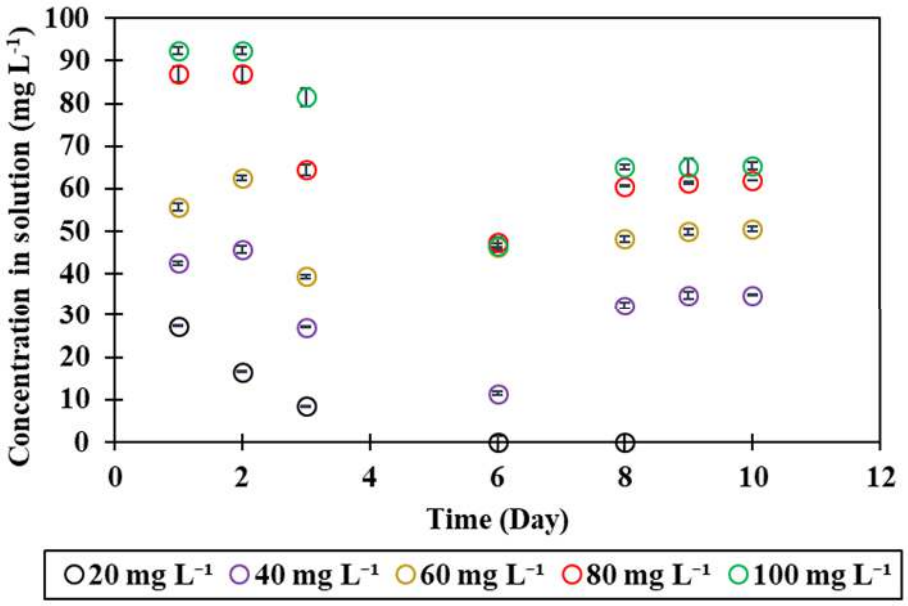

Figure 4.14 Tetracycline profile of concentration in manure as a function of time (symbols) for different initial concentrations. Error bars are standard deviation for duplicate sampling.

As can be seen in Figure 4.14, tetracycline concentration fluctuates over the time. For both initial concentrations, after 7 days, the concentration becomes stable. Therefore, constant point was selected to 8 days. This reduction in tetracycline concentration could occur because of the existence of macromolecular or chelates in liquid manure. The existence of these compounds in manure could deactivate tetracycline molecules. Kuhne et al. [89] investigated the stability of tetracycline in liquid porcine manure. According to the authors, tetracycline concentration became stable after 8 days.

4.3.6.2. Adsorption in the manure

The possibility of the adsorption process in liquid manure was studied based on the procedure explained in section 3.2.4. Figure 4.15 demonstrates the results obtained through tetracycline adsorption in liquid manure at room temperature using different adsorbent loading. The adsorption capacity for different adsorbent usage can be calculated using Eq. (3.1) described in section 3.5.1. The results are summarized in Table 4.11.

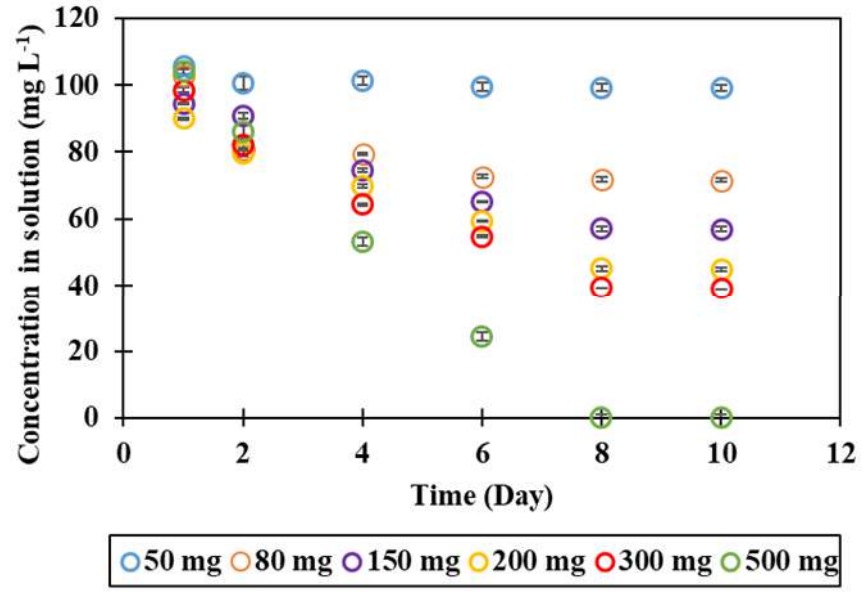

Figure 4.15 Tetracycline adsorption for 100 mg L^{-1} solution using different amount of activated carbon at room temperature. Error bars are standard deviation for duplicate sampling.

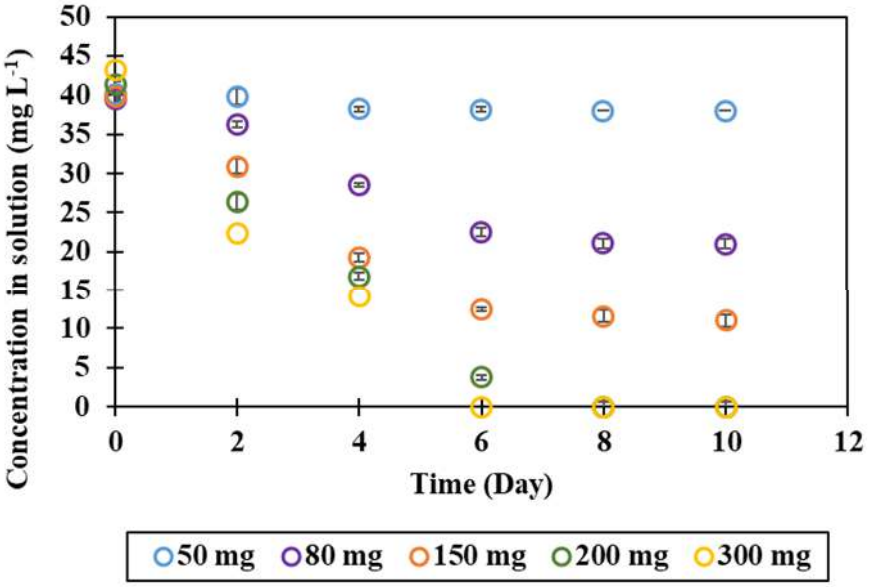

Figure 4.16 Tetracycline adsorption for 40 mg L^{-1} solution using different amount of activated carbon at room temperature. Error bars are standard deviation for duplicate sampling.

Table 4.11 Determination of adsorption capacity for different amount of activated carbon used for tetracycline removal in the manure

	40 mg L^{-1}	**100 mg L^{-1}**
Adsorbent dosage (mg)	**Adsorption capacity** (mg L^{-1})	**Adsorption capacity** (mg L^{-1})
80	23	38
150	19	24
200	-	22
300	-	20

According to Figure 4.15 and Figure 4.16, increasing the amount of activated carbon could adsorb more tetracycline in solution. This could occur because the more activated carbon in the solution provides more adsorbing sites for activated carbon. Based on Figure 4.15 and Figure 4.16, 50 mg of activated carbon could not adsorb tetracycline in liquid manure. This might occur because of the existence of different components in liquid manure which cover activated carbon adsorbing sites [89]. However, by increasing activated carbon amount in the solution, tetracycline concentration approaches zero.

The obtained adsorption capacity for 40 and 100 mg L^{-1} in manure is lower compared with the results obtained for tetracycline adsorption in the water. This might happen because, manure is a complex medium with different compounds and activated carbon could adsorb other compounds rather than tetracycline.

Fukahori et al. [90] studied adsorption of sulfonamide antibiotics in the distillated water and real porcine urine on HSZ-385. They found that the adsorption efficiency for removal of sulfonamide decreased in the real porcine urine compared the results in the water. This was attributed to the adsorption of organic matter which existed in real porcine on HSZ-385.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In the present study, the performance of activated carbon in removal of tetracycline and lincomycin from water either as an individual antibiotic or in the mixture was analyzed. The effect of initial concentration on the adsorption process was investigated. To understand whether temperature can affect adsorption process or not, both single-solute and binary adsorption were carried out at different temperatures. Feasibility of adsorption process in removing of tetracycline in the manure was explored.

Conclusions

Adsorption experimental data for both single-solute system and binary system indicated that for temperatures evaluated in this work higher temperature was more favorable for the adsorption process. More uptake occurred for both lincomycin and tetracycline either as an individual antibiotic or in the multicomponent system at higher temperatures.

Initial concentration could affect the adsorption process. The results demonstrated that increasing initial concentration of lincomycin or tetracycline in the single-solute or binary adsorption process would lead to more uptake.

The experimental data pattern for single-solute and binary adsorption demonstrate that in binary system adsorption capacity for both antibiotics is lower compare with the results obtained through single-solute system.

Single-solute adsorption experimental data was fitted with different isotherm models namely Langmuir, Freundlich, and Sip. The results obtained from each isotherm demonstrated that Sip model could predict the experimental data for both lincomycin and tetracycline well compared to other isotherms based on R-square and Chi-square. Additionally, the mixture adsorption experimental data was fitted with extended Langmuir and extended Sip isotherm. The obtained results indicated that extended Sip model provided a better fit compared to extended Langmuir model based on more favorable R-square and Chi-square.

The obtained results from Sip and extended Sip model indicated that maximum adsorption capacity for tetracycline was greater compared to lincomycin at all temperatures. This means that activated carbon could adsorb more tetracycline compared to lincomycin.

Thermodynamic parameters for both single-solute and binary adsorption process were determined. The results indicated that both processes were endothermic and entropy increased in the systems. The value of enthalpy for both systems demonstrated that physisorption process was more dominant.

The results obtained through stability of tetracycline in the manure showed that tetracycline concentration decreased with time. Also, the results from the adsorption process indicated that the concentration of activated carbon in the deionized water (100 mg L^{-1}) was insufficient. The effect of adsorbent dosage on the manure adsorption demonstrated that the required concentration of activated carbon to remove tetracycline in the manure was 1.5 g L^{-}

Recommendations for future work

The results obtained in the present study opens opportunities for additional research related to the application of adsorption technology for removing antibiotics from real manure. The following recommendations can be made.

- Extended Sip and extended Langmuir isotherm describe the binary adsorption process well; however, IAST (Ideal Adsorbed Solution Theory) might provide more information about the process and should be evaluated.
- Although adsorption isotherm and thermodynamic parameters provide crucial information for understanding the single-solute and binary adsorption of tetracycline and lincomycin, the kinetic study could provide additional information and is recommended.
- Effect of initial concentration variations on adsorption capacity in the manure is recommended.
- Determination of thermodynamic parameters for tetracycline adsorption in manure is recommended to understand the mechanism of the adsorption process.

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APPENDIX A. Calibration curves for detection of tetracycline and lincomycin concentration

Tetracycline and lincomycin concentrations in water were determined using HPLC as mentioned in section 3.2.4. In addition, tetracycline in manure slurry was detected following the procedure explained in section 3.2.4. Figure A.1 and Figure A.2 demonstrates tetracycline and lincomycin calibration curves in the deionized water respectively. Figure A.3 shows tetracycline calibration curve in manure slurry.

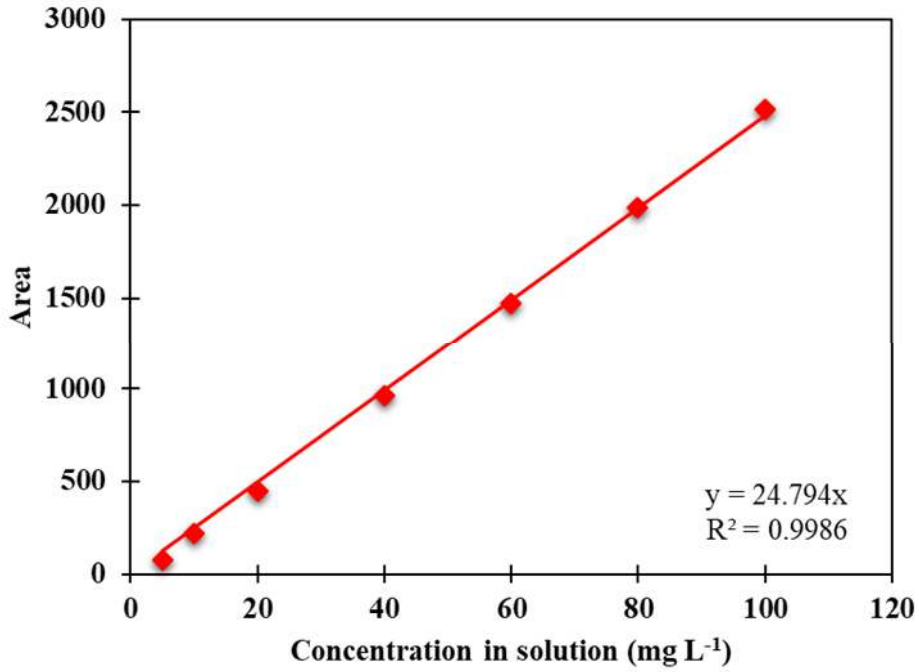

Figure A.1 Tetracycline calibration curve in the deionized water

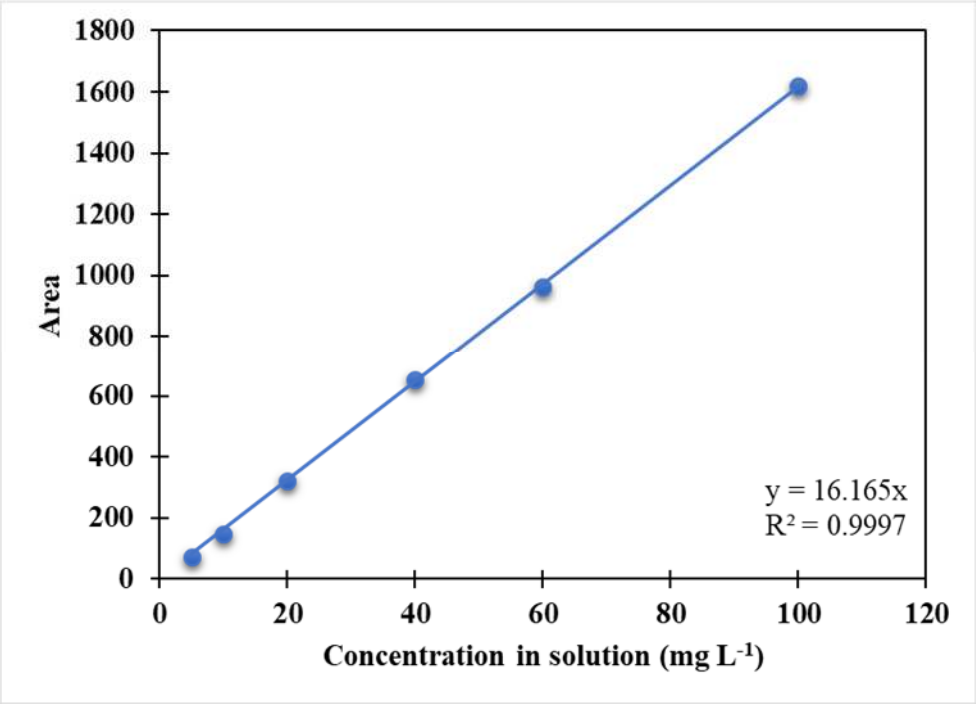

Figure A.2 Lincomycin calibration curve in the deionized water

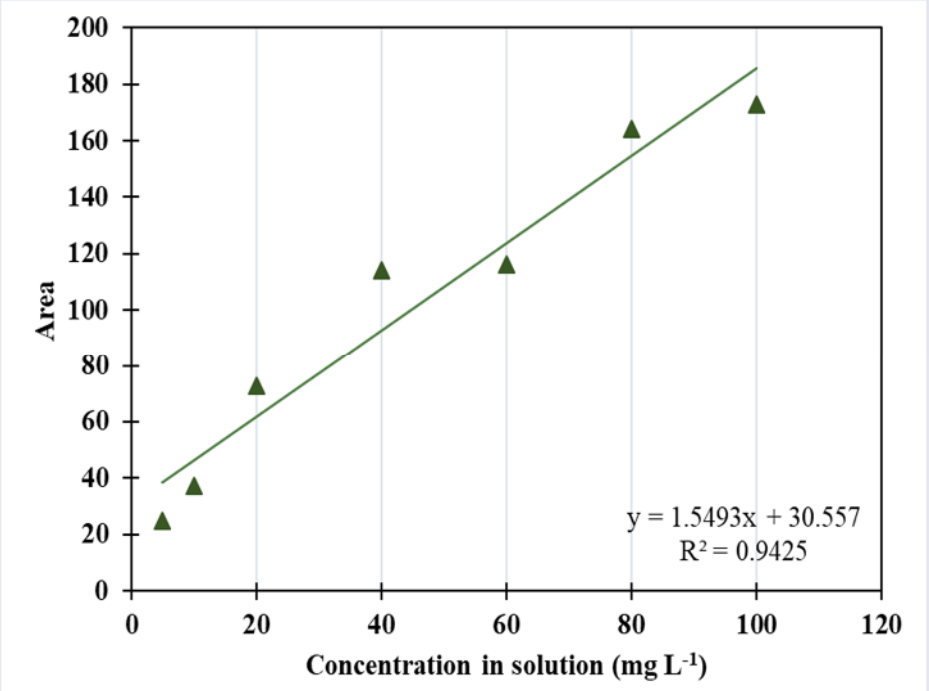

Figure A.3 Tetracycline calibration curve in the manure

APPENDIX B. Adsorption isotherms for tetracycline and lincomycin as an individual antibiotic in deionized water at different temperatures

Isotherms obtained through fitting single-solute and binary adsorption experimental data at different temperatures are presented below. Langmuir (Eq. (2.2)) and Freundlich (Eq. (2.5)) parameters calculated through linearization based on the procedure explained in chapter two are presented below. The results obtained from linearization for Langmuir and Freundlich isotherms for both single-solute and binary adsorption are listed in Table B.1 and Table B.2.

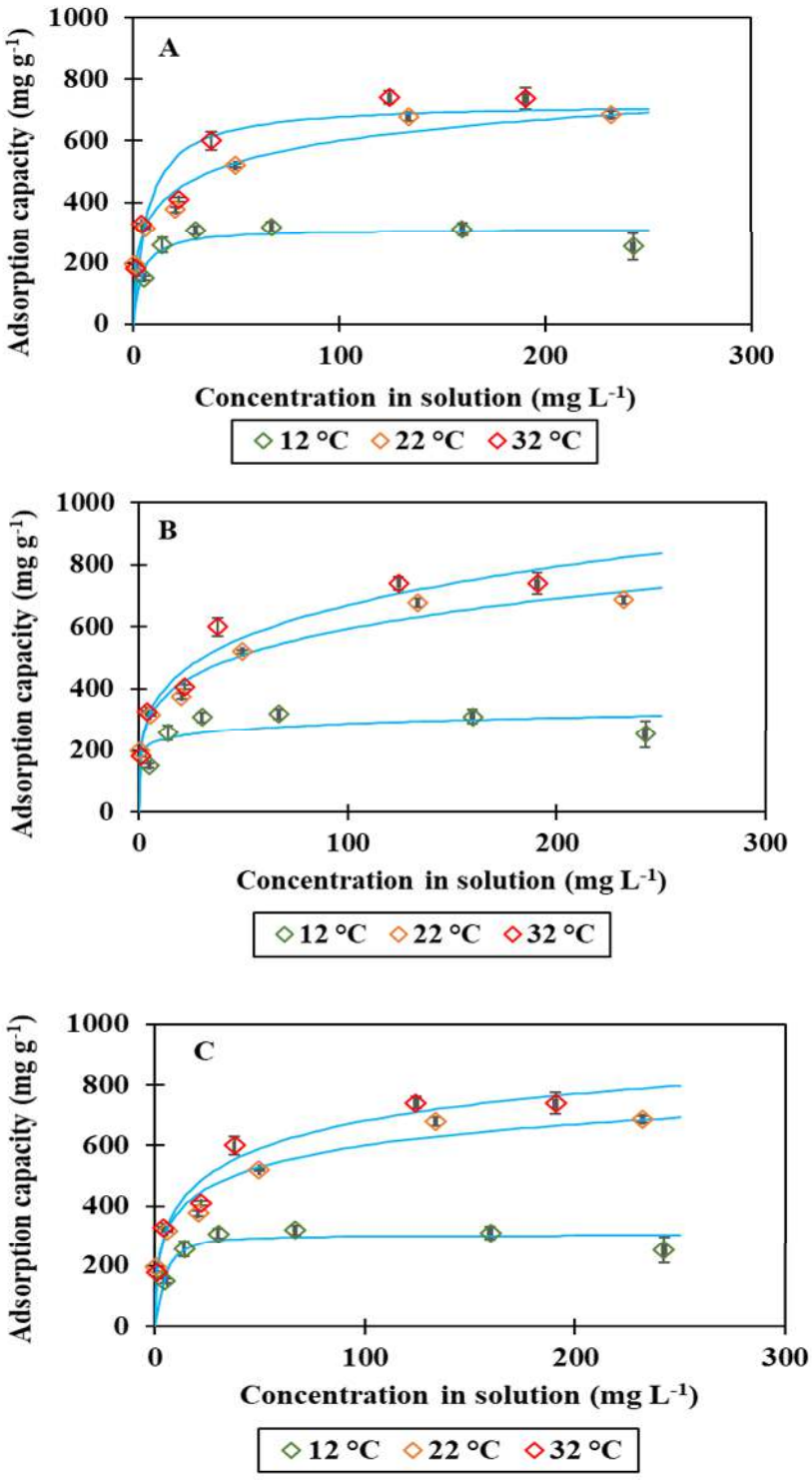

Figure B.1 Tetracycline experimental data (symbols) and fitted isotherms (lines) including: (A) Langmuir, (B) Freundlich, (C) Sip at different temperatures

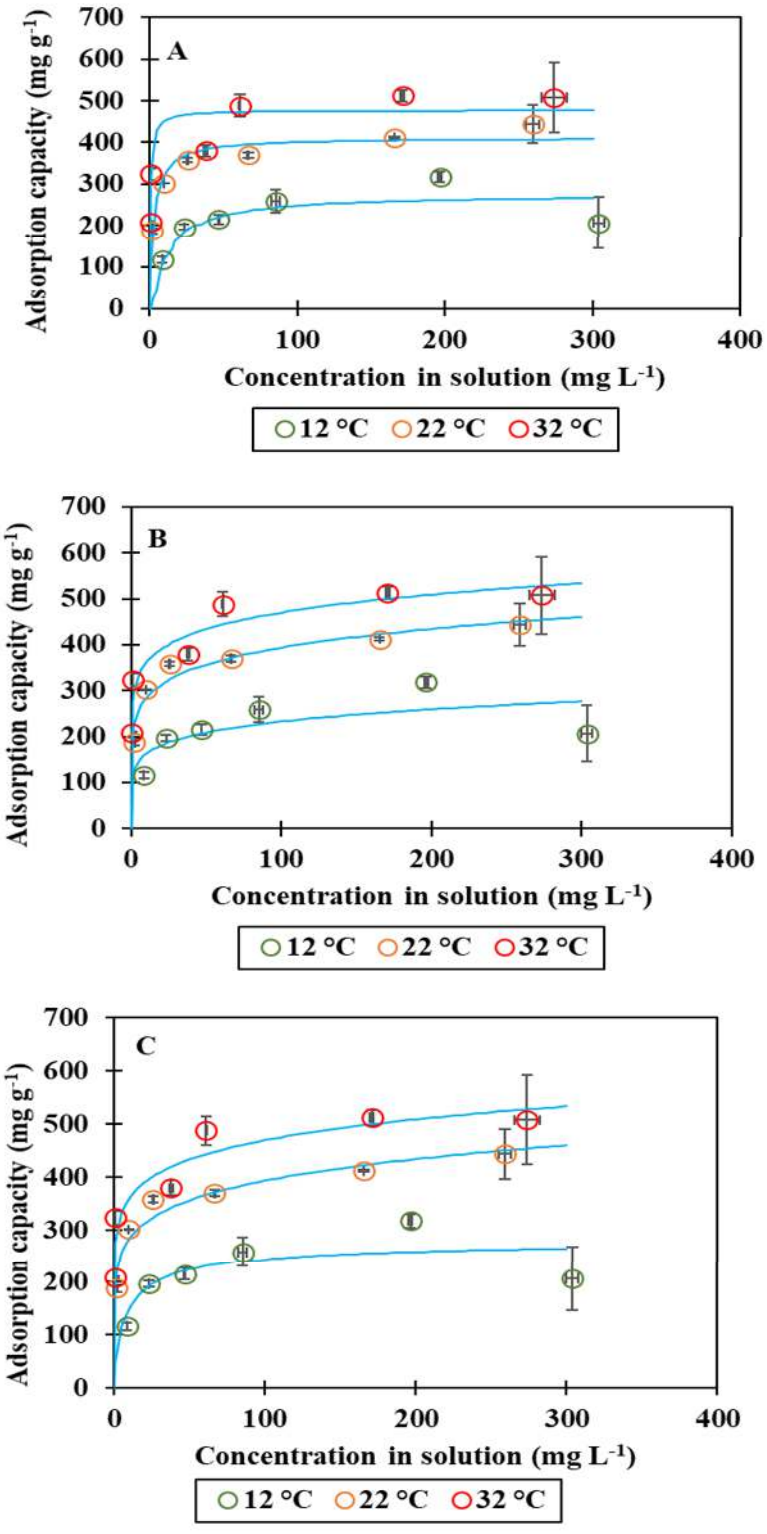

Figure B.2 Lincomycin experimental data (symbols) and fitted isotherms (lines) including: (A) Langmuir, (B) Freundlich, (C) Sip at different temperatures

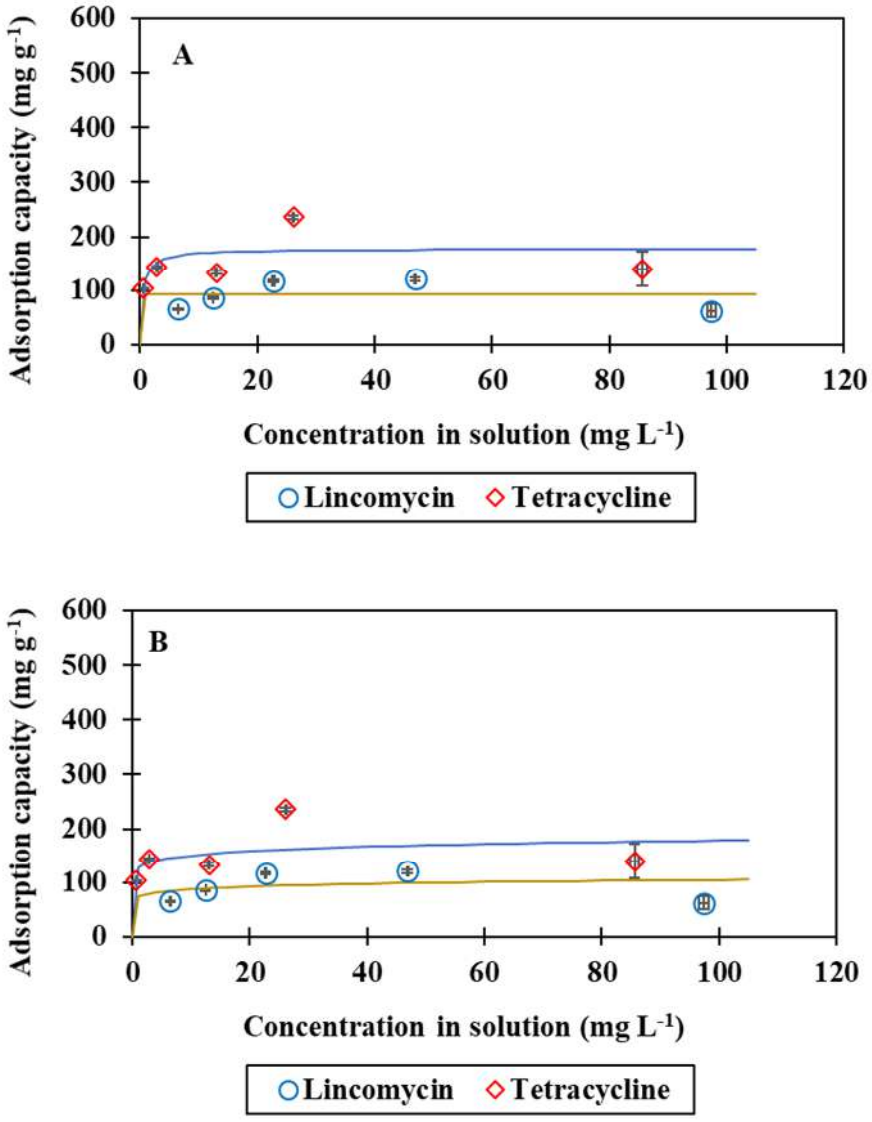

Figure B.3 Mixture experimental data (symbols) and fitted isotherms (lines) including: (A) extended Langmuir and (B) extended Sip at 12 °C

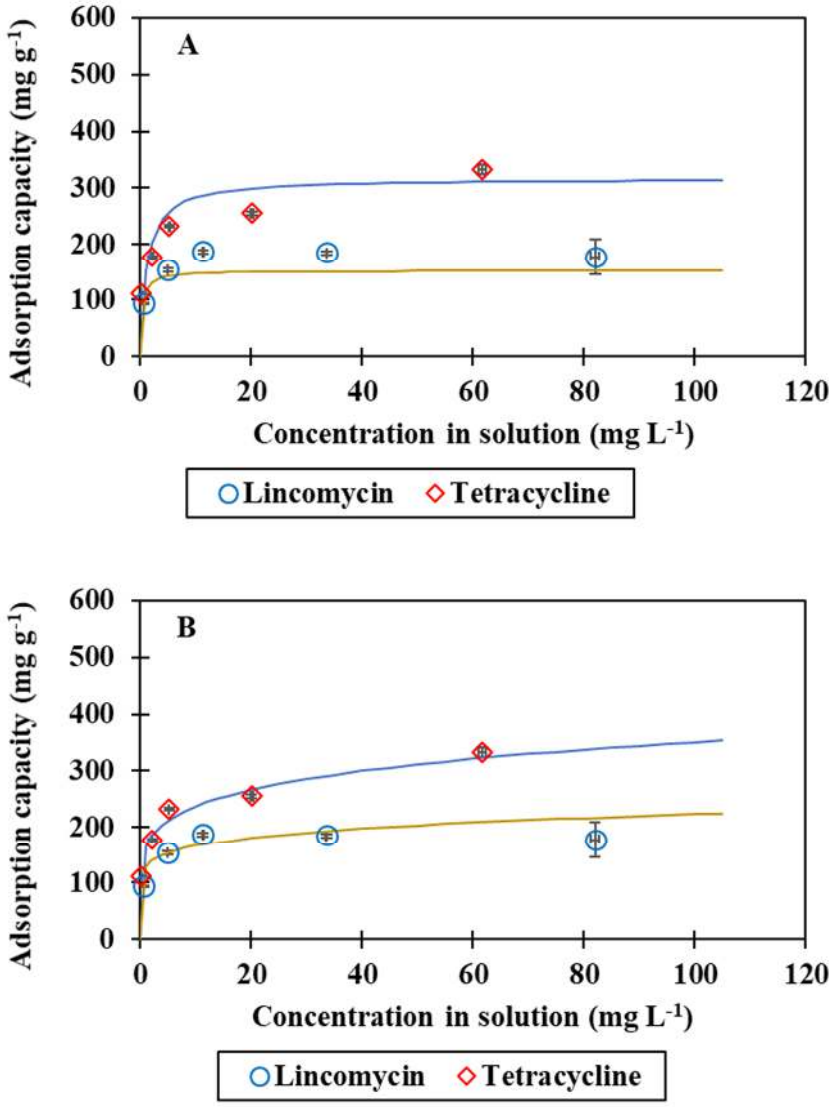

Figure B.4 Mixture experimental data (symbols) and fitted isotherms (lines) including: (A) extended Langmuir and (B) extended Sip at 22 °C

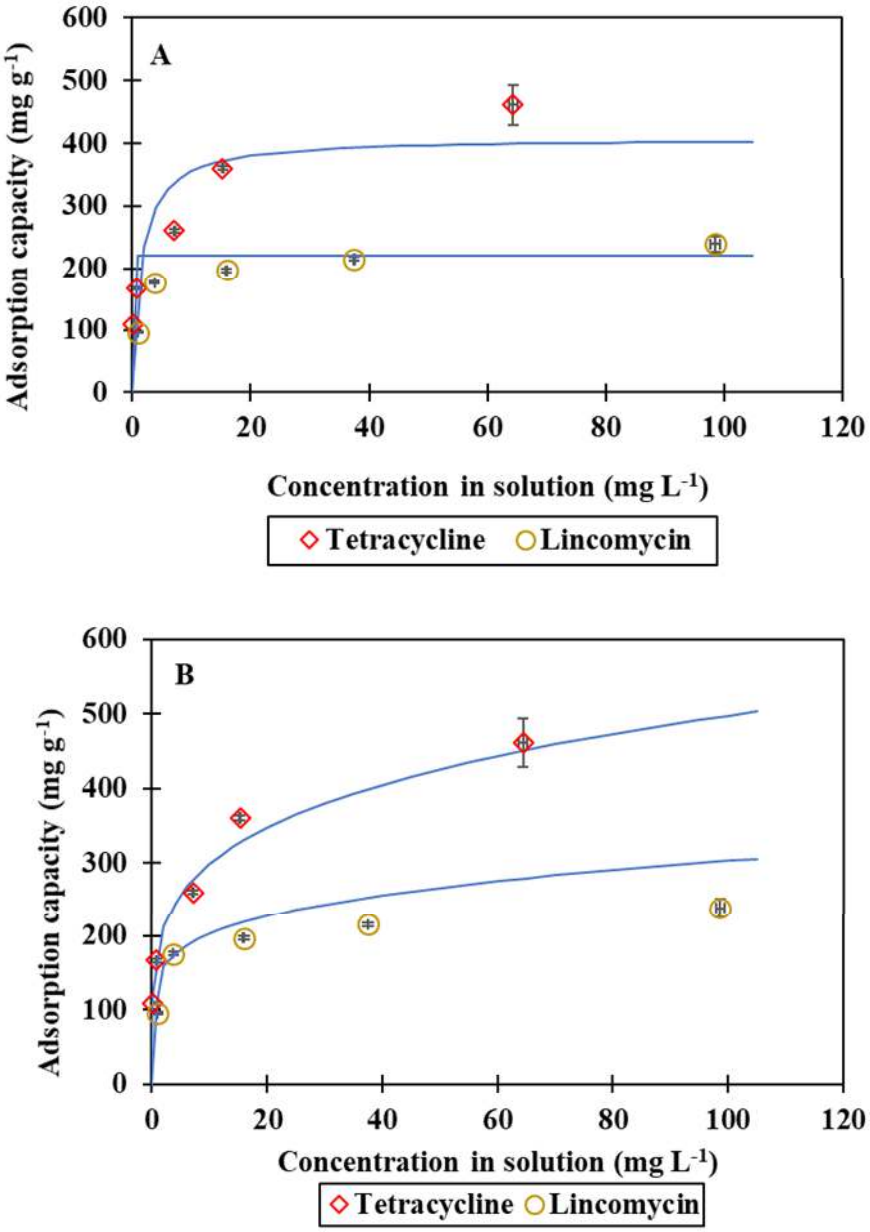

Figure B.5 Mixture experimental data (symbols) and fitted isotherms (lines) including: (A) extended Langmuir and (B) extended Sip at 32 °C

Table B.1 Langmuir and Freundlich parameters calculated from linearization for single-solute

Single-solute adsorption						
Langmuir						
	Tetracycline			**Lincomycin**		
Temperature (℃)	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_L}$ ($L\ mg^{-1}$)	$\mathbf{R^2}$	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_L}$ ($L\ mg^{-1}$)	$\mathbf{R^2}$
5	285	8.75	0.998	238	0.14	0.994
12	322	0.35	0.998	344	0.04	0.993
22	714	0.09	0.994	434	0.15	0.997
32	769	0.1	0.994	526	0.24	0.997
Freundlich						
	Tetracycline			**Lincomycin**		
Temperature (℃)	$\mathbf{K_F}$	**n**	$\mathbf{R^2}$	$\mathbf{K_F}$	**n**	$\mathbf{R^2}$
5	159	0.12	0.642	96	0.17	0.880
12	160	7.8	0.451	93	0.19	0.602
22	226	0.21	0.979	194	0.140	0.919
32	195	0.27	0.949	267	0.12	0.860

Table B.2 Langmuir and Freundlich parameters calculated from linearization for binary adsorption

Binary adsorption						
Langmuir						
	Tetracycline			**Lincomycin**		
Temperature (℃)	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_L}$ ($L\ mg^{-1}$)	$\mathbf{R^2}$	$\mathbf{q_{max}}$ ($mg\ g^{-1}$)	$\mathbf{K_L}$ ($L\ mg^{-1}$)	$\mathbf{R^2}$
5	148	0.93	0.701	85	0.67	0.285
12	170	2.44	0.285	101	0.46	0.144
22	338	0.51	0.737	170	2.10	0.436
32	408	0.67	0.812	229	0.74	0.971
Freundlich						
	Tetracycline			**Lincomycin**		
Temperature (℃)	$\mathbf{K_F}$	$\boldsymbol{n}$	$\mathbf{R^2}$	$\mathbf{K_F}$	**n**	$\mathbf{R^2}$
5	159	0.12	0.642	68	0.04	0.069
12	107	0.07	0.321	81	0.03	0.015
22	157	0.18	0.983	133	0.05	0.094
32	183	0.21	0.982	123	0.15	0.910

APPENDIX C. Equilibrium constant and distribution coefficient calculated for single-solute and binary adsorption

Equilibrium constant can be determined through using distribution coefficient based on the procedure proposed by Singh et al. [50] explained in chapter two. Distribution coefficient can be determined through plotting ln $(\frac{q_e}{C_e})$ vs C_e and extrapolating C_e to zero. However, distribution coefficient calculated from this method has dimension and in order to convert it to dimensionless unit, Milonjic [59] proposed a method which was explained in chapter 2. The results for distribution coefficient and equilibrium constant are presented in Table C.1 and Table C.2 respectively.

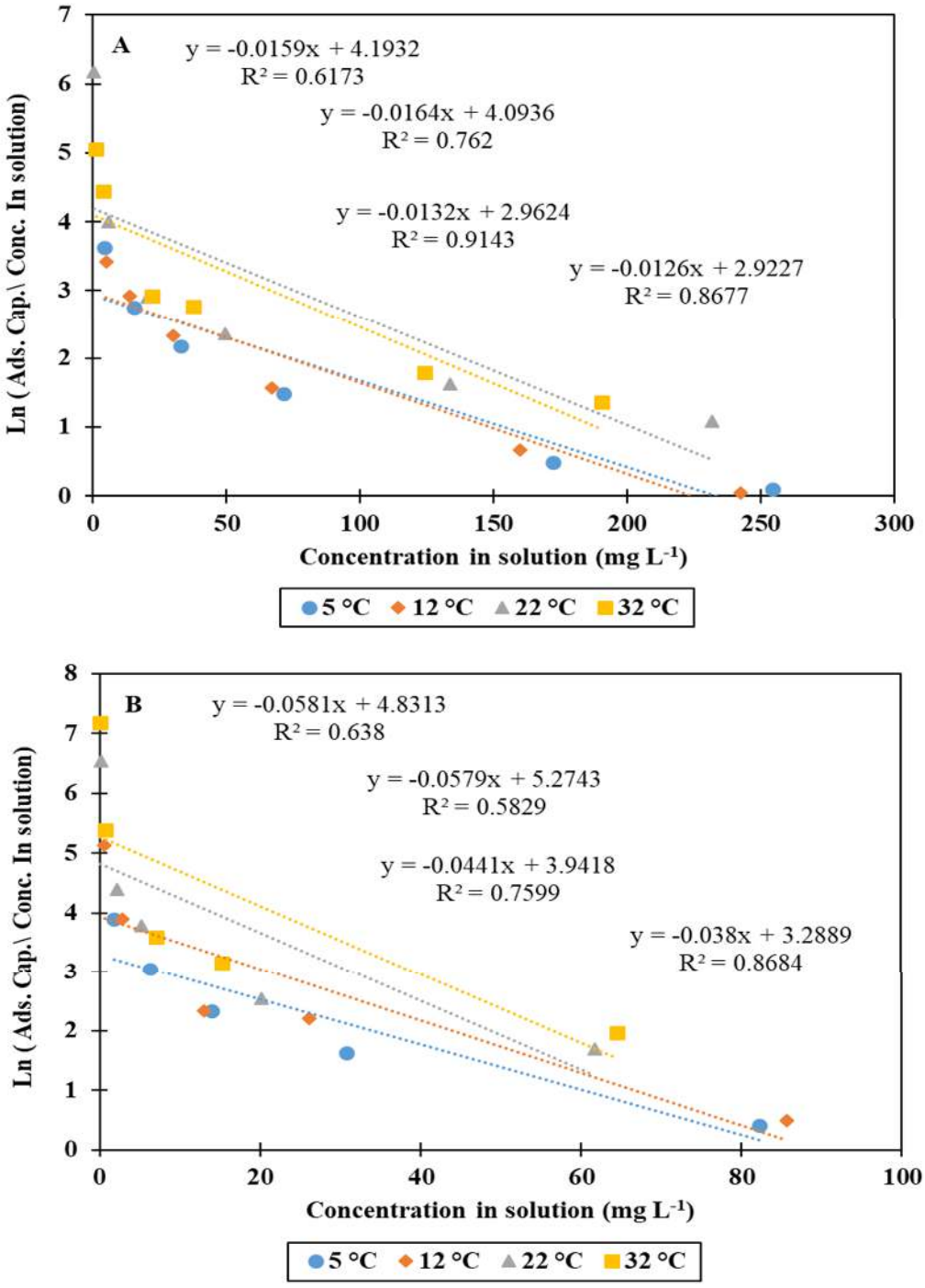

Figure C.1 Ln (adsorption capacity/concentration in solution) vs concentration in solution plot for tetracycline (A) single-solute adsorption and (B) Binary adsorption

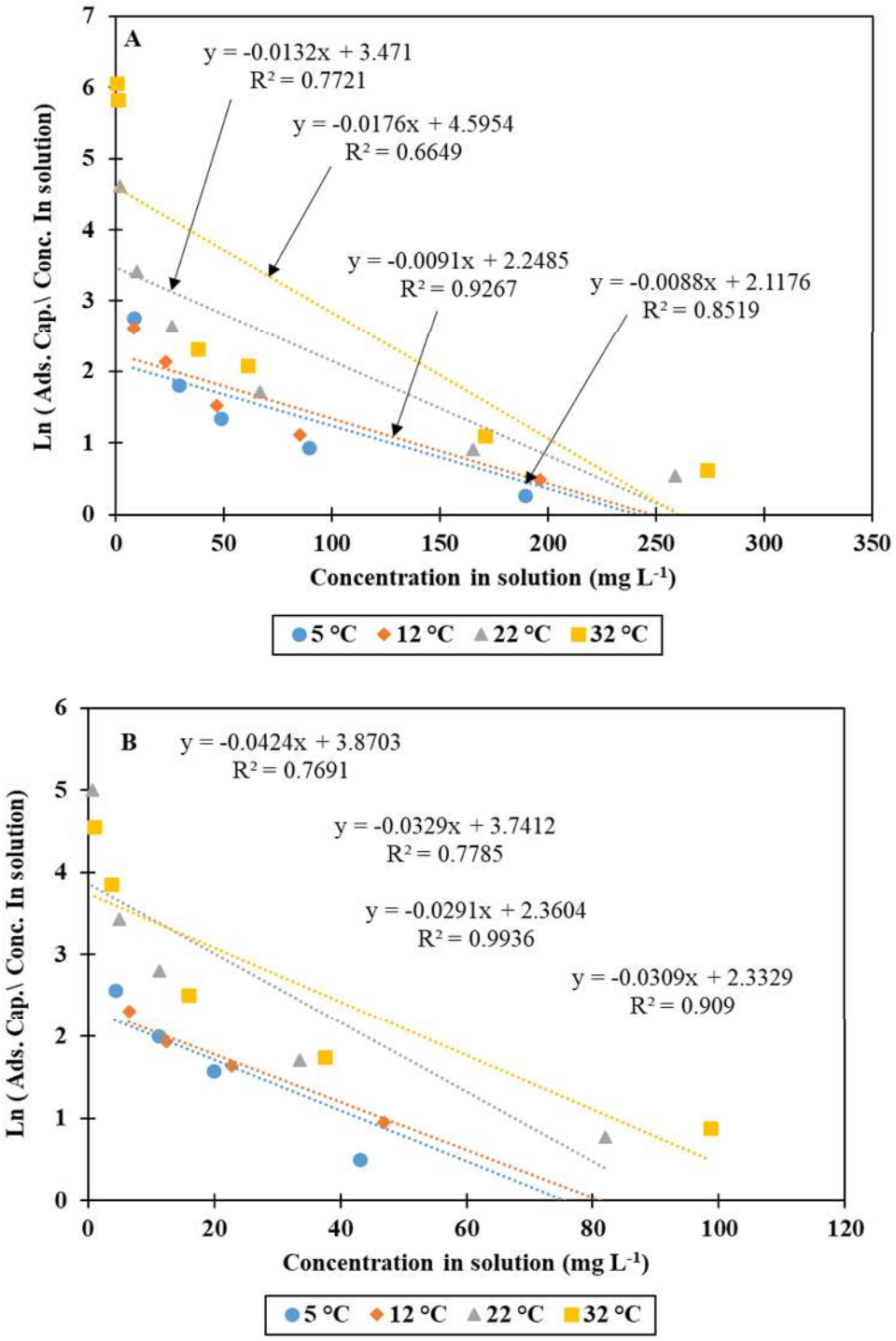

Figure C.2 Ln (adsorption capacity/concentration in solution) vs concentration in solution plot for lincomycin (A) single-solute adsorption and (B) Binary adsorption

Table C.1 Distribution coefficient determined for single-solute and binary adsorption at different temperatures

	Single-solute		**Binary**	
	Tetracycline	**Lincomycin**	**Tetracycline**	**Lincomycin**
Temperature (°C)	Ln (K_d) ($L\ g^{-1}$)	Ln (K_d) ($L\ g^{-1}$)	Ln (K_d) ($L\ g^{-1}$)	Ln (K_d) ($L\ g^{-1}$)
5	2.92	2.11	3.28	2.33
12	2.96	2.24	3.94	2.36
22	4.09	3.47	4.83	3.74
32	4.19	4.59	5.27	3.87

Table C.2 Equilibrium constant determined for single-solute and binary adsorption at different temperatures

	Single-solute		**Binary**	
	Tetracycline	**Lincomycin**	**Tetracycline**	**Lincomycin**
Temperature (°C)	Ln (K_c)	Ln (K_c)	Ln (K_c)	Ln (K_c)
5	9.83	9.02	10.19	9.23
12	9.87	9.15	10.84	9.26
22	11.10	10.37	11.73	10.77
32	11.00	11.50	12.18	10.64

APPENDIX D. Van’t Hoff plots for determination of thermodynamic parameters of single-solute and binary adsorption

Thermodynamic parameters can be determined using Van’t Hoff plots based on procedure mentioned in chapter two. Van’t Hoff plots for tetracycline and lincomycin in single-solute and binary adsorption are presented as below. Thermodynamic parameters calculated using equilibrium constant are listed in Table D.1.

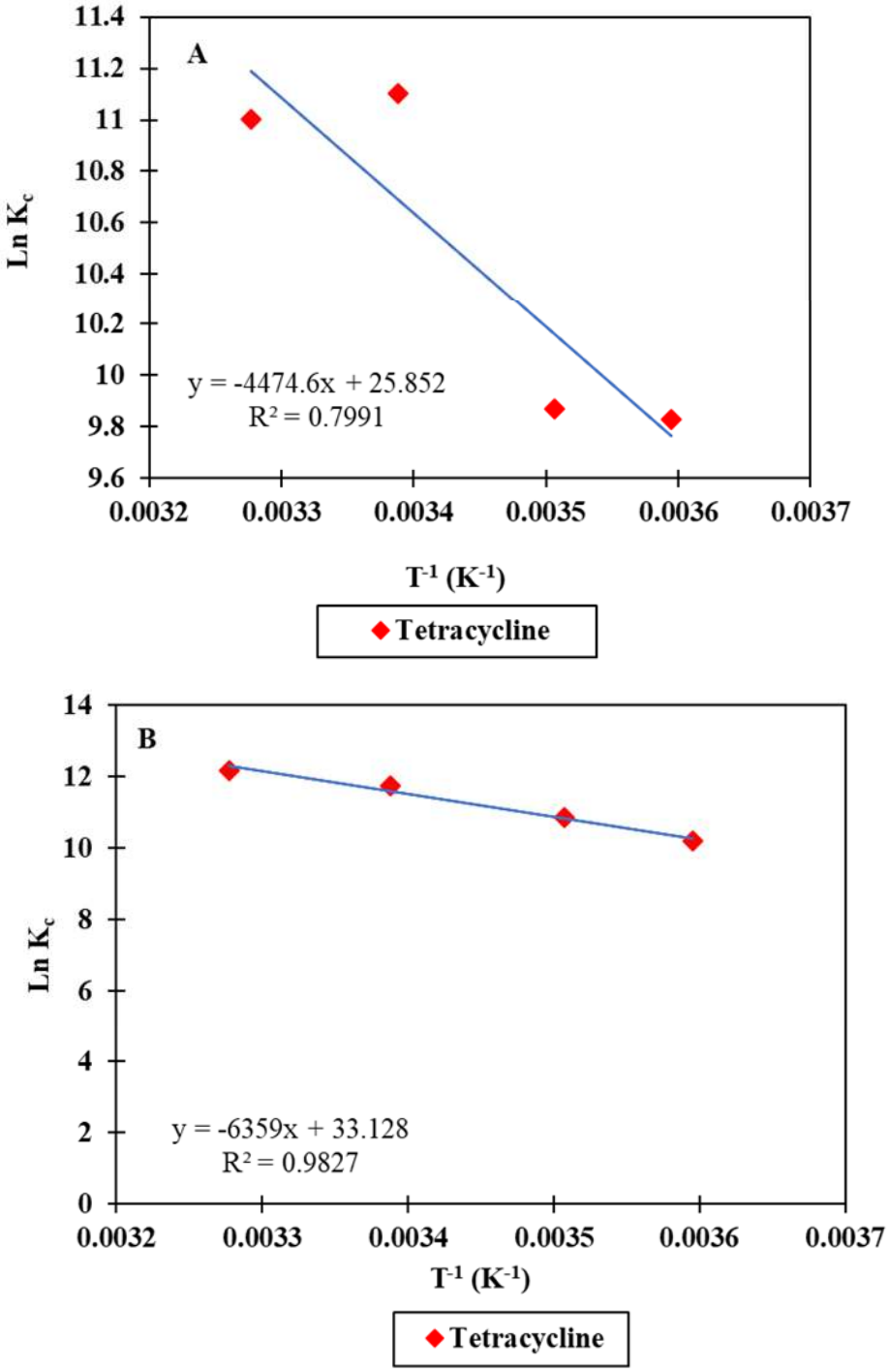

Figure D.1 Van't Hoff plot for tetracycline in (A) single-solute adsorption and (B) binary adsorption

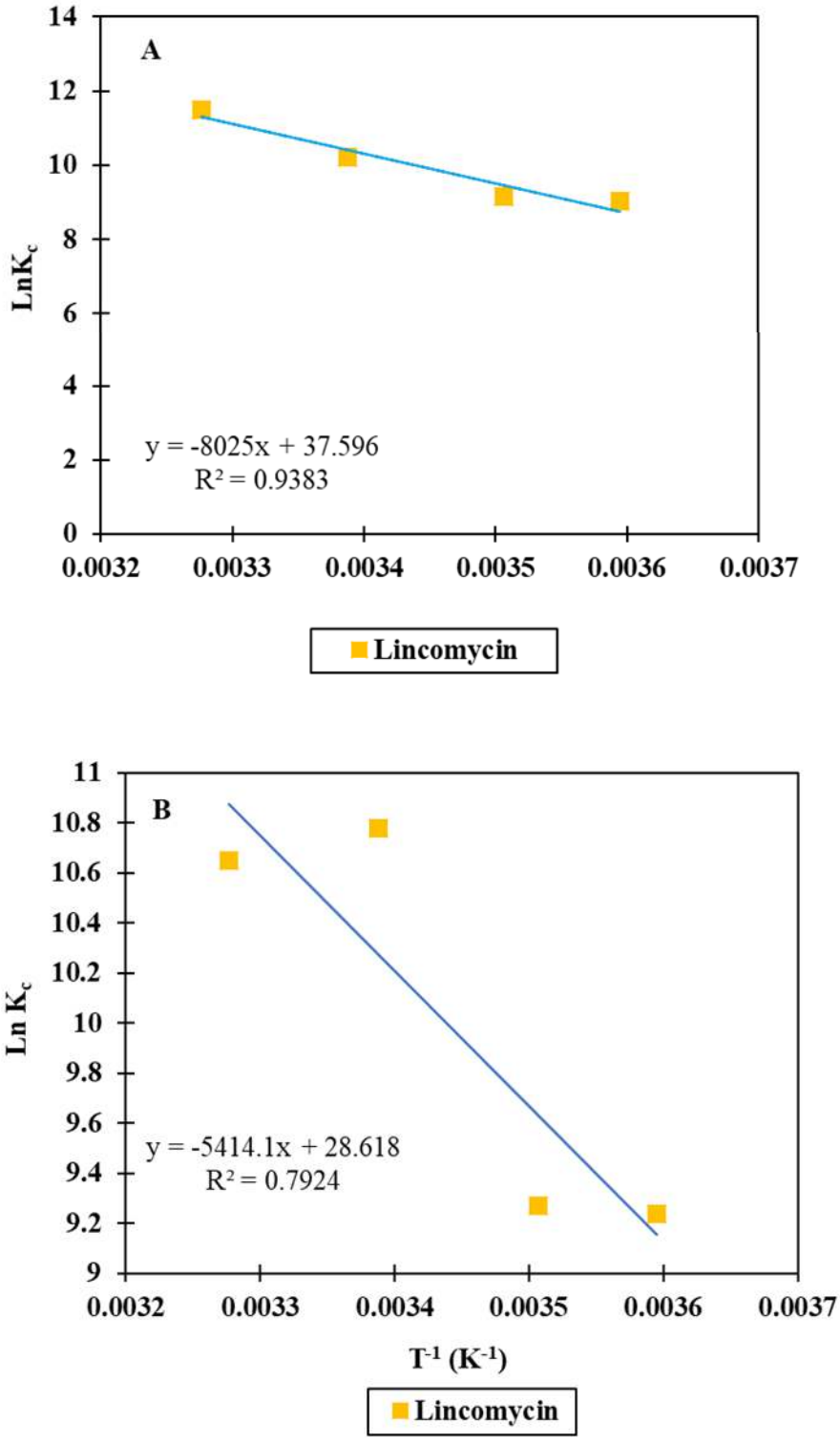

Figure D.2 Van't Hoff plot for tetracycline in (A) single-solute adsorption and (B) binary adsorption

Table D.1 Thermodynamic parameters calculated for single-solute and binary adsorption

Sing-solute adsorption			
Tetracycline		**Lincomycin**	
ΔH ($J\ mol^{-1}$)	**ΔS** ($J\ mol^{-1}\ K^{-1}$)	**ΔH** ($J\ mol^{-1}$)	**ΔS** ($J\ mol^{-1}\ K^{-1}$)
36667	213	66720	312
Binary adsorption			
Tetracycline		**Lincomycin**	
ΔH ($J\ mol^{-1}$)	**ΔS** ($J\ mol^{-1}\ K^{-1}$)	**ΔH** ($J\ mol^{-1}$)	**ΔS** ($J\ mol^{-1}\ K^{-1}$)
52372	272	45012	241